

Electronic Supplementary Information

Between porphyrins and phthalocyanines: 10,20-diaryl-5,15-tetrabenzodiazaporphyrins

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Synthesis

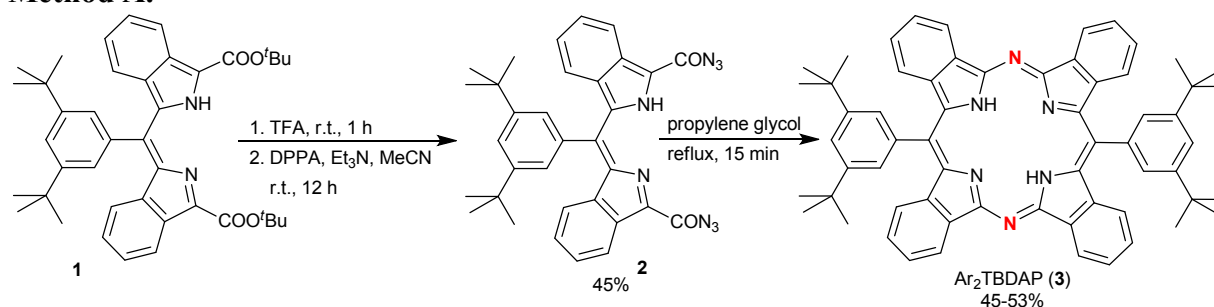
General information

Reagents and solvents, unless stated otherwise, were purchased from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed with pre-coated silica gel plates and visualized by UV light ($\lambda = 254$ nm). Silica gel 60 for column chromatography was purchased from Macherey-Nagel. Melting points were determined in open capillaries and were uncorrected. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance 400 MHz spectrometer in CDCl_3 with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, br s = broad singlet, m = multiplet), coupling constant in Hz]. UV/vis absorption spectra were measured on PerkinElmer Lambda 40, quartz cuvette 1.00 cm. Photoluminescence spectra were obtained on Horibu Jobin Yvonne FluoroMax-2 fluorimeter, quartz cuvette, 1.00 cm. Quantum yields were measured using rhodamine 6G as external standard. MALDI-TOF spectra were measured on Bruker Autoflex II mass spectrometer equipped with a nitrogen laser ($\lambda=337$ nm.). X-ray crystallographic analysis was performed with a STOE StadiVari PILATUS-100K diffractometer.

Dipyrromethenes (**1**) was prepared as it has been described in the previous report.¹

Synthetic Procedures

Method A.

