

Supporting Information

Dual Function of Carbon tetrachloride: Synthesis of Chlorinated Heterocycles

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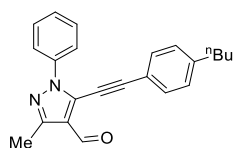
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General Experimental

General Method. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in CDCl_3 . Chemical shifts for protons and carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, coupling constants in Hertz and integration. High-resolution mass spectra were recorded on electrospray mass spectrometer. Crystal structure analysis was accomplished on single needles X-ray diffractometer. TLC analysis was performed on commercially prepared 60 F₂₅₄ silica gel plates and visualized by either UV irradiation or by staining with I_2 . All purchased chemicals were used as received. All melting points are uncorrected.

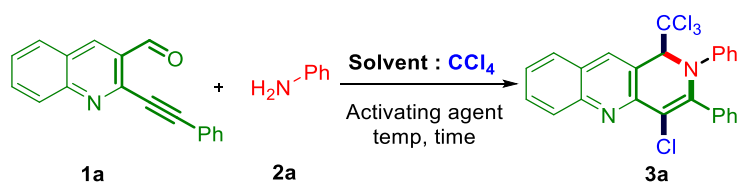
Starting Materials Synthesis: The starting materials **1** were prepared by Sonogashira coupling using the reported procedure. The structure and purity of known starting materials were confirmed by comparison of their physical and spectral data (^1H NMR and ^{13}C NMR) with those reported in literature¹



5-((4-Butylphenyl)ethynyl)-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde (1x). The product was obtained as a brown solid, mp: 98–100°C (153.9 mg, 90%); ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 1H), 7.83–7.81 (m, 2H), 7.51–7.47 (m, 2H), 7.41–7.37 (m, 3H), 7.16 (d, J = 7.8 Hz, 2H), 2.60 (t, J = 7.8 Hz, 2H), 2.57 (s, 3H), 1.61–1.54 (m, 2H), 1.38–1.25 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.0, 150.9, 145.6, 138.9, 131.8, 131.0, 129.1, 128.9, 128.4, 123.5, 123.4, 118.1, 101.8, 75.5, 35.8, 33.4, 22.4, 14.0, 13.6; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}]$ 343.1810, found 343.1813.

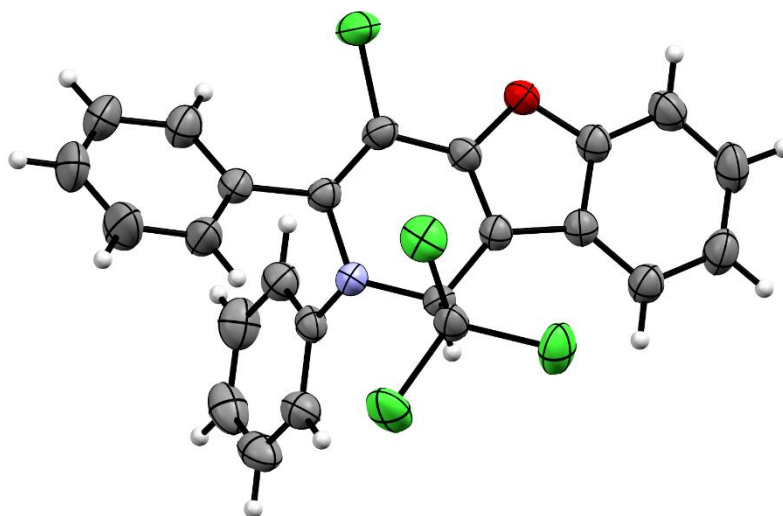
¹ (a) A. K. Verma, V. Rustagi, T. Aggarwal, A. P. Singh, *J. Org. Chem.* 2010, **75**, 7691–7703. (b) T. Aggarwal, M. Imam, N. K. Kaushik, V. S. Chauhan, A. K. Verma, *ACS Comb Sci.* 2011, **13**, 530–536. (c) V. Rustagi, R. K. Tiwari, A. K. Verma, *Eur. J. Org. Chem.* 2012, **24**, 4590–4602. (d) V. Rustagi, T. Aggarwal, A. K. Verma, *Green Chem.* 2011, **13**, 1640–1643. (e) S. P. Shukla, R. K. Tiwari, A. K. Verma, *Tetrahedron* 2012, **68**, 9035–9044. (f) A. K. Verma, D. Choudhary, R. K. Saunthwal, V. Rustagi, M. Patel, R. K. Tiwari, *J. Org. Chem.* 2013, **78**, 6657–6669. (g) R. R. Jha, R. K. Saunthwal, A. K. Verma, *Org. Biomol. Chem.* 2014, **12**, 552–556. (h) R. R. Jha, A. K. Danodia, S. Kumar, A. K. Verma, *Tetrahedron Lett.* 2014, **55**, 610–615. (i) S. Kumar, C. Cruz, S. Pal, R. K. Saunthwal, R. K. Tiwari, E. Juaristi, A. K. Verma, *J. Org. Chem.* 2015, **80**, 10548–10560. (j) P. K. Mishra, A. K. Verma, *Green Chem.* 2016, **18**, 6367–6372. (k) S. Pal, D. Choudhary, M. Jainth, S. Kumar, R. K. Tiwari, A. K. Verma, *J. Org. Chem.* 2016, **81**, 9356–9371.

Table 1. Optimising the tandem cyclization



Entry	Activating agent	Solvent	Temp (°C)	Time (h)	Yield (%) ^b 3a
1	AgOTf	carbon tetrachloride	80	24	-
2	AgOTf	Dichloromethane	80	24	-
3	K ₂ CO ₃	carbon tetrachloride	80	24	-
4	Et ₃ N	carbon tetrachloride	80	24	-
5	AgOTf	1,2-dichloroethane : carbon tetrachloride (9:1)	80	16	20
6	-	1,2-dichloroethane : carbon tetrachloride (9:1)	80	16	80
7	-	1,2-dichloroethane : carbon tetrachloride (9:1)	100	12	87
8	-	1,2-dichloroethane : carbon tetrachloride (9:1)	120	10	84
9	-	1,2-dichloroethane : carbon tetrachloride(9:1)	100	10	65 ^c
10	-	tetrahydrofuran : carbon tetrachloride (9:1)	100	12	60
11	-	1,4-dioxane : carbon tetrachloride (9:1)	100	12	50
12	-	<i>N,N</i> -dimethylformaldehyde: carbon tetrachloride (9:1)	100	16	65
13	-	dimethyl sulfoxide : carbon tetrachloride (9:1)	100	16	40
14	-	<i>N</i> -Methyl-2-pyrrolidone : carbon tetrachloride (9:1)	100	16	45
15	-	1,2-dichloroethane : carbon tetrachloride (1:1)	100	16	50
16	-	carbon tetrachloride	100	10	25

^aReaction conditions: 2-(phenylethynyl)quinoline-3-carbaldehyde **1a** (0.50 mmol), aniline **2a** (0.51 mmol), solvent (2.0 mL), heated in a sealed tube. ^bIsolated yield. ^c30% SM was recovered.

Table 2. Crystal data and structure refinement for **5a**.

Identification code	shelx	
Empirical formula	C ₂₄ H ₁₅ Cl ₄ N O	
Formula weight	475.17	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 10.0953(5) Å	a = 90°.
	b = 26.4194(9) Å	b = 114.895(6)°.
	c = 8.7916(5) Å	g = 90°.
Volume	2126.9(2) Å ³	
Z	4	
Density (calculated)	1.484 Mg/m ³	
Absorption coefficient	0.573 mm ⁻¹	
F(000)	968	
Crystal size	? x ? x ? mm ³	
Theta range for data collection	3.447 to 24.995°.	
Index ranges	-11 ≤ h ≤ 11, -31 ≤ k ≤ 31, -10 ≤ l ≤ 10	
Reflections collected	26358	
Independent reflections	3733 [R(int) = 0.0428]	
Completeness to theta = 24.995°	99.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3733 / 0 / 275	
Goodness-of-fit on F ²	1.010	
Final R indices [I > 2σ(I)]	R1 = 0.0417, wR2 = 0.0946	

R indices (all data)	R1 = 0.0488, wR2 = 0.0985
Extinction coefficient	n/a
Largest diff. peak and hole	0.196 and -0.304 e.Å ⁻³

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	8354(1)	6643(1)	4314(1)	51(1)
Cl(2)	10948(1)	6511(1)	7366(1)	57(1)
Cl(4)	5170(1)	5399(1)	2498(1)	53(1)
Cl(3)	8806(1)	7249(1)	7202(1)	57(1)
O(1)	7910(2)	4983(1)	5229(2)	39(1)
N(1)	6711(2)	6324(1)	6505(2)	32(1)
C(19)	9723(2)	5331(1)	7565(3)	33(1)
C(8)	6084(2)	6361(1)	7696(3)	33(1)
C(7)	5757(2)	6114(1)	4928(3)	31(1)
C(16)	7535(2)	5466(1)	5453(3)	33(1)
C(14)	8290(2)	6229(1)	7176(3)	31(1)
C(17)	6157(2)	5683(1)	4413(3)	34(1)
C(15)	8572(2)	5699(1)	6793(3)	32(1)
C(1)	4427(2)	6417(1)	3978(3)	35(1)
C(20)	9271(3)	4906(1)	6532(3)	36(1)
C(24)	11049(3)	5312(1)	8979(3)	41(1)
C(9)	5008(3)	6022(1)	7620(3)	41(1)
C(13)	6530(3)	6735(1)	8926(3)	43(1)
C(21)	10067(3)	4468(1)	6790(4)	46(1)
C(2)	3060(3)	6198(1)	3143(3)	46(1)
C(23)	11849(3)	4866(1)	9286(4)	50(1)
C(18)	9051(3)	6636(1)	6535(3)	38(1)
C(10)	4377(3)	6063(1)	8726(4)	53(1)
C(12)	5883(3)	6766(1)	10031(3)	52(1)
C(22)	11381(3)	4457(1)	8204(4)	53(1)
C(6)	4560(3)	6936(1)	3873(4)	52(1)
C(11)	4802(3)	6435(1)	9925(4)	55(1)
C(3)	1869(3)	6496(1)	2207(4)	57(1)

C(4)	2020(3)	7008(1)	2074(4)	67(1)
C(5)	3365(3)	7226(1)	2909(4)	70(1)

Table 4. Bond lengths [Å] and angles [°] for **5a**.

Cl(1)-C(18)	1.775(3)
Cl(2)-C(18)	1.769(2)
Cl(4)-C(17)	1.726(2)
Cl(3)-C(18)	1.774(2)
O(1)-C(16)	1.370(3)
O(1)-C(20)	1.385(3)
N(1)-C(7)	1.426(3)
N(1)-C(8)	1.436(3)
N(1)-C(14)	1.470(3)
C(19)-C(24)	1.393(3)
C(19)-C(20)	1.394(3)
C(19)-C(15)	1.446(3)
C(8)-C(9)	1.387(3)
C(8)-C(13)	1.392(3)
C(7)-C(17)	1.347(3)
C(7)-C(1)	1.483(3)
C(16)-C(15)	1.350(3)
C(16)-C(17)	1.425(3)
C(14)-C(15)	1.496(3)
C(14)-C(18)	1.558(3)
C(14)-H(14)	0.96(2)
C(1)-C(6)	1.385(4)
C(1)-C(2)	1.387(3)
C(20)-C(21)	1.371(3)
C(24)-C(23)	1.389(4)
C(24)-H(24)	0.9300
C(9)-C(10)	1.372(4)
C(9)-H(9)	0.9300
C(13)-C(12)	1.383(4)
C(13)-H(13)	0.9300
C(21)-C(22)	1.385(4)
C(21)-H(21)	0.9300
C(2)-C(3)	1.382(4)
C(2)-H(2)	0.9300

C(23)-C(22)	1.385(4)
C(23)-H(23)	0.9300
C(10)-C(11)	1.373(4)
C(10)-H(10)	0.9300
C(12)-C(11)	1.370(4)
C(12)-H(12)	0.9300
C(22)-H(22)	0.9300
C(6)-C(5)	1.378(4)
C(6)-H(6)	0.9300
C(11)-H(11)	0.9300
C(3)-C(4)	1.370(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.370(4)
C(4)-H(4)	0.9300
C(5)-H(5)	0.9300

C(16)-O(1)-C(20)	104.80(17)
C(7)-N(1)-C(8)	114.28(17)
C(7)-N(1)-C(14)	119.83(18)
C(8)-N(1)-C(14)	117.09(18)
C(24)-C(19)-C(20)	118.7(2)
C(24)-C(19)-C(15)	136.3(2)
C(20)-C(19)-C(15)	105.0(2)
C(9)-C(8)-C(13)	119.1(2)
C(9)-C(8)-N(1)	119.8(2)
C(13)-C(8)-N(1)	121.1(2)
C(17)-C(7)-N(1)	118.8(2)
C(17)-C(7)-C(1)	126.5(2)
N(1)-C(7)-C(1)	114.69(19)
C(15)-C(16)-O(1)	112.9(2)
C(15)-C(16)-C(17)	124.5(2)
O(1)-C(16)-C(17)	122.5(2)
N(1)-C(14)-C(15)	110.27(18)
N(1)-C(14)-C(18)	110.74(18)
C(15)-C(14)-C(18)	113.31(19)
N(1)-C(14)-H(14)	108.6(14)
C(15)-C(14)-H(14)	110.3(14)
C(18)-C(14)-H(14)	103.3(14)

C(7)-C(17)-C(16)	118.3(2)
C(7)-C(17)-Cl(4)	124.34(18)
C(16)-C(17)-Cl(4)	117.23(17)
C(16)-C(15)-C(19)	106.2(2)
C(16)-C(15)-C(14)	118.1(2)
C(19)-C(15)-C(14)	135.7(2)
C(6)-C(1)-C(2)	118.7(2)
C(6)-C(1)-C(7)	118.8(2)
C(2)-C(1)-C(7)	122.4(2)
C(21)-C(20)-O(1)	124.6(2)
C(21)-C(20)-C(19)	124.3(2)
O(1)-C(20)-C(19)	111.08(19)
C(23)-C(24)-C(19)	117.7(2)
C(23)-C(24)-H(24)	121.1
C(19)-C(24)-H(24)	121.1
C(10)-C(9)-C(8)	120.2(2)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(12)-C(13)-C(8)	119.6(3)
C(12)-C(13)-H(13)	120.2
C(8)-C(13)-H(13)	120.2
C(20)-C(21)-C(22)	116.1(2)
C(20)-C(21)-H(21)	121.9
C(22)-C(21)-H(21)	121.9
C(3)-C(2)-C(1)	120.0(3)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(22)-C(23)-C(24)	121.8(2)
C(22)-C(23)-H(23)	119.1
C(24)-C(23)-H(23)	119.1
C(14)-C(18)-Cl(2)	109.54(16)
C(14)-C(18)-Cl(3)	110.59(17)
Cl(2)-C(18)-Cl(3)	108.15(13)
C(14)-C(18)-Cl(1)	112.15(16)
Cl(2)-C(18)-Cl(1)	108.34(14)
Cl(3)-C(18)-Cl(1)	107.95(13)
C(11)-C(10)-C(9)	120.8(3)
C(11)-C(10)-H(10)	119.6

C(9)-C(10)-H(10)	119.6
C(11)-C(12)-C(13)	120.9(3)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(23)-C(22)-C(21)	121.3(2)
C(23)-C(22)-H(22)	119.3
C(21)-C(22)-H(22)	119.3
C(5)-C(6)-C(1)	120.5(3)
C(5)-C(6)-H(6)	119.8
C(1)-C(6)-H(6)	119.8
C(10)-C(11)-C(12)	119.4(3)
C(10)-C(11)-H(11)	120.3
C(12)-C(11)-H(11)	120.3
C(4)-C(3)-C(2)	120.8(3)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(5)-C(4)-C(3)	119.4(3)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	120.6(3)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^* 2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Cl(1)	59(1)	48(1)	51(1)	8(1)	27(1)	-2(1)
Cl(2)	31(1)	50(1)	84(1)	5(1)	20(1)	-4(1)
Cl(4)	55(1)	45(1)	42(1)	-12(1)	2(1)	1(1)
Cl(3)	62(1)	29(1)	85(1)	-10(1)	36(1)	-6(1)
O(1)	40(1)	27(1)	43(1)	-3(1)	12(1)	2(1)
N(1)	26(1)	33(1)	33(1)	-3(1)	10(1)	1(1)
C(19)	31(1)	30(1)	39(1)	3(1)	16(1)	0(1)
C(8)	33(1)	32(1)	34(1)	4(1)	14(1)	7(1)
C(7)	29(1)	30(1)	33(1)	-1(1)	11(1)	-2(1)

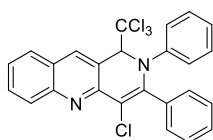
C(16)	36(1)	25(1)	37(1)	1(1)	14(1)	1(1)
C(14)	29(1)	30(1)	31(1)	-2(1)	9(1)	0(1)
C(17)	32(1)	32(1)	33(1)	-2(1)	8(1)	-4(1)
C(15)	30(1)	29(1)	35(1)	2(1)	13(1)	0(1)
C(1)	31(1)	39(1)	33(1)	-1(1)	11(1)	1(1)
C(20)	34(1)	29(1)	42(1)	4(1)	15(1)	1(1)
C(24)	34(1)	38(1)	47(2)	2(1)	12(1)	-1(1)
C(9)	42(1)	38(1)	42(1)	2(1)	16(1)	0(1)
C(13)	48(2)	39(1)	43(1)	-2(1)	20(1)	1(1)
C(21)	48(2)	33(1)	58(2)	-2(1)	23(1)	4(1)
C(2)	35(1)	48(2)	50(2)	3(1)	14(1)	-1(1)
C(23)	35(1)	47(2)	58(2)	7(1)	9(1)	6(1)
C(18)	33(1)	28(1)	50(2)	-3(1)	15(1)	0(1)
C(10)	48(2)	60(2)	58(2)	13(2)	30(1)	1(1)
C(12)	68(2)	50(2)	37(1)	-2(1)	22(1)	12(1)
C(22)	42(2)	40(2)	73(2)	10(1)	21(1)	13(1)
C(6)	40(1)	37(1)	61(2)	-7(1)	5(1)	3(1)
C(11)	63(2)	63(2)	51(2)	16(2)	36(2)	20(2)
C(3)	33(1)	69(2)	57(2)	-5(2)	7(1)	3(1)
C(4)	46(2)	64(2)	71(2)	0(2)	5(2)	23(2)
C(5)	58(2)	39(2)	90(2)	-3(2)	7(2)	13(1)

General Procedure for the Synthesis of Chlorinated Heterocycles.

In an oven-dried sealed tube, a solution of *ortho*-alkynylaldehyde **1** (0.50 mmol), aniline **2** (0.51 mmol) were added in 2.0 mL of 1,2-ethylenedichloride : carbontetrachloride (9:1) . The resulting reaction mixture was heated at 100 °C for 12–16 h. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the reaction was cooled to room temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and water (15 mL). The layers were separated, and the organic layer was washed with aqueous saturated brine solution and dried over Na₂SO₄. Organic layer was concentrated under reduced pressure. The crude material so obtained was purified by column chromatography on silica gel (100–200) (hexane:ethyl acetate). The structure and purity of known starting materials were confirmed by comparison of their physical and spectral data (¹H NMR, ¹³C NMR, and HRMS).

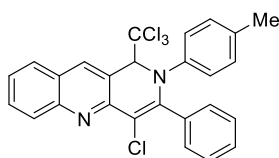
Note: The Carbon tetrachloride is Carcinogen, Target Organ Effect, Toxic by inhalation. Toxic by ingestion, Toxic by skin absorption. Please, obtain special instructions before use. Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray. Wash skin thoroughly after handling. Wear protective gloves/ protective clothing/ eye protection/ face protection. If inhaled: Remove person to fresh air and keep comfortable for breathing. call a poison center/doctor if you feel unwell. exposed or concerned: Get medical advice/ attention.

Analytical Data for the of Chlorinated Heterocycles



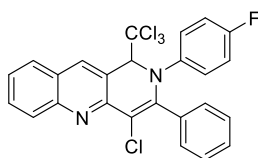
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3a).

The product was obtained as a yellow solid, mp: 148–150°C (211.5 mg, 87%); ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.19 (s, 1H), 7.91–7.88 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.81–7.77 (m, 1H), 7.56–7.52 (m, 1H), 7.35–7.31 (m, 2H), 7.29–7.23 (m, 3H), 7.14–7.09 (m, 2H), 6.96–6.93 (m, 1H), 5.57 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 149.3, 148.8, 147.1, 144.0, 138.6, 135.0, 131.4, 131.0, 129.9, 129.5, 129.4, 128.2, 128.0, 127.4, 126.9, 125.2, 123.9, 120.6, 119.6, 102.4, 78.5; HRMS (ESI) [M+H]⁺ Calcd for [C₂₅H₁₆Cl₄N₂] 485.0146, found 485.0153.



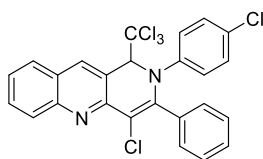
4-Chloro-3-phenyl-2-(*p*-tolyl)-1-(trichloromethyl)-1,2-

dihydrobenzo[*b*][1,6]naphthyridine (3b). The product was obtained as a yellow solid, mp: 218–220°C (225.3 mg, 90%); ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.5 Hz, 1H), 8.13 (s, 1H), 7.89–7.86 (m, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.80–7.76 (m, 1H), 7.55–7.51 (m, 1H), 7.35–7.31 (m, 2H), 7.29–7.25 (m, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 5.50 (s, 1H), 2.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 148.7, 144.6, 144.2, 138.4, 135.0, 134.9, 131.2, 130.8, 129.8, 129.7, 129.3, 128.0, 127.9, 127.2, 126.7, 123.9, 120.2, 118.9, 102.2, 78.4, 20.8; HRMS (ESI) [M+H]⁺ Calcd for [C₂₆H₁₈Cl₄N₂] 499.0302, found 499.0286.



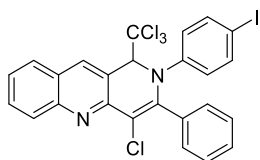
4-Chloro-2-(4-fluorophenyl)-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[*b*][1,6]naphthyridine (3c). The product was obtained as a yellow solid, mp: 148–150°C (201.1 mg, 80%); ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 7.87–7.85 (m, 3H), 7.83–7.78 (m, 1H), 7.58–7.54 (m, 1H), 7.37–7.33 (m, 2H), 7.31–7.27 (m, 1H), 7.24–7.21 (m, 2H), 6.84–6.78 (m, 2H), 5.48 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0 (d, *J*_{C-F} = 245.6 Hz), 149.0, 148.7, 144.1, 143.1, 138.5, 134.7, 131.1, 131.0, 129.6 (d, *J*_{C-F} = 23.1 Hz), 128.1, 127.9, 127.3, 126.9, 125.9 (d, *J*_{C-F} = 7.7 Hz), 120.0, 119.2, 116.1 (d, *J*_{C-F} = 23.1 Hz), 102.1, 78.5; HRMS (ESI) [M+H]⁺ Calcd for [C₂₅H₁₅Cl₄FN₂] 503.0052, found 503.0085.



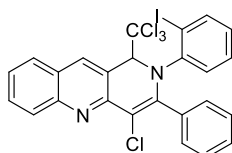
4-Chloro-2-(4-chlorophenyl)-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[*b*][1,6]naphthyridine (3d). The product was obtained as a yellow solid, mp: 184–186°C (202.2 mg, 78%); ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.7 Hz, 1H), 8.20 (s, 1H), 7.89–7.84 (m, 3H), 7.82–7.78 (m, 1H), 7.557–7.53 (m, 1H), 7.37–7.28 (m, 3H), 7.20–7.17 (m, 2H), 7.09–7.06 (m, 2H), 5.50 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.9, 148.7, 145.5, 143.3, 138.4, 134.5, 131.1, 131.0, 130.5, 129.7, 129.6, 129.3, 128.2, 127.9, 127.3, 127.0, 125.0, 120.2, 119.9, 101.9, 78.3; HRMS (ESI) [M+H]⁺ Calcd for [C₂₅H₁₅Cl₅N₂] 518.9756, found 518.9751.



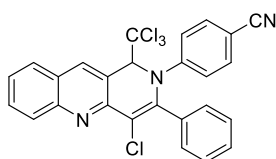
4-Chloro-2-(4-iodophenyl)-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[b][1,6]naphthyridine (3e). The product was obtained as a yellow solid, mp: 225–227°C (263.5 mg, 86%); ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, J = 8.7 Hz, 1H), 8.22 (s, 1H), 7.89–7.87 (m, 2H), 7.85–7.79 (m, 2H), 7.58–7.54 (m, 1H), 7.43–7.40 (m, 2H), 7.38–7.29 (m, 3H), 7.02–7.00 (m, 2H), 5.52 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.6, 148.4, 146.4, 142.7, 138.2, 137.9, 134.2, 130.8, 131.7, 129.5, 129.3, 127.9, 127.6, 127.0, 126.7, 125.2, 120.0, 119.9, 101.7, 88.8, 77.9; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{25}\text{H}_{15}\text{Cl}_4\text{IN}_2]$ 610.9112, found 610.9084.



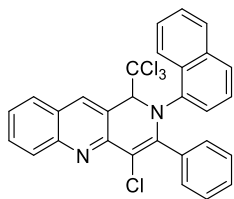
4-Chloro-2-(2-iodophenyl)-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[b][1,6]naphthyridine (3f). The product was obtained as a yellow solid, mp: 115–117°C (260.1 mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ 8.26–8.25 (m, 2H), 7.89 (d, J = 7.1 Hz, 1H), 7.80–7.75 (m, 1H), 7.72–7.66 (m, 2H), 7.55–7.49 (m, 3H), 7.30–7.25 (m, 3H), 7.10–7.06 (m, 1H), 6.81–6.77 (m, 1H), 5.49 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 148.9, 148.1, 145.6, 141.1, 138.9, 136.0, 135.2, 131.0, 130.0, 129.9, 129.7, 129.5, 128.4, 128.34, 128.3, 127.5, 126.5, 121.4, 114.9, 103.4, 99.3, 77.8; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{25}\text{H}_{15}\text{Cl}_4\text{IN}_2]$ 610.9112, found 610.9092.



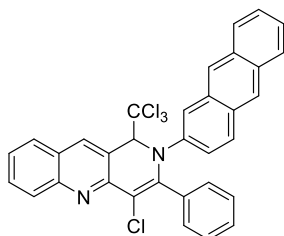
4-(4-Chloro-3-phenyl-1-(trichloromethyl)benzo[b][1,6]naphthyridin-2(1H)-

yl)benzonitrile (3g). The product was obtained as a yellow solid, mp: 187–189°C (153.8 mg, 60%); ^1H NMR (400 MHz, CDCl_3) δ 8.27–8.25 (m, 2H), 7.90–7.88 (m, 2H), 7.85–7.78 (m, 2H), 7.58–7.54 (m, 1H), 7.39–7.36 (m, 3H), 7.34–7.29 (m, 4H), 5.65 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 148.6, 148.5, 141.4, 138.2, 134.0, 133.1, 131.1, 130.9, 129.7, 128.3, 127.8, 127.3, 122.6, 121.9, 120.5, 118.4, 107.3, 101.4, 77.3; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{26}\text{H}_{15}\text{Cl}_4\text{N}_3]$ 510.0098, found 510.0069.



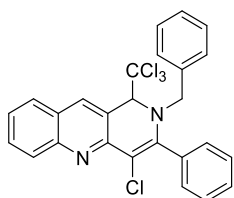
4-Chloro-2-(naphthalen-1-yl)-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[b][1,6]naphthyridine (3h). The product was obtained as a light brown solid, mp: 219–221°C (198.7 mg, 74%); ^1H NMR (400 MHz, CDCl_3) δ 8.33 (d, J = 8.5 Hz, 1H), 8.23 (s, 1H), 7.88–7.81 (m, 3H), 7.74 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.58–7.53 (m, 1H), 7.35–7.22 (m, 4H), 7.20–7.08 (m, 5H), 5.53 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9, 148.8, 148.6, 142.1, 138.7, 135.1, 134.6, 132.5, 131.5, 130.9, 129.7, 129.7, 129.0, 128.9, 128.6, 128.1, 127.9, 127.3, 127.3, 126.3, 126.1, 124.9, 122.2, 119.4, 112.6, 103.10, 77.6; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{29}\text{H}_{18}\text{Cl}_4\text{N}_2]$ 535.0302, found 535.0312.



2-(Anthracen-2-yl)-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-

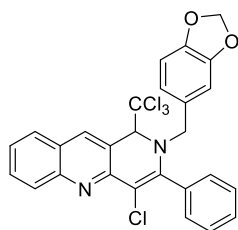
dihydrobenzo[b][1,6]naphthyridine (3i). The product was obtained as a brown semi solid, mp: 228–230°C (175.9 mg, 60%); ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, J = 8.5 Hz, 1H), 8.24–8.23 (m, 2H), 8.15 (s, 1H), 8.02–8.00 (m, 2H), 7.89–7.87 (m, 2H), 7.84–7.78 (m, 3H), 7.73–7.72 (m, 1H), 7.56–7.51 (m, 2H), 7.42–7.38 (m, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.24–7.20 (m, 1H), 5.76 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 149.2, 148.7, 143.7, 143.6, 138.5, 134.9, 132.2, 131.5, 131.4, 131.1, 130.9, 129.8, 129.7, 129.4, 129.2, 128.2, 128.1, 127.9, 127.8, 127.3, 126.8, 126.1, 125.9, 125.7, 125.4, 122.7, 121.1, 120.5, 119.8, 102.1, 78.0; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{33}\text{H}_{20}\text{Cl}_4\text{N}_2]$ 585.0459, found 585.047.



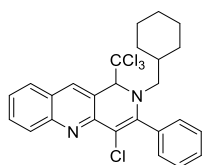
2-Benzyl-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine

(3j). The product was obtained as a yellow solid, mp: 92–94°C (185.9 mg, 75%); ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, J = 8.5 Hz, 1H), 8.00 (s, 1H), 7.78–7.73 (m, 2H), 7.71–7.68 (m,

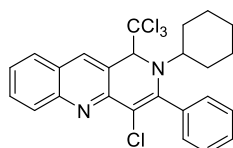
2H), 7.52–7.46 (m, 4H), 7.09–7.06 (m, 3H), 6.93–6.91 (m, 2H), 5.25 (s, 1H), 4.60–4.56 (m, 1H), 4.47–4.43 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.3, 148.6, 148.2, 137.8, 137.6, 134.6, 130.7, 130.4, 129.7, 129.4, 128.8, 128.6, 127.8, 127.2, 127.0, 126.0, 119.4, 111.6, 103.6, 74.81, 59.7; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{26}\text{H}_{18}\text{Cl}_4\text{N}_2]$ 499.0302, found 499.0341.



2-(Benzo[d][1,3]dioxol-5-ylmethyl)-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3k). The product was obtained as a yellow solid, mp: 164–166°C (217.4 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, J = 8.7 Hz, 1H), 8.04 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.79–7.68 (m, 3H), 7.51–7.40 (m, 4H), 6.52–6.50 (m, 1H), 6.40–6.38 (m, 2H), 5.78–5.75 (m, 2H), 5.25 (s, 1H), 4.45 (d, J = 15.6 Hz, 1H), 4.30 (d, J = 15.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.2, 148.4, 148.2, 148.0, 147.3, 138.0, 134.5, 131.1, 130.8, 130.4, 129.8, 129.2, 128.7, 127.9, 127.0, 126.1, 120.9, 119.4, 111.6, 108.4, 107.7, 103.6, 101.1, 74.4, 59.6; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{27}\text{H}_{18}\text{Cl}_4\text{N}_2\text{O}_2]$ 543.0201, found 543.0174.

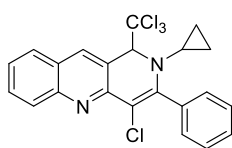


4-Chloro-2-(cyclohexylmethyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3l). The product was obtained as a yellow solid, mp: 195–197°C (177.8 mg, 70%); ^1H NMR (400 MHz, CDCl_3) δ 8.23–8.21 (m, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.77–7.73 (m, 1H), 7.68–7.66 (m, 2H), 7.52–7.43 (m, 4H), 5.21 (s, 1H), 3.31–3.25 (m, 1H), 3.13–3.08 (m, 1H), 1.48–1.34 (m, 4H), 1.28–1.24 (m, 2H), 1.03–0.83 (m, 3H), 0.71–0.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.5, 148.7, 148.3, 137.9, 134.5, 130.7, 129.5, 129.4, 128.4, 127.9, 127.1, 125.9, 119.7, 110.6, 103.6, 75.9, 63.0, 39.0, 30.9, 30.5, 26.1, 25.8, 25.7; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{26}\text{H}_{24}\text{Cl}_4\text{N}_2]$ 505.0772, found 505.0747.



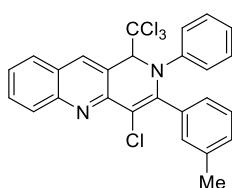
4-Chloro-2-cyclohexyl-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[*b*][1,6]naphthyridin (3m). The product was obtained as a yellow solid, mp:169–171°C (196.5 mg, 80%); ¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.89–7.83 (m, 3H), 7.78–7.73 (m, 1H), 7.54–7.45 (m, 4H), 5.19 (s, 1H), 3.01–2.94 (m, 1H), 2.17–2.14 (m, 1H), 1.86–1.73 (m, 1H), 1.61–1.55 (m, 1H), 1.48–1.40 (m, 2H), 1.30–1.23 (m, 1H), 1.02–0.85 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 149.9, 148.6, 147.8, 137.7, 135.9, 130.5, 130.45, 129.6, 128.3, 127.8, 127.4, 126.2, 122.0, 116.5, 102.8, 76.8, 69.7, 63.3, 32.1, 30.9, 25.9, 25.4; HRMS (ESI) [M+H]⁺ Calcd for [C₂₅H₂₂Cl₄N₂] 491.0615, found 491.0638.



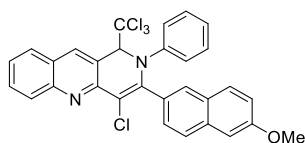
4-4-Chloro-2-cyclopentyl-3-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[*b*][1,6]naphthyridine (3n). The product was obtained as a brown solid, mp:109–111°C (199.8 mg, 89%); ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.24 (s, 1H), 7.87–7.84 (m, 1H), 7.77–7.72 (m, 3H), 7.53–7.47 (m, 3H), 7.45–7.41 (m, 1H), 5.39 (s, 1H), 3.17–3.12 (m, 1H), 0.71–0.66 (m, 1H), 0.53–0.47 (m, 2H), 0.35–0.28 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 149.1, 148.5, 148.4, 138.1, 135.4, 131.1, 130.5, 129.5, 129.3, 128.4, 128.0, 127.1, 126.4, 120.2, 110.5, 103.8, 77.7, 39.7, 12.3, 9.5; HRMS (ESI) [M+H]⁺ Calcd for [C₂₂H₁₆Cl₄N₂] 449.0146, found 449.0132.



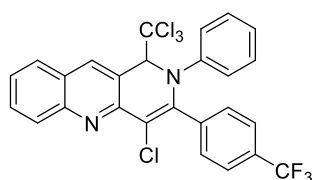
4-Chloro-2-phenyl-3-(*m*-tolyl)-1-(trichloromethyl)-1,2-

dihydrobenzo[*b*][1,6]naphthyridine (3o). The product was obtained as a yellow solid, mp 188–191°C (219.6 mg, 88%); ¹H NMR (400 MHz, CDCl₃) δ 8.29–8.26 (m, 1H), 8.21 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.81–7.77 (m, 1H), 7.69 (d, *J* = 9.6 Hz, 2H), 7.56–7.52 (m, 1H), 7.27–7.20 (m, 4H), 7.14–7.08 (m, 2H), 6.98–6.94 (m, 1H), 5.57 (s, 1H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 148.7, 146.9, 144.0, 138.3, 137.5, 134.7, 131.7, 130.8, 130.2, 129.7, 129.2, 128.4, 127.8, 127.2, 126.7, 125.0, 123.8, 120.4, 102.2, 78.3, 21.7; HRMS (ESI) [M+H]⁺ Calcd for [C₂₆H₁₈Cl₄N₂] 499.0302, found 499.0298.



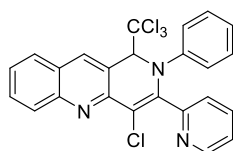
4-Chloro-3-(6-methoxynaphthalen-2-yl)-2-phenyl-1-(trichloromethyl)-1,2-

dihydrobenzo[b][1,6]naphthyridine (3p). The product was obtained as a brown solid, mp: 218–221°C (237.2 mg, 84%); ^1H NMR (400 MHz, CDCl_3) δ 8.31–8.27 (m, 2H), 8.22 (s, 1H), 7.98–7.95 (m, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.81–7.77 (m, 1H), 7.73 (d, J = 8.9 Hz, 1H), 7.67 (d, J = 8.7 Hz, 1H), 7.56–7.52 (m, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.12–7.05 (m, 4H), 6.90–6.86 (m, 1H), 5.62 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 149.6, 148.9, 147.3, 144.3, 138.7, 135.1, 131.5, 131.1, 130.6, 130.4, 129.9, 129.5, 128.9, 128.5, 128.1, 127.5, 127.0, 126.6, 125.2, 123.9, 120.7, 119.4, 105.9, 102.5, 78.7, 55.7; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{30}\text{H}_{20}\text{Cl}_4\text{N}_2\text{O}]$ 565.0408, found 565.0394.



4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-

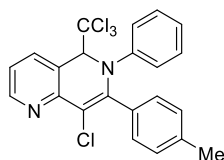
dihydrobenzo[b][1,6]naphthyridine (3q). The product was obtained as a yellow solid, mp: 228–230°C (193.8 mg, 70%); ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, J = 8.5 Hz, 1H), 8.18 (s, 1H), 8.02 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.82–7.78 (m, 1H), 7.60–7.58 (m, 2H), 7.56–7.54 (m, 1H), 7.23 (d, J = 7.8 Hz, 2H), 7.16–7.12 (m, 2H), 7.00–6.96 (m, 1H), 5.56 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.6, 146.4, 142.1, 138.4, 131.3, 130.9, 129.6, 129.4, 127.8, 127.3, 127.0, 125.3, 124.9 (d, $J_{\text{C-F}}$ = 2.9 Hz), 123.6, 120.7, 120.2, 101.9, 78.1; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{26}\text{H}_{15}\text{Cl}_4\text{F}_3\text{N}_2]$ 553.0020, found 553.0033.



4-Chloro-2-phenyl-3-(pyridin-2-yl)-1-(trichloromethyl)-1,2-

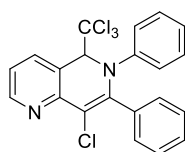
dihydrobenzo[b][1,6]naphthyridine (3r). The product was obtained as a yellow solid, mp: 148–150°C (187.5 mg, 77%); ^1H NMR (400 MHz, CDCl_3) δ 8.72–8.71 (m, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.24 (s, 1H), 7.86–7.77 (m, 3H), 7.66–7.62 (m, 1H), 7.57–7.53 (m, 1H), 7.37–7.34 (m, 2H), 7.20–7.11 (m, 3H), 6.98–6.93 (m, 1H), 5.65 (s, 1H); ^{13}C NMR (100 MHz,

CDCl₃) δ 154.2, 149.1, 148.8, 148.7, 146.6, 142.0, 138.3, 136.5, 130.8, 129.9, 129.2, 129.1, 127.8, 127.3, 126.9, 125.2, 124.8, 123.4, 123.2, 121.4, 120.3, 120.1, 102.3, 78.1; HRMS (ESI) [M+H]⁺ Calcd for [C₂₄H₁₅Cl₄N₃] 486.0098, found 486.0084.

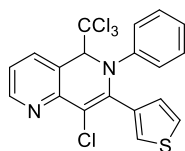


8-Chloro-6-phenyl-7-(p-tolyl)-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine(4a).

The product was obtained as a brown solid, mp: 165–167°C (173.9 mg, 77%); ¹H NMR (400 MHz, CDCl₃) δ 8.80–8.79 (m, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.73–7.71 (m, 1H), 7.30–7.23 (m, 3H), 7.15–7.10 (m, 4H), 6.97–6.93 (m, 1H), 5.43 (s, 1H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.5, 149.5, 146.6, 141.8, 139.1, 137.9, 131.5, 130.8, 128.9, 128.6, 124.6, 123.3, 122.0, 120.7, 118.2, 115.0, 101.7, 76.7, 21.1; HRMS (ESI) [M+H]⁺ Calcd for [C₂₂H₁₆Cl₄N₂] 449.0146, found 449.0151.

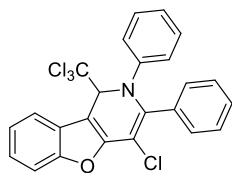


8-Chloro-6,7-diphenyl-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4b). The product was obtained as a brown solid, mp: 182–184°C (174.5 mg, 80%); ¹H NMR (400 MHz, CDCl₃) δ 8.81–8.80 (m, 1H), 7.88–7.85 (m, 2H), 7.74–7.72 (m, 1H), 7.33–7.24 (m, 6H), 7.14–7.10 (m, 2H), 6.97–6.93 (m, 1H), 5.44 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 149.6, 146.7, 142.0, 138.2, 134.6, 131.1, 129.2, 129.1, 128.0, 125.0, 123.6, 122.3, 120.9, 118.8, 101.9, 77.9; HRMS (ESI) [M+H]⁺ Calcd for [C₂₁H₁₄Cl₄N₂] 434.9989, found 434.9993.



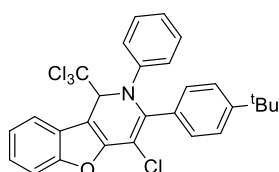
8-Chloro-6-phenyl-7-(thiophen-3-yl)-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4c). The product was obtained as a brown solid, mp: 192–194°C (163.5 mg, 74%); ¹H NMR (400 MHz, CDCl₃) δ 8.80–8.79 (m, 1H), 7.87–7.86 (m, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 5.0 Hz, 1H), 7.30–7.26 (m, 1H), 7.22–7.20 (m, 3H), 7.15 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.1 Hz, 1H), 5.44 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 149.6, 147.1, 138.0, 137.0,

136.0, 129.7, 129.6, 129.2, 124.8, 124.6, 122.5, 122.3, 121.3, 118.6, 102.0, 76.8; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{19}H_{12}Cl_4N_2S]$ 440.9554, found 440.9550.