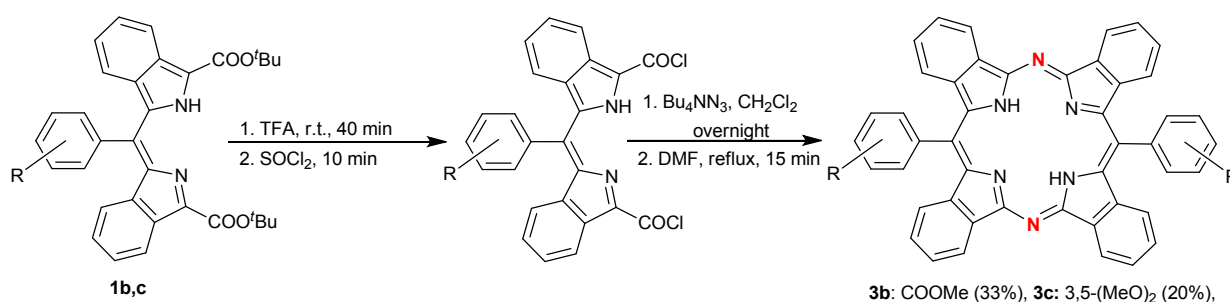


Diazide (2): To dipyrromethene (**1**) (365 mg, 0.576 mmol) 5 mL of TFA were added and stirred at room temperature for 1 h, then TFA was evaporated to dryness *in vacuo*. Dark residue was dissolved in 5 mL of dry acetonitrile, triethylamine (0.26 mL, 2.5 eq.), and diphenylphosphoryl azide (DPPA) (0.28 mL, 2.2 eq.) were added, and the mixture was stirred at room temperature overnight (control by TLC, elution by DCM, fast moving deep blue spot turning green on heating). The reaction mixture was then evaporated *in vacuo*, dissolved in DCM, washed by water (3x100 mL), dried over Na_2SO_4 , concentrated and purified by column chromatography on silica gel with DCM eluent, collecting the first deep-blue fraction. Yield of the diazide (**2**) (150 mg, 45%), deep-blue crystals, m.p. - fast decomposition above 120 °C; UV/vis: λ_{max} (CH_2Cl_2)/nm ($\log \varepsilon/\log(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1})$) 591 (4.51); ^1H NMR (400MHz, CDCl_3 , Me_4Si) δ 14.72 (s, 1H), 8.23 (d, $J=8.08$ Hz, 2H), 7.74 (t, $J=1.77$ Hz, 1H) 7.39 (d, $J=1.77$ Hz, 2H), 7.29 (ddd, $J=7.53, 1.01$ Hz, 2H), 7.01 (ddd, $J=7.71, 1.01$ Hz, 2H), 6.17 (d, $J=8.34$ Hz, 2H), 1.37 (s, 18H); ^{13}C NMR (400MHz, CDCl_3 , Me_4Si) δ 166.2, 152.4, 138.1, 137.1, 135.9, 134.7, 131.9, 127.3, 126.9, 123.4, 122.7, 122.5, 35.2, 31.4; MALDI-TOF (matrix - dithranol): (m/z) calcd for $\text{C}_{33}\text{H}_{30}\text{N}_8\text{O}_2$ 570.25, found 514.3 [(M-2N₂)⁺], 515.3 [(MH-2N₂)⁺].

Ar₂TBDAP (3a): To diazide (**2**), 100 mg (0.175 mmol), placed into 100 mL flask, equipped with a magnetic stirrer, 4 mL of propylene glycol was added. The resulting heterogeneous mixture was promptly heated (**attention: azides can be explosive, wear safety glasses**) in open air using a heat gun (**fast and intense heating by a heat gun, or using a microwave oven, or a pre-heated oil bath is important for achieving maximum yields, while careful slow heating on a stirring plate gave inferior yields. When reproducing this technique, it is advised first to do trial runs with small portions of diazide to adjust optimal heating regime. The appearance of dirty-green color of reaction mixture, particularly well seen in**

drops of reaction mixture splashing onto the walls of tube, can be used as a visual token of success. Instrumental control is performed by TLC – appearance of fast-moving green spot, or by UV-vis spectroscopy by distinct narrow band near 680 nm) to ca. 200 °C, and refluxed for 15 minutes, with vigorous stirring. The reaction mixture was then cooled to r.t. and DCM was added. The resulting solution was washed by water (2x200 mL) and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluted with DCM, collecting an emerald-green fast running band (R_f ca 0.9). Deep-green crystalline solid (42 mg, 53% based on diazide, 24% overall yield based on starting dipyrromethene **1a**), mp > 300 °C; UV/vis: λ_{\max} (THF)/nm 386 ($\log\epsilon/\log(\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$ 4.75), 426 (4.83), 608 (4.49), 635 (4.47), 683 (5.02); ^1H NMR (400MHz, CDCl_3 , Me_4Si) δ 9.84 (d, $J=7.58$ Hz, 4H), 8.12 (s+dd overlapped, 10H) 7.76 (dd, $J_{\text{app}}=7.82$ Hz, 4H), 7.31 (d, $J=8.07$ Hz, 4H), 1.57 (s, 36H), -0.68 (s, 2H); ^{13}C NMR (400MHz, CDCl_3 , Me_4Si) δ 152.1, 146.9, 142.9, 139.3, 138.0, 137.5, 128.3, 127.8, 126.9, 124.9, 123.2, 122.3, 120.4, 35.4, 31.7; MALDI-TOF (matrix- Proton Sponge©) (m/z) calcd for $\text{C}_{62}\text{H}_{60}\text{N}_6$ -888.49, found -888.19 [M^-].

Method B.



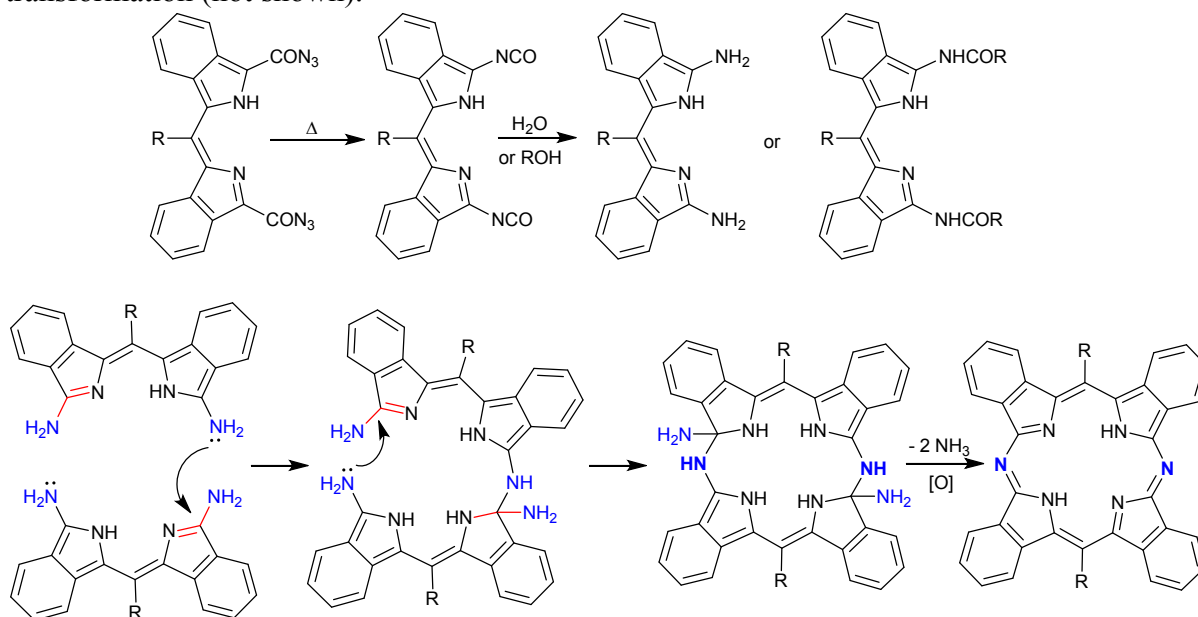
Ar₂TBDAP (3c): To dipyrromethene **1c** 170 mg (292 μmol) 5 mL of TFA were added and stirred at room temperature for 40 minutes, then TFA was evaporated to dryness *in vacuo*. To the dry residue 2 mL of thionyl chloride were added and the mixture was stirred at 40 °C for 10 minutes. The reaction mixture was then evaporated *in vacuo* to dryness and the flask was purged a few minutes with dry argon to remove remaining hydrogen chloride. The dark solid residue was dissolved in dry DCM, and the solution of tetrabutylammonium azide (TBAA) (285 mg, 1.18 mmol, **attention: an extremely hygroscopic solid – all manipulations in open air should be done as promptly as possible**) in DCM was added and stirred at room temperature overnight. The reaction mixture was then washed by water (3x100 mL), dried under Na_2SO_4 and concentrated *in vacuo* to afford a dark blue solid, which was used in the following reaction without isolation and purification. To this residue, placed into 25 mL flask, equipped with a magnetic stirrer, 2 mL of wet dimethylformamide (“wet” in this context means that solvent grade DMF was used as received without further purification, in an open-air setup) were added. The resulting mixture was promptly heated in open air using a heat gun to boiling and intensely refluxed for 15 minutes with vigorous stirring. After cooling to r.t., 25 ml of DCM were added, the solution was washed by water (3x100 mL) and evaporated *in vacuo* to dryness. The dark-green residue was purified by column chromatography on silica gel eluted with CH_2Cl_2 , collecting an emerald-green fraction moving ahead of all bands ($R_f \sim 0.7$). Dark-green crystals **3c** (22 mg, 20%), m.p. > 300 °C; UV/vis: λ_{\max} (tetrahydrofuran)/nm 385 ($\log\epsilon/\log(\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$ 4.92), 424 (4.97), 608 (4.66), 635 (4.69), 683 (5.21); ^1H NMR (400MHz, CDCl_3 , Me_4Si) δ 9.79 (d, $J=7.58$ Hz, 4H), 8.11 (dd, $J_{\text{app}}=7.34$ Hz, 4H), 7.84 (dd, $J_{\text{app}}=7.34$ Hz, 4H), 7.58 (d, $J=8.07$ Hz, 4H), 7.43 (d, $J=2.2$ Hz, 4H), 7.17 (dd, $J_{\text{app}}=2.2$ Hz, 2H), 3.99 (s, 12H), -0.80 (s, 2H); ^{13}C NMR could not be measured because of low solubility of the compound. MALDI-TOF (matrix dithranol) (m/z) calcd for $\text{C}_{50}\text{H}_{36}\text{N}_6\text{O}_4$ 784.28, found 784.19 [M^+]