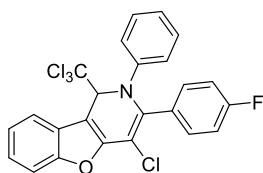
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5a).

The product was obtained as a pale yellow solid, mp:174–176°C (208.0 mg, 88%); 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.58–7.56 (m, 2H), 7.34–7.21 (m, 7H), 7.12 (t, J = 7.8 Hz, 2H), 6.96–6.93 (m, 1H), 5.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 151.6, 147.4, 140.6, 134.0, 130.9, 129.2, 128.1, 126.9, 125.1, 124.8, 123.9, 123.7, 120.5, 111.9, 108.2, 106.1, 103.2, 75.2; (ESI) $[M+H]^+$ Calcd for $[C_{24}H_{15}Cl_4NO]$ 473.9986, found 473.9975.



3-(4-(tert-Butyl)phenyl)-4-chloro-2-phenyl-1-(trichloromethyl)-1,2-

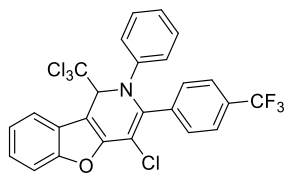
dihydrobenzofuro[3,2-c]pyridine (5b). The product was obtained as a yellow solid, mp: 127–129°C (225.1 mg, 85%); 1H NMR (400 MHz, $CDCl_3$) δ 7.79–7.76 (m, 2H), 7.59–7.56 (m, 2H), 7.35–7.31 (m, 5H), 7.29–7.27 (m, 1H), 7.17–7.12 (m, 2H), 6.96 (t, J = 7.4 Hz, 1H), 5.70 (s, 1H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 152.2, 151.7, 147.6, 140.4, 131.0, 130.5, 129.1, 126.9, 125.0, 124.7, 124.6, 123.7, 123.5, 120.4, 111.8, 108.0, 106.0, 103.0, 75.2, 34.81, 31.2; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{28}H_{23}Cl_4NO]$ 530.0612, found 530.0596.



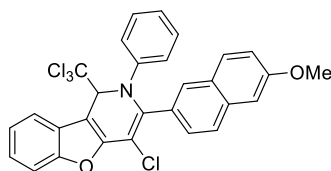
4-Chloro-3-(4-fluorophenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-

c]pyridine (5c). The product was obtained as a yellow solid, mp:178–180°C (196.5 mg, 80%); 1H NMR (400 MHz, $CDCl_3$) δ 7.76–7.73 (m, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.26–7.21 (m, 3H), 7.19–7.18 (m, 2H), 7.08 (t, J = 7.3 Hz, 2H), 6.95–6.91 (m, 2H), 5.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 147.2, 139.6, 132.9 (d, J_{C-F} = 8.7 Hz), 129.2, 126.6, 124.8

(d, $J_{C-F} = 45.3$ Hz), 123.9, 123.8, 120.5, 115.3 (d, $J_{C-F} = 21.2$ Hz), 111.9, 106.2, 103.1, 75.2; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{24}H_{14}Cl_4FNO]$ 491.9892, found 491.9848.

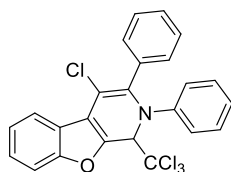


4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5d). The product was obtained as a brown solid, mp: 152–154°C (210.5 mg, 78%); 1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, $J = 7.8$ Hz, 2H), 7.64–7.53 (m, 4H), 7.36–7.28 (m, 4H), 7.18–7.14 (m, 2H), 7.03–6.99 (m, 1H), 5.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 150.9, 146.8, 138.7, 137.4, 131.0, 129.3, 126.5, 125.3, 125.0, 124.9 (q, $J_{C-F} = 2.9$ Hz) 123.8, 123.6, 120.5, 111.8, 106.7, 102.8, 75.0; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{25}H_{14}Cl_4F_3NO]$ 541.9860, found 541.9855.



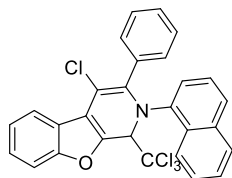
H

4-Chloro-3-(6-methoxynaphthalen-2-yl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5e). The product was obtained as a yellow solid, mp: 210–212°C (240.3 mg, 87%); 1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.93–7.90 (m, 1H), 7.73 (d, $J = 9.1$ Hz, 1H), 7.66–7.63 (m, 1H), 7.60–7.59 (m, 2H), 7.40–7.37 (m, 2H), 7.32–7.23 (m, 2H), 7.13–7.07 (m, 3H), 7.04 (d, $J = 2.3$ Hz, 1H), 6.92–6.88 (m, 1H), 5.75 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 155.9, 151.8, 147.6, 140.8, 134.6, 131.0, 130.3, 129.4, 129.2, 128.4, 128.3, 127.0, 126.4, 125.1, 124.7, 123.8, 120.5, 119.2, 111.9, 105.7, 103.3, 75.3, 55.5; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{29}H_{19}Cl_4NO_2]$ 553.0170, found 554.0249.

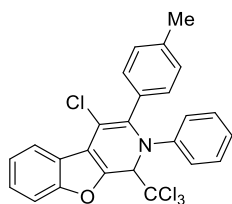


4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6a). The product was obtained as a brown semi-solid (210.6 mg, 89%); 1H NMR (400 MHz,

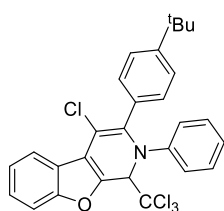
CDCl₃) δ 8.19–8.16 (m, 1H), 7.87–7.85 (m, 2H), 7.53–7.51 (m, 1H), 7.38–7.36 (m, 2H), 7.32–7.28 (m, 4H), 7.23–7.20 (m, 1H), 7.14–7.10 (m, 2H), 6.96–6.92 (m, 1H), 5.72 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 147.2, 142.8, 135.3, 134.2, 130.9, 129.2, 128.6, 128.0, 125.6, 124.9, 124.3, 123.7, 123.1, 121.7, 116.9, 112.4, 112.1, 100.8, 74.7; HRMS (ESI) [M+H]⁺ Calcd for [C₂₄H₁₅Cl₄NO] 473.9986, found 473.9981.



4-Chloro-2-(naphthalen-1-yl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6b). The product was obtained as a brown solid, mp: 190–192°C (191.5 mg, 73%); ¹H NMR (400 MHz, CDCl₃) δ 8.26–8.24 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.72–7.70 (m, 1H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.49–7.35 (m, 4H), 7.22–7.13 (m, 7H), 5.71 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.2, 143.0, 141.1, 139.7, 134.7, 134.4, 132.2, 130.2, 128.9, 128.6, 128.5, 127.8, 127.6, 126.1, 125.7, 124.7, 124.3, 123.6, 122.0, 116.9, 114.1, 112.2, 102.3, 74.5; HRMS (ESI) [M+H]⁺ Calcd for [C₂₈H₁₇Cl₄NO] 524.0143, found 524.0112.

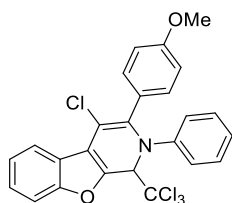


4-Chloro-2-phenyl-3-(p-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6c). The product was obtained as a brown solid, mp: 135–137°C (209.2 mg, 86%); ¹H NMR (400 MHz, CDCl₃) δ 8.18–8.16 (m, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.53–7.51 (m, 1H), 7.40–7.36 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.15–7.11 (m, 4H), 6.96 (t, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 156.3, 147.5, 142.9, 138.7, 135.5, 131.3, 130.9, 129.3, 128.9, 125.7, 124.9, 124.5, 123.8, 123.2, 121.7, 112.2, 100.9, 74.9, 21.6; HRMS (ESI) [M+H]⁺ Calcd for [C₂₅H₁₇Cl₄NO] 488.0143, found 488.0175.

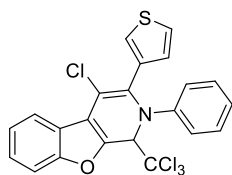


3-(4-(*tert*-Butyl)phenyl)-4-chloro-2-phenyl-1-(trichloromethyl)-1,2-

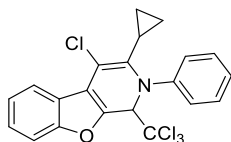
dihydrobenzofuro[2,3-*c*]pyridine (6d). The product was obtained as a yellow solid, mp: 230–232°C (230.3 mg, 87%); ^1H NMR (400 MHz, CDCl_3) δ 8.18–8.16 (m, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.52–7.50 (m, 1H), 7.36 (t, J = 4.1 Hz, 2H), 7.31 (d, J = 8.2 Hz, 4H), 7.15–7.11 (m, 2H), 6.94 (t, J = 7.3 Hz, 1H), 5.70 (s, 1H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.1, 151.5, 147.4, 142.8, 135.1, 131.0, 130.5, 129.1, 125.5, 124.9, 124.6, 124.3, 123.6, 122.8, 121.6, 117.0, 112.1, 100.8, 74.7, 34.7, 31.3; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{28}\text{H}_{23}\text{Cl}_4\text{NO}]$ 529.0534, found 530.0613.



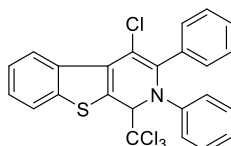
4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-*c*]pyridine (6e). The product was obtained as a green solid, mp: 182–184°C (214.4 mg, 85%); ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.07 (m, 1H), 7.71 (d, J = 8.2 Hz, 2H), 7.44–7.42 (m, 1H), 7.31–7.26 (m, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.04 (t, J = 7.6 Hz, 2H), 6.88–6.85 (m, 1H), 6.75 (d, J = 8.2 Hz, 2H), 5.62 (s, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 155.7, 147.0, 142.2, 134.7, 131.8, 128.7, 126.1, 125.1, 124.3, 123.9, 123.2, 122.6, 121.1, 116.6, 113.0, 111.7, 110.8, 100.4, 74.3, 55.8; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{25}\text{H}_{17}\text{Cl}_4\text{NO}_2]$ 504.0092, found 504.0106.



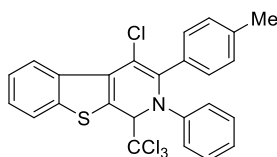
4-Chloro-2-phenyl-3-(thiophen-3-yl)-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-*c*]pyridine (6f). The product was obtained as a brown solid, mp: 184–186°C (208.5 mg, 90%); ^1H NMR (400 MHz, CDCl_3) δ 8.19–8.15 (m, 1H), 7.78–7.77 (m, 1H), 7.60–7.58 (m, 1H), 7.53–7.50 (m, 1H), 7.40–7.36 (m, 2H), 7.30–7.28 (m, 2H), 7.22–7.19 (m, 1H), 7.18–7.14 (m, 2H), 7.00–7.96 (m, 1H), 5.70 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 147.4, 142.9, 135.6, 130.4, 129.2, 129.1, 127.7, 125.4, 124.6, 124.4, 124.1, 123.5, 121.9, 121.4, 116.7, 112.1, 111.9, 74.4; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{22}\text{H}_{13}\text{Cl}_4\text{NOS}]$ 479.9550, found 479.9526.



4-Chloro-3-cyclopropyl-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6g). The product was obtained as a brown solid, mp:178–180°C (175.5 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ 8.21–8.17 (m, 1H), 7.55–7.50 (m, 1H), 7.40–7.32 (m, 6H), 7.17–7.14 (m, 1H), 5.58 (s, 1H), 2.10–2.03 (m, 1H), 1.00–0.96 (m, 1H), 0.94–0.86 (m, 1H), 0.75–0.79 (m, 1H), 0.60–0.53 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 147.8, 142.0, 135.7, 129.4, 125.4, 124.8, 123.9, 123.6, 121.9, 121.5, 116.5, 114.8, 112.1, 101.0, 74.9, 12.8, 8.0, 6.2; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{21}\text{H}_{15}\text{Cl}_4\text{NO}]$ 437.9986, found 437.9988.

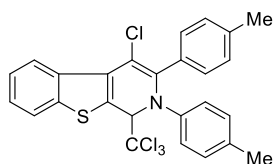


4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7a). The product was obtained as a brown solid, mp:164–166°C (171.7 mg, 70%); ^1H NMR (400 MHz, CDCl_3) δ 8.74 (d, J = 8.1 Hz, 1H), 7.89–7.87 (m, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.49–7.45 (m, 1H), 7.42–7.38 (m, 1H), 7.33–7.29 (m, 2H), 7.27–7.22 (m, 3H), 7.12–7.08 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 5.66 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.6, 140.8, 137.1, 134.8, 134.1, 131.1, 128.9, 128.6, 127.8, 125.8, 125.3, 124.7, 124.6, 124.5, 122.8, 122.4, 115.7, 101.4, 75.9; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{24}\text{H}_{15}\text{Cl}_4\text{NS}]$ 489.9758, found 489.9721.

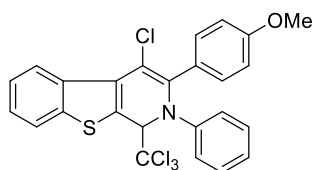


4-Chloro-2-phenyl-3-(p-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7b). The product was obtained as a yellow solid, mp:156–158°C (171.5 mg, 68%); ^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, J = 8.1 Hz, 1H), 7.81–7.76 (m, 3H), 7.49–7.45 (m, 1H), 7.42–7.38 (m, 1H), 7.26–7.24 (m, 2H), 7.13–7.08 (m, 4H), 6.92 (t, J = 7.4 Hz, 1H), 5.65 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 141.0, 138.8, 137.3, 135.1,

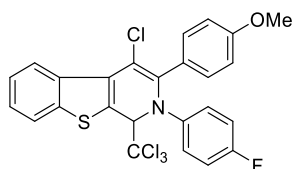
131.2, 129.1, 128.9, 125.8, 125.4, 124.8, 124.7, 124.6, 122.9, 122.6, 115.5, 101.6, 76.2, 21.6; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{25}H_{17}Cl_4NS]$ 503.9914, found 503.9901.



4-Chloro-2,3-di-p-tolyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7c). The product was obtained as a yellow solid, mp: 160–162°C (163.5 mg, 63%); 1H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 8.2 Hz, 1H), 7.80 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.49–7.45 (m, 1H), 7.42–7.38 (m, 1H), 7.15–7.11 (m, 4H), 6.90 (d, J = 8.2 Hz, 2H), 5.62 (s, 1H), 2.29 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 141.2, 138.9, 137.7, 135.3, 134.5, 131.7, 131.3, 130.6, 129.8, 128.9, 125.7, 125.5, 125.0, 124.8, 123.2, 122.8, 115.1, 101.9, 76.5, 21.7, 21.0; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{26}H_{19}Cl_4NS]$ 518.0071, found 518.0052.

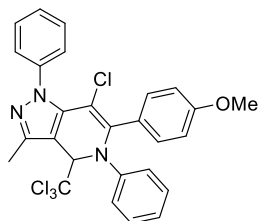


4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7d). The product was obtained as a brown semisolid (166.5 mg, 64%); 1H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.2 Hz, 1H), 7.84–7.81 (m, 3H), 7.50–7.46 (m, 1H), 7.43–7.39 (m, 1H), 7.26–7.24 (m, 2H), 7.14–7.10 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.86–6.83 (m, 2H), 5.65 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 146.7, 140.7, 136.7, 134.8, 132.4, 130.3, 128.8, 126.4, 125.4, 125.2, 124.6, 124.5, 124.3, 122.7, 122.3, 114.6, 113.3, 101.4, 75.9, 55.0; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{25}H_{17}Cl_4NS]$ 519.9863, found 519.9842.

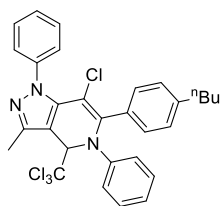


4-Chloro-2-(4-fluorophenyl)-3-(4-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7e). The product was obtained as a brown solid,

mp:152–154°C (161.9 mg, 60%); ^1H NMR (400 MHz, CDCl_3) δ 8.73 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.78–7.74 (m, 2H), 7.50–7.46 (m, 1H), 7.44–7.40 (m, 1H), 7.22–7.18 (m, 2H), 6.86–6.77 (m, 4H), 5.53 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 159.7 (d, $J_{\text{C-F}}$ = 251.4 Hz), 159.7, 143.1, 141.0, 137.2, 135.0, 132.6, 130.5, 126.3, 125.5, 124.9 (d, $J_{\text{C-F}}$ = 7.7 Hz), 124.7 (d, $J_{\text{C-F}}$ = 9.6 Hz), 122.59, 115.8 (d, $J_{\text{C-F}}$ = 23.1 Hz), 114.2, 113.3, 101.4, 76.5, 55.3; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{25}\text{H}_{16}\text{Cl}_4\text{FNOS}]$ 537.9769, found 537.9741.

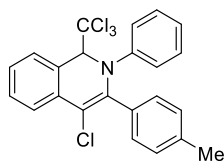


7-Chloro-6-(4-methoxyphenyl)-3-methyl-1,5-diphenyl-4-(trichloromethyl)-4,5-dihydro-1H-pyrazolo[4,3-c]pyridine (8a). The product was obtained as a yellow solid, mp: 91–93°C (239.7 mg, 88%); ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.45–7.41 (m, 1H), 7.29–7.25 (m, 2H), 7.19–7.15 (m, 2H), 7.00–6.96 (m, 1H), 6.80 (d, J = 8.7 Hz, 2H), 5.43 (s, 1H), 3.74 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 147.0, 146.1, 140.6, 139.8, 137.7, 132.6, 129.1, 128.8, 128.3, 126.3, 126.1, 124.3, 122.5, 115.2, 113.5, 111.9, 106.8, 103.6, 74.1, 55.3, 13.5; HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd for $[\text{C}_{27}\text{H}_{21}\text{Cl}_4\text{N}_3\text{O}]$ 544.0517, found 544.0522.

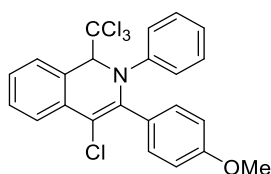


6-(4-Butylphenyl)-7-chloro-3-methyl-1,5-diphenyl-4-(trichloromethyl)-4,5-dihydro-1H-pyrazolo[4,3-c]pyridine (8b). The product was obtained as a red semisolid (236.5 mg, 83%); ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.54–7.49 (m, 2H), 7.45–7.41 (m, 1H), 7.27 (t, J = 8.5 Hz, 2H), 7.17 (t, J = 7.8 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.98–6.94 (t, J = 7.3 Hz, 1H), 5.44 (s, 1H), 2.55–2.50 (m, 2H), 2.38 (s, 3H), 1.57–1.50 (m, 2H), 1.33–1.25 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.0, 146.0, 144.2, 140.8, 139.7, 137.6, 131.2, 131.0, 129.1, 128.8, 128.3, 128.0, 126.1,

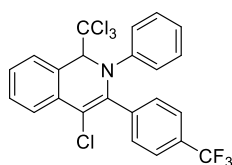
124.2, 122.4, 112.0, 107.5, 103.4, 74.1, 35.6, 33.2, 22.5, 14.0, 13.5; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{30}H_{27}Cl_4N_3]$ 570.1037, found 570.1046.



4-Chloro-2-phenyl-3-(*p*-tolyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (9a). The product was obtained as a colourless solid, mp:148–150°C (197.5 mg, 88%); 1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.55–7.51 (m, 1H), 7.43–7.41 (m, 1H), 7.37–7.33 (m, 1H), 7.25–7.23 (m, 2H), 7.14–7.10 (m, 4H), 6.92 (t, J = 7.3 Hz, 1H), 5.45 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 138.7, 137.4, 133.0, 132.2, 131.1, 130.3, 129.6, 129.0, 128.7, 127.5, 125.5, 124.3, 124.2, 123.1, 118.5, 102.6, 78.1, 21.5; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{23}H_{17}Cl_4N]$ 448.0193 found 448.0180.

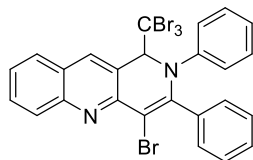


4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (9b). The product was obtained as a green solid, mp:146–148°C (194.8 mg, 84%); 1H NMR (400 MHz, $CDCl_3$) δ 7.91–7.77 (m, 3H), 7.55–7.50 (m, 1H), 7.42–7.32 (m, 2H), 7.28–7.20 (m, 2H), 7.15–7.09 (m, 2H), 6.93–6.82 (m, 3H), 5.43 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 147.3, 137.2, 133.2, 132.7, 130.4, 129.7, 129.1, 127.5, 125.7, 124.4, 124.2, 123.2, 118.2, 113.5, 102.8, 78.2, 55.4; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{23}H_{17}Cl_4NO]$ 464.0143, found 464.0142.



4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinoline (9c). The product was obtained as a brown solid, mp:129–131°C (200.6 mg, 80%); 1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.96 (m, 2H), 7.89–7.86 (m, 1H), 7.57–7.52 (m, 3H), 7.44–7.36 (m, 2H), 7.23–7.20 (m, 2H), 7.14–7.09 (m, 2H), 6.96–6.92 (m, 1H), 5.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 138.7, 135.9, 132.4, 131.4, 130.4, 129.7,

129.2, 128.2, 125.6, 124.9 (q, $J_{C-F} = 3.8$ Hz), 124.6, 124.5, 123.0, 120.3, 102.4, 77.9; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{23}H_{14}Cl_4F_3N]$ 501.9911, found 502.9928.

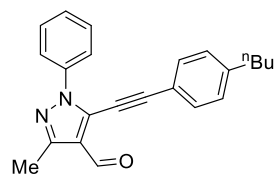


4-Bromo-2,3-diphenyl-1-(tribromomethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (10).

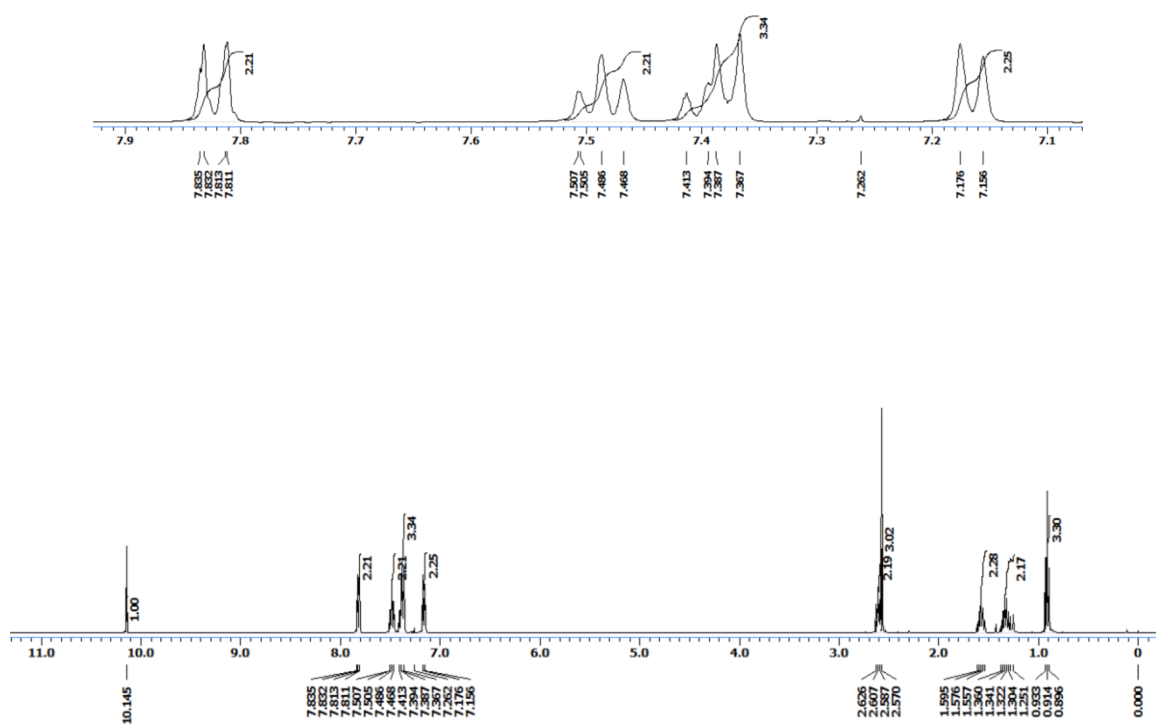
The product was obtained as a brown solid, mp:120–122°C (199.2 mg, 60%); 1H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (m, 2H), 7.96–7.94 (m, 2H), 7.88–7.85 (m, 1H), 7.83–7.79 (m, 1H), 7.56–7.52 (m, 1H), 7.35–7.28 (m, 5H), 7.12–7.08 (m, 2H), 6.96 (t, $J = 7.4$ Hz, 1H), 5.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 147.9, 146.6, 139.2, 135.9, 131.3, 130.8, 129.3, 129.2, 128.9, 127.6, 127.5, 127.0, 126.7, 125.2, 124.1, 120.3, 79.2, 49.9; HRMS (ESI) $[M+H]^+$ Calcd for $[C_{25}H_{16}Br_4N_2]$ 660.8125, found 660.8135.

Copies of ^1H and ^{13}C NMR

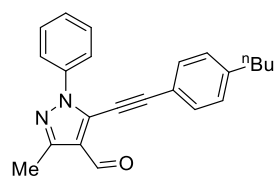
¹H NMR



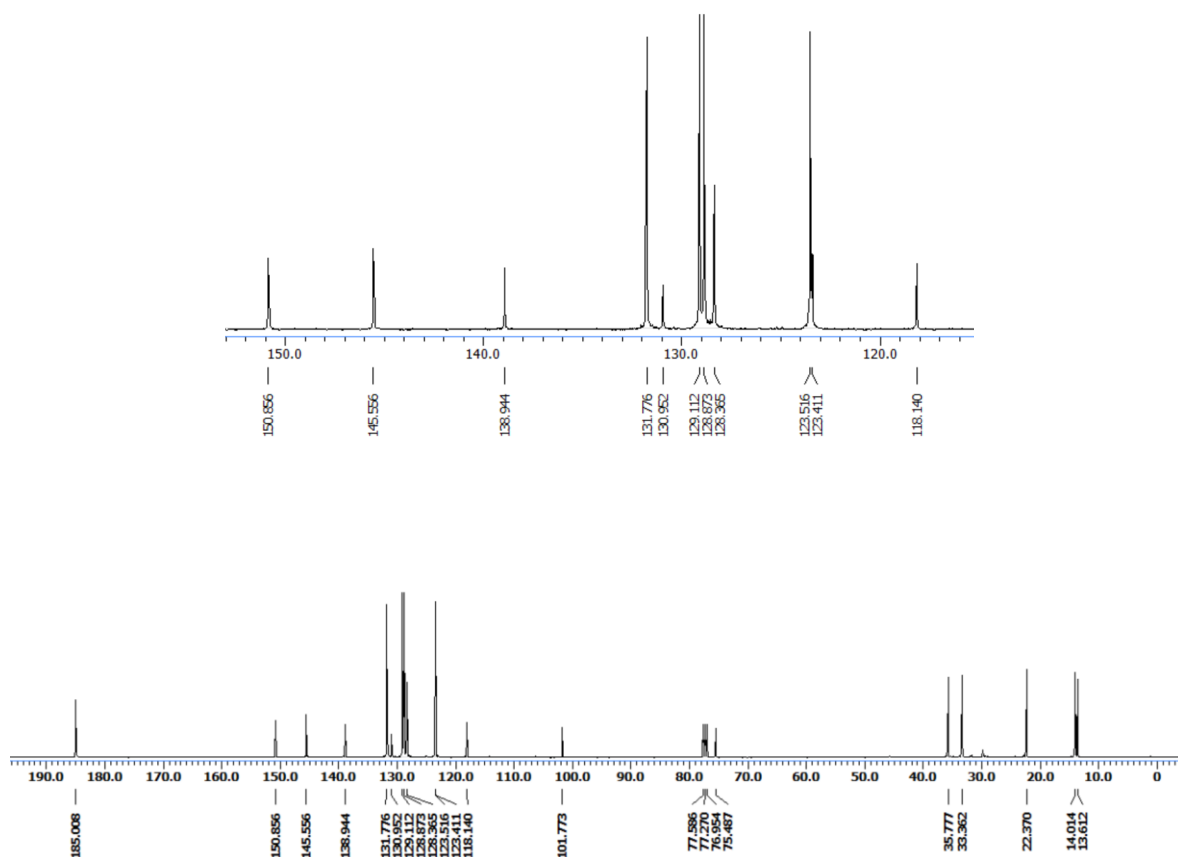
5-((4Butylphenyl)ethynyl)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (1x)



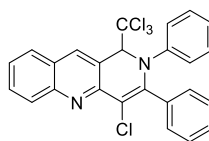
¹³C NMR



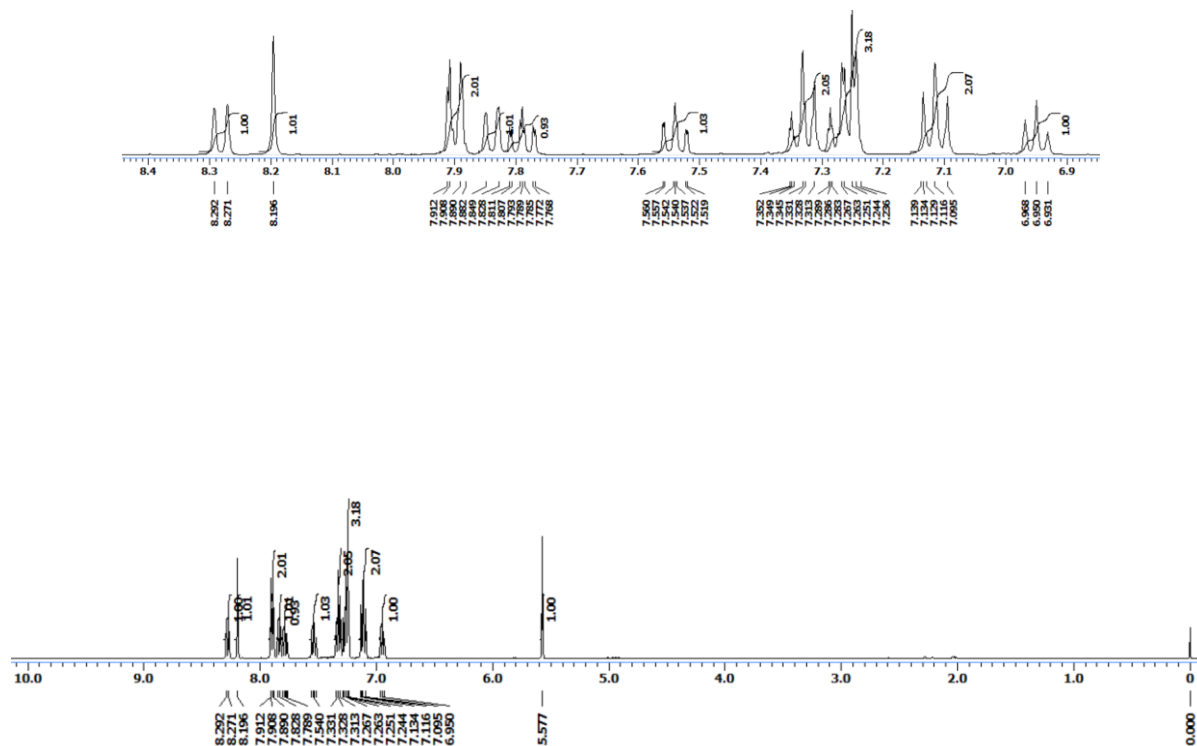
5-((4Butylphenyl)ethynyl)-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (1x)



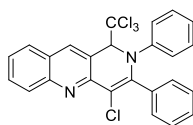
¹H NMR



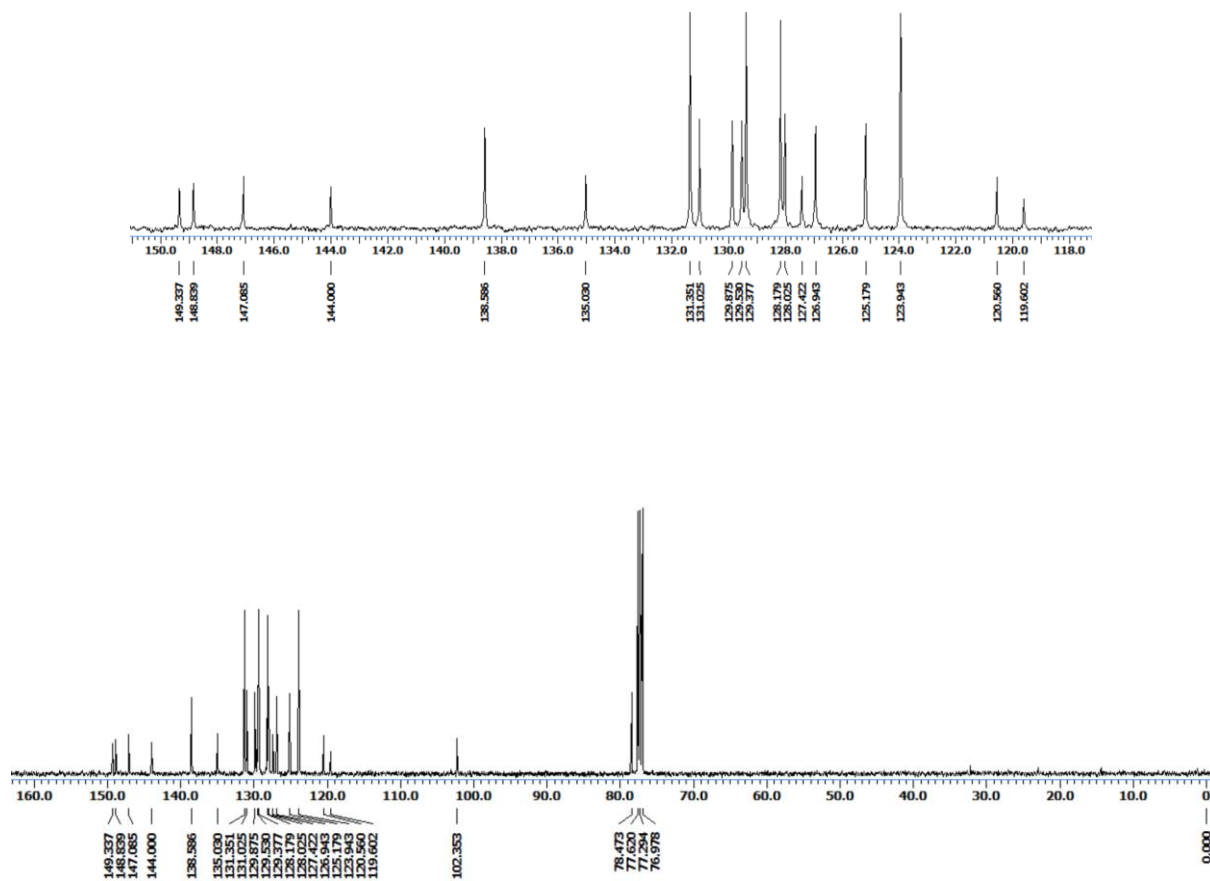
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (3a)



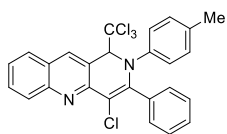
¹³C NMR



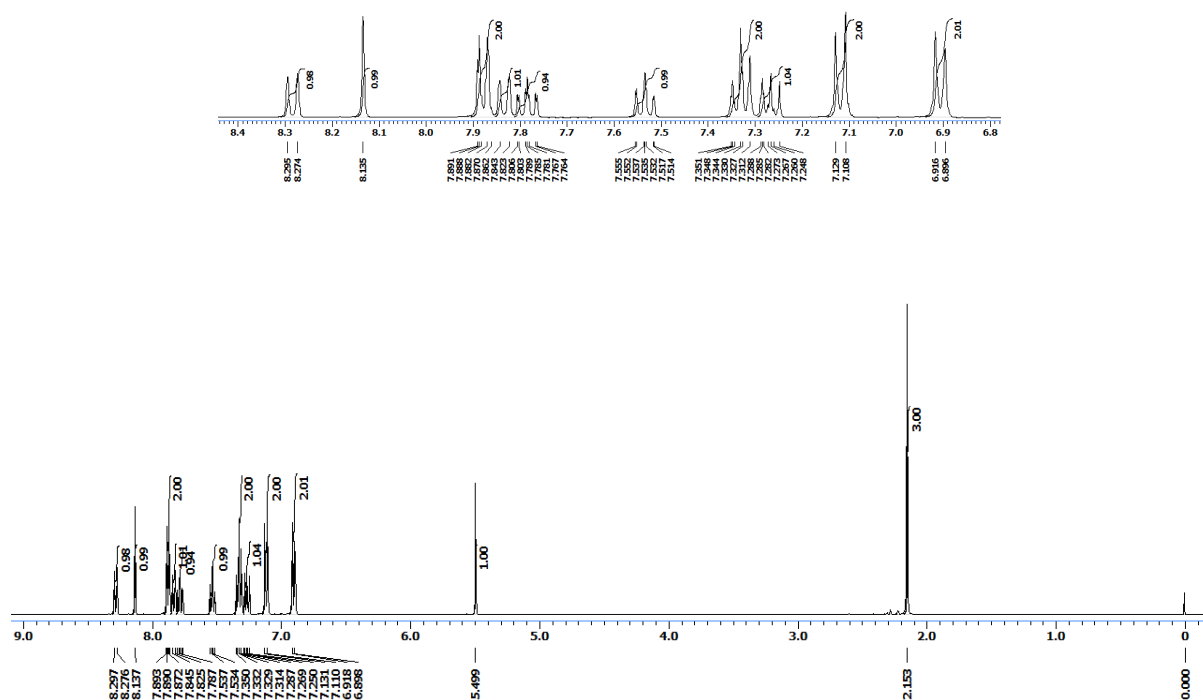
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (3a)



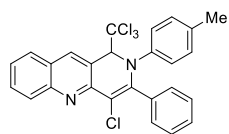
¹H NMR



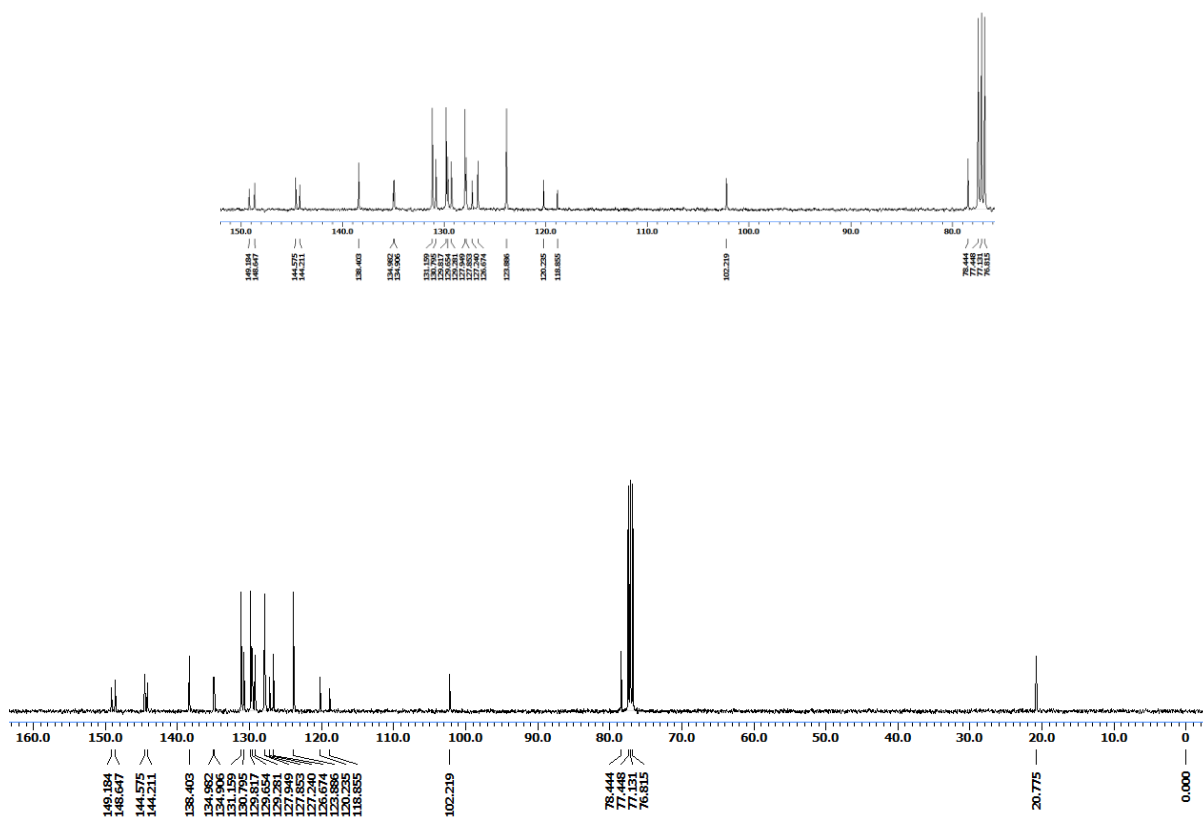
4-Chloro-3-phenyl-2-(p-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3b)



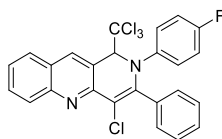
¹³C NMR



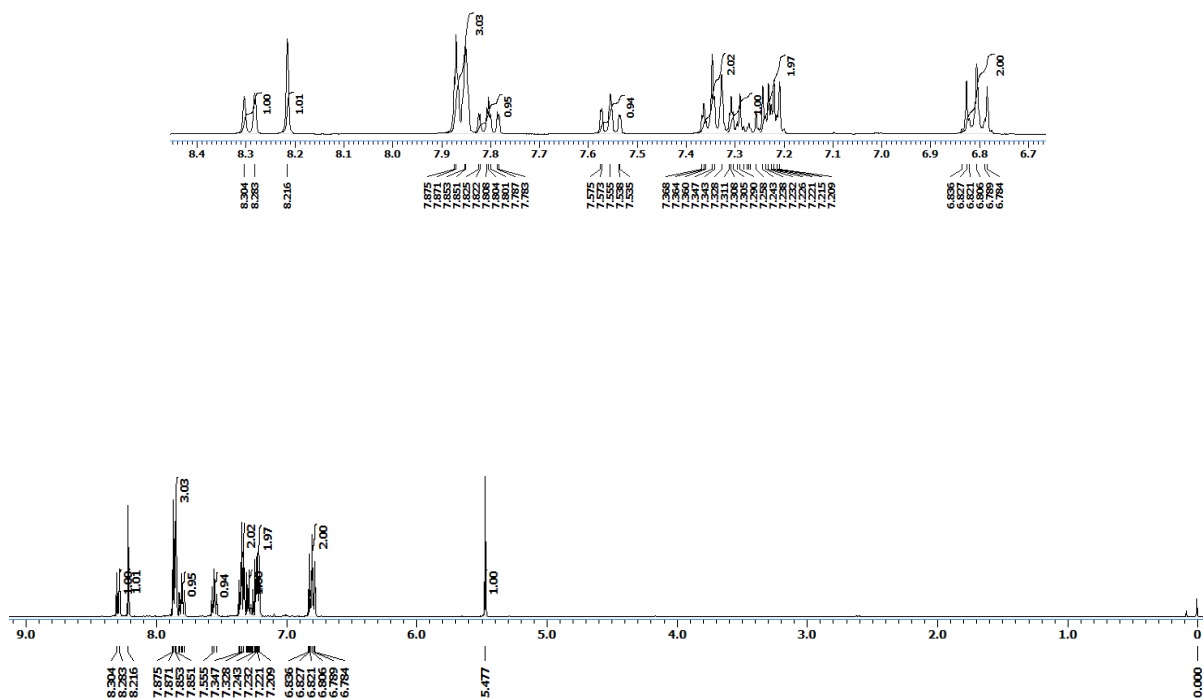
4-Chloro-3-phenyl-2-(p-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3b)

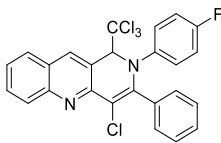


¹H NMR

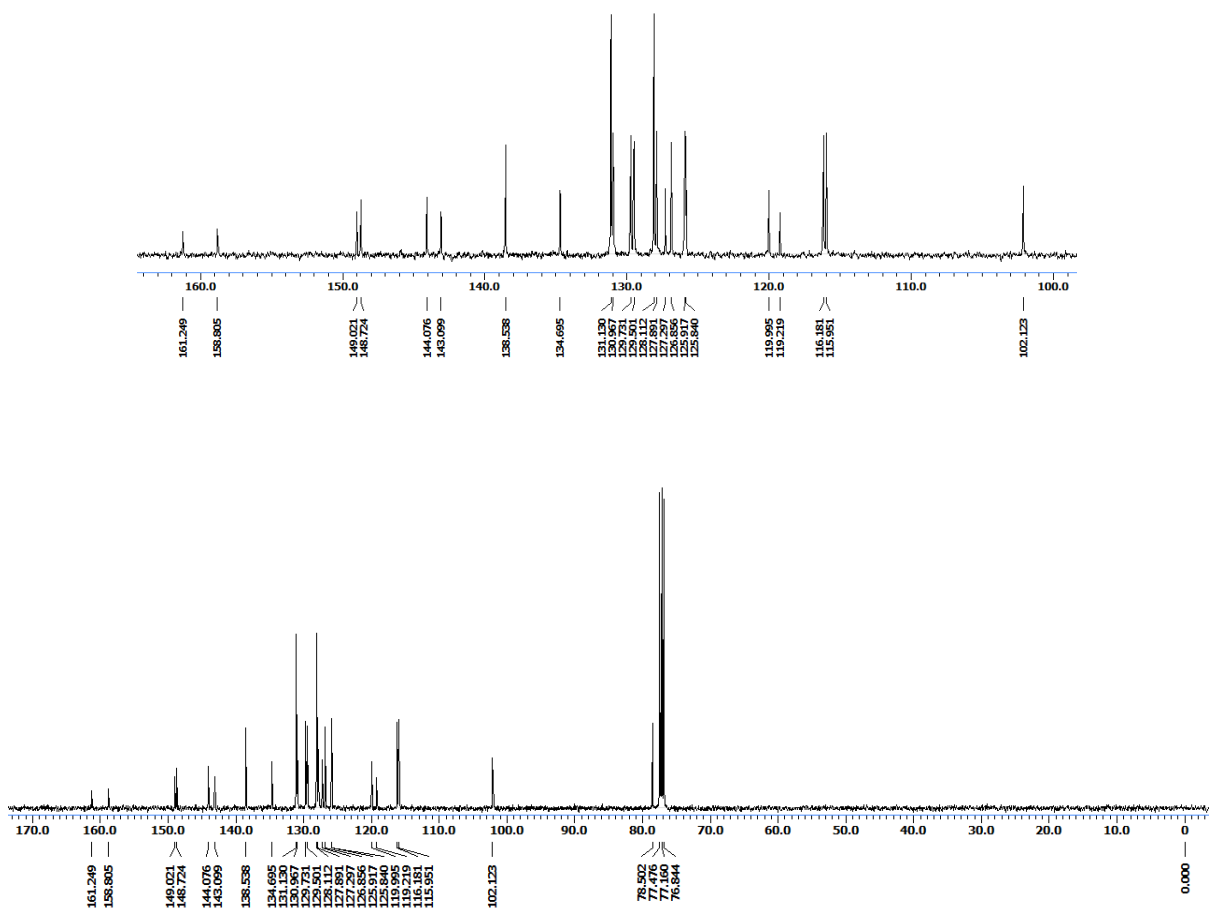


4-Chloro-2-(4-fluorophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3c)

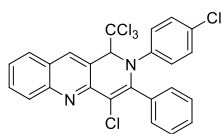


¹³C NMR

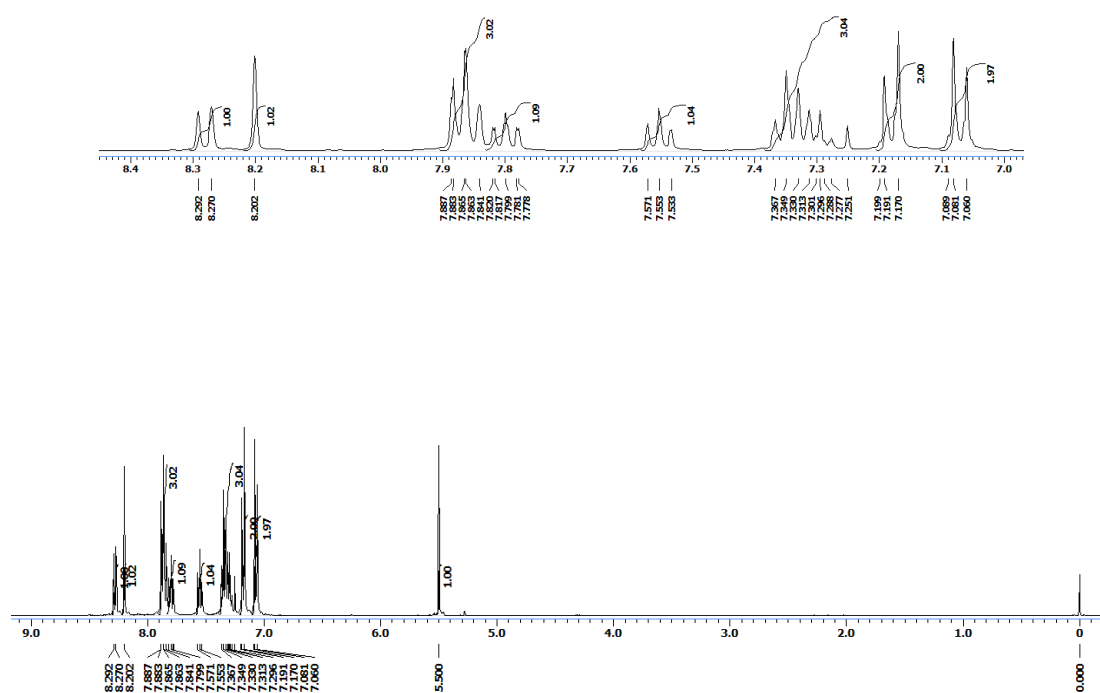
4-Chloro-2-(4-fluorophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3c)



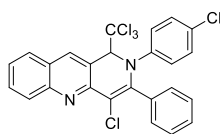
¹H NMR



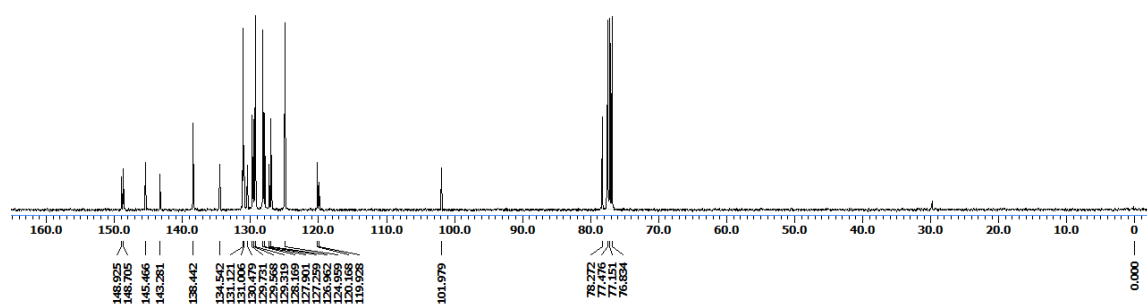
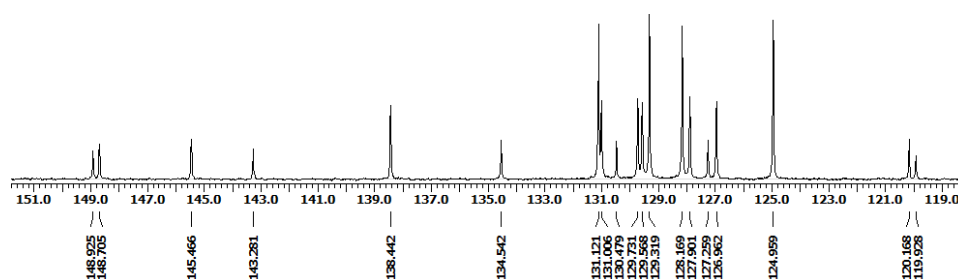
4-Chloro-2-(4-chlorophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3d)



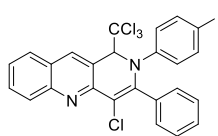
¹³C NMR



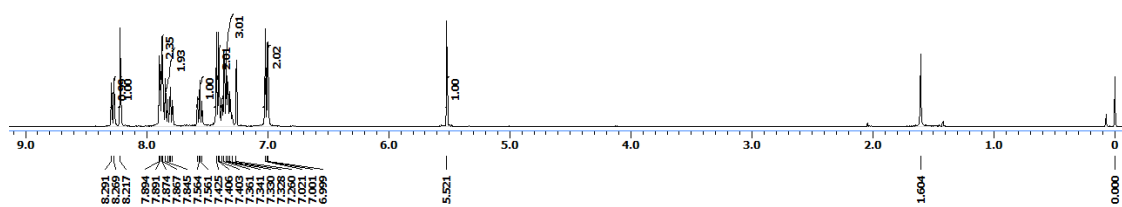
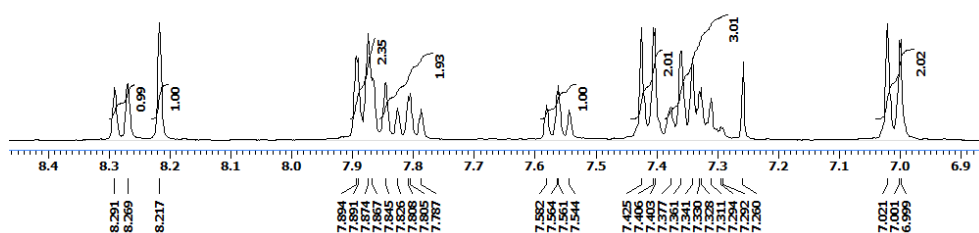
4-Chloro-2-(4-chlorophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3d)



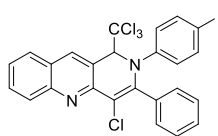
¹H NMR



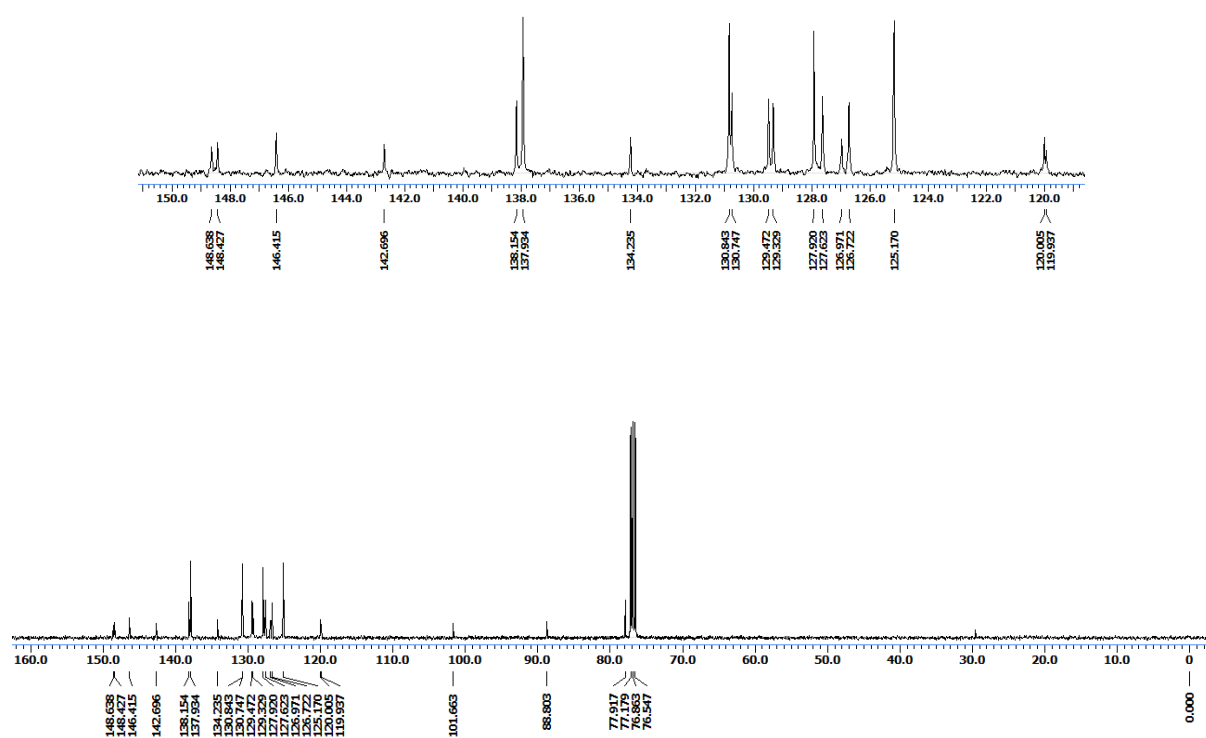
4-Chloro-2-(4-iodophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (3e)



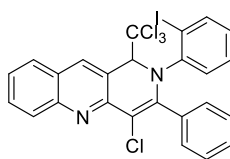
¹³C NMR



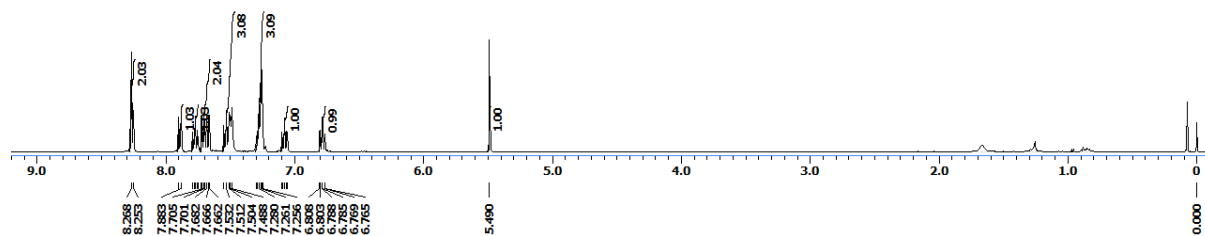
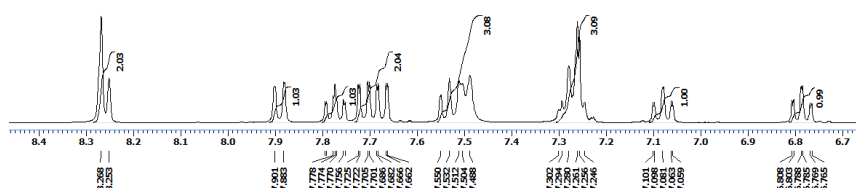
4-Chloro-2-(4-iodophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3e)



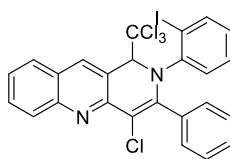
¹H NMR



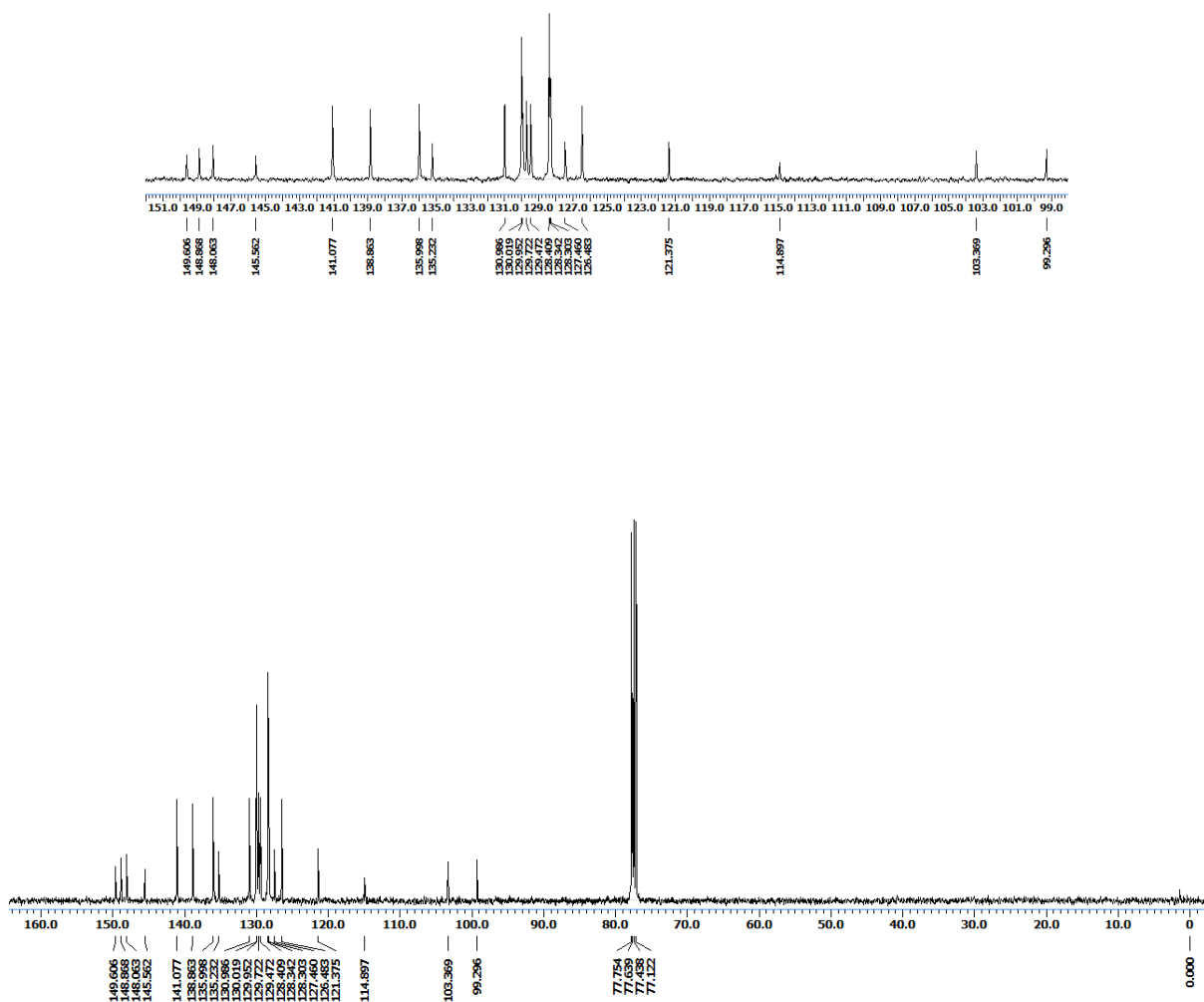
4-Chloro-2-(2-iodophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3f)



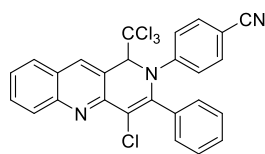
¹³C NMR



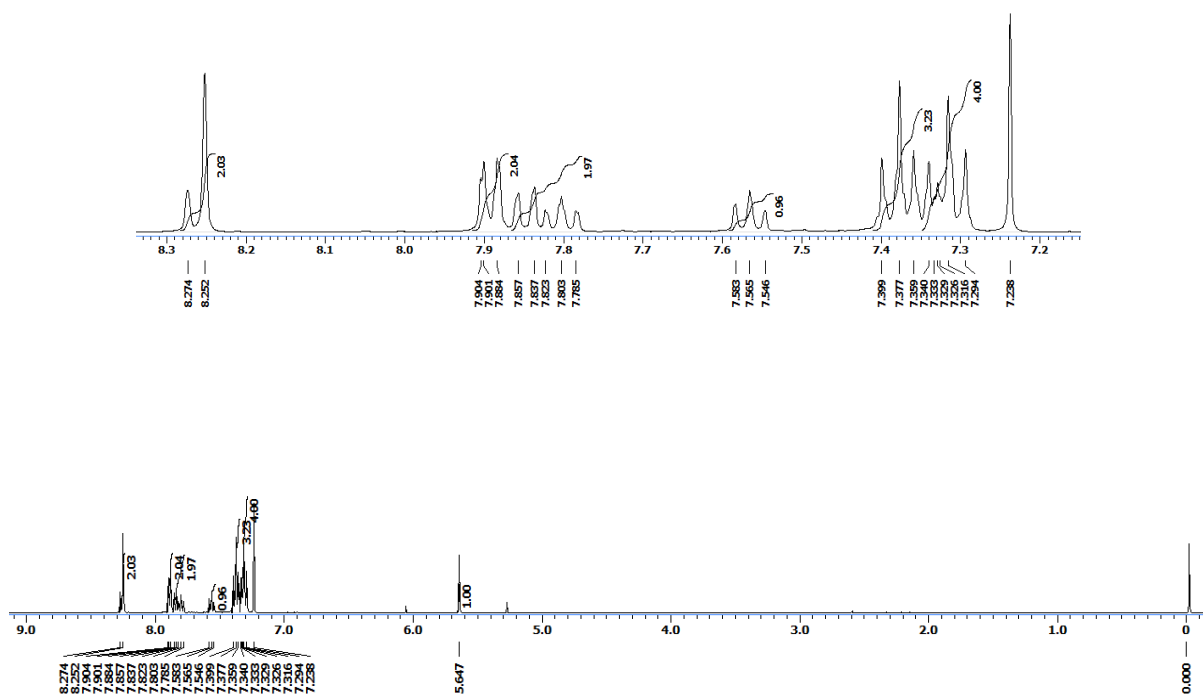
4-Chloro-2-(2-iodophenyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3f)



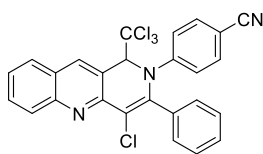
¹H NMR



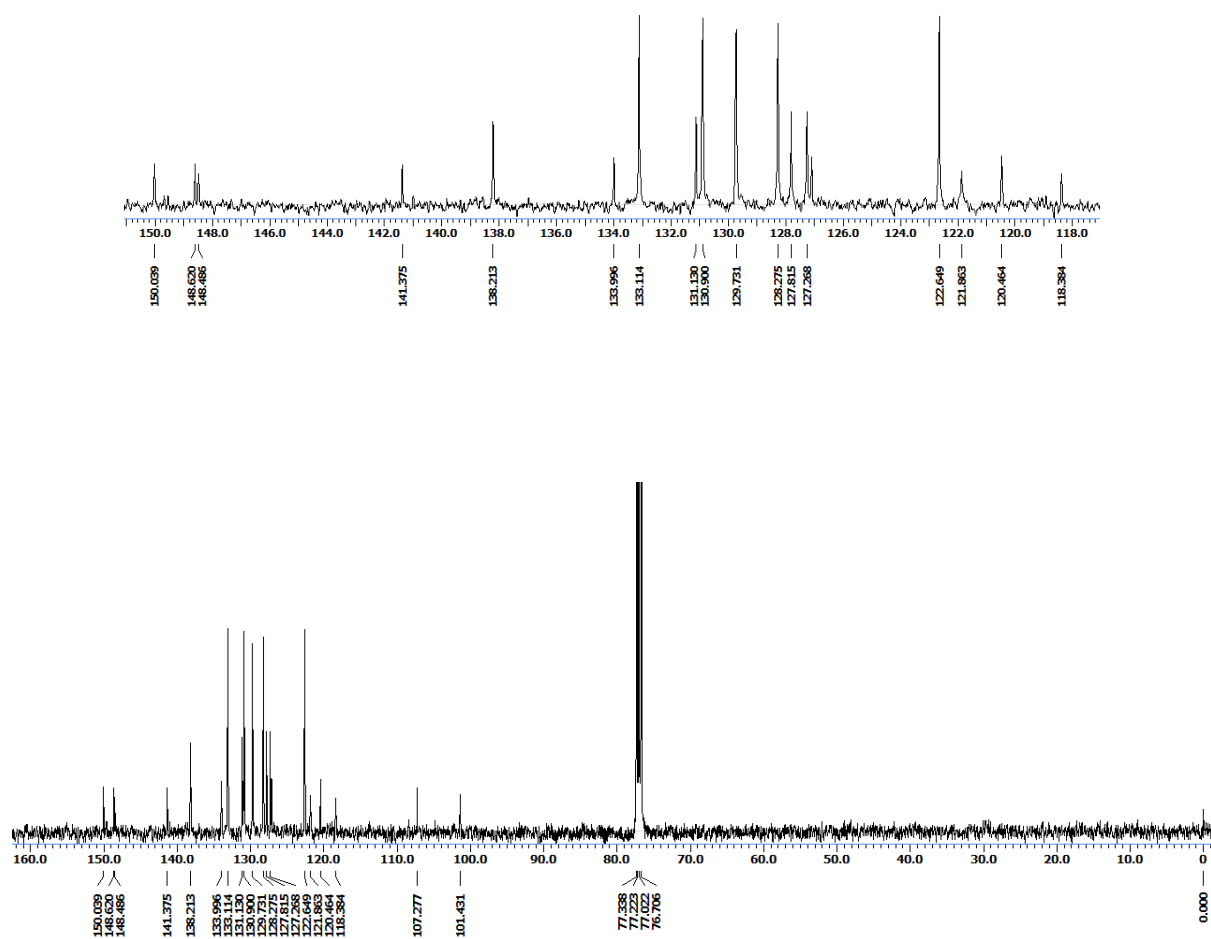
4-(4-chloro-3-phenyl-1-(trichloromethyl)benzo[b][1,6]naphthyridin-2(1H)-yl)benzonitrile (3g)



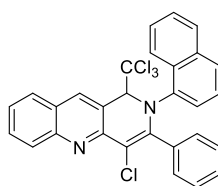
¹³C NMR



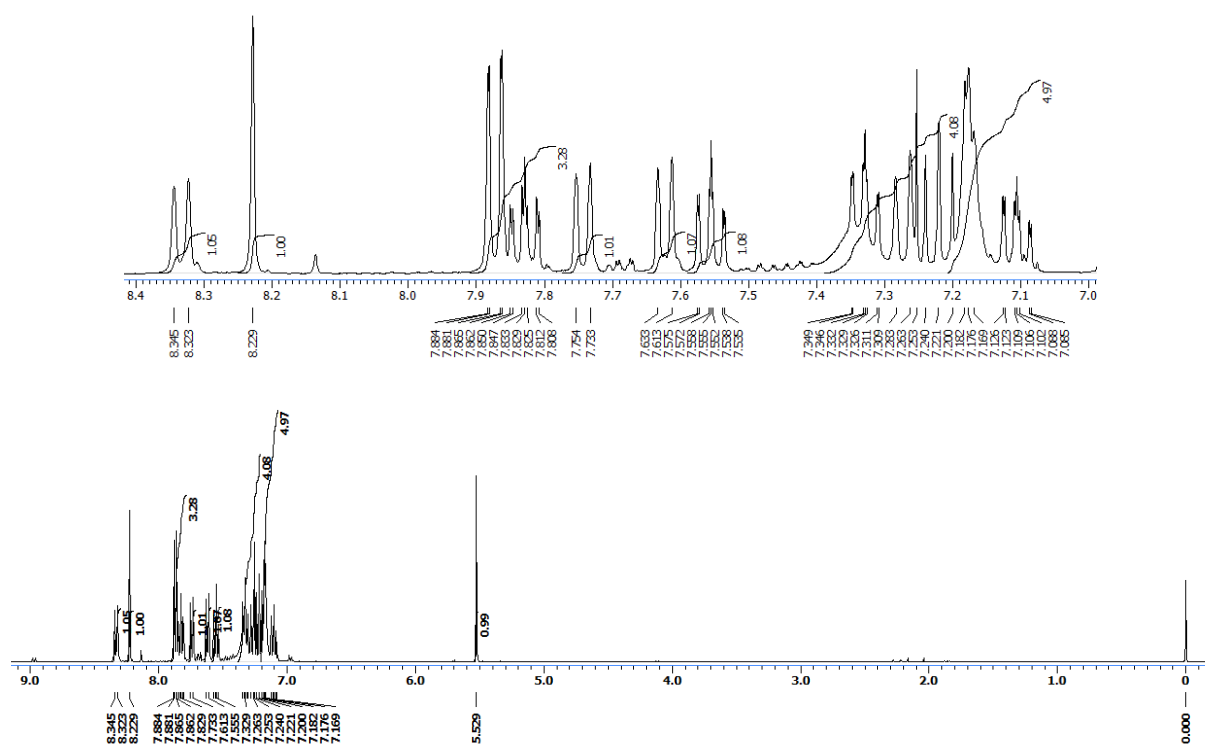
4-(4-chloro-3-phenyl-1-(trichloromethyl)benzo[*b*][1,6]naphthyridin-2(1*H*)-yl)benzonitrile (3g)



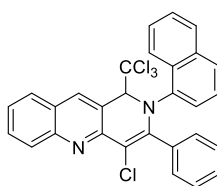
¹H NMR



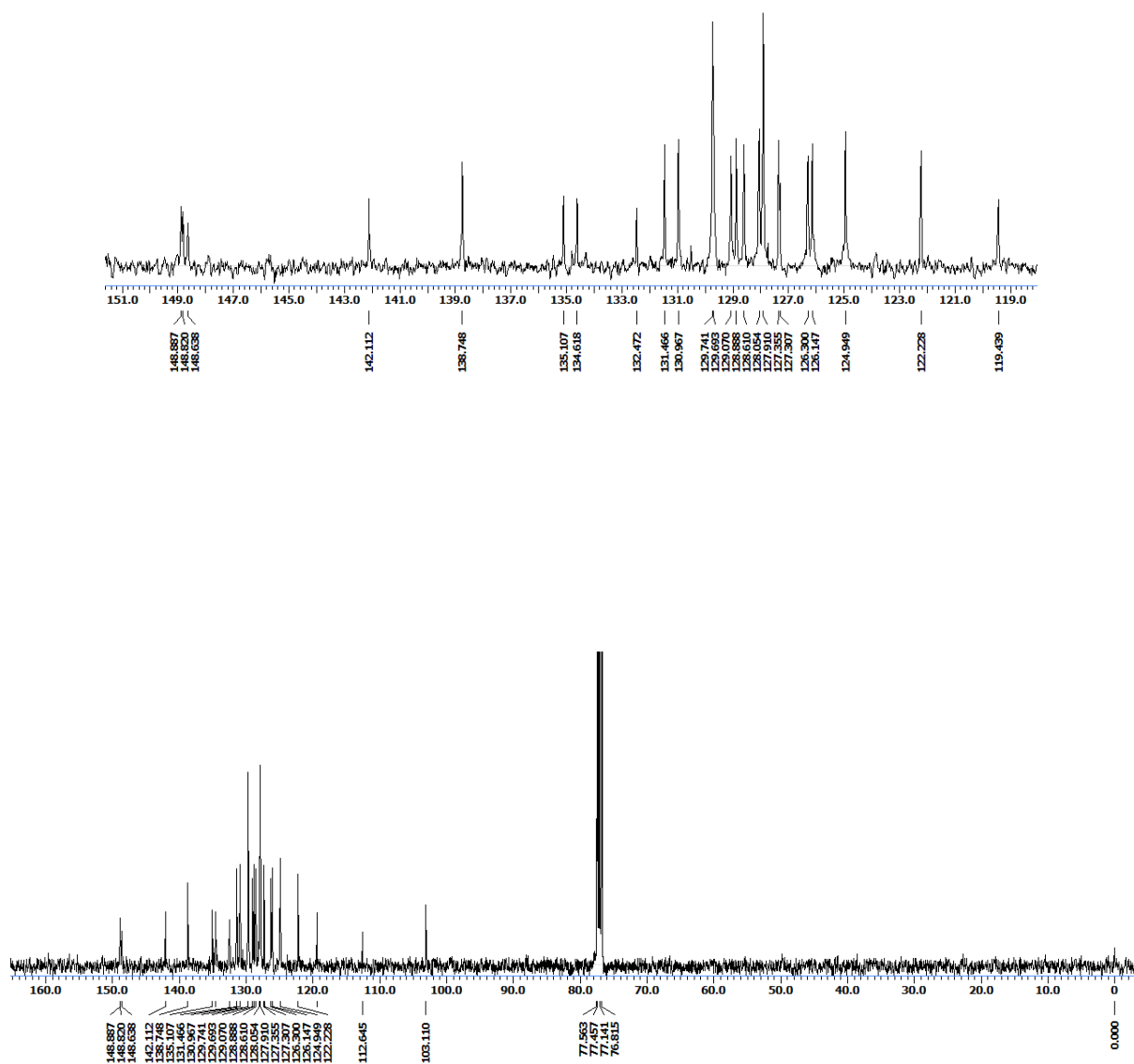
4-Chloro-2-(naphthalen-1-yl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3h)



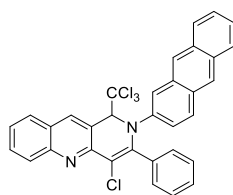
¹³C NMR



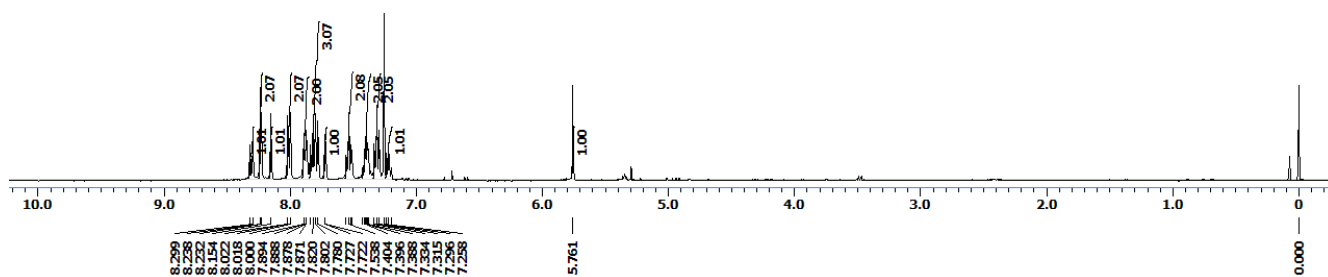
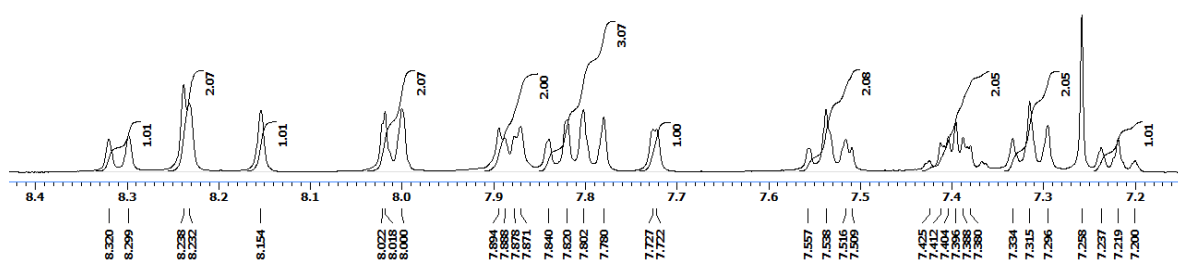
4-Chloro-2-(naphthalen-1-yl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (3h)



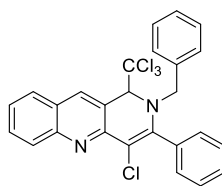
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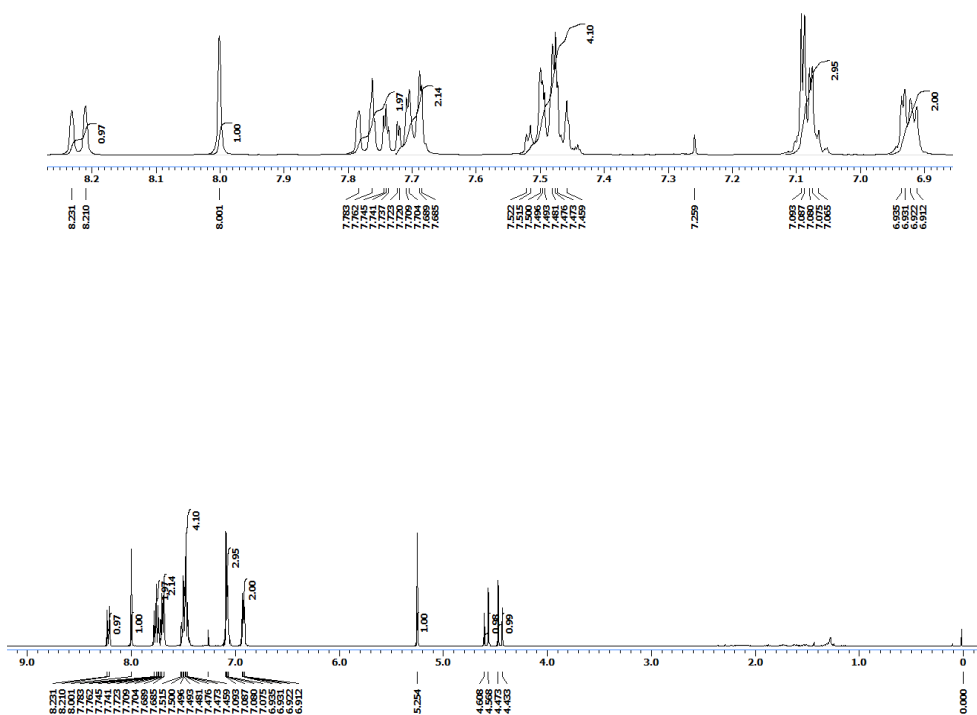
2-(Anthracen-2-yl)-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3i)



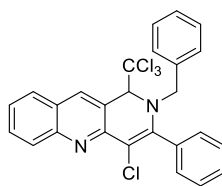
¹H NMR



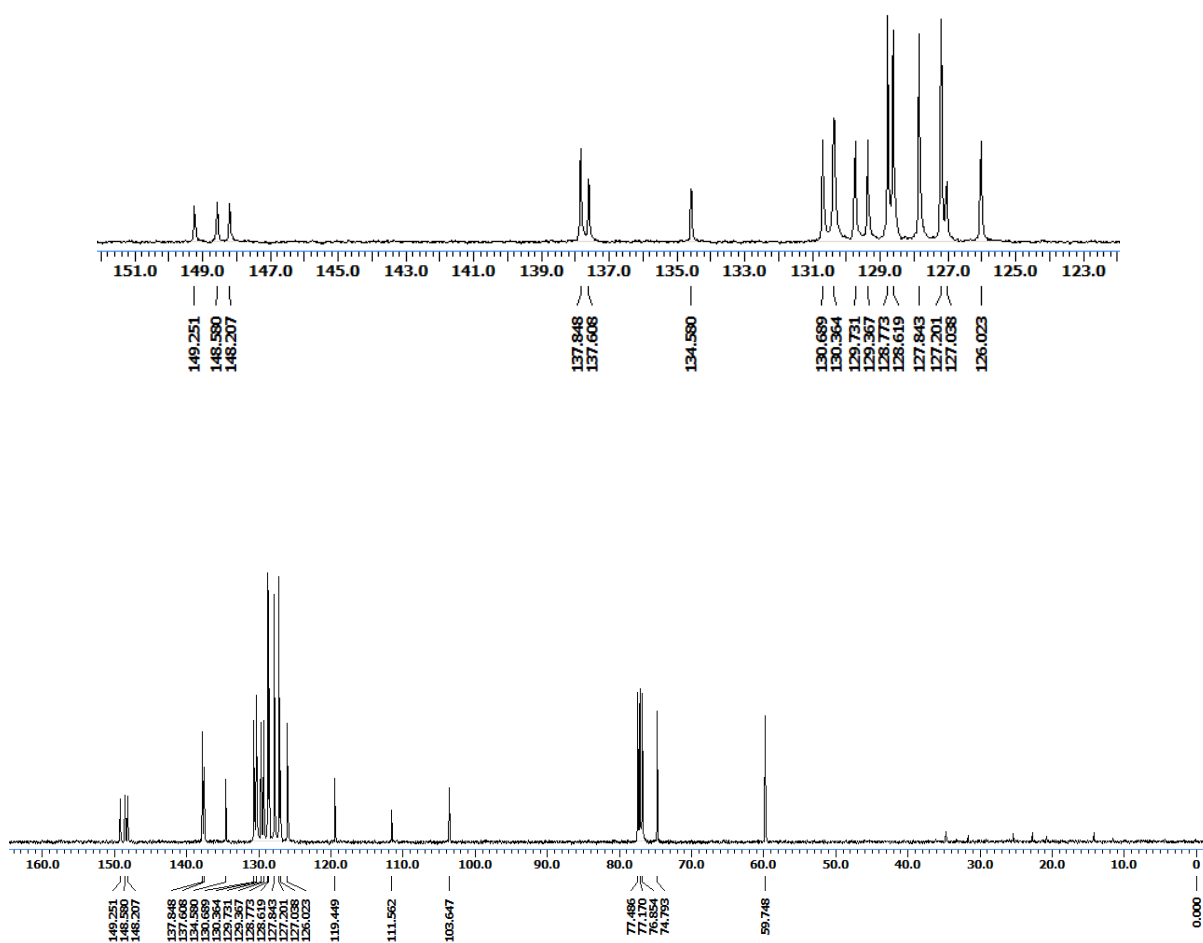
2-Benzyl-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine
(3j)