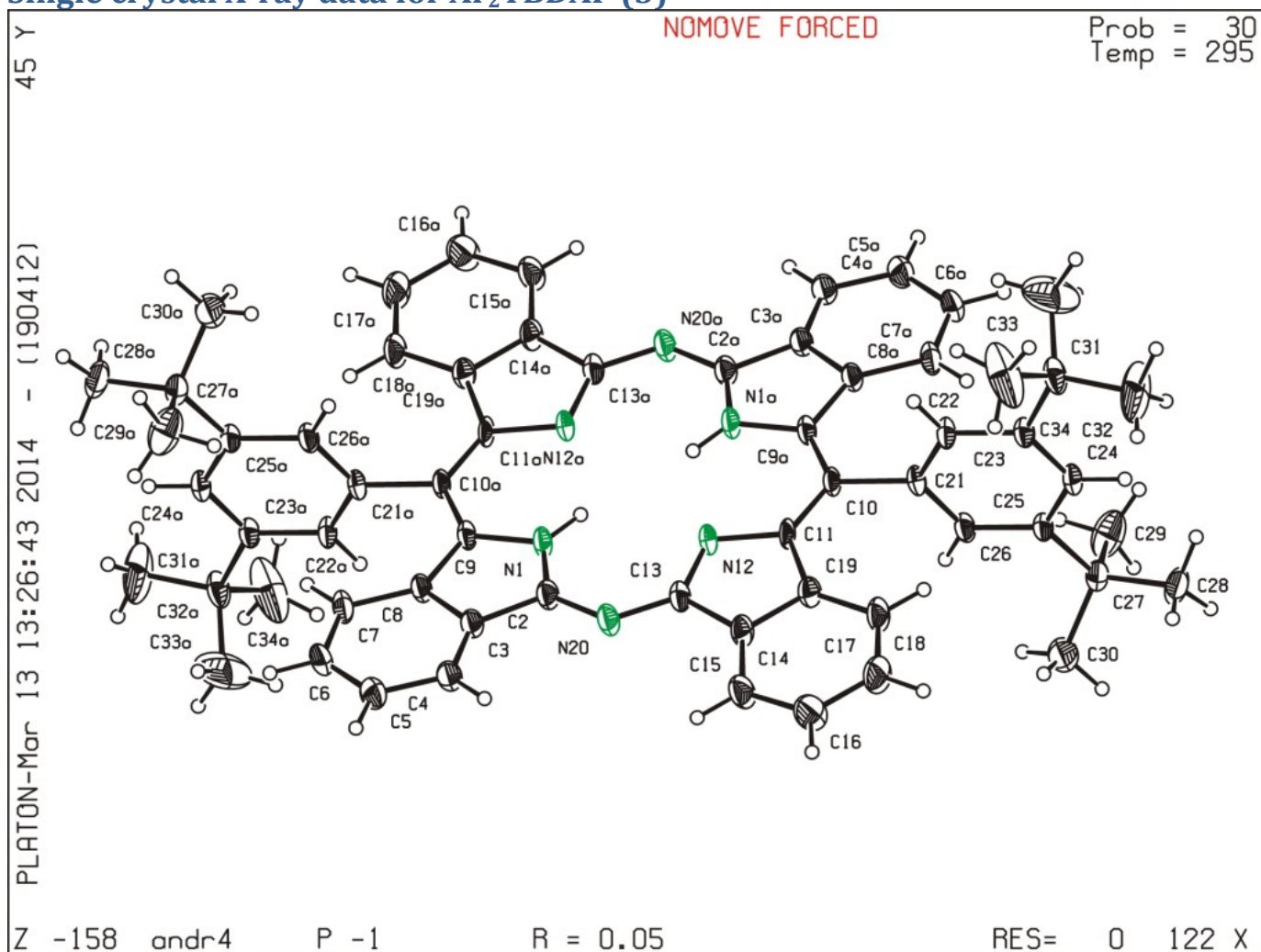
Ar₂TBDAP (3b): Obtained similarly from dipyrromethene **1b** (245 mg, 423 μmol). Dark-green crystals **3b** (55 mg, 33%), mp > 300 °C (from CH_2Cl_2); UV/vis: λ_{\max} (tetrahydrofuran)/nm 386 ($\log\epsilon/\log(\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$ 4.75), 423 (4.76), 608 (4.42), 636 (4.46), 684 (4.97); ^1H NMR (400MHz, CDCl_3 +TFA, Me_4Si) δ 10.1-9.10 (broad s, TFA), 9.14 (d, $J=7.34$ Hz, 4H), 8.68 (d, $J=7.70$ Hz, 4H), 8.52 (d, $J=7.70$ Hz, 4H), 8.12 (dd, $J_{\text{app}}=7.34$ Hz, 4H), 7.81 (dd, $J_{\text{app}}=7.58$ Hz, 4H), 7.41 (d, $J=7.34$ Hz, 4H); ^{13}C NMR could not be measured