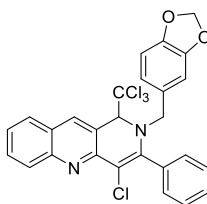
¹³C NMR



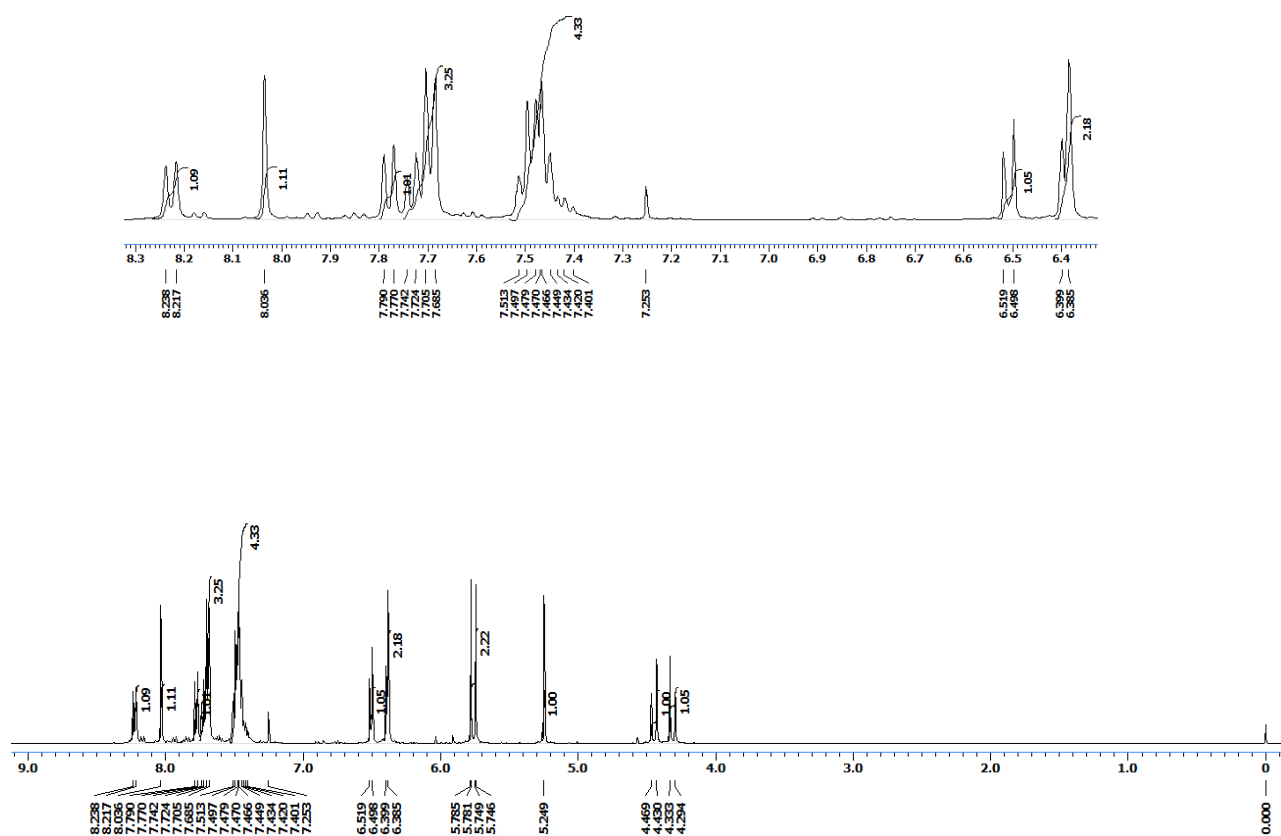
2-Benzyl-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine
(3j)



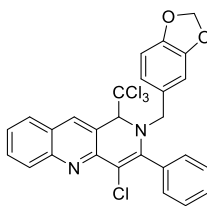
¹H NMR



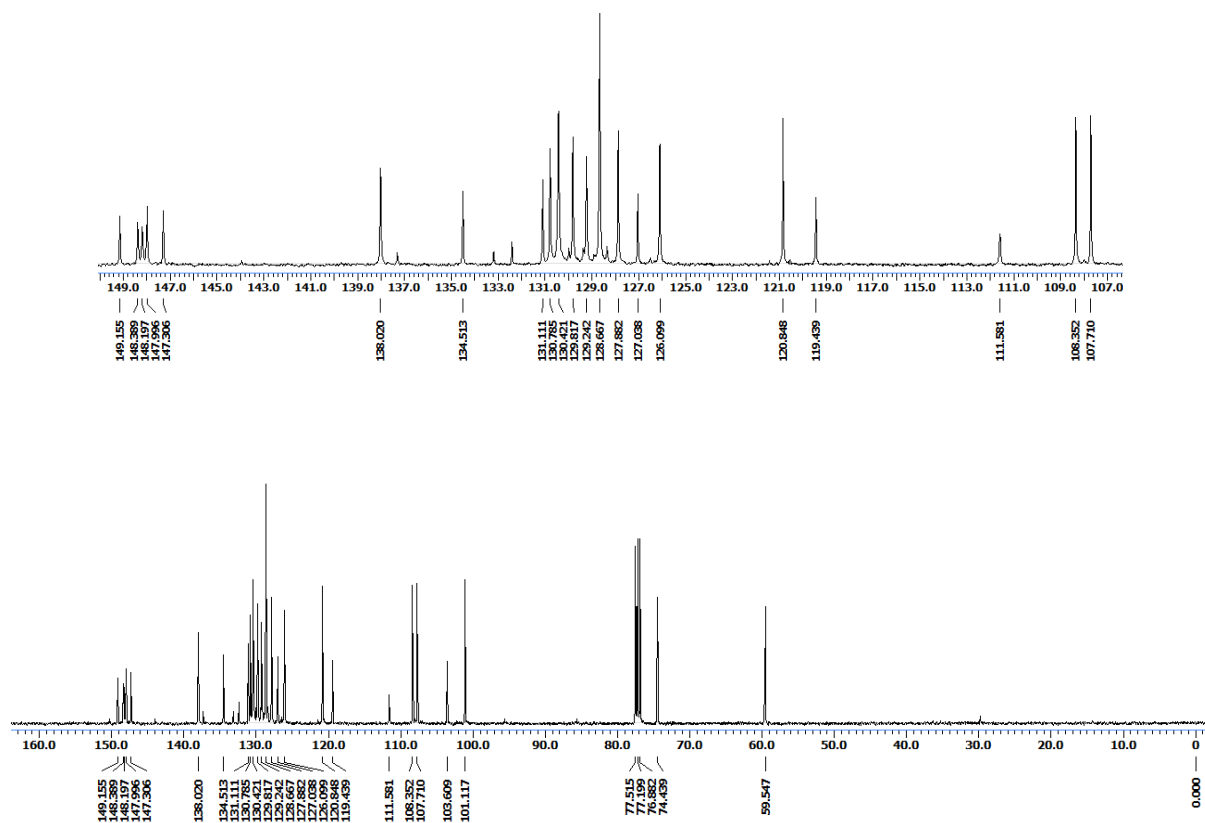
2-(Benzo[d][1,3]dioxol-5-ylmethyl)-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3k)



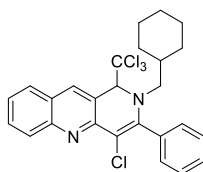
¹³C NMR



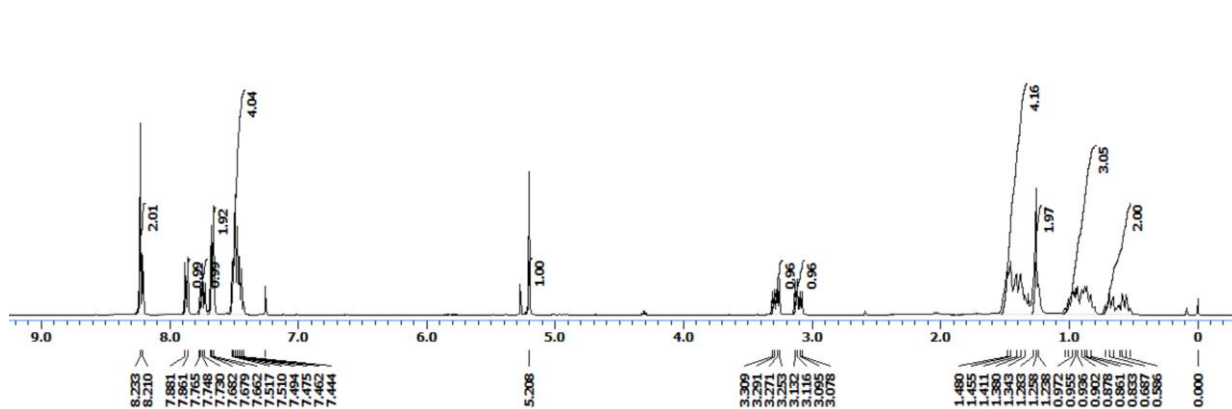
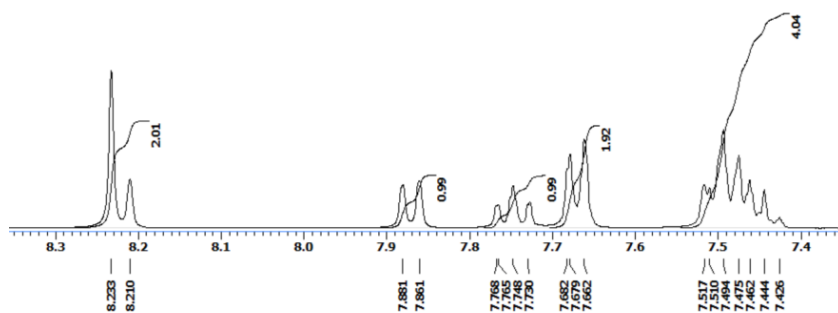
2-(Benzo[d][1,3]dioxol-5-ylmethyl)-4-chloro-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3k)



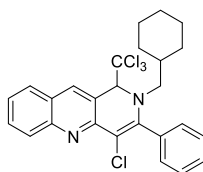
¹H NMR



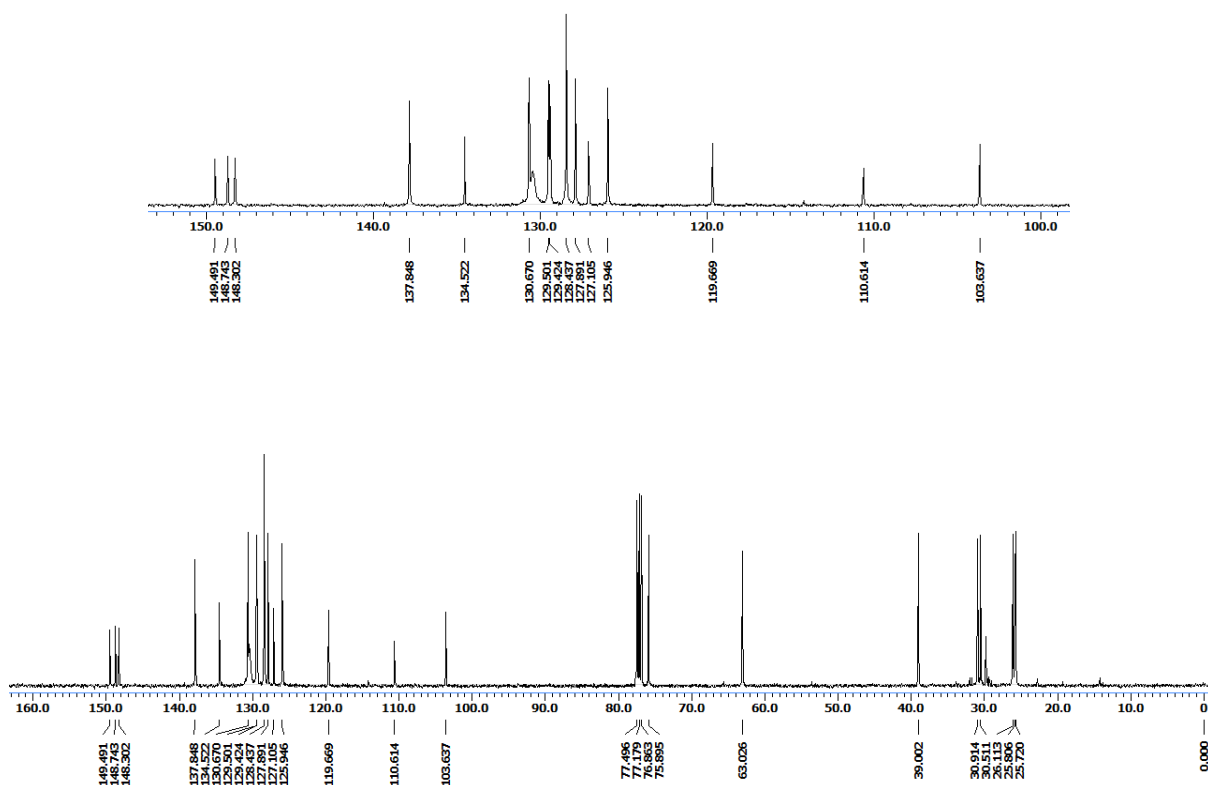
4-Chloro-2-(cyclohexylmethyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3l)



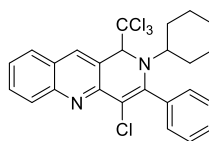
¹³C NMR



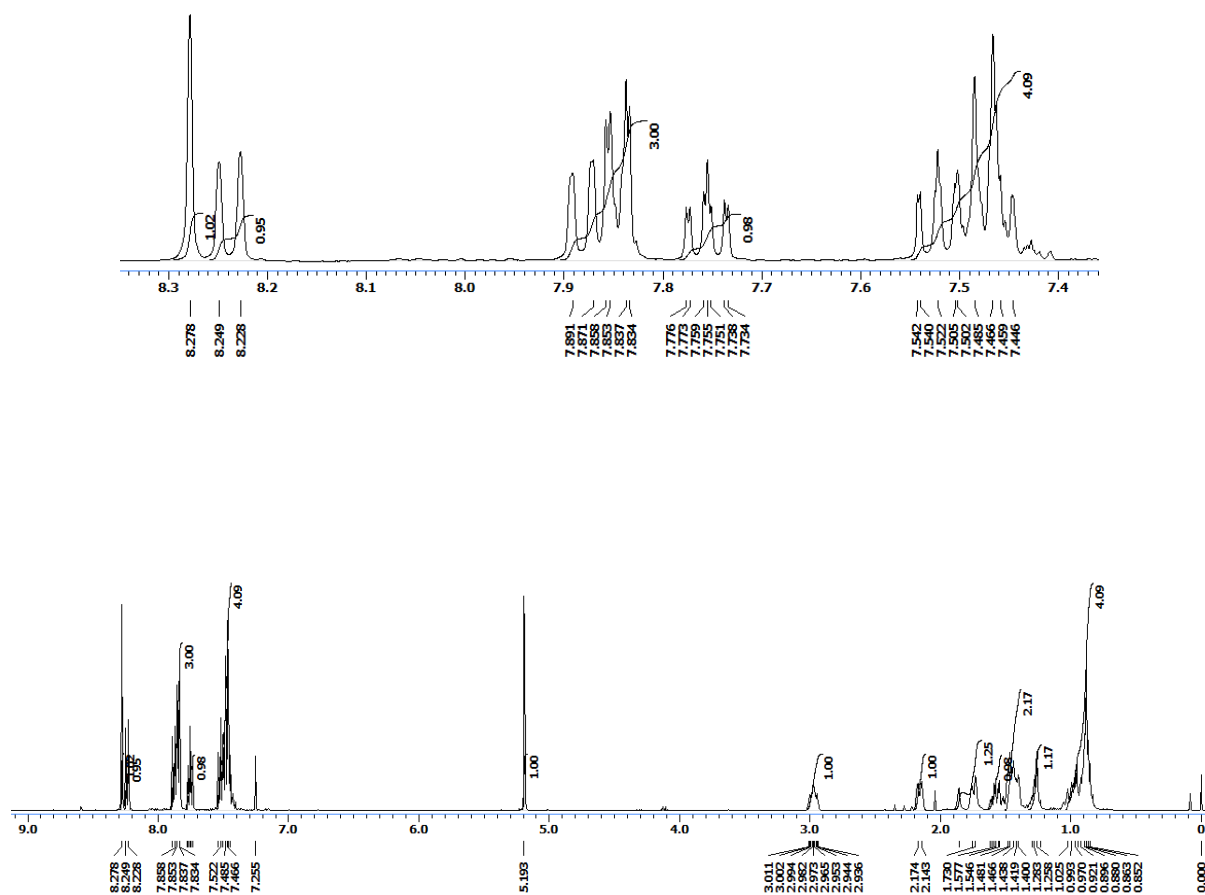
4-Chloro-2-(cyclohexylmethyl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3l)



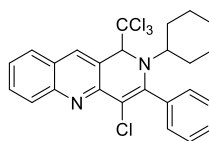
¹H NMR



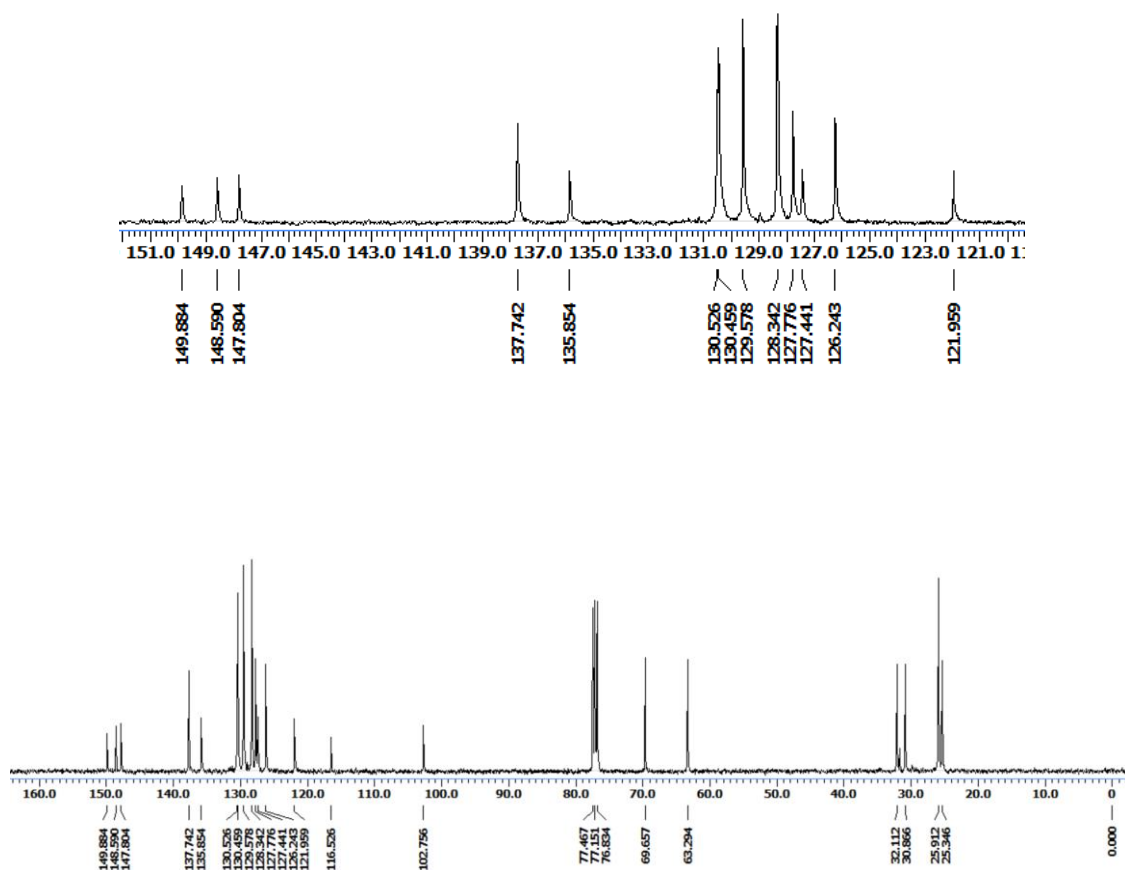
4-Chloro-2-cyclohexyl-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridin (3m)



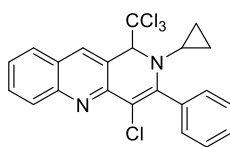
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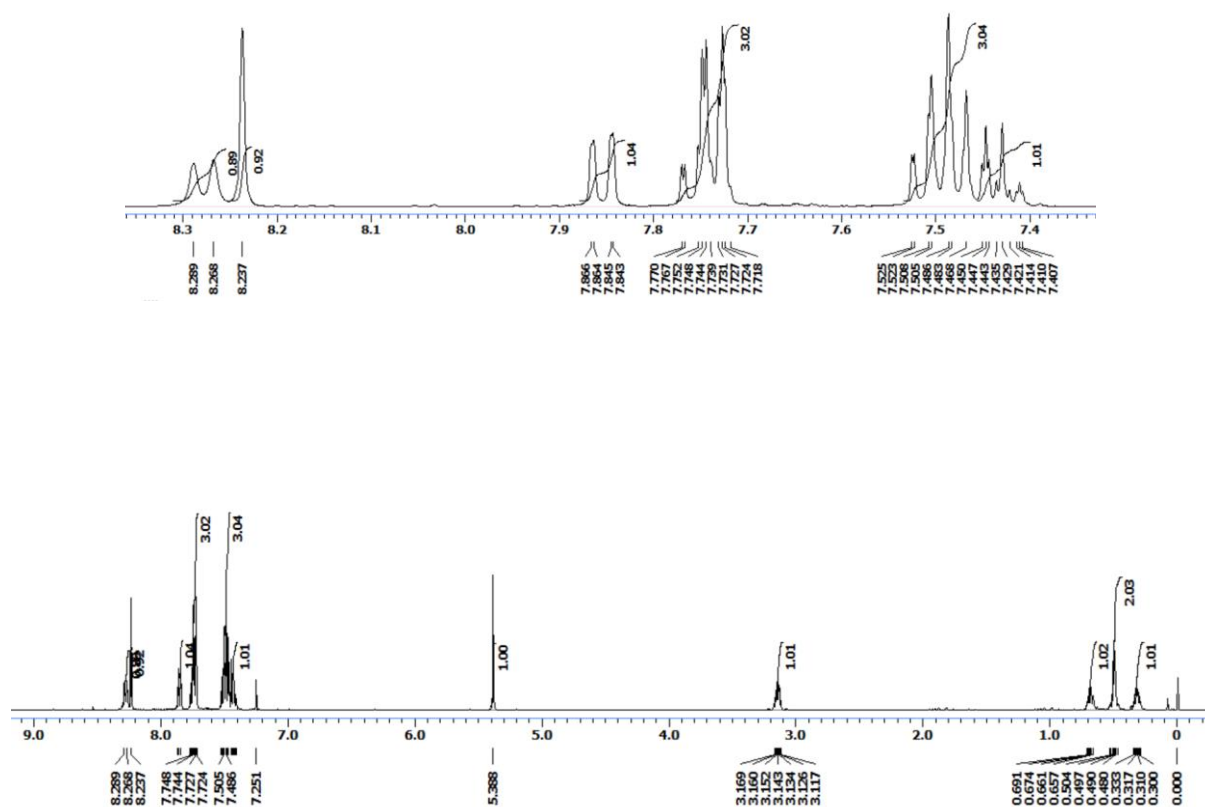
4-Chloro-2-cyclohexyl-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridin (3m)



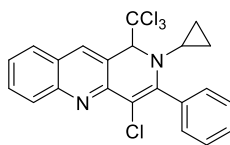
¹H NMR



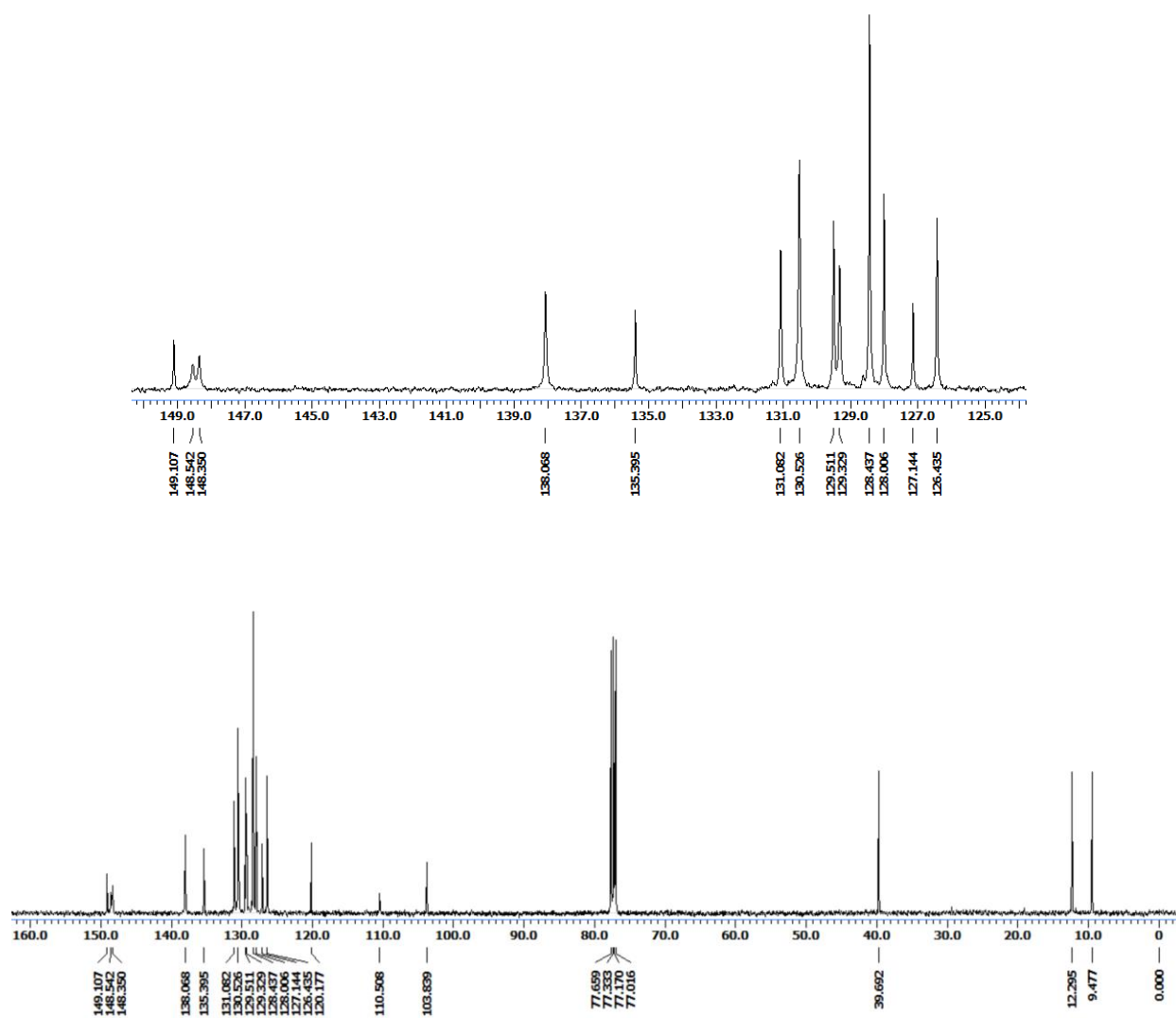
4-Chloro-2-cyclopropyl-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3n)

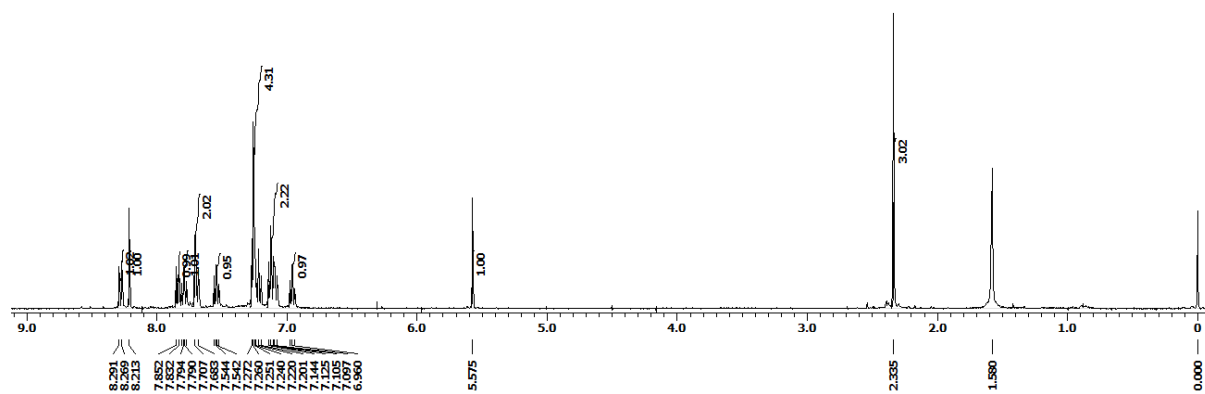


¹³C NMR

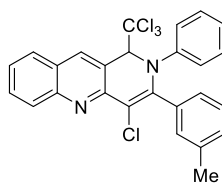


4-Chloro-2-cyclopropyl-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3n)

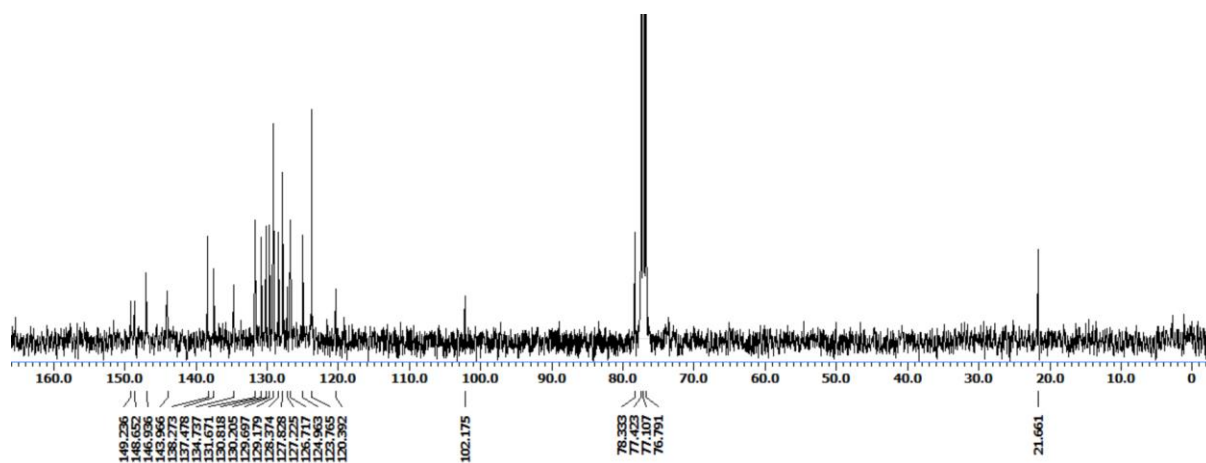
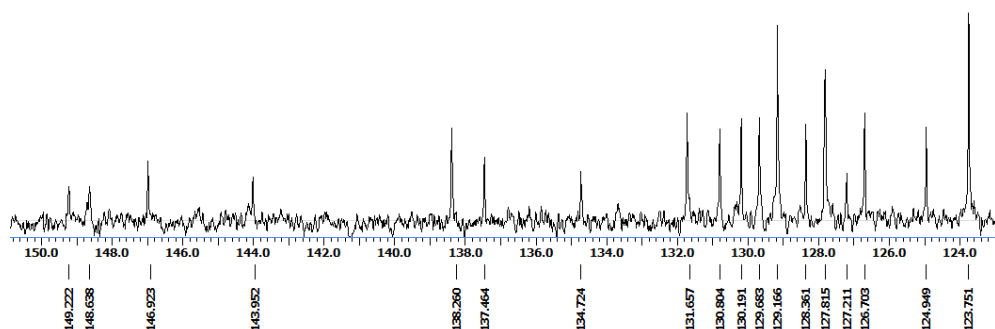


Cc1ccc(cc1C2=C(Cl)N(C(=C2)c3cccnc3)c4ccccc4)C5(Cl)(Cl)Cl

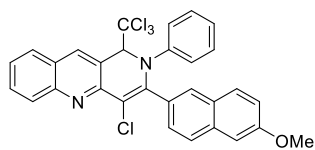
¹³C NMR



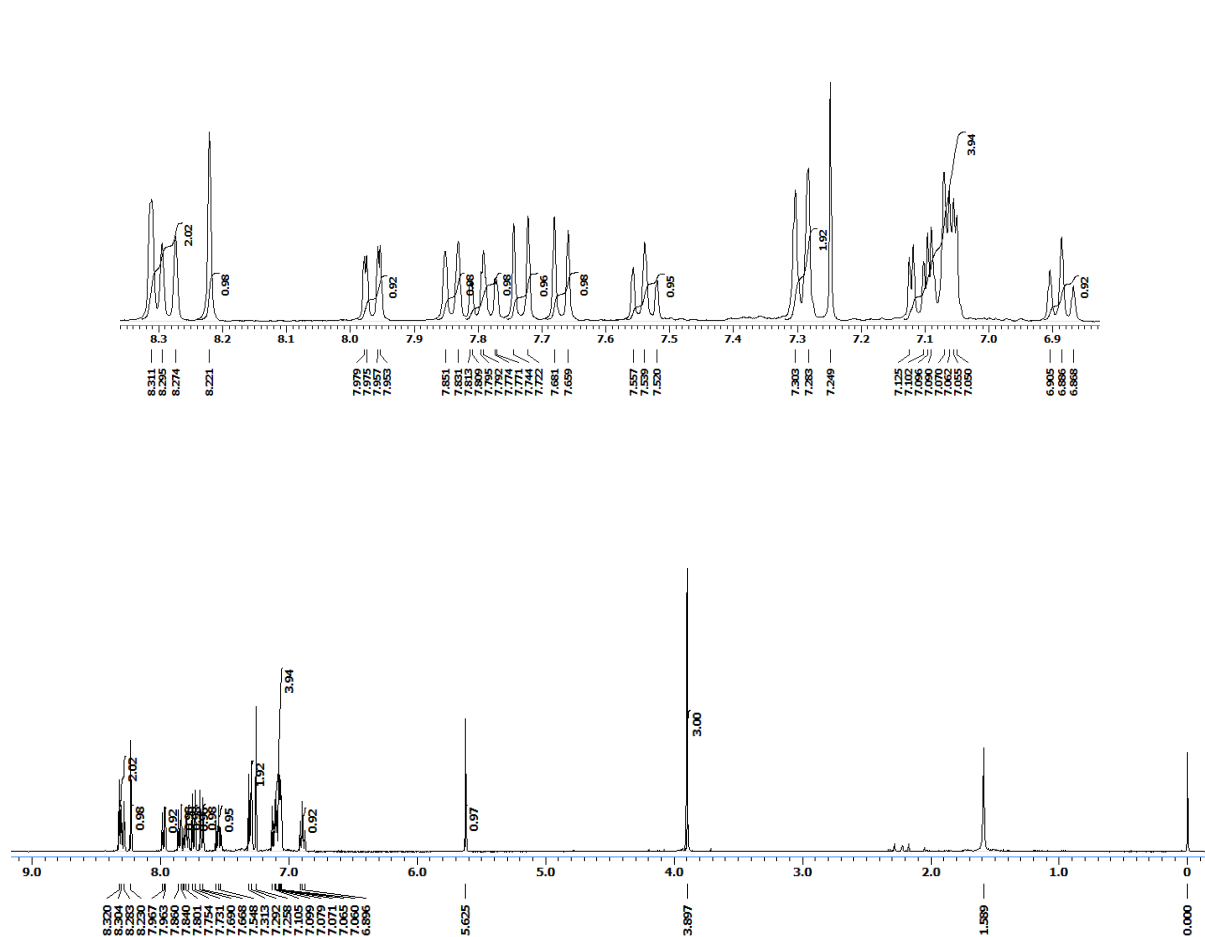
4-Chloro-2-phenyl-3-(m-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3o)

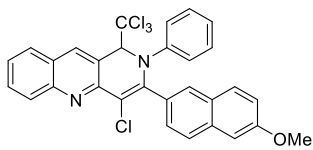


¹H NMR

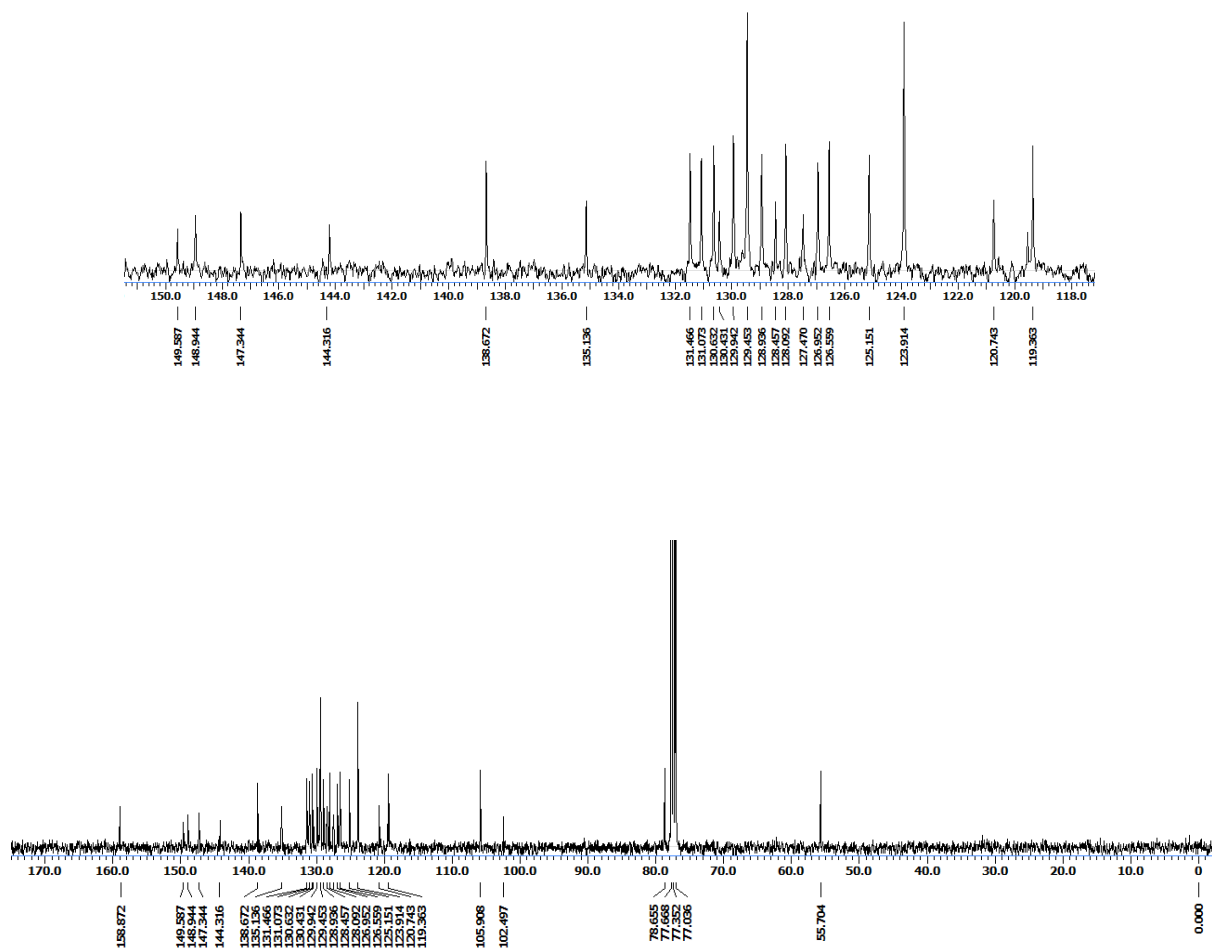


4-Chloro-3-(6-methoxynaphthalen-2-yl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3p)

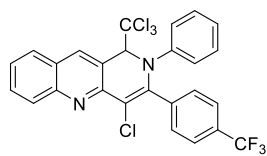


¹³C NMR

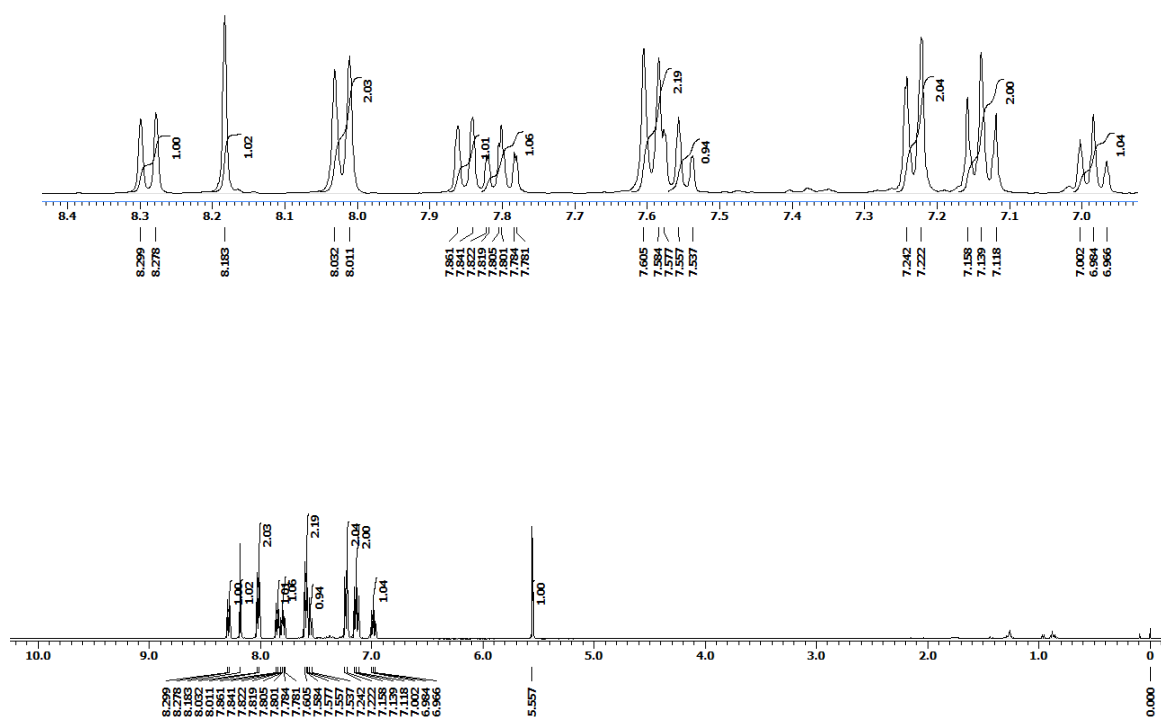
4-Chloro-3-(6-methoxynaphthalen-2-yl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (3p)



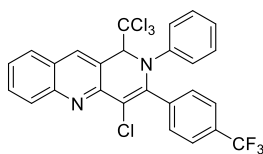
¹H NMR



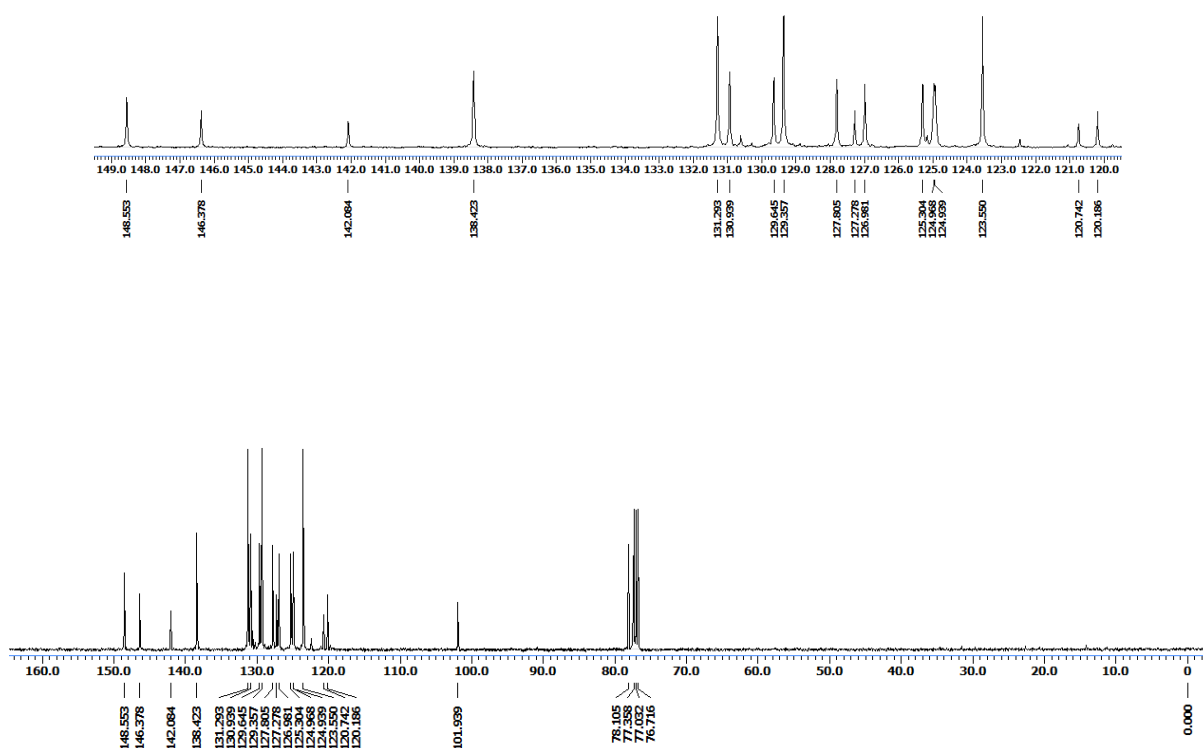
4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3q)



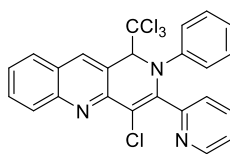
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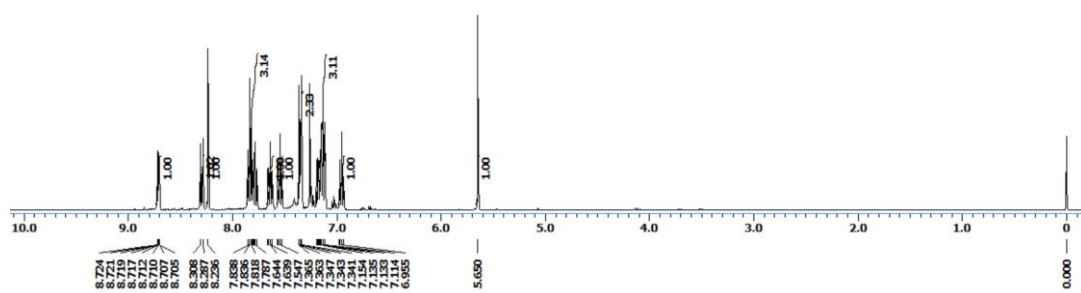
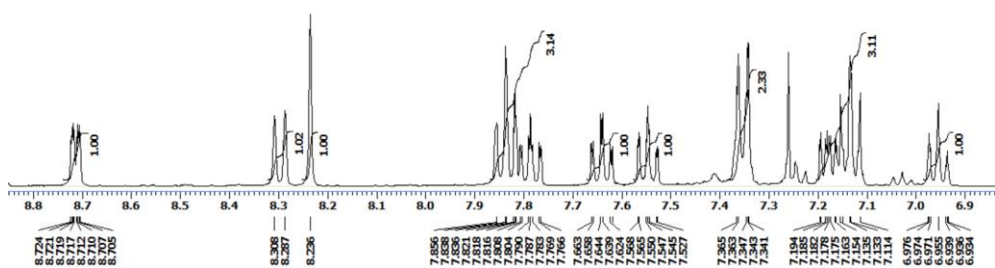
4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3q)



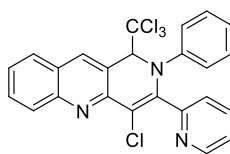
¹H NMR



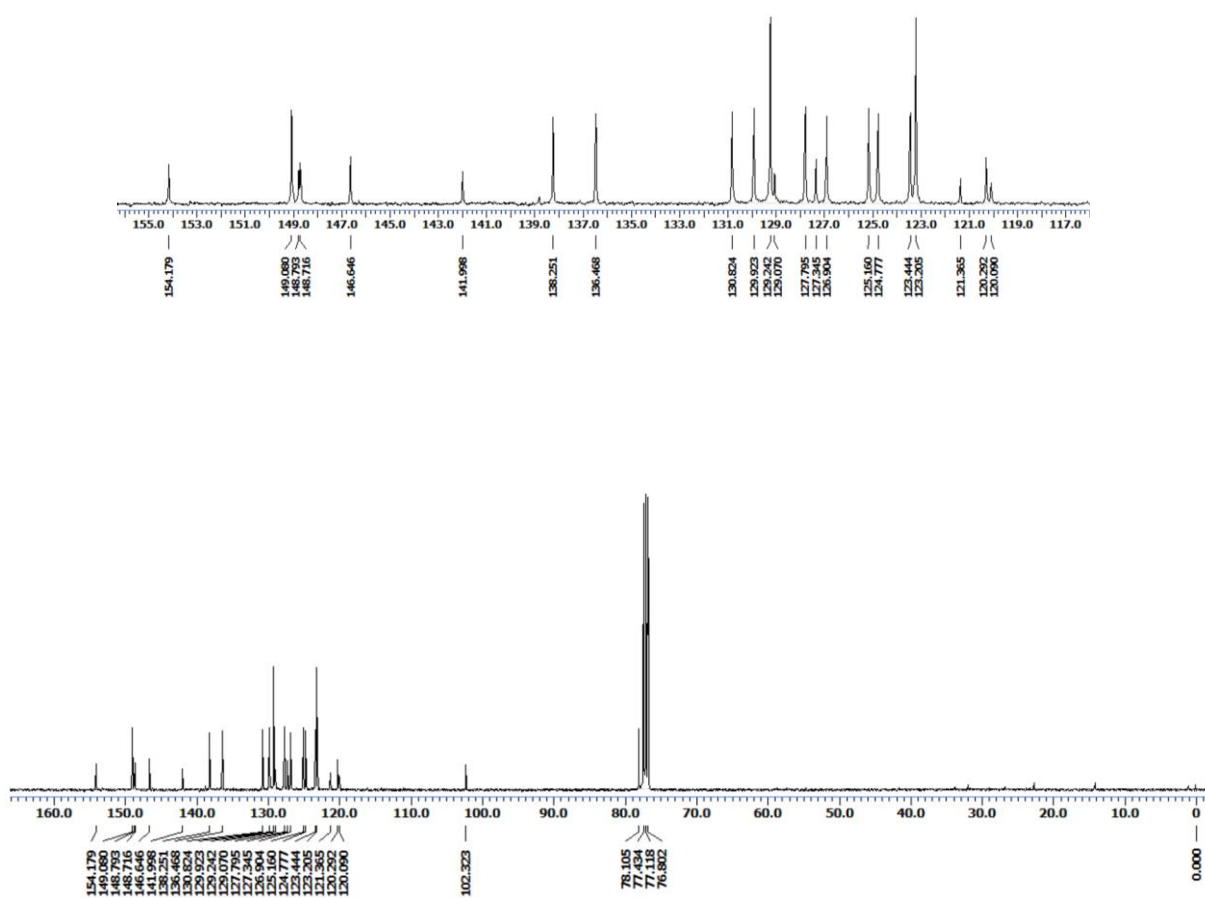
4-Chloro-2-phenyl-3-(pyridin-2-yl)-1-(trichloromethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (3r)



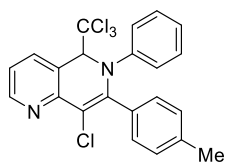
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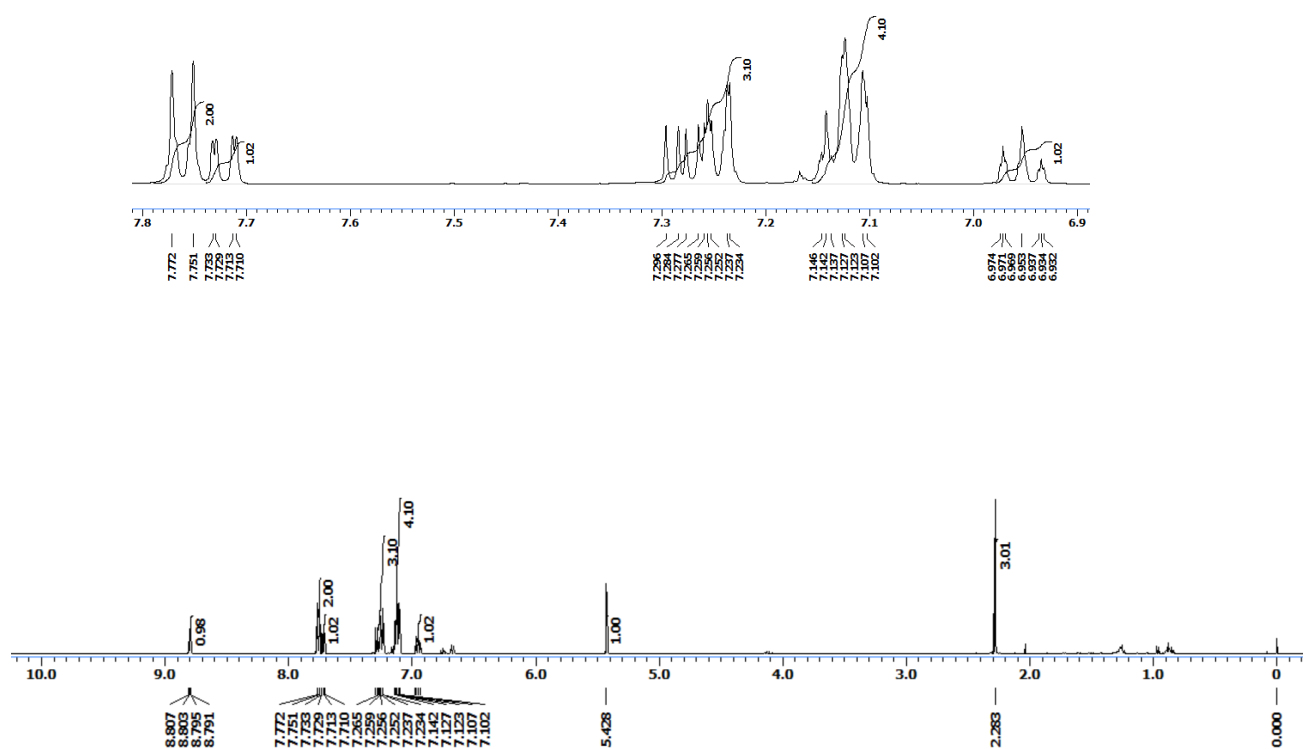
4-Chloro-2-phenyl-3-(pyridin-2-yl)-1-(trichloromethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (3r)



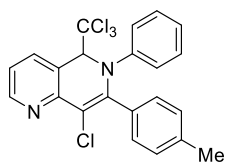
¹H NMR



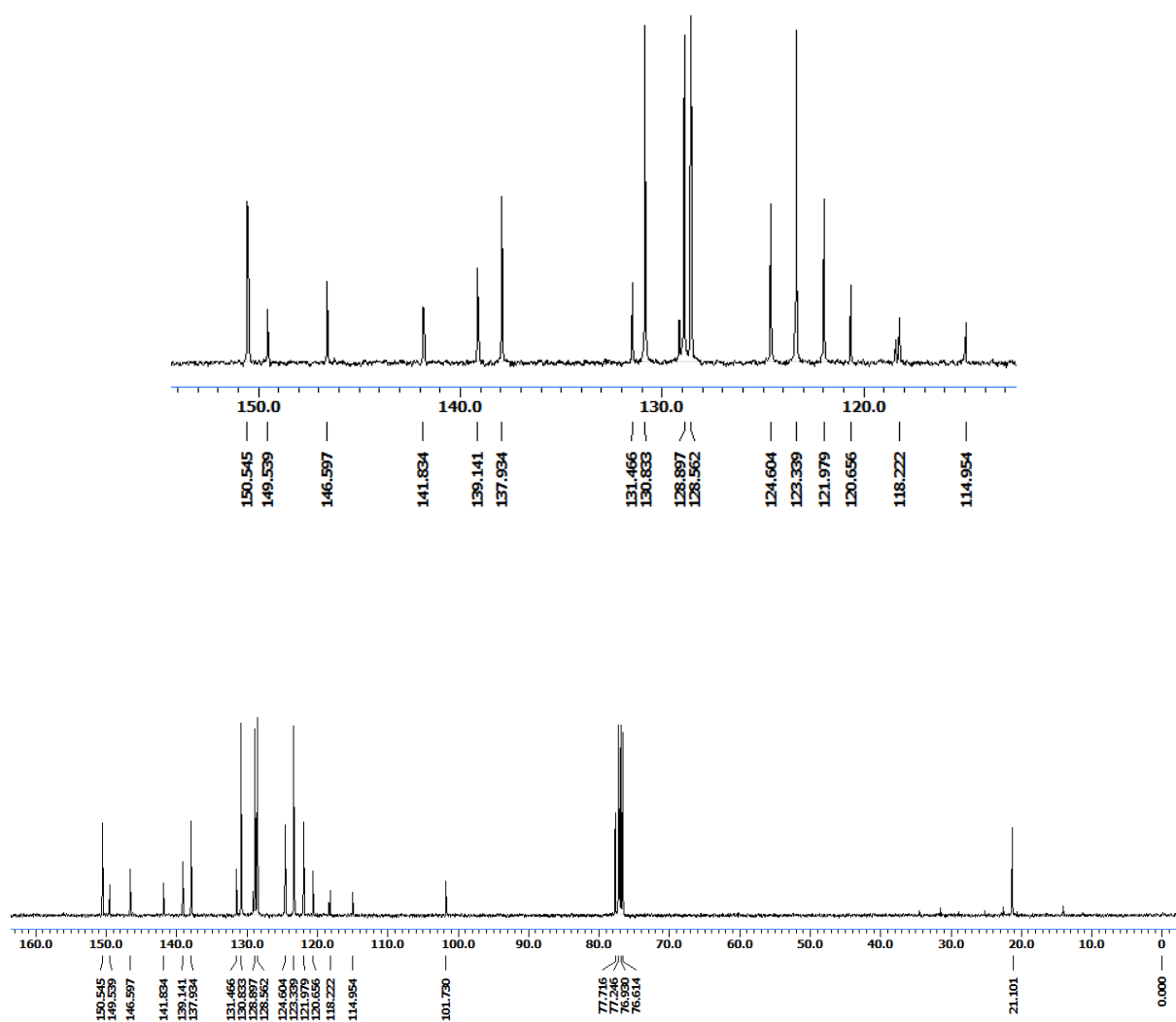
8-Chloro-6-phenyl-7-(*p*-tolyl)-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4a)



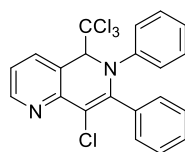
¹³C NMR



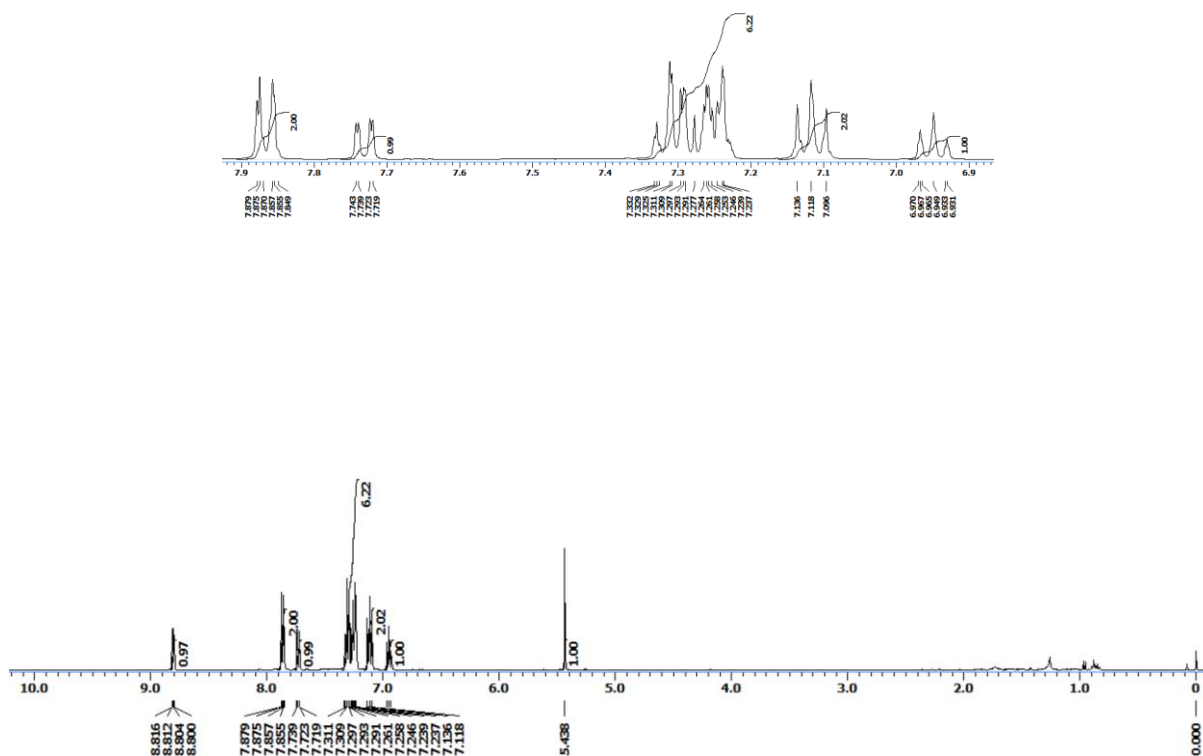
8-Chloro-6-phenyl-7-(*p*-tolyl)-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4a)



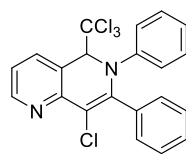
¹H NMR



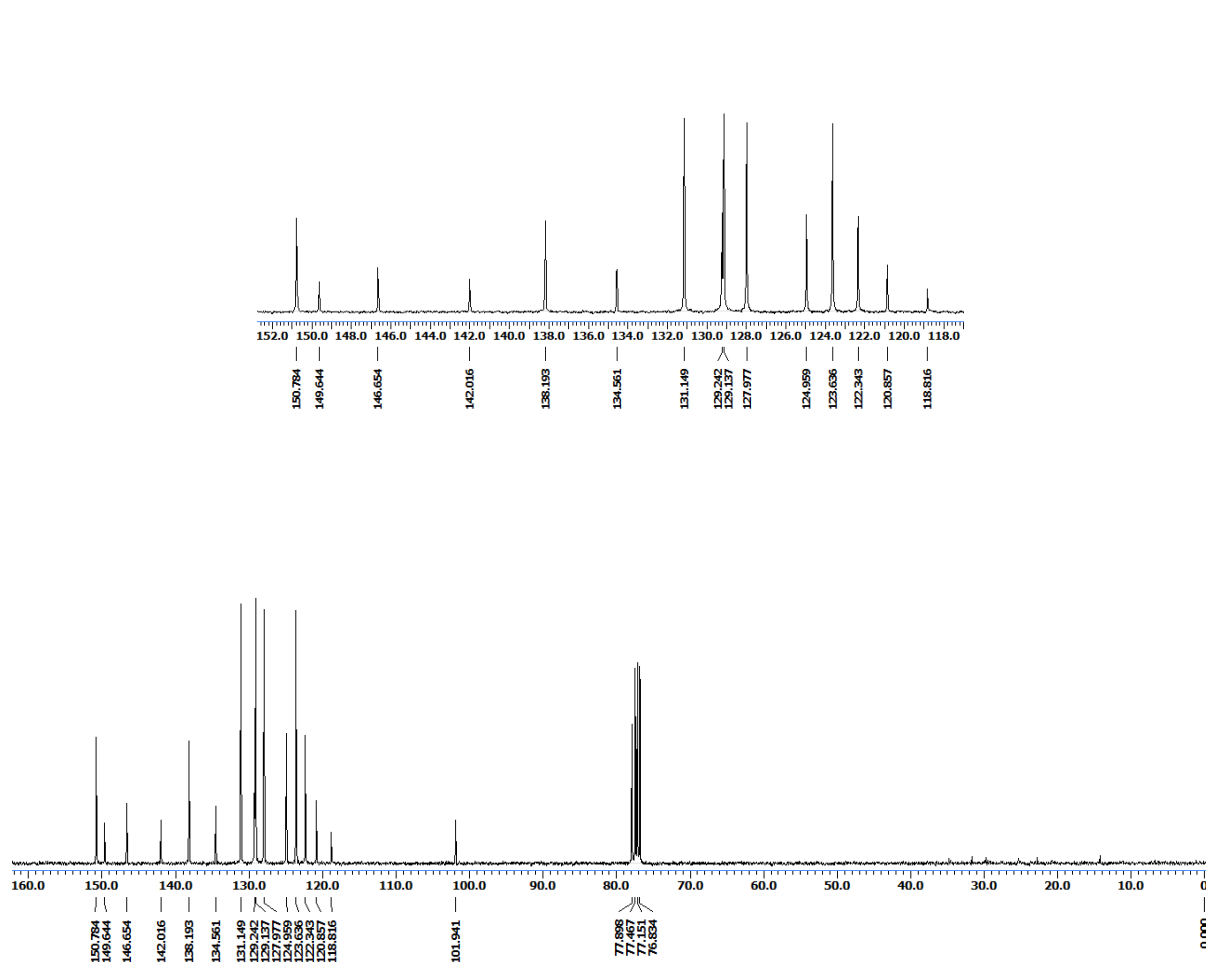
8-Chloro-6,7-diphenyl-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4b)



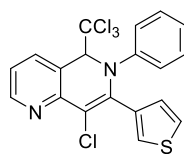
¹³C NMR



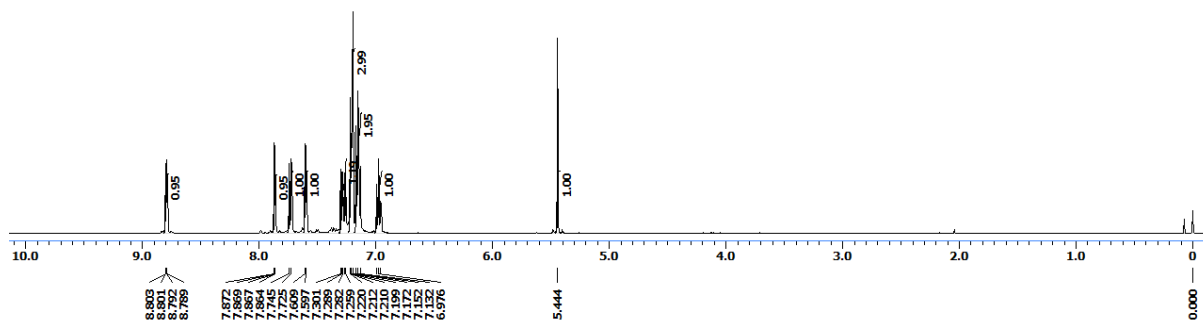
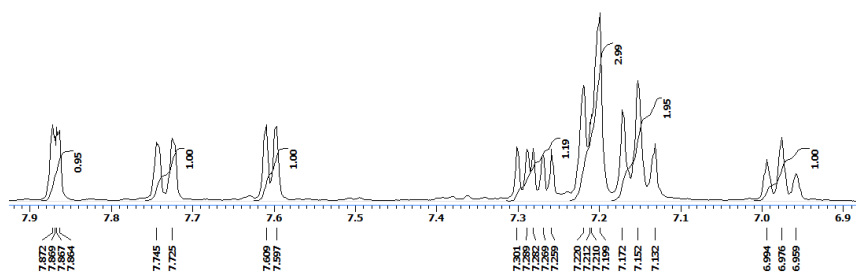
8-Chloro-6,7-diphenyl-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4b)



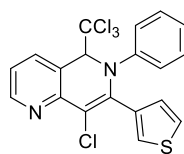
¹H NMR



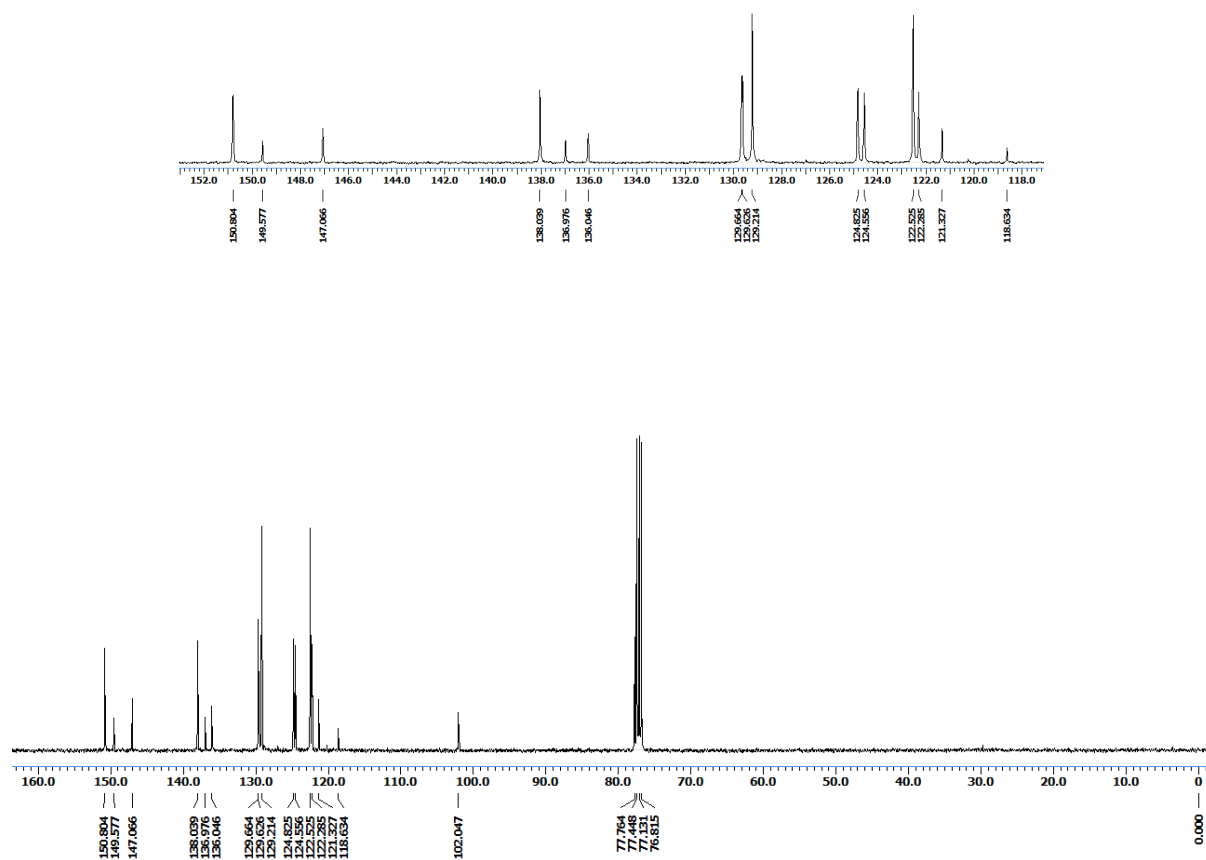
8-Chloro-6-phenyl-7-(thiophen-3-yl)-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4c)



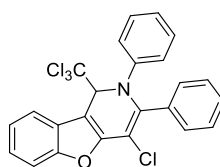
¹³C NMR



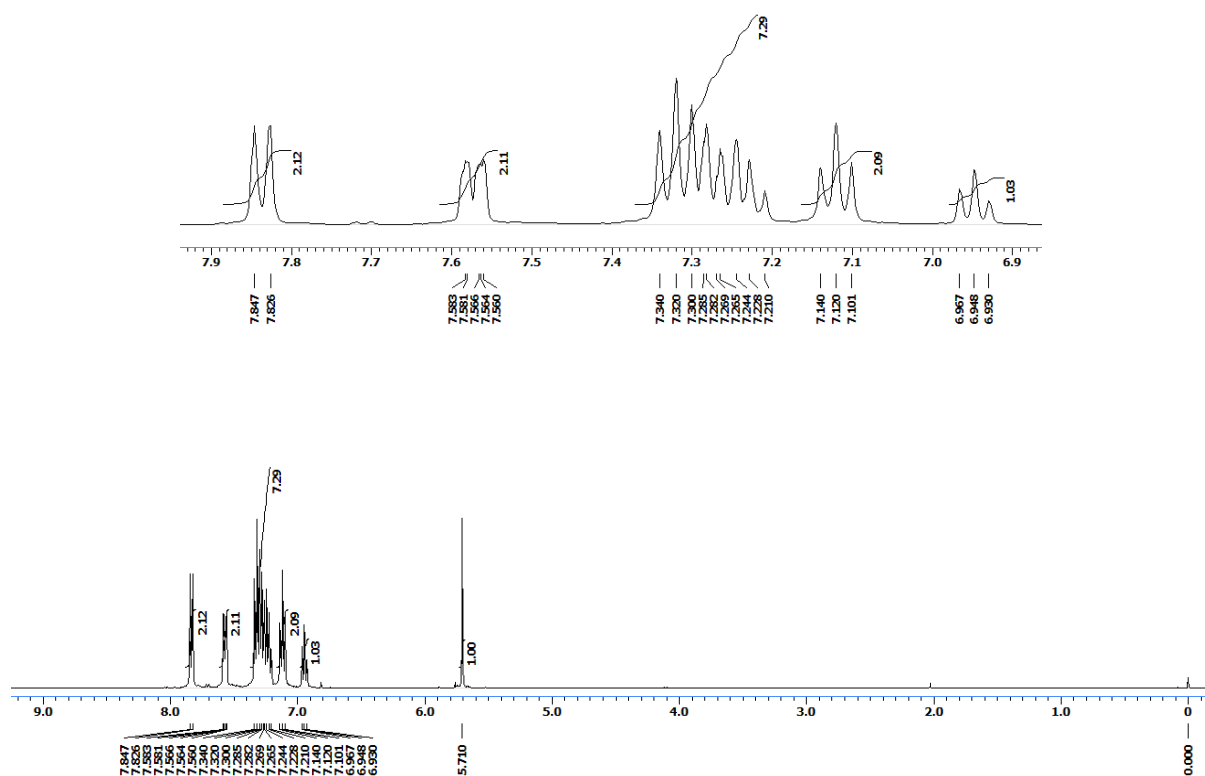
8-Chloro-6-phenyl-7-(thiophen-3-yl)-5-(trichloromethyl)-5,6-dihydro-1,6-naphthyridine (4c)



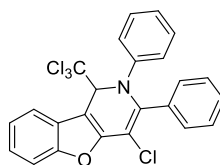
¹H NMR



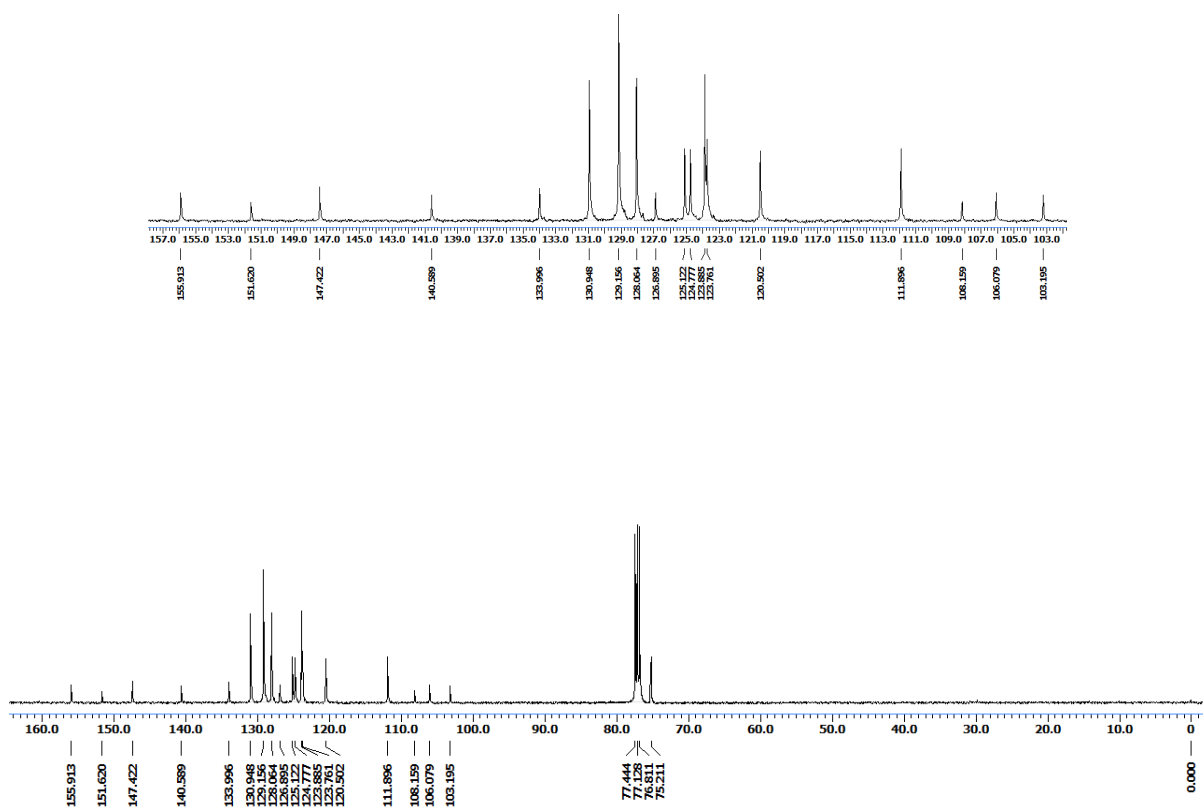
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5a)



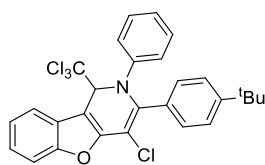
¹³C NMR



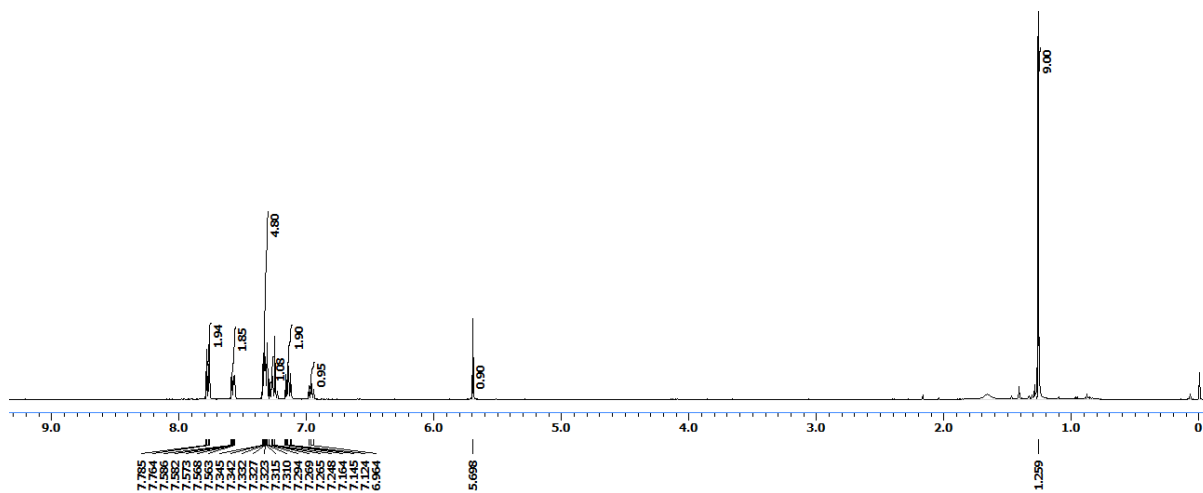
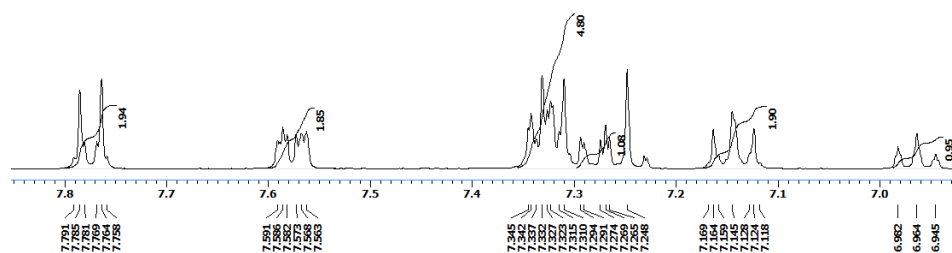
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5a)

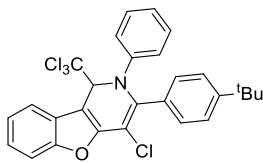


¹H NMR

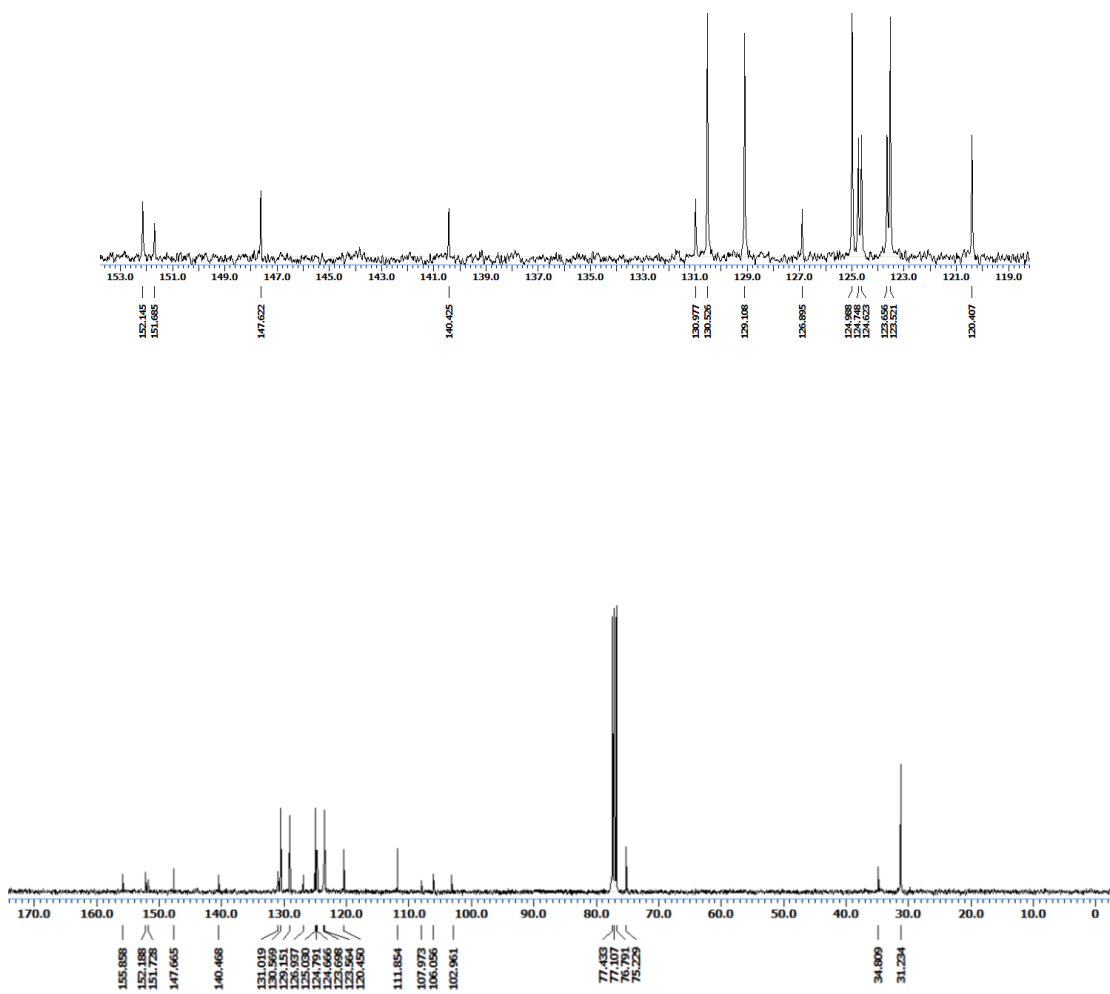


3-(4-(*Tert*-butyl)phenyl)-4-chloro-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-*c*]pyridine (5b)