because of low solubility of the compound. MALDI-TOF (matrix- dithranol) (m/z) calcd for $C_{50}H_{32}N_6O_4$ 780.25, found 781.34 $[(M+H)^+]$

Tentative mechanism of TBDAP formation

Tentative mechanism includes the Curtius rearrangement, which affords either diamine or the respective carbamate by reaction of isocyanate with spurious water of hydroxylic solvent, such as propylene glycol. The diamine undergoes a stepwise macrocyclization through the attack of nucleophilic nitrogen atom at electrophilic amidine-type carbon atom (fragment marked by red), followed by aromatization through ammonia elimination (like what happens in the classical Fischer indole synthesis), and spontaneous oxidative dehydrogenation. Carbamate nitrogen atoms may as well be hypothesized to take part in such transformation (not shown).



Single crystal X-ray data for Ar₂TBDAP (3)

Crystal data for TBDAP (1): C₆₂H₆₀N₆, *M* = 889.16, triclinic, *a* = 9.1332(15) Å, *b* = 11.8576(18) Å, *c* = 13.566(2) Å, α = 84.777(12)°, β = 83.980(13)°, γ = 72.609(12)°, *V* = 1391.5(4) Å³, *T* = 295(2) K, space group *P* $\bar{1}$, *Z* = 1, μ (CuK α) = 0.478 mm⁻¹, 4785 reflections measured, 4785 independent reflections (*R*_{int} = 0.0). The final *R*₁ values were 0.0537 (*I* > 2 σ (*I*)). The final *wR*(*F*²) values were 0.1176 (*I* > 2 σ (*I*)). The final *R*₁ values were 0.0876 (all data). The final *wR*(*F*²) values were 0.1269 (all data). The goodness of fit on *F*² was 0.864. CCDC number CCDC 989911.