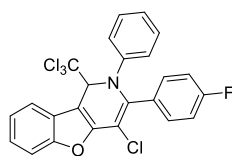


¹³C NMR

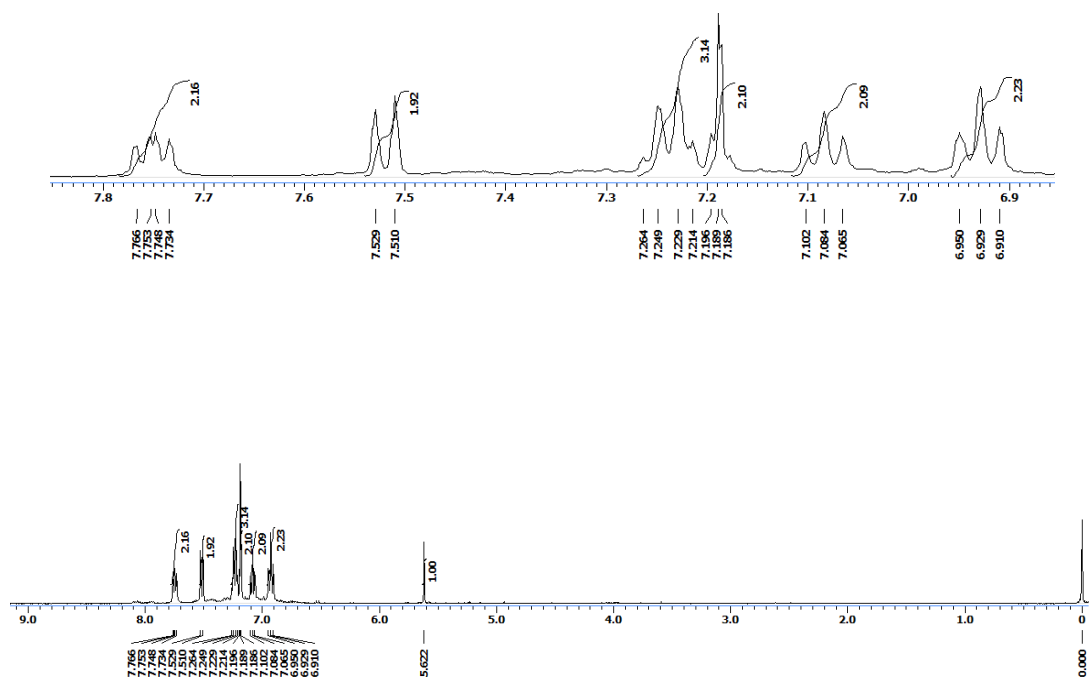
3-(4-(*Tert*-butyl)phenyl)-4-chloro-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-*c*]pyridine (5b)



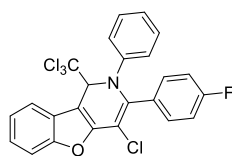
¹H NMR



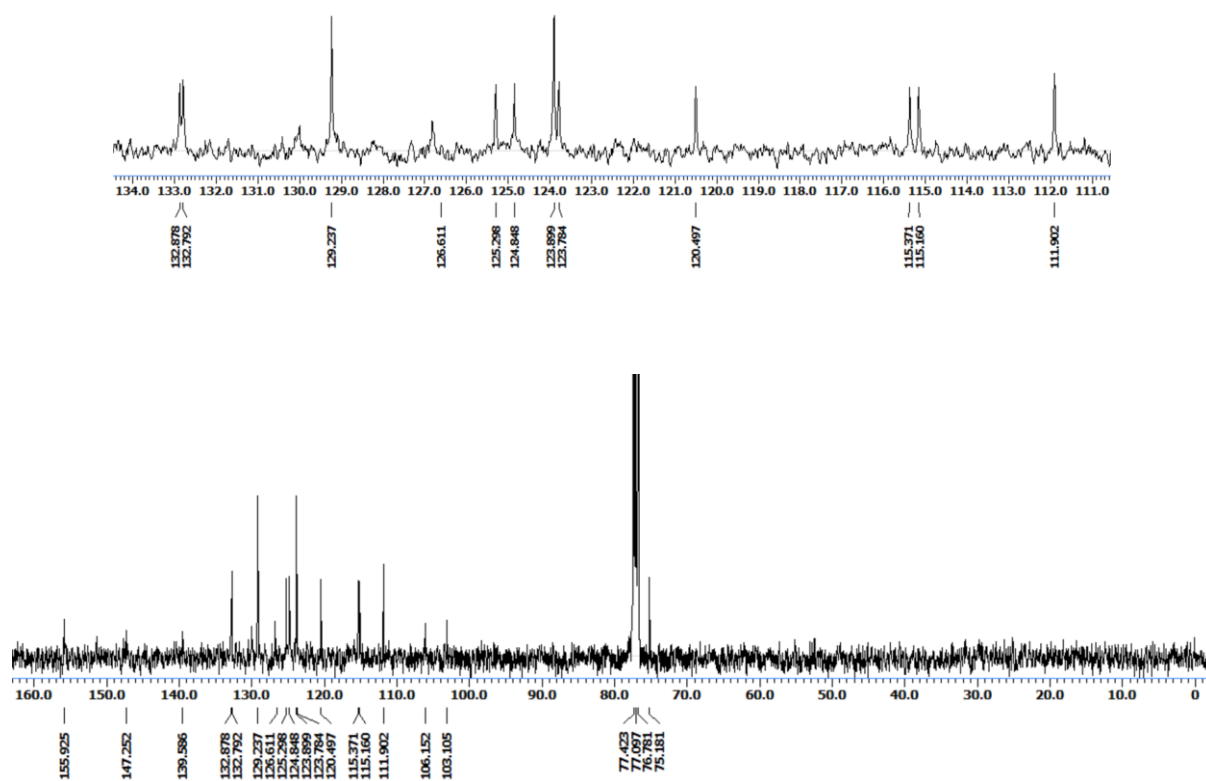
4-Chloro-3-(4-fluorophenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5c)



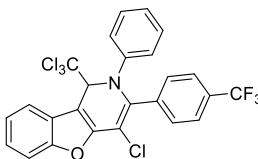
¹³C NMR



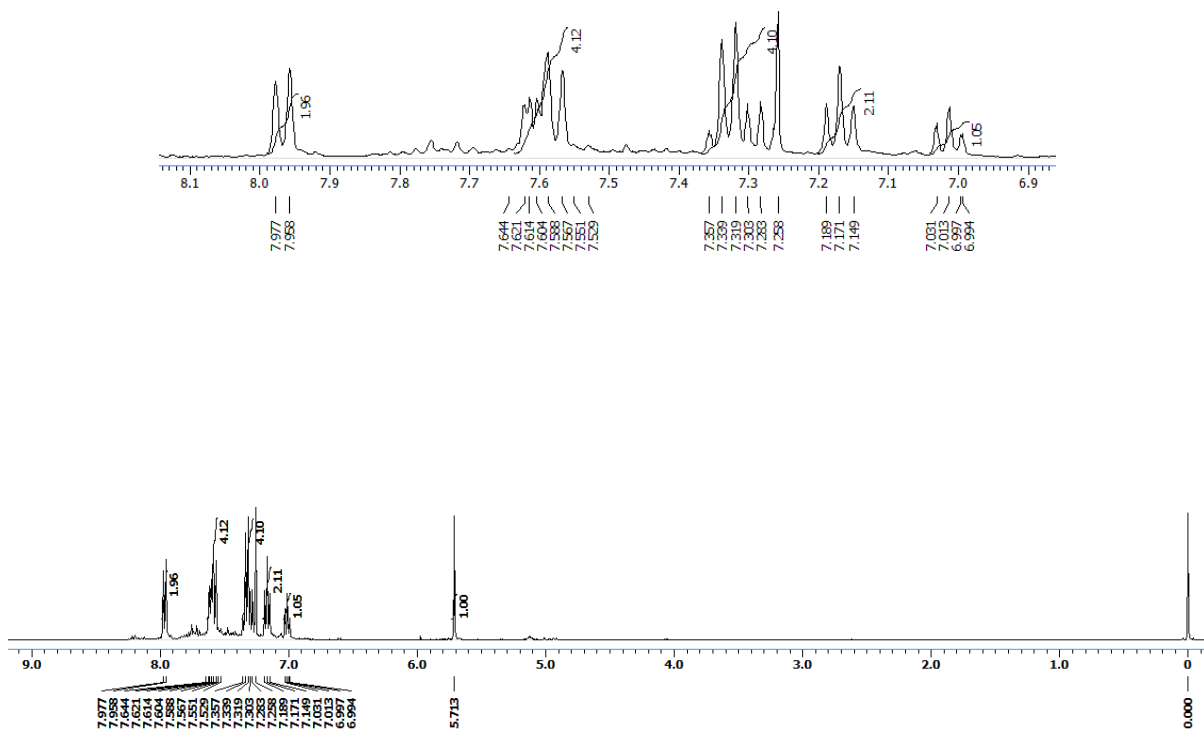
4-Chloro-3-(4-fluorophenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5c)



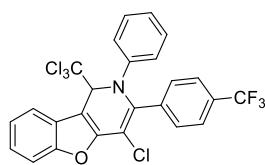
¹H NMR



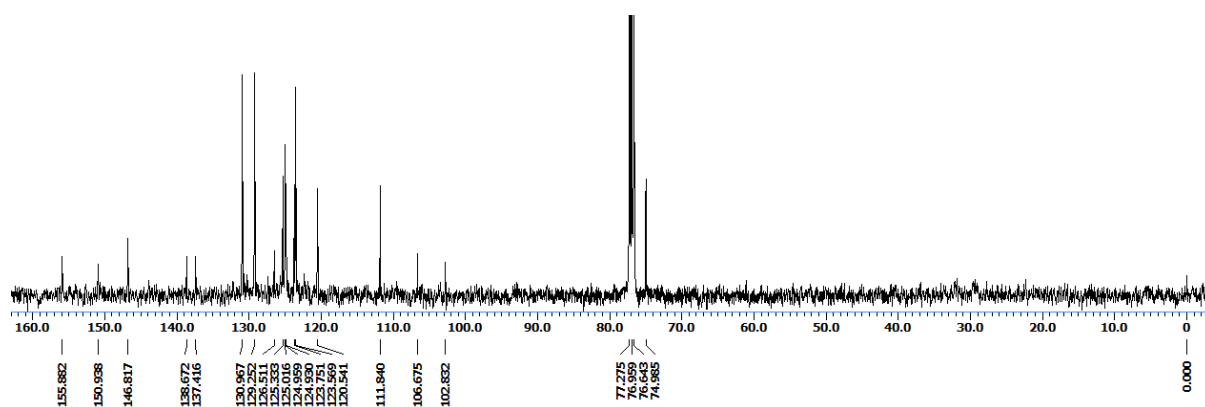
4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzofuro[3,2-c]pyridine(5d)



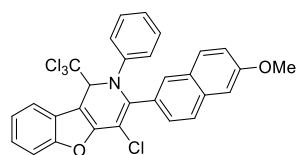
¹³C NMR



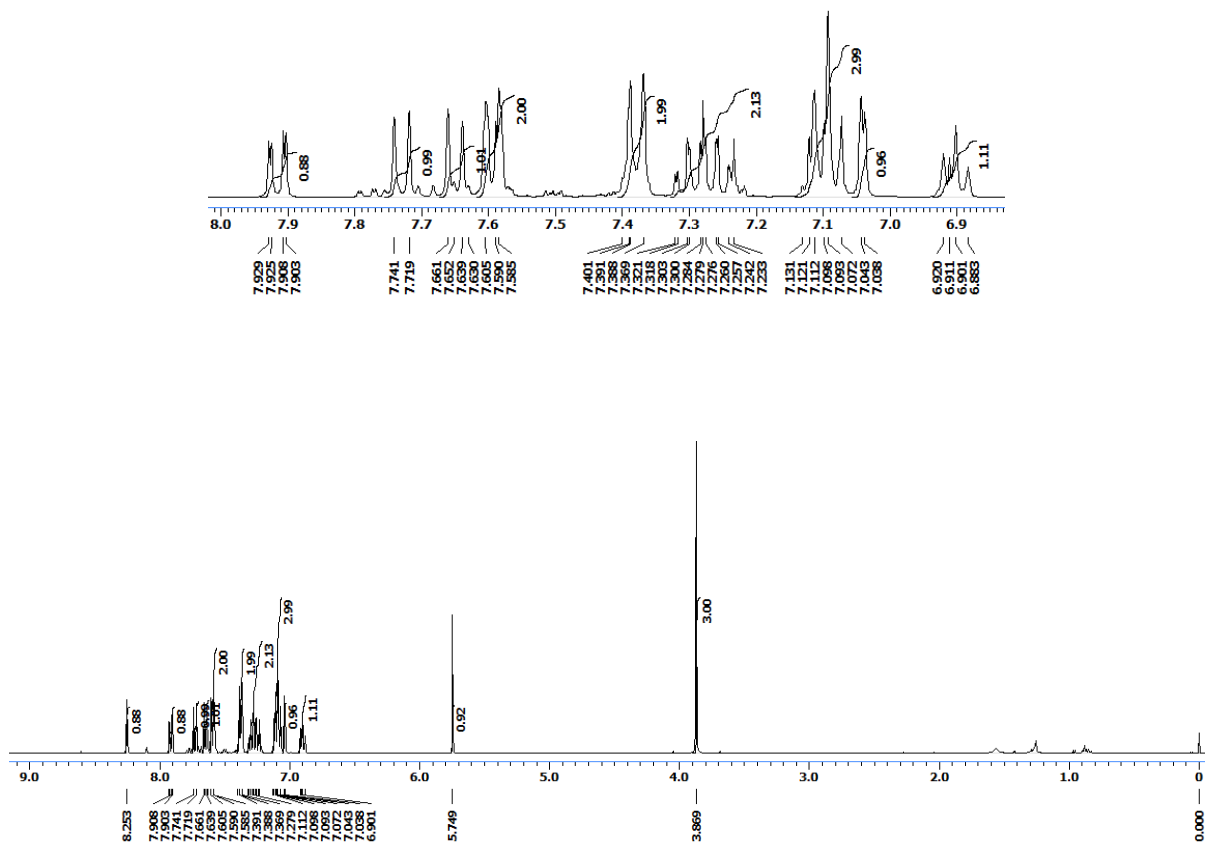
4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzofuro[3,2-*c*]pyridine (5d)



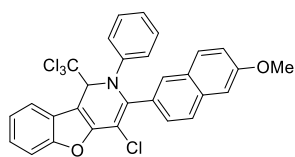
¹H NMR



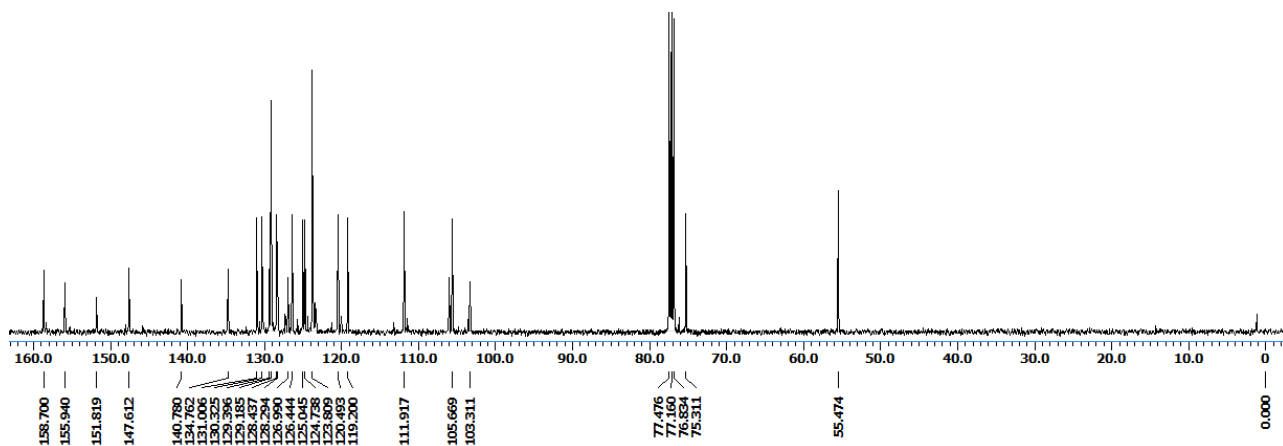
4-Chloro-3-(6-methoxynaphthalen-2-yl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5e)



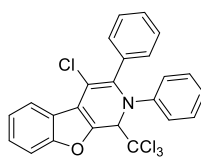
¹³C NMR



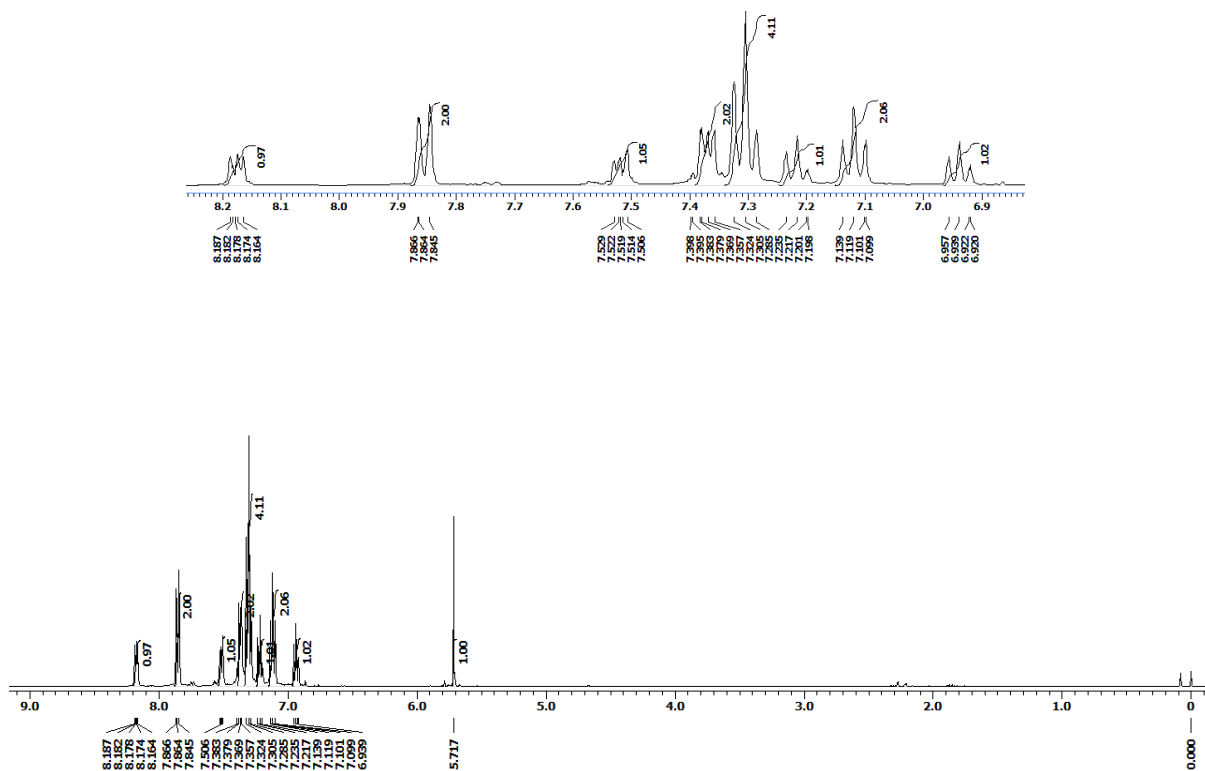
4-Chloro-3-(6-methoxynaphthalen-2-yl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[3,2-c]pyridine (5e)



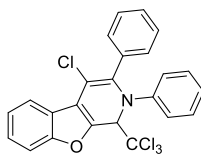
¹H NMR



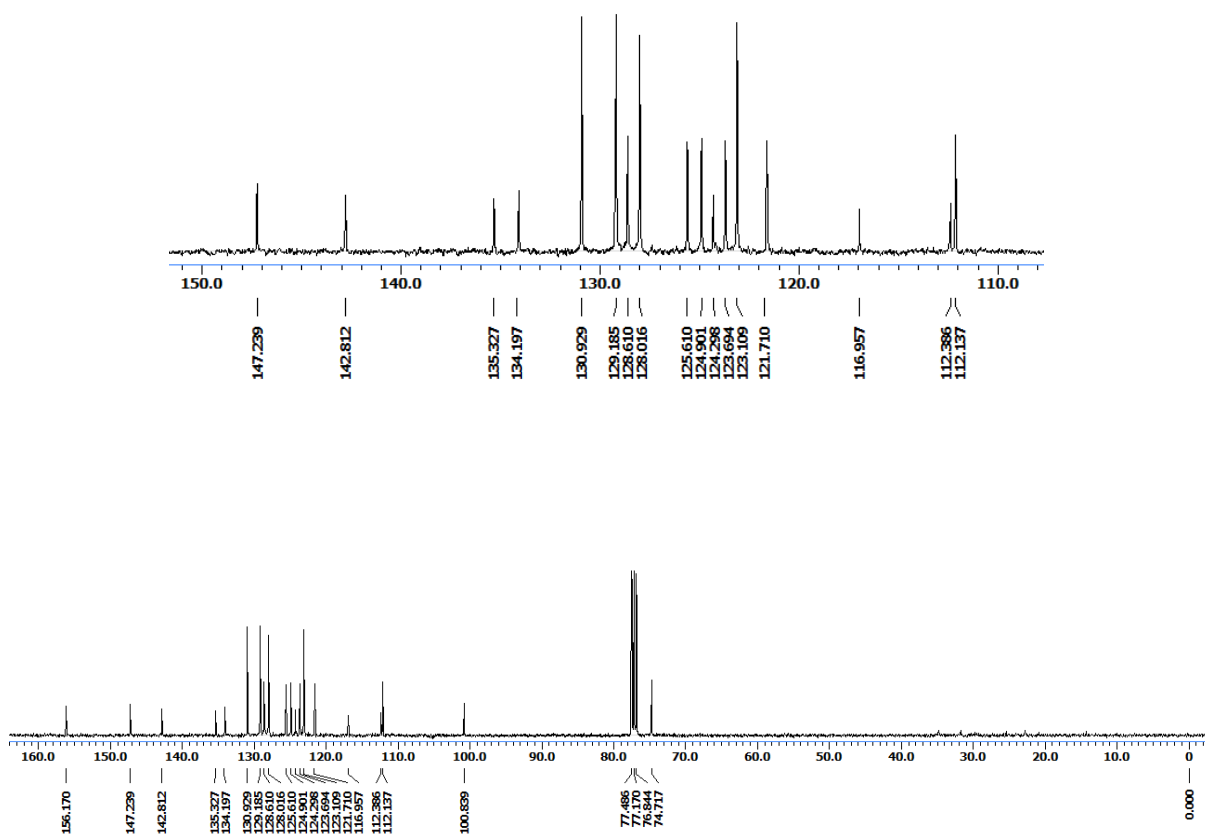
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6a)



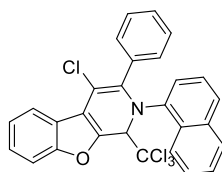
¹³C NMR



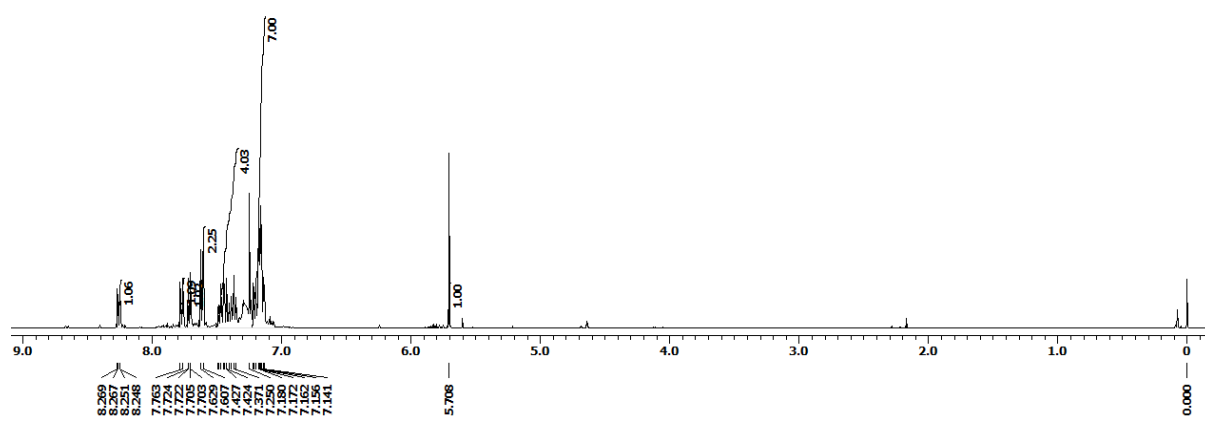
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6a)



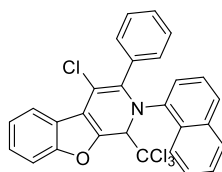
¹H NMR



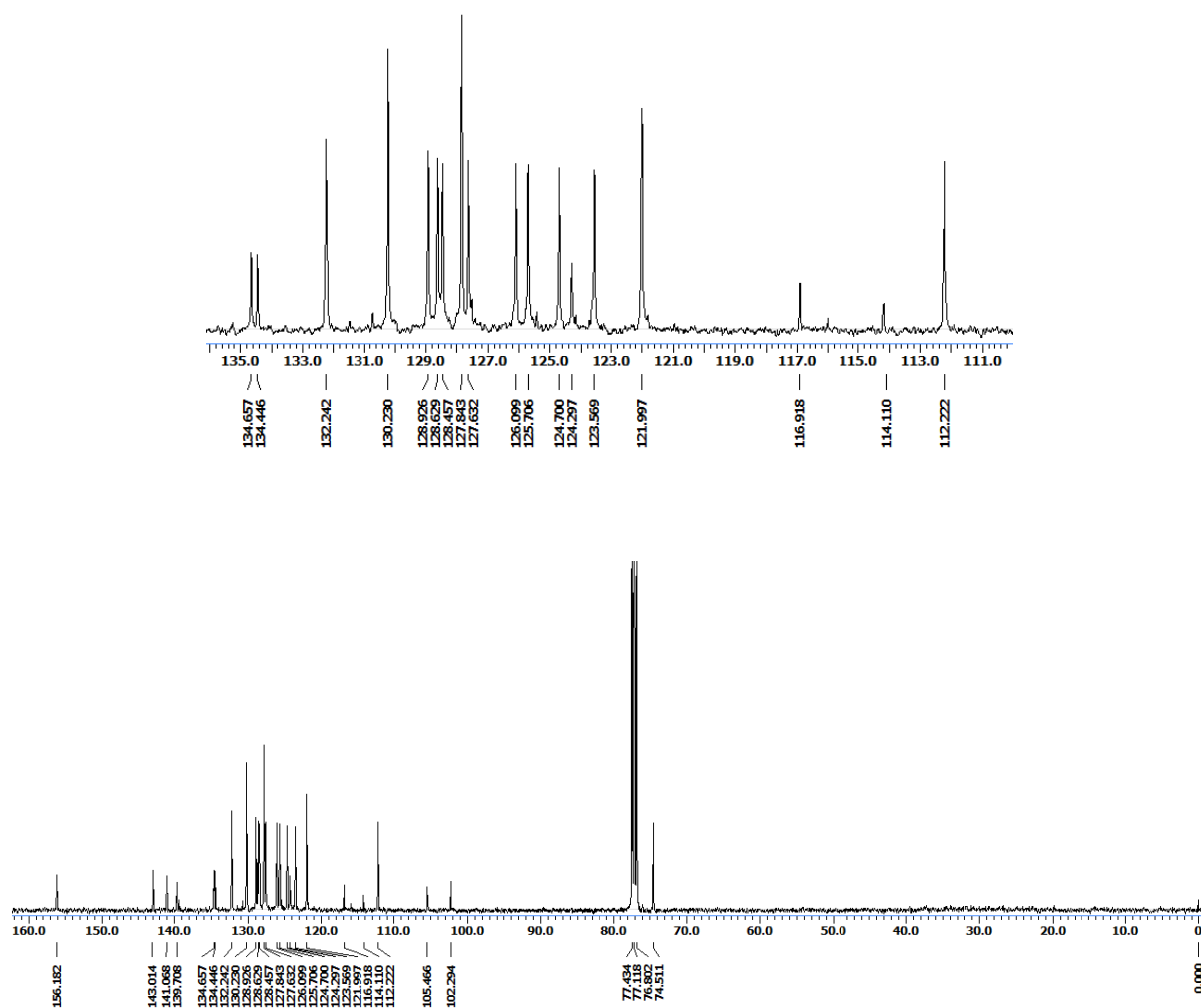
4-Chloro-2-(naphthalen-1-yl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6b)



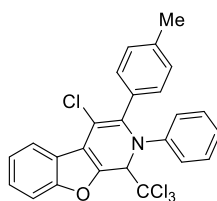
¹³C NMR



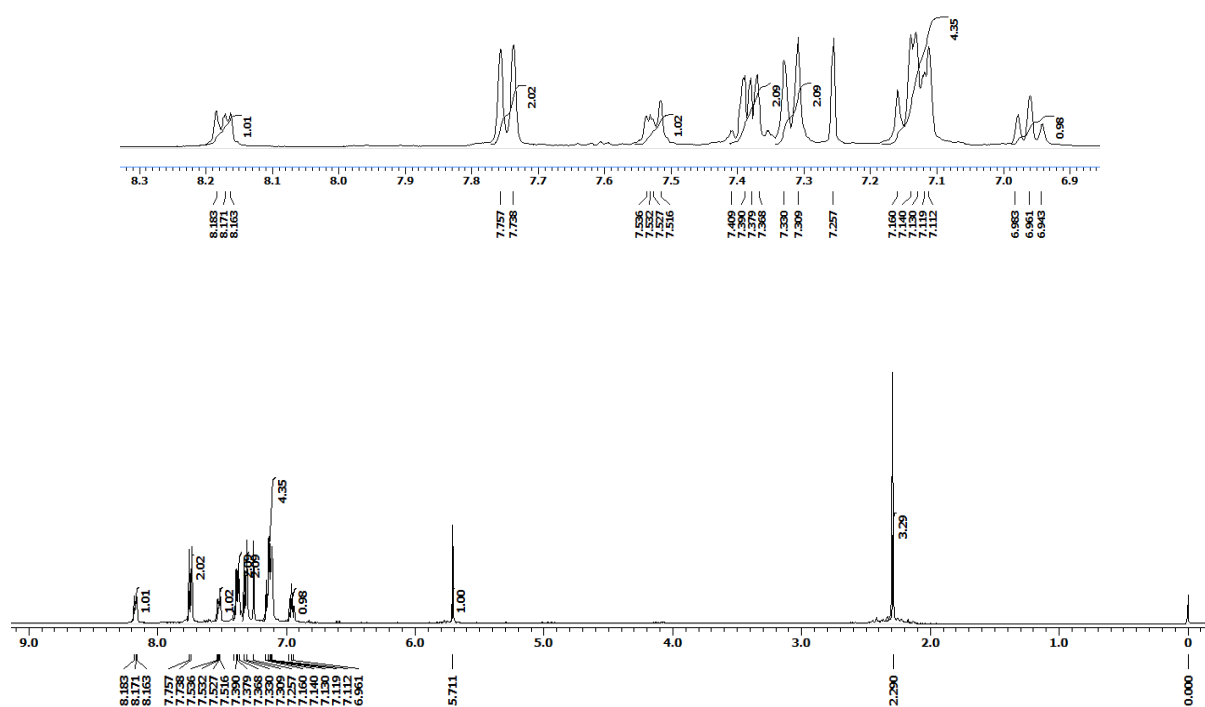
4-Chloro-2-(naphthalen-1-yl)-3-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6b)



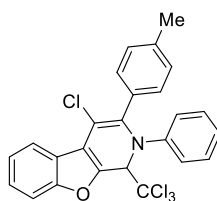
¹H NMR



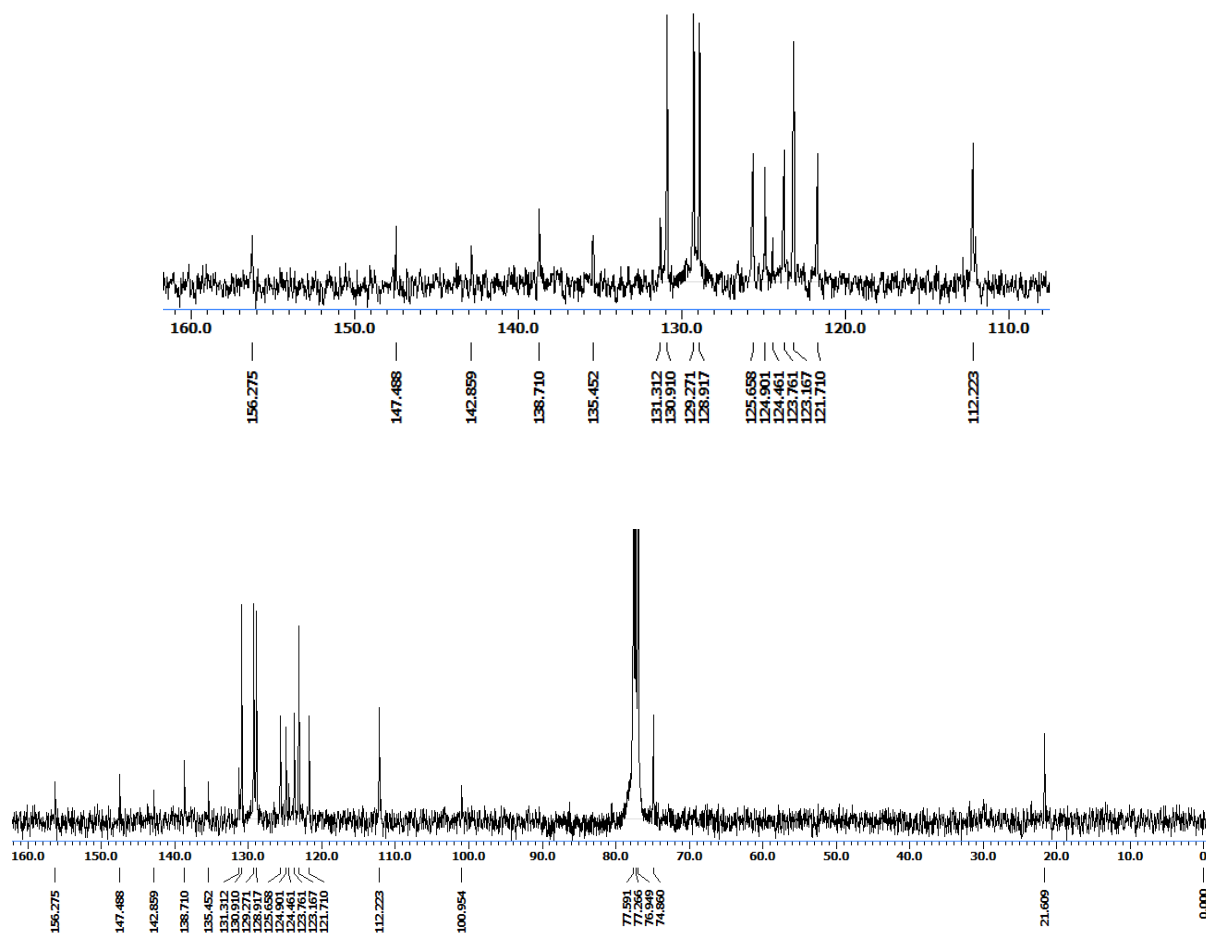
4-Chloro-2-phenyl-3-(*p*-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-*c*]pyridine (6c)



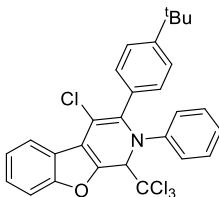
¹³C NMR



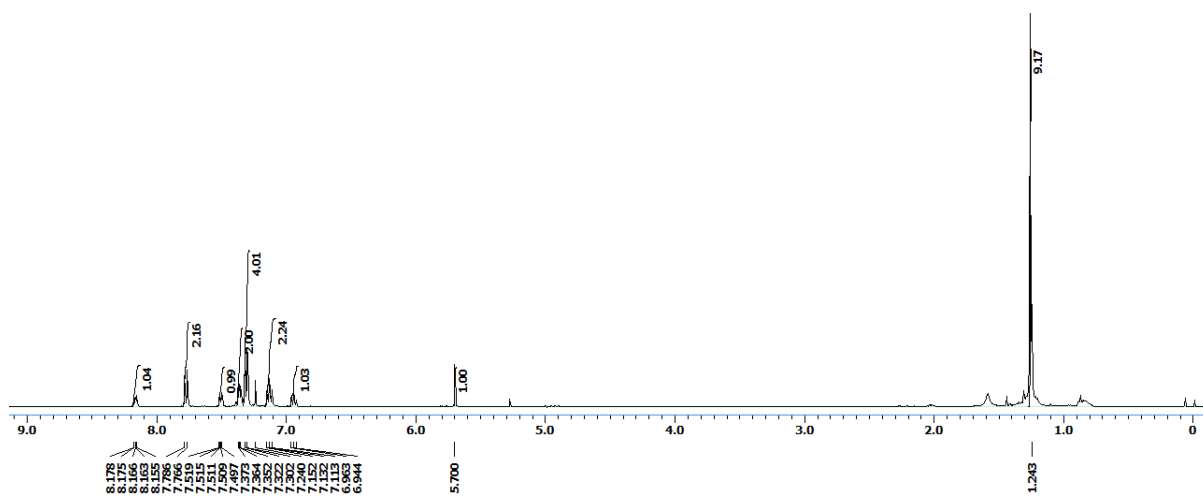
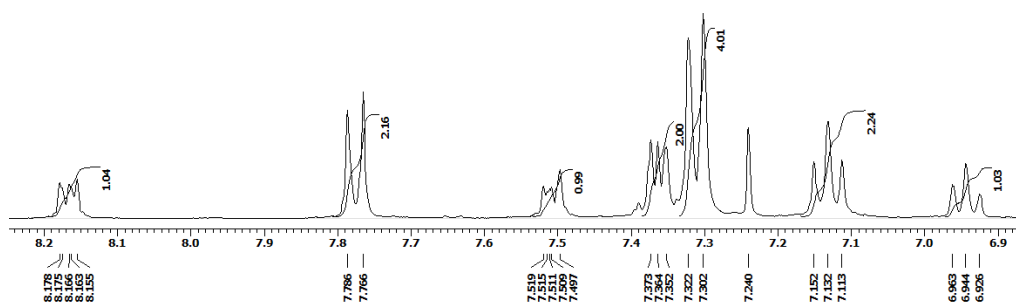
4-Chloro-2-phenyl-3-(*p*-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-*c*]pyridine (6c)



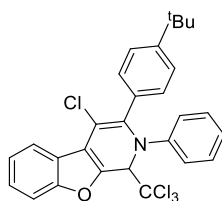
¹H NMR



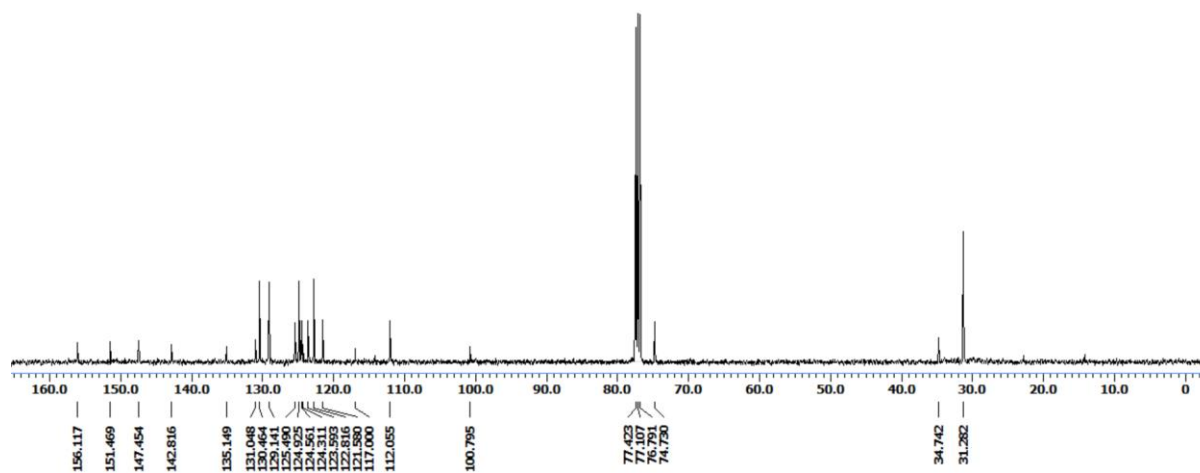
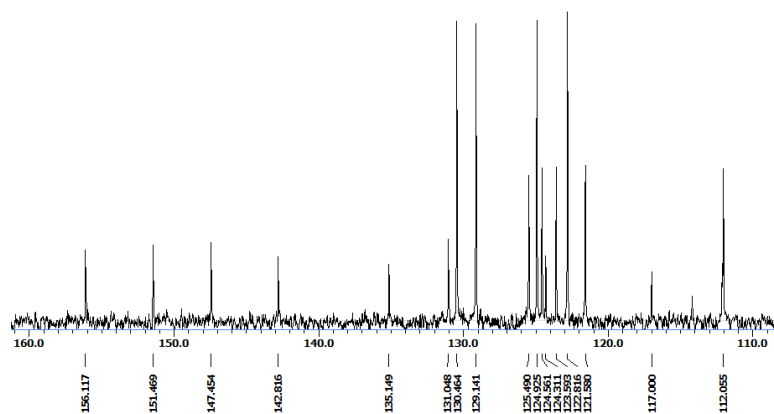
3-(4-(*Tert*-butyl)phenyl)-4-chloro-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-*c*]pyridine (6d)