Table 1. Selected bond distances

Entry	Atom 1	Atom 2	Length, Å
1	C10	C21	1.505(2)
2	C10	C9	1.396(3)
3	C9	C8	1.462(2)
4	C8	C3	1.400(3)
5	C3	C2	1.454(3)
6	C2	N1	1.365(2)
7	C2	N20	1.325(2)
8	N20	C13	1.331(3)
9	C13	N12	1.350(2)
10	N12	C11	1.400(3)
11	C11	C19	1.463(3)
12	C19	C14	1.404(3)
13	C14	C15	1.393(3)

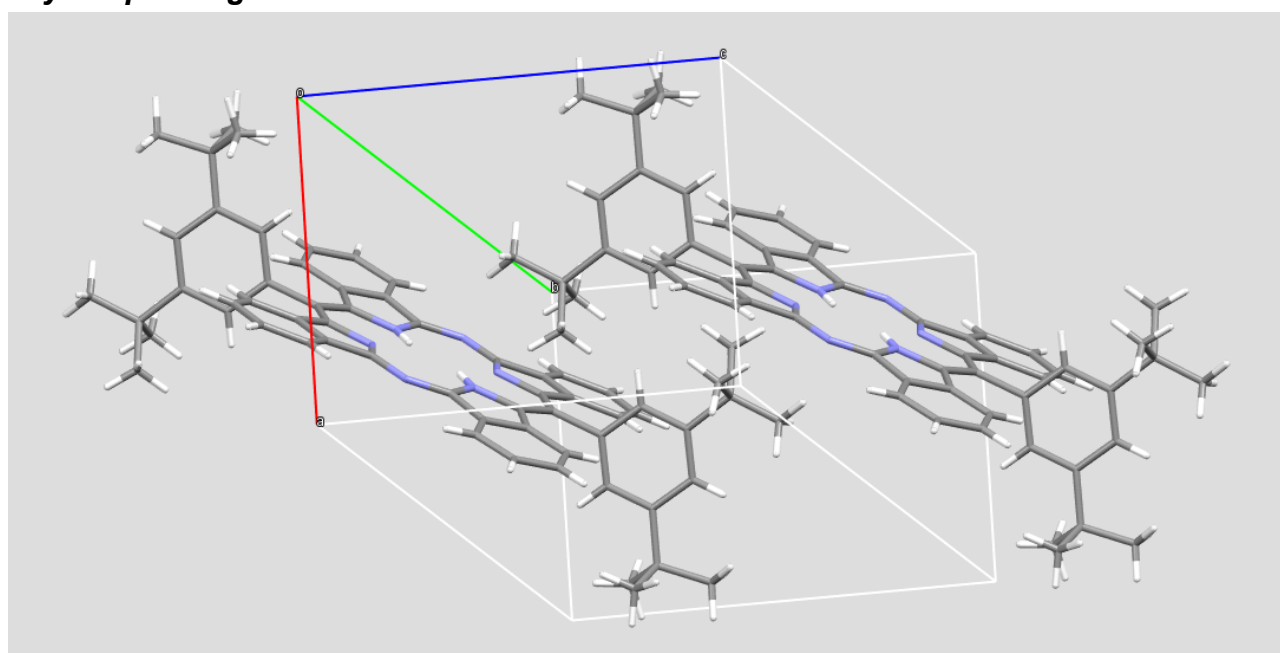
14	C15	C16	1.376(4)
15	C16	C17	1.391(4)
16	C17	C18	1.366(3)
17	C11	C10	1.377(2)

Table 2. Selected Angles

Entry	Atom 1	Atom 2	Atom 3	Angle, deg
1	C21	C10	C9	115.5(1)
2	C9	C8	C3	106.5(2)
3	C8	C3	C2	106.5(2)
4	C3	C2	N1	109.6(2)
5	C2	N1	C9	108.5(2)
6	C3	C8	C7	118.3(2)
7	C8	C7	C6	117.7(2)
8	C7	C6	C5	122.4(2)
9	C2	N20	C13	126.3(1)
10	C13	N12	C11	109.9(2)
11	N12	C11	C19	107.5(2)
12	C11	C19	C14	106.2(2)
13	C19	C14	C13	107.7(2)
14	C19	C18	C17	118.5(2)
15	C18	C17	C16	122.7(2)

Table 3. Selected Torsions

Entry	Atom 1	Atom 2	Atom 3	Atom 4	Torsion, deg
1	C26	C21	C10	C9	-89.4(2)
2	C3	C2	N20	C13	177.9(2)
3	C8	C9	C10	C11	-175.8(2)

Crystal packing**Figure 1. Unit cell**

In the arrangement of molecules in crystals the molecules are arranged as one-molecule-thick belts, stacked above each other at a distance of 7.6 Å, far beyond effective stacking interaction.