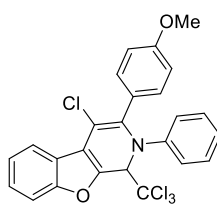
¹³C NMR



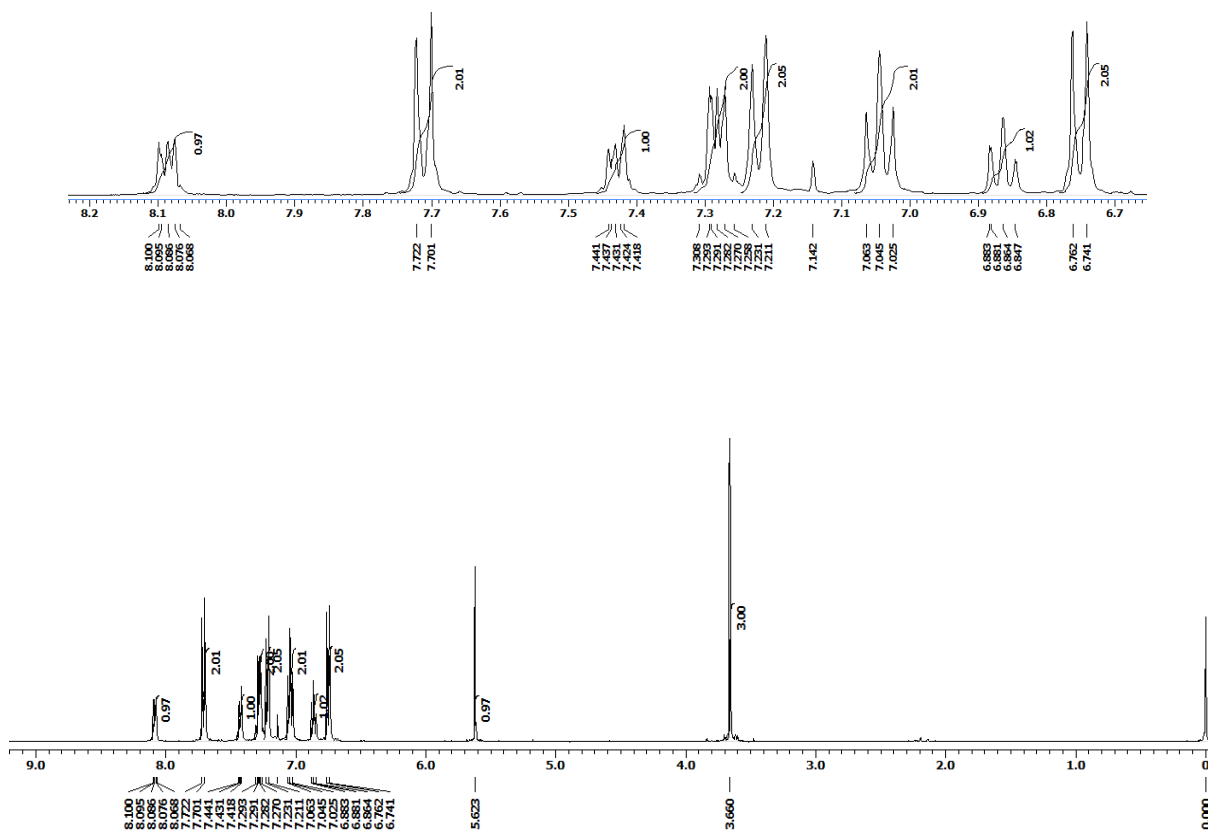
3-(4-(*Tert*-butyl)phenyl)-4-chloro-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-*c*]pyridine (6d)



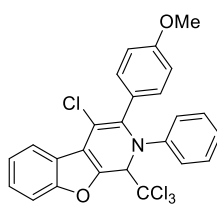
¹H NMR



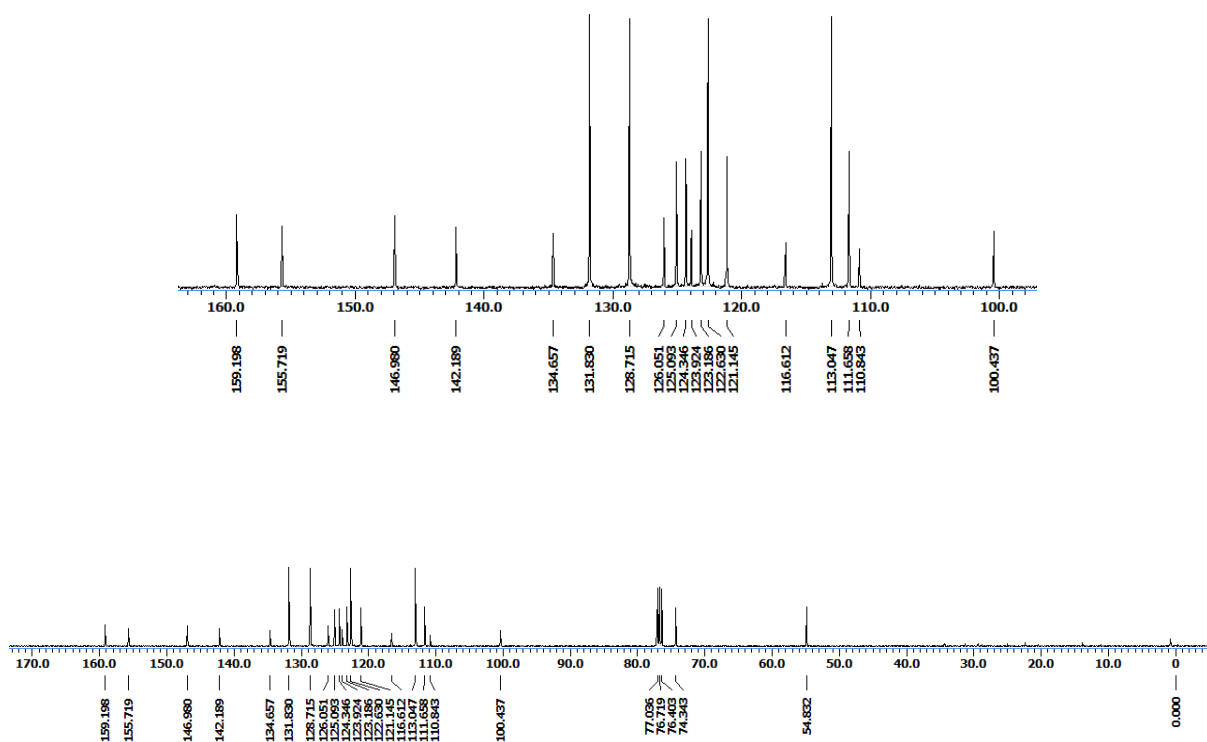
4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6e)



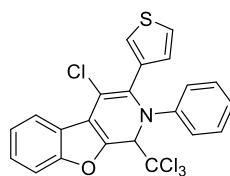
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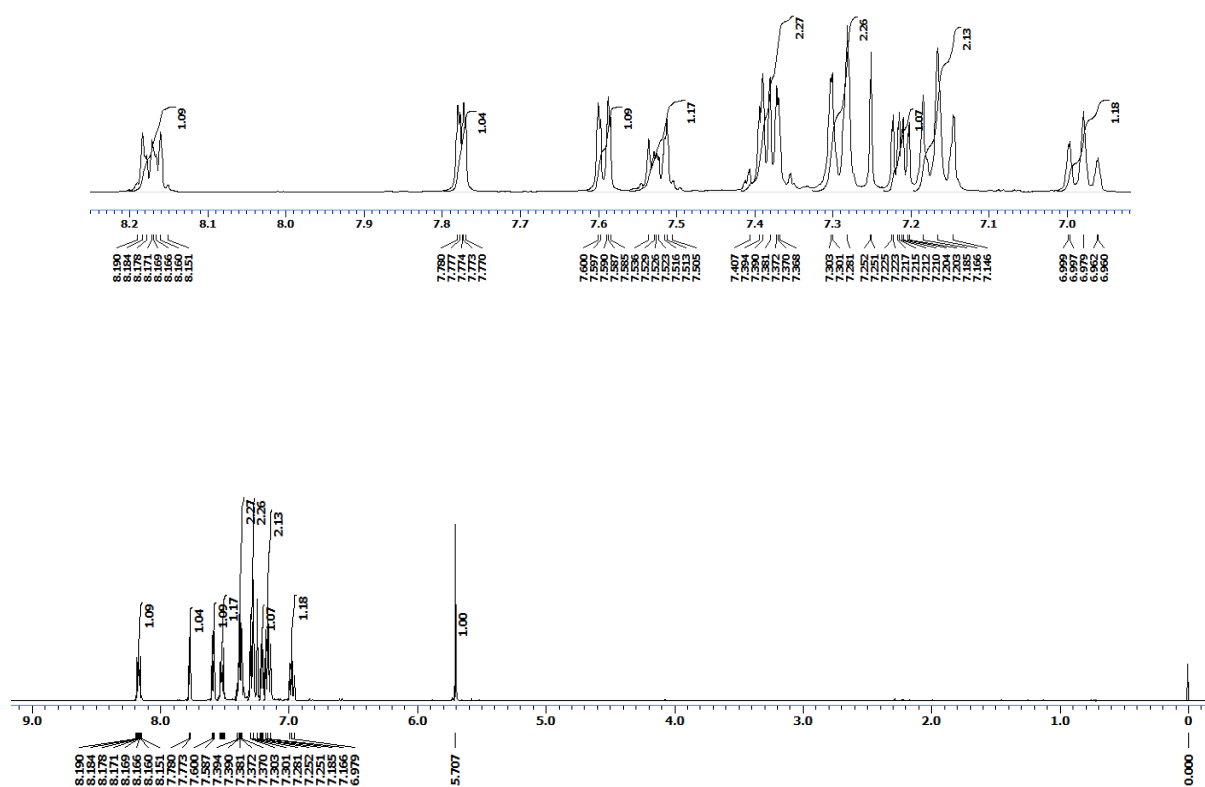
4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6e)



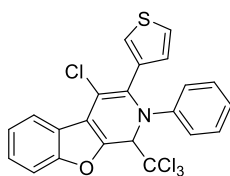
¹H NMR



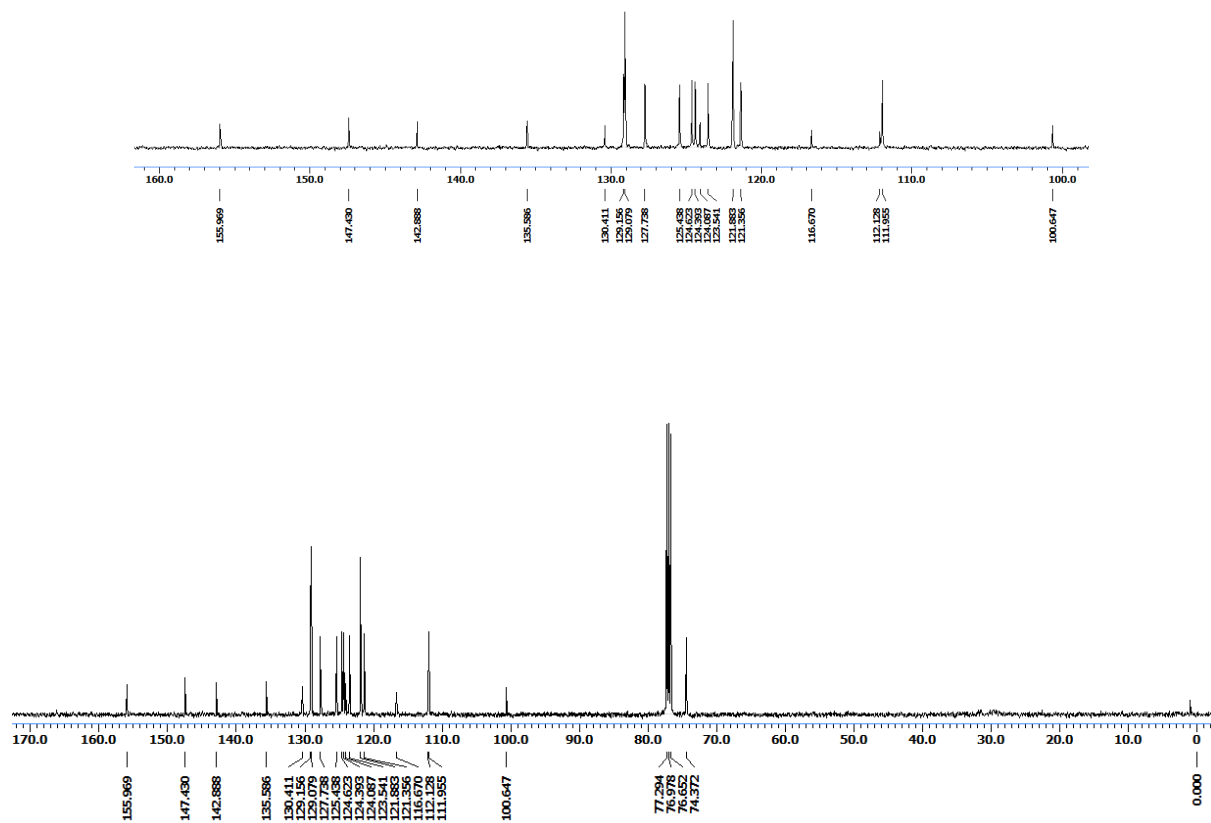
4-Chloro-2-phenyl-3-(thiophen-3-yl)-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6f)



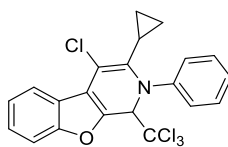
¹³C NMR



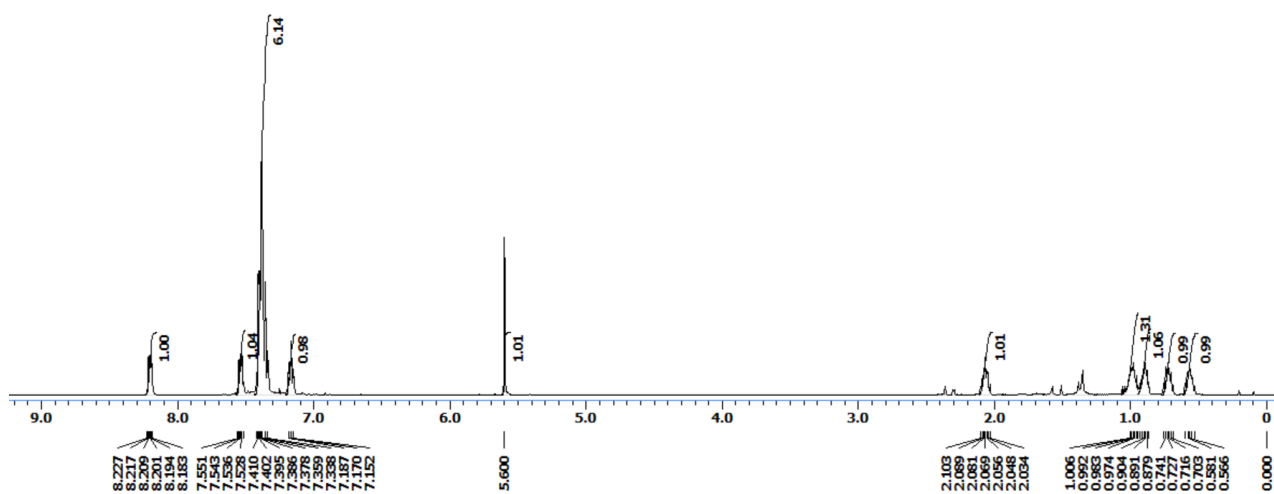
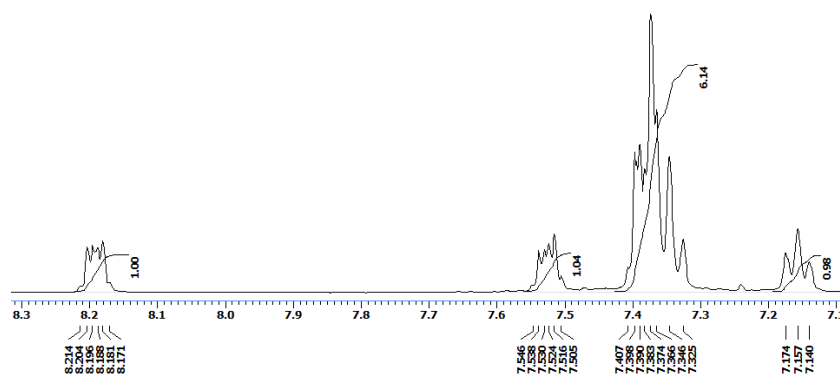
4-Chloro-2-phenyl-3-(thiophen-3-yl)-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6f)

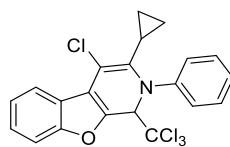


¹H NMR

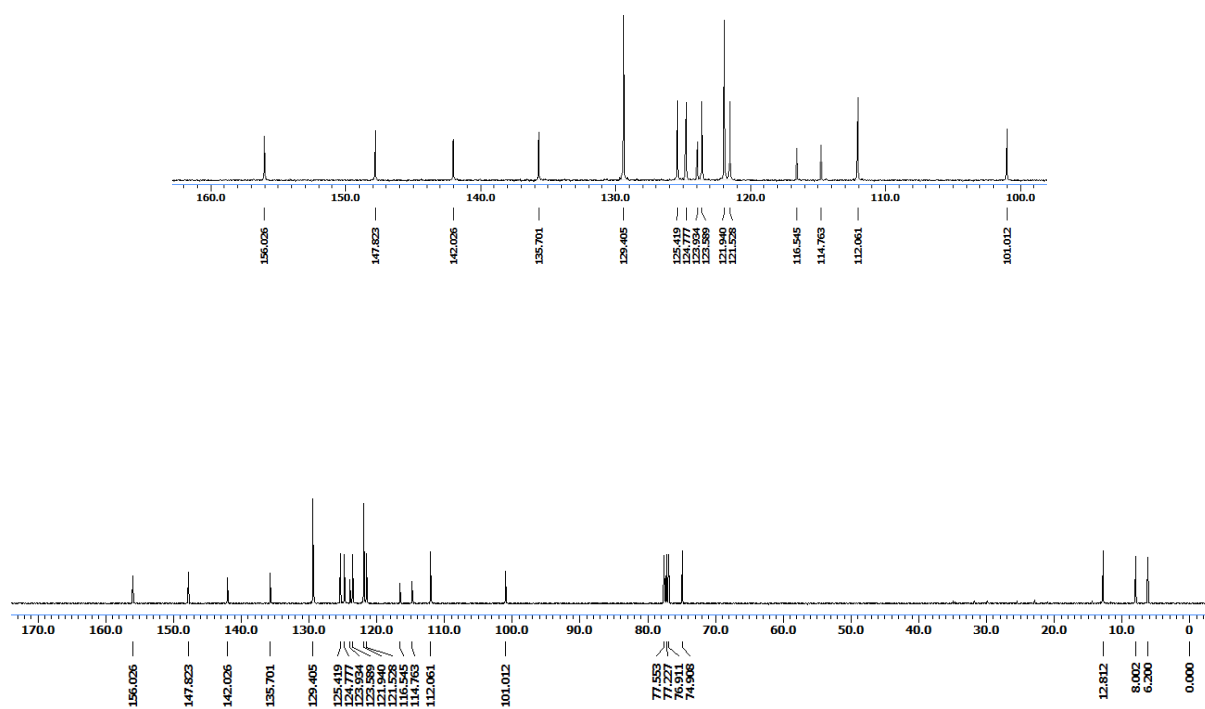


4-Chloro-3-cyclopropyl-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6g)

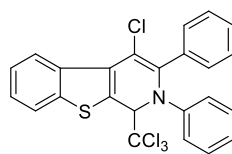


¹³C NMR

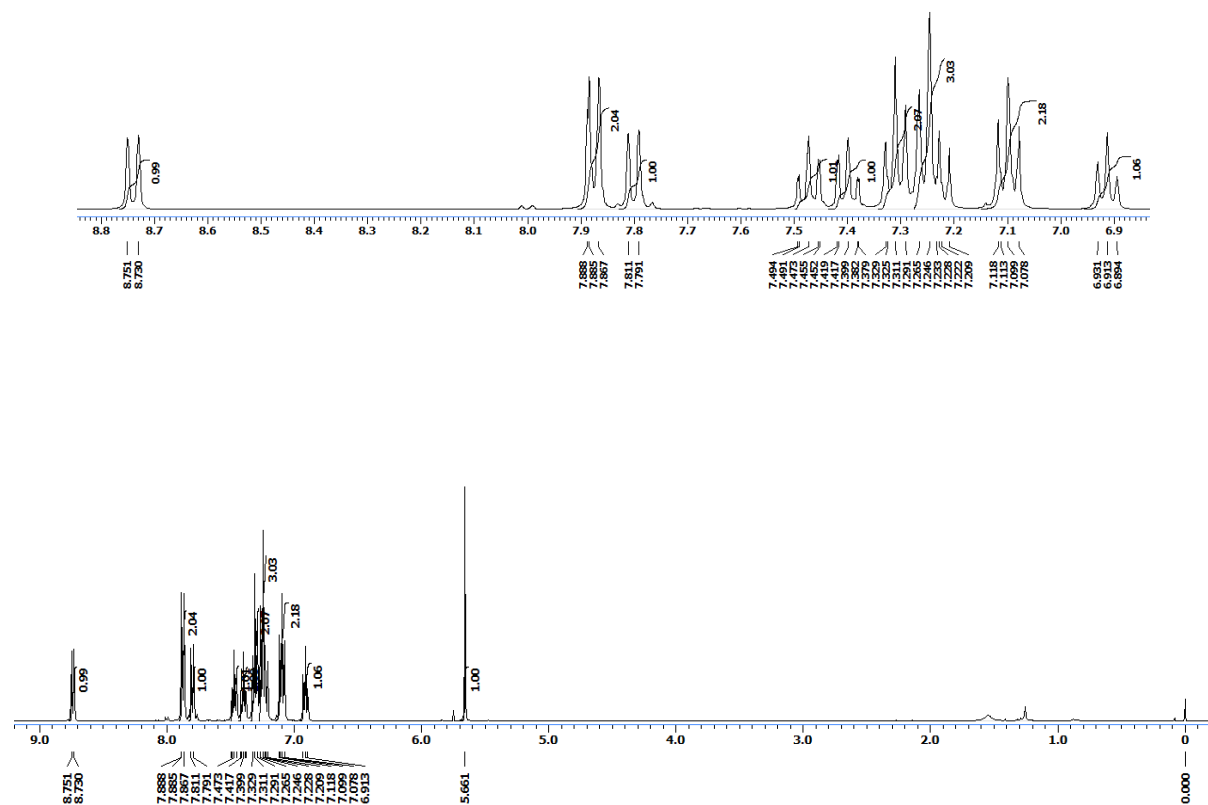
4-Chloro-3-cyclopropyl-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzofuro[2,3-c]pyridine (6g)



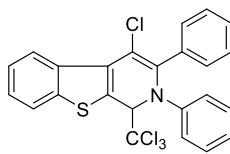
¹H NMR



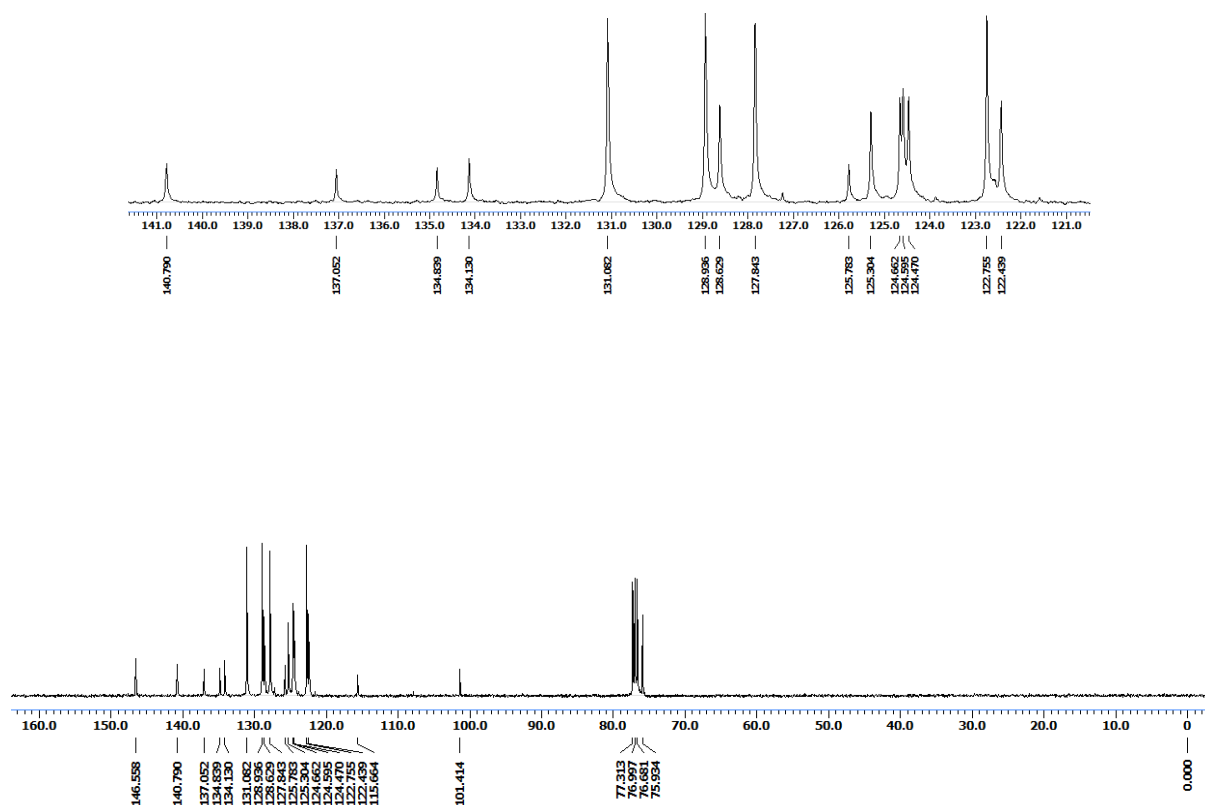
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7a)



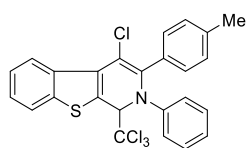
¹³C NMR



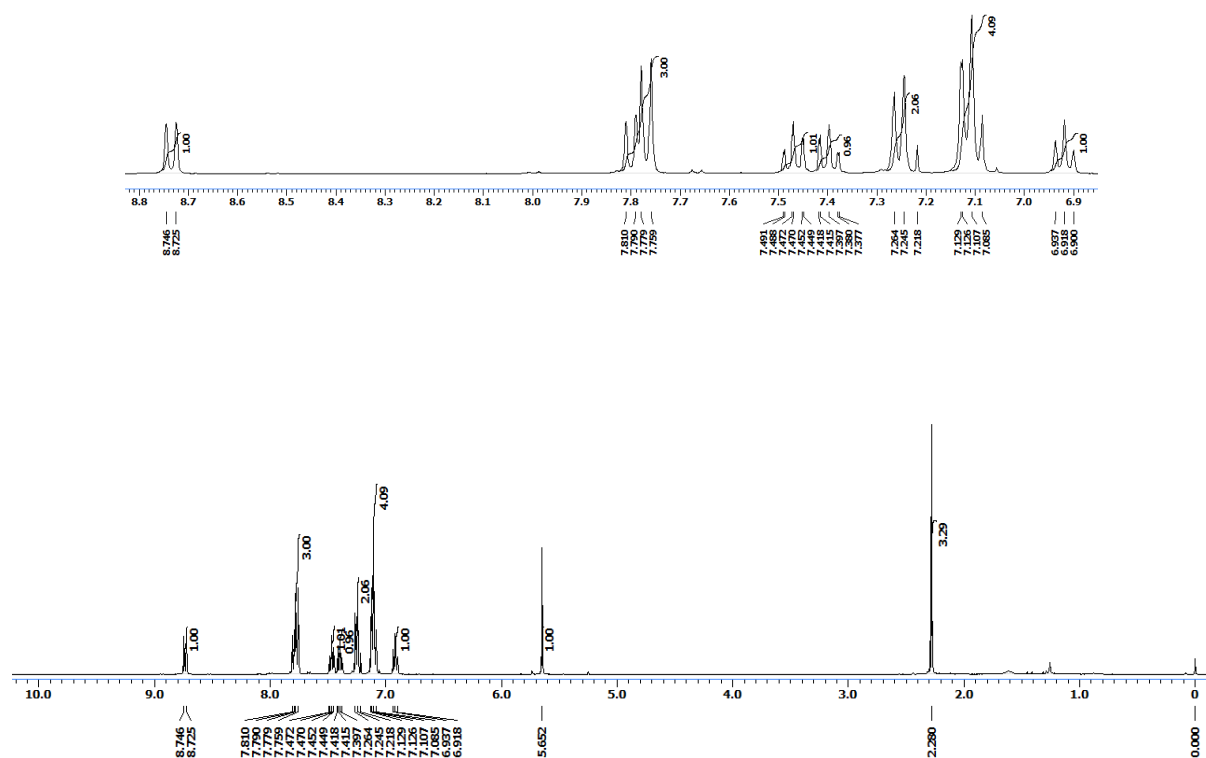
4-Chloro-2,3-diphenyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7a)



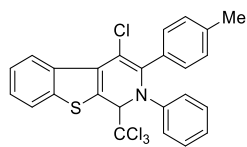
¹H NMR



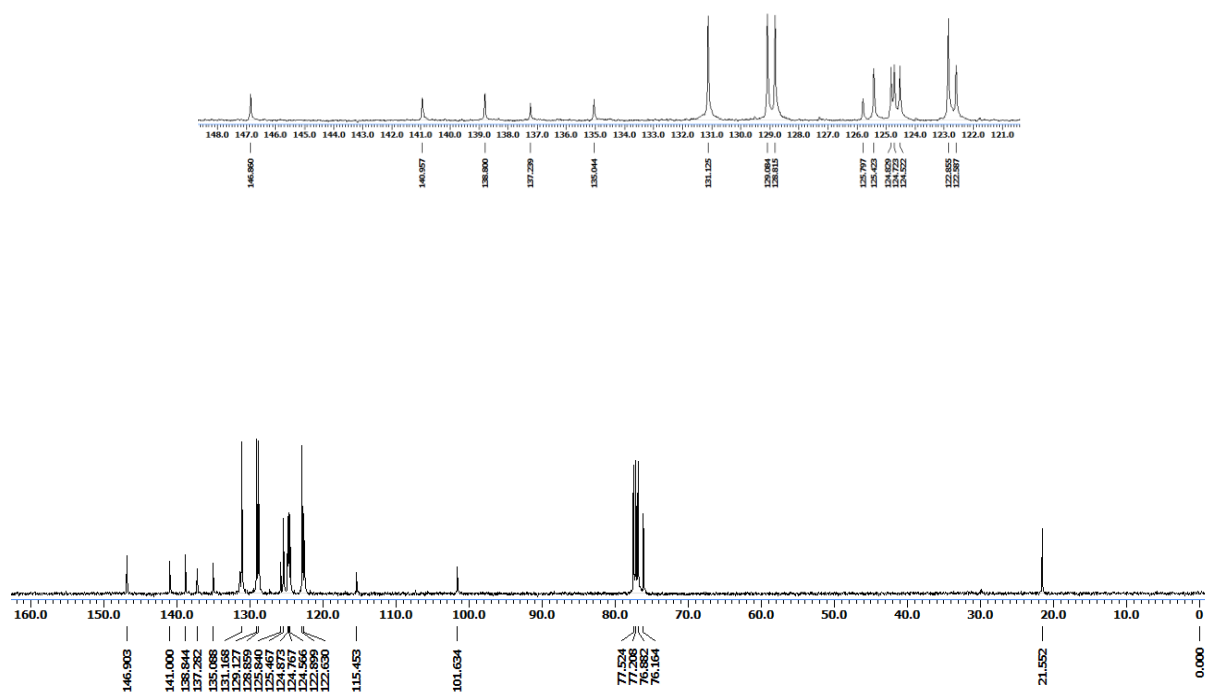
4-Chloro-2-phenyl-3-(p-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7b)



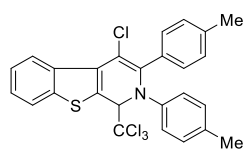
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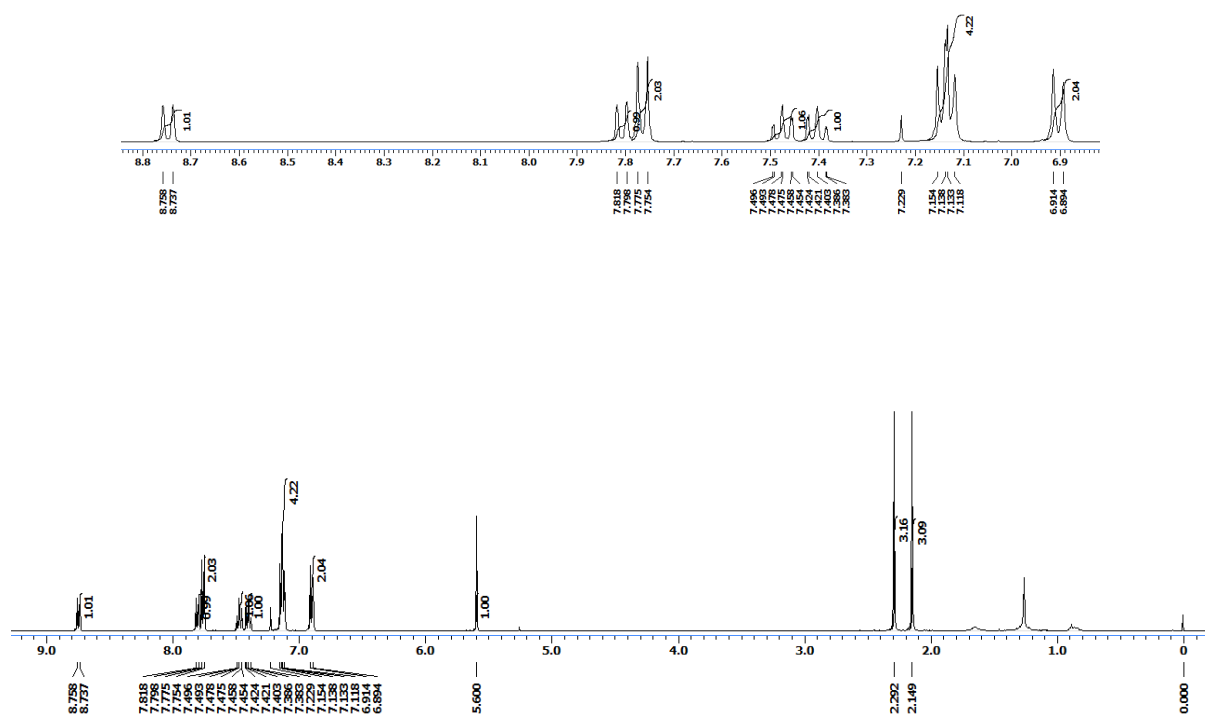
4-Chloro-2-phenyl-3-(p-tolyl)-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7b)



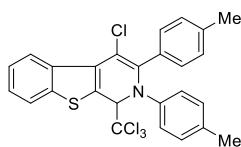
¹H NMR



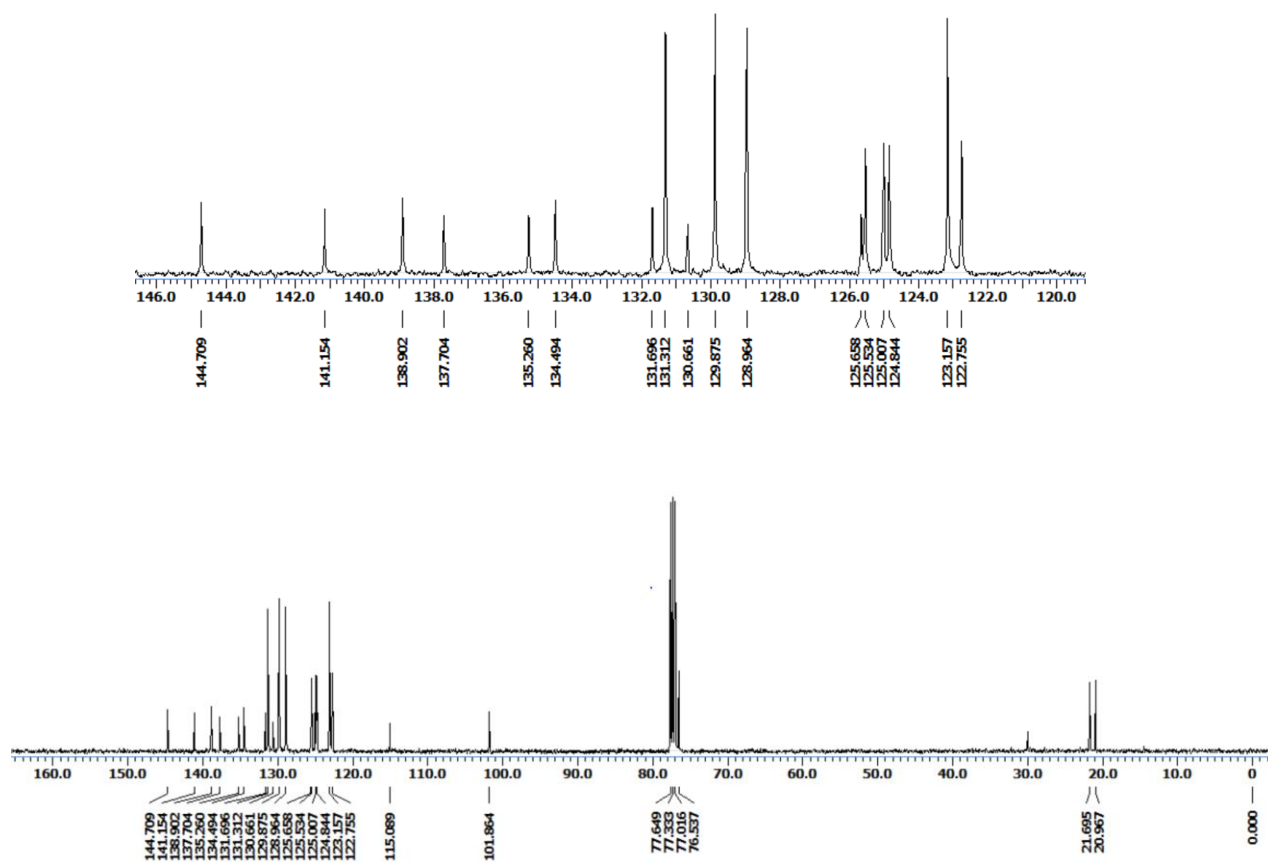
4-Chloro-2,3-di-p-tolyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7c)



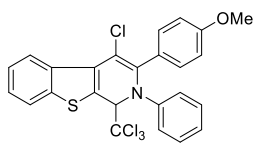
¹³C NMR



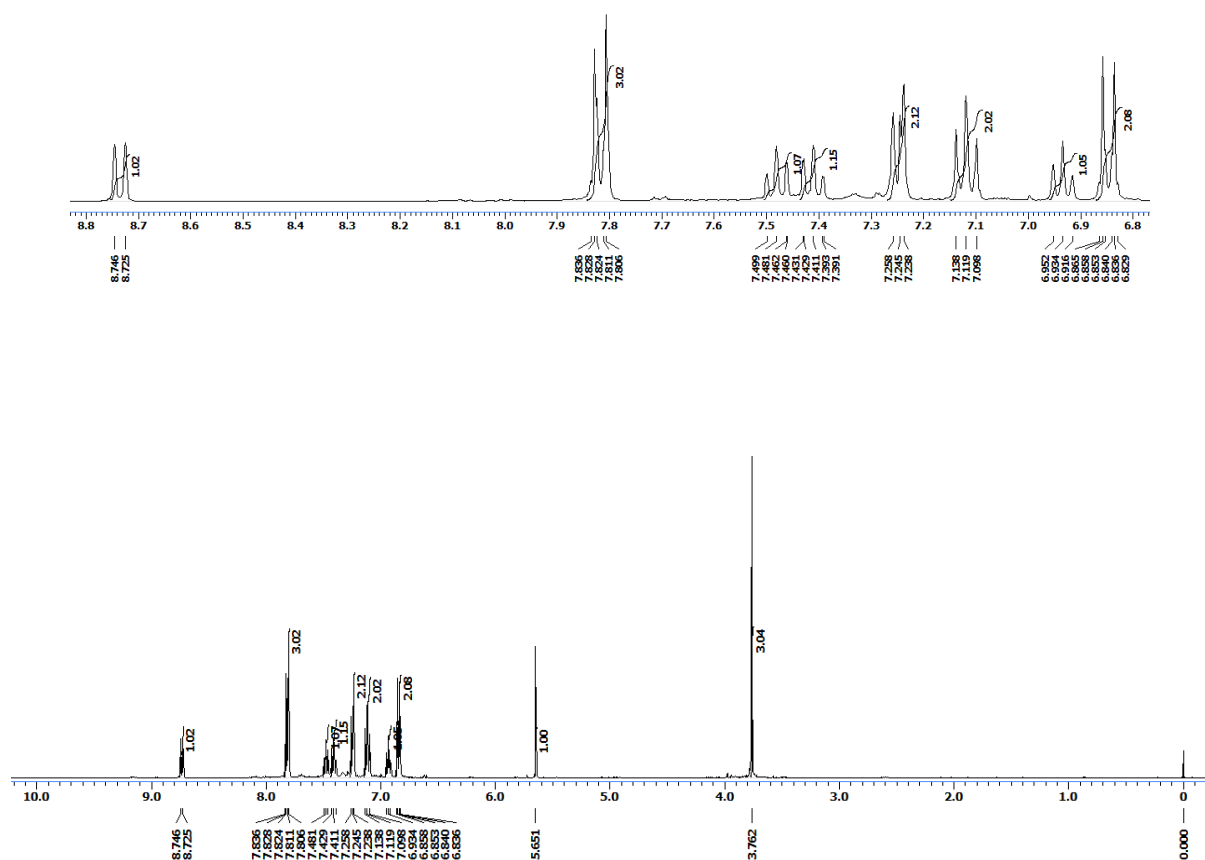
4-Chloro-2,3-di-p-tolyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine
(7c)

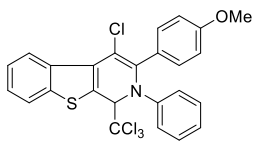


¹H NMR

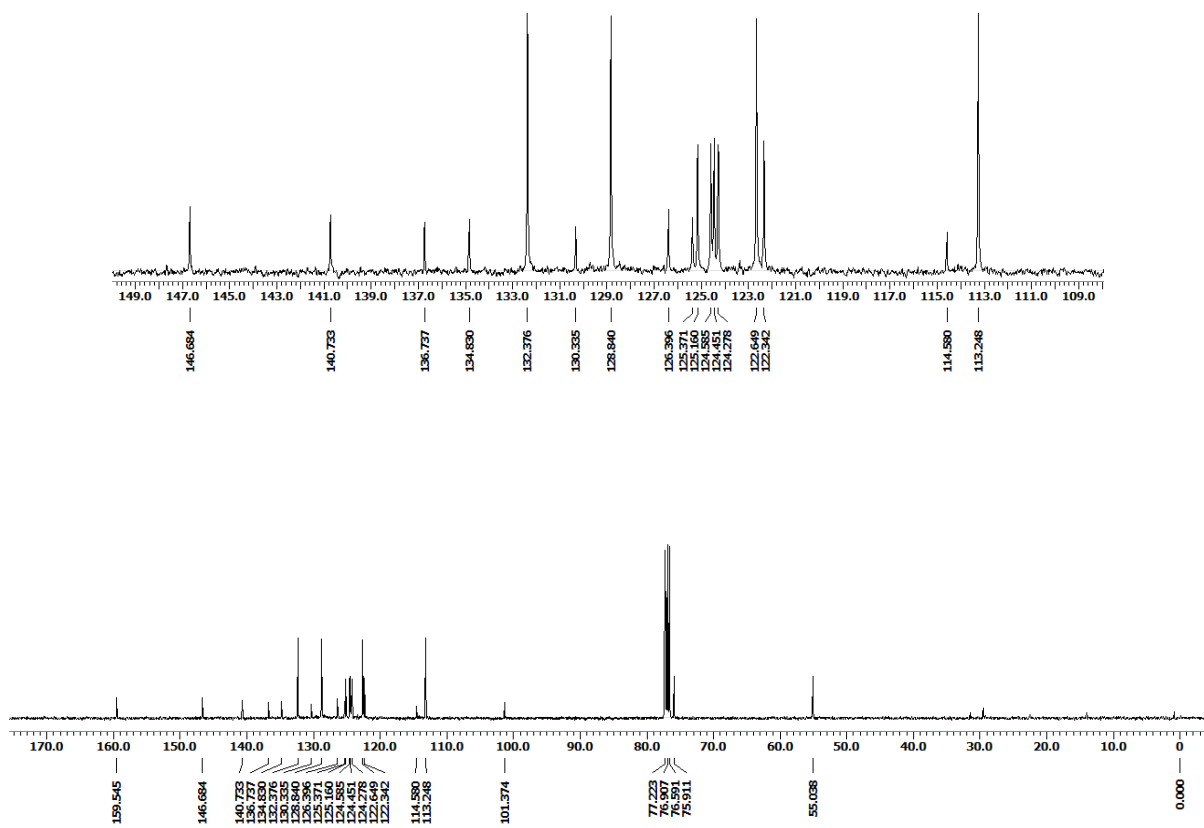


4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7d)

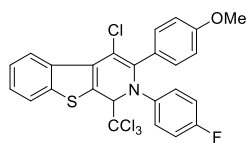


¹³C NMR

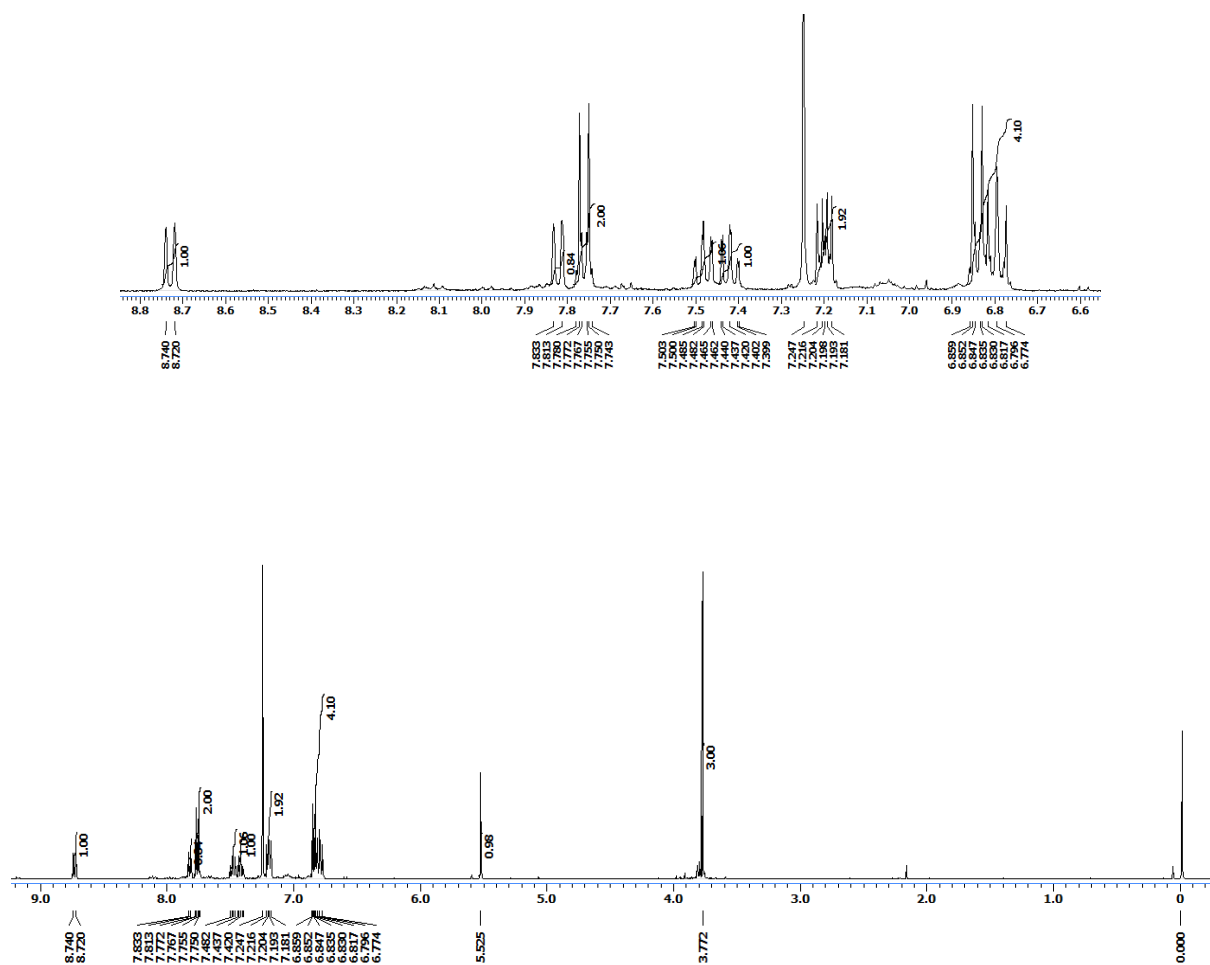
4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-*c*]pyridine (7d)



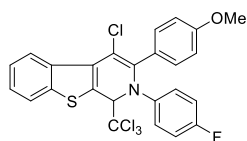
¹H NMR



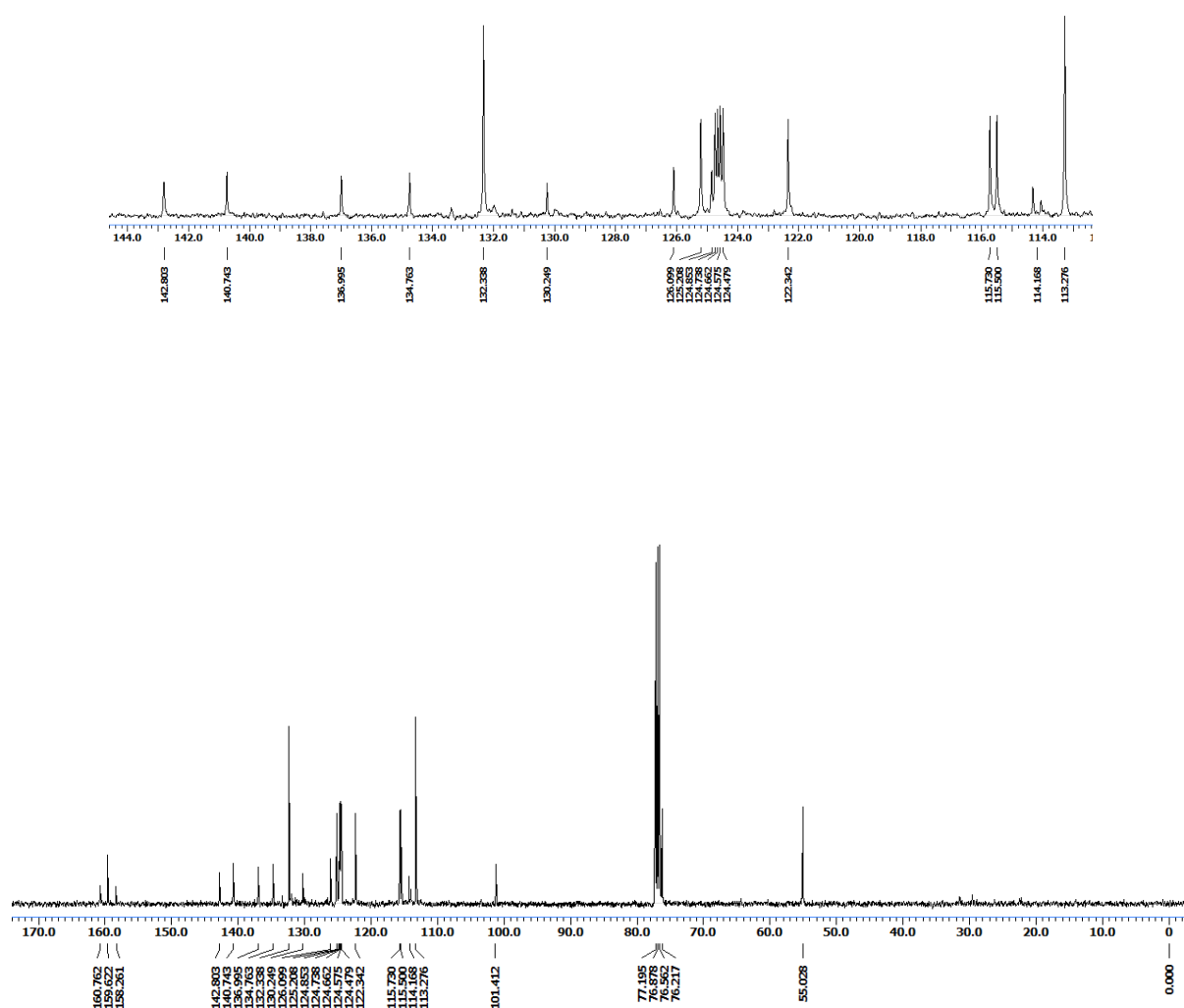
4-Chloro-2-(4-fluorophenyl)-3-(4-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7e)



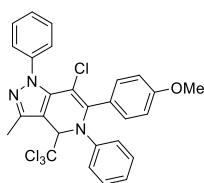
¹³C NMR



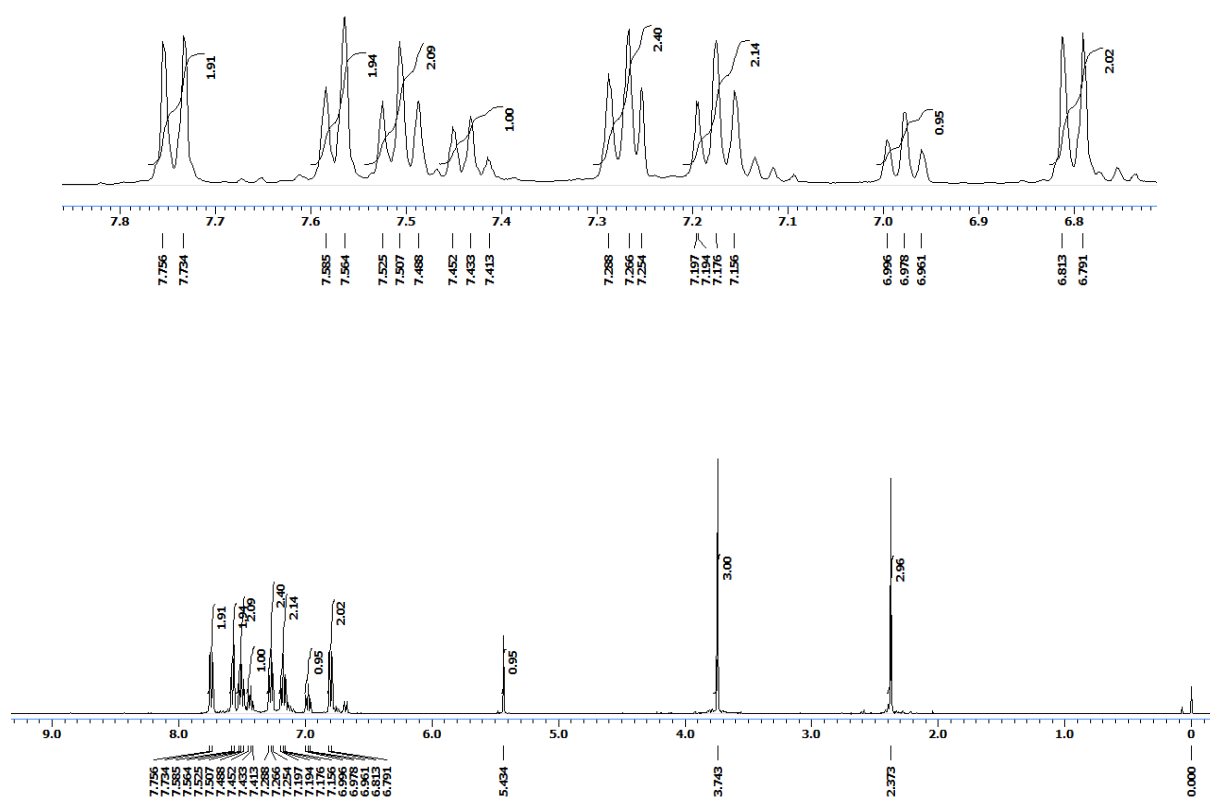
4-Chloro-2-(4-fluorophenyl)-3-(4-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydrobenzo[4,5]thieno[2,3-c]pyridine (7e)



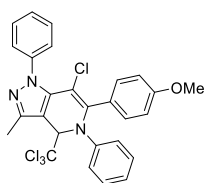
¹H NMR



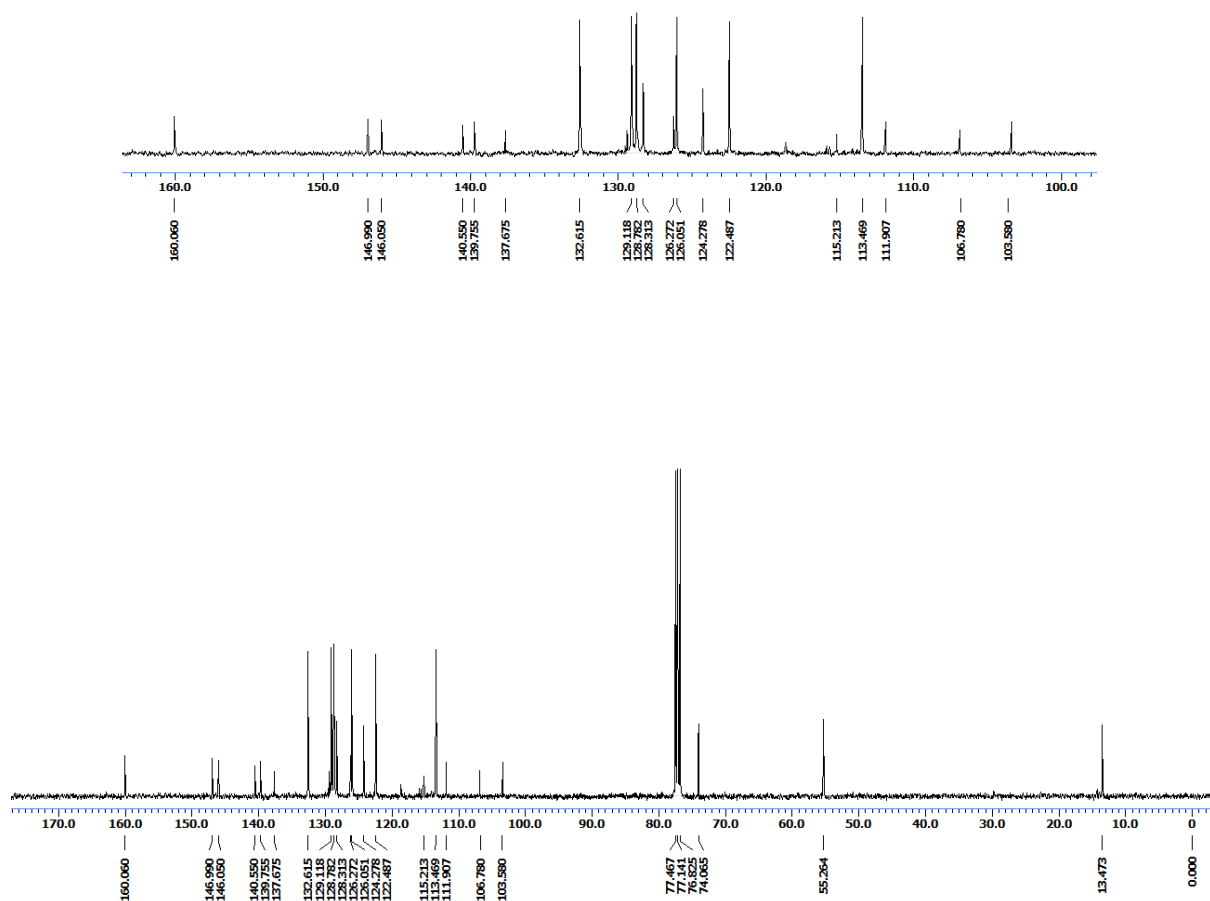
7-Chloro-6-(4-methoxyphenyl)-3-methyl-1,5-diphenyl-4-(trichloromethyl)-4,5-dihydro-1H-pyrazolo[4,3-c]pyridine (8a)



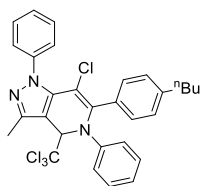
¹³C NMR



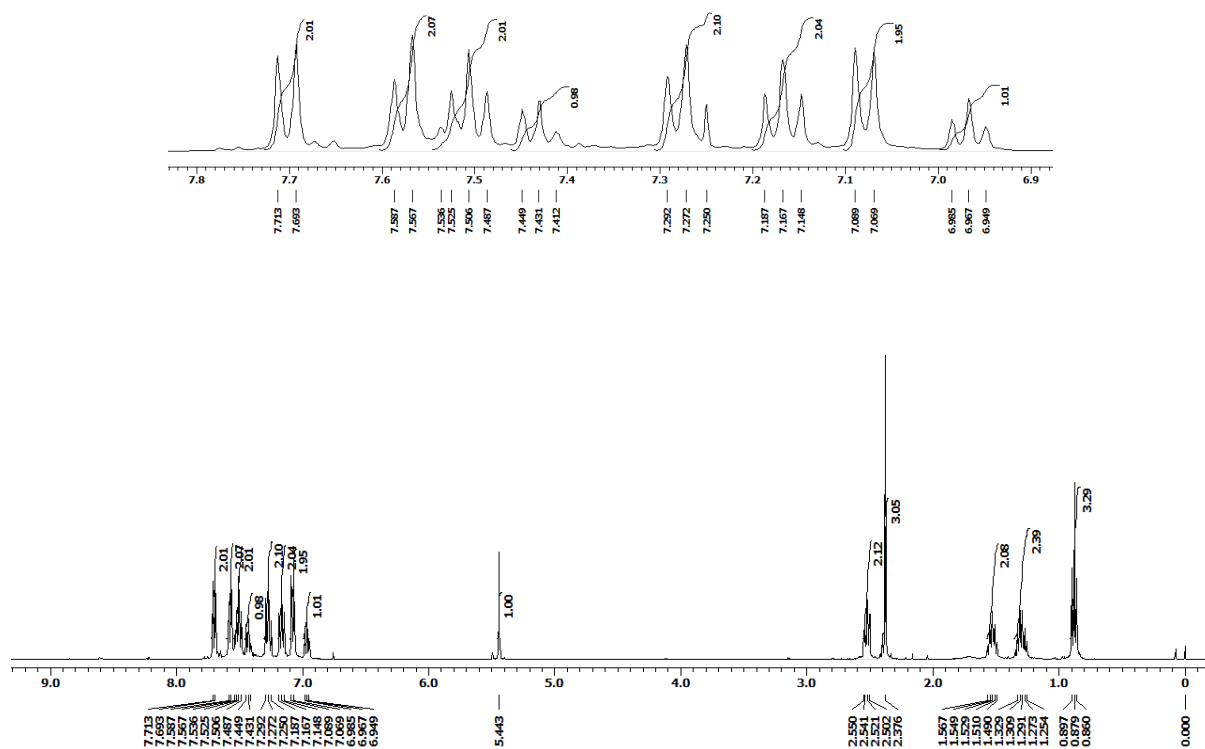
7-Chloro-6-(4-methoxyphenyl)-3-methyl-1,5-diphenyl-4-(trichloromethyl)-4,5-dihydro-1H-pyrazolo[4,3-c]pyridine (8a)



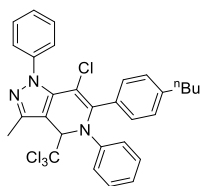
¹H NMR



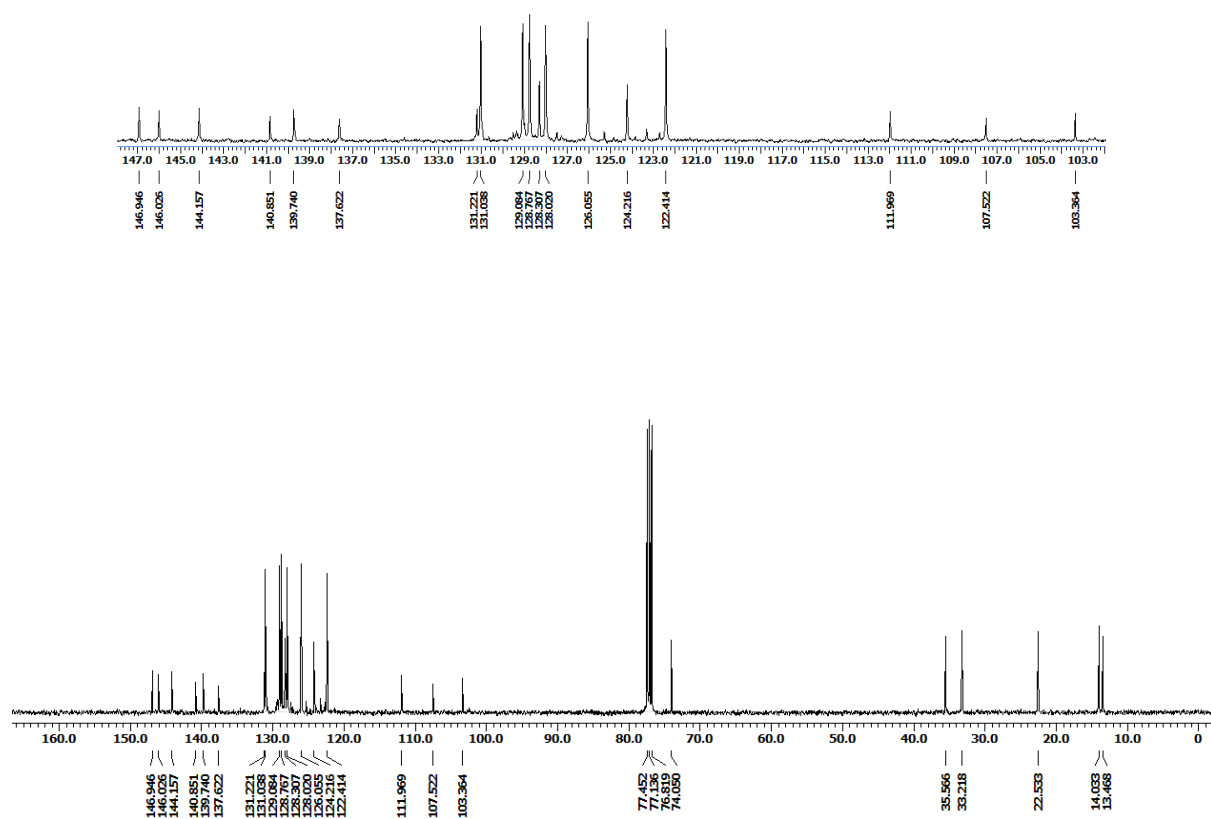
6-(4-Butylphenyl)-7-chloro-3-methyl-1,5-diphenyl-4-(trichloromethyl)-4,5-dihydro-1H-pyrazolo[4,3-c]pyridine (8b)



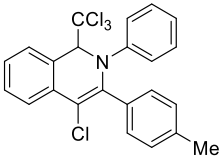
¹³C NMR



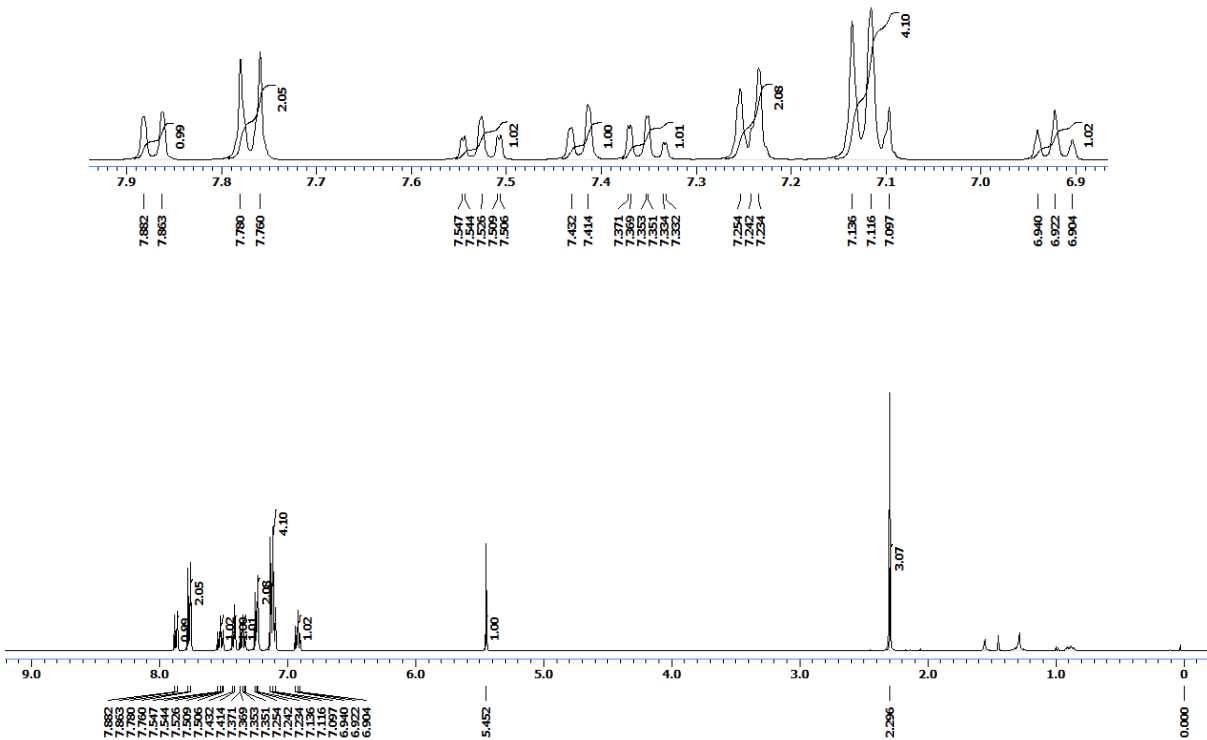
6-(4-Butylphenyl)-7-chloro-3-methyl-1,5-diphenyl-4-(trichloromethyl)-4,5-dihydro-1H-pyrazolo[4,3-c]pyridine (8b)



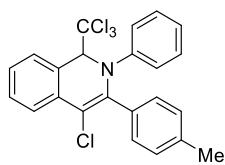
¹H NMR



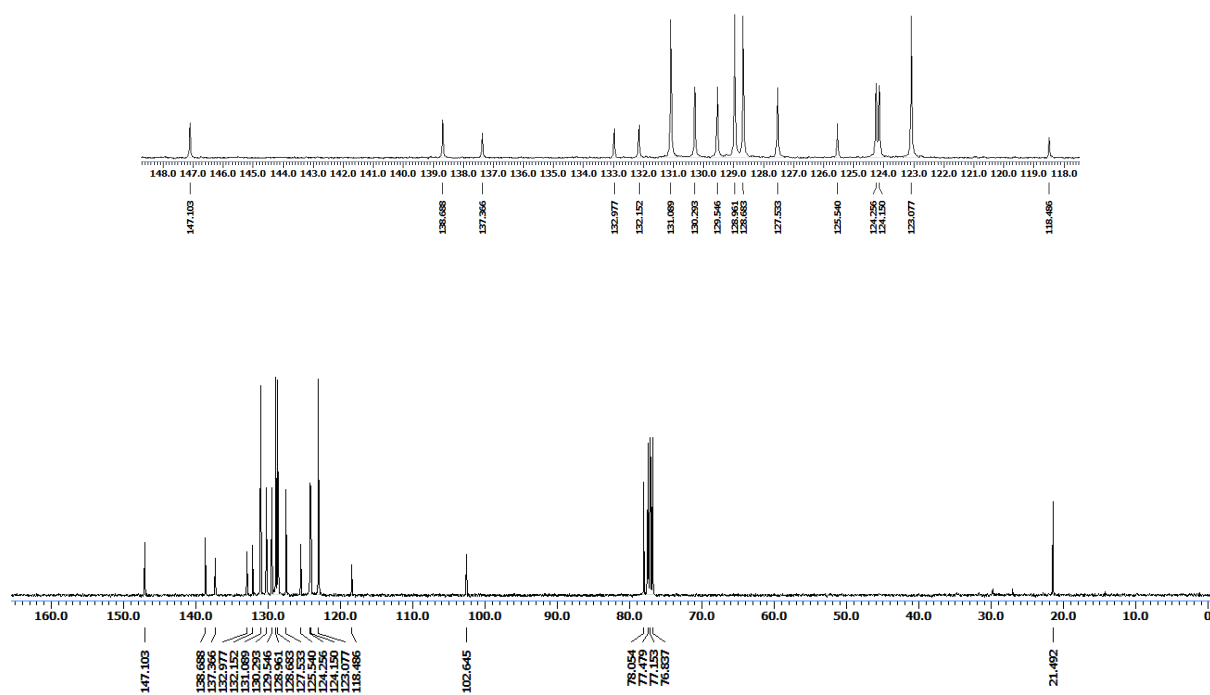
4-Chloro-2-phenyl-3-(*p*-tolyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (9a)



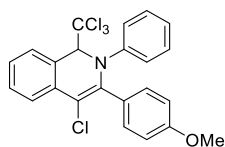
¹³C NMR



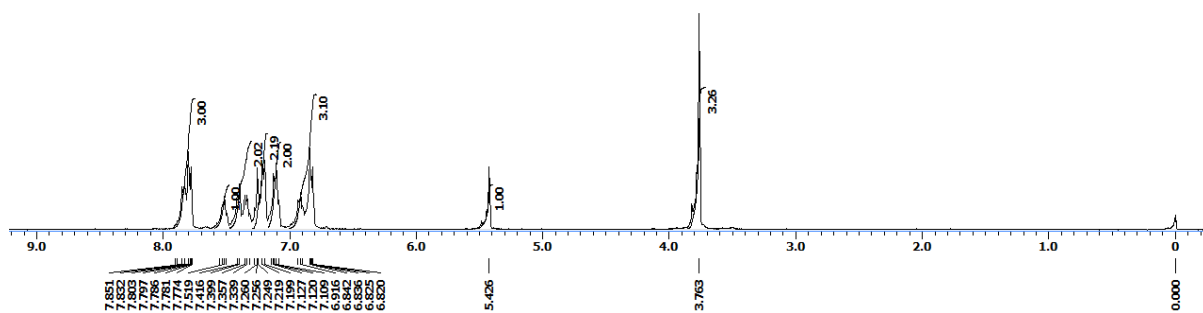
4-Chloro-2-phenyl-3-(*p*-tolyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (9a)



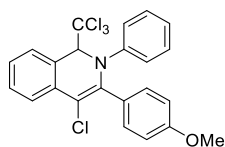
¹H NMR



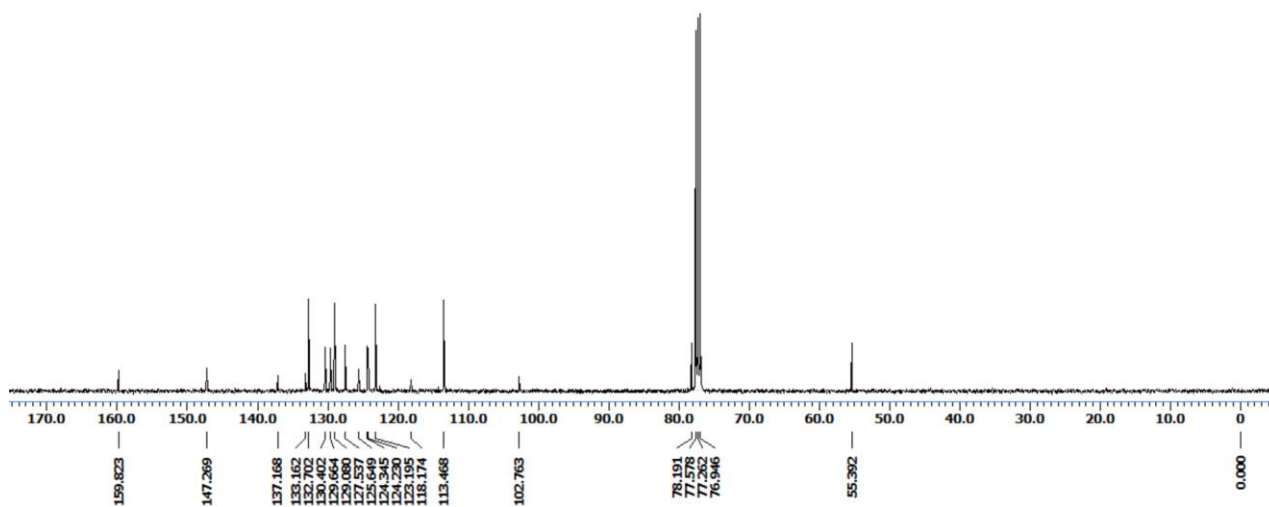
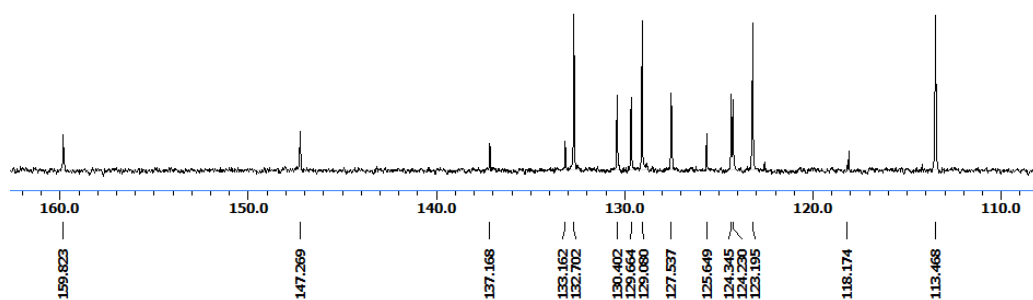
4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (9b)



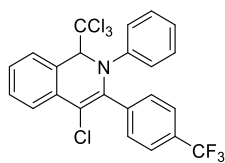
¹³C NMR



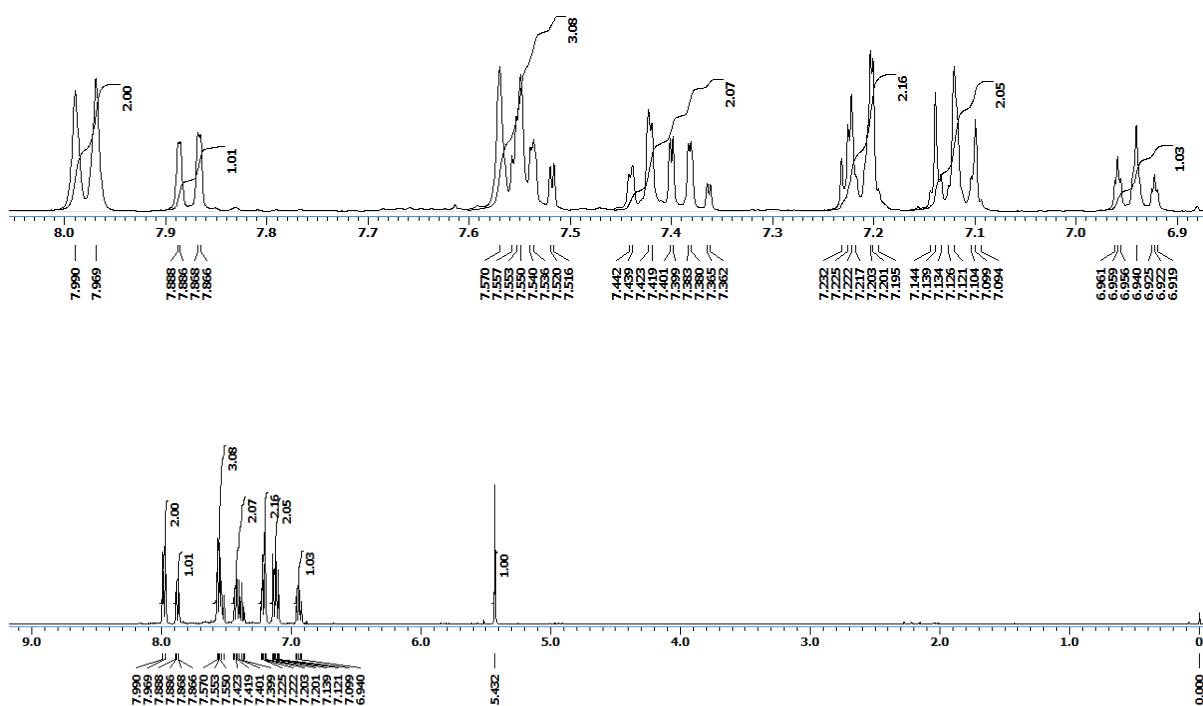
4-Chloro-3-(4-methoxyphenyl)-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (9b)



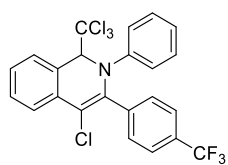
¹H NMR



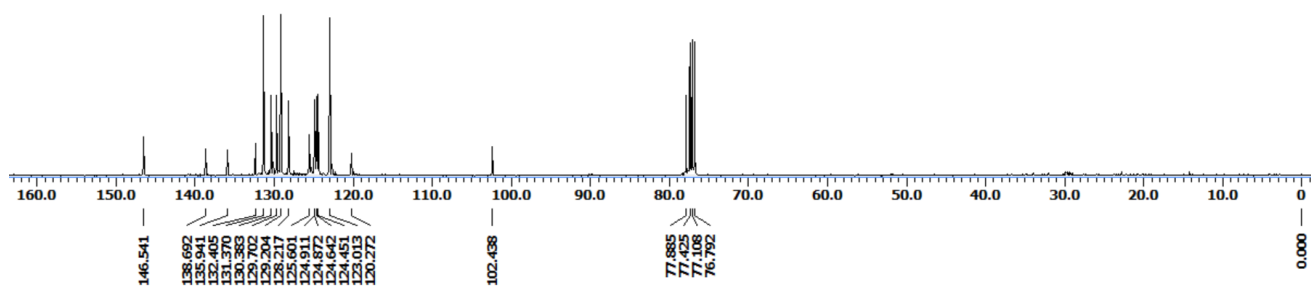
4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinoline (9c)



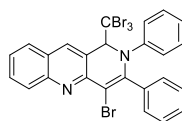
¹³C NMR



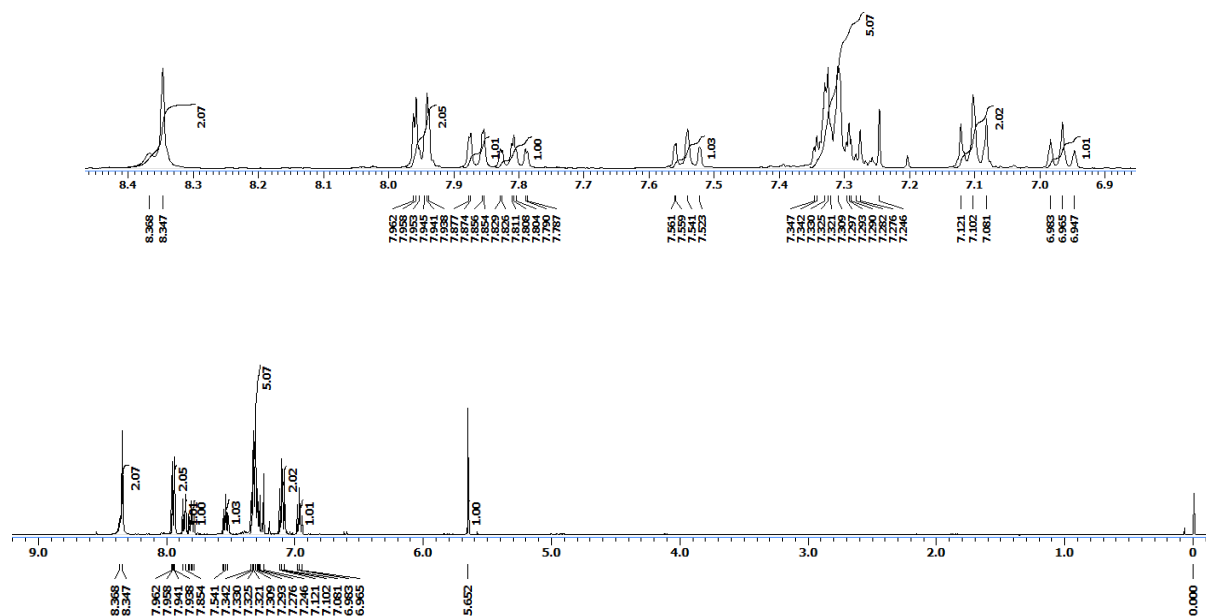
4-Chloro-2-phenyl-1-(trichloromethyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinoline (9c)



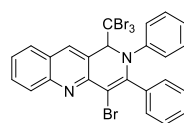
¹H NMR



4-Bromo-2,3-diphenyl-1-(tribromomethyl)-1,2-dihydrobenzo[b][1,6]naphthyridine (10)



¹³C NMR



4-Bromo-2,3-diphenyl-1-(tribromomethyl)-1,2-dihydrobenzo[*b*][1,6]naphthyridine (10).