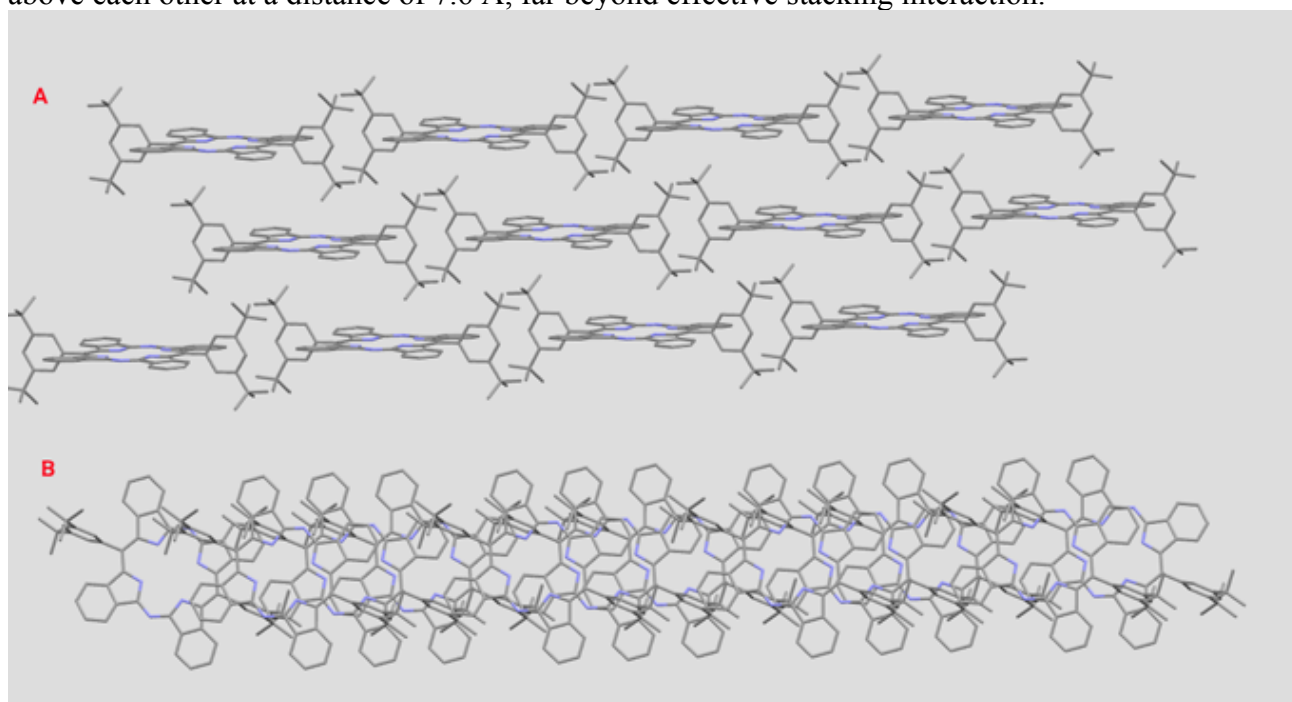


Figure 2. Arrangement of Ar₂TBDAP (3) molecules in crystal, part 1. A – one-molecule-thick flat belts, side view; B – view from above.

There is another pattern, in which each second belt is shifted sideways, so that the marginal benzo-rings stack above each other at a distance of 3.9 Å, compatible with effective π -stacking interaction. In this pattern, such belts are situated as a ladder, with each belt sticking to one above and to one below through these benzo-rings (marked below by pink and greenish color).

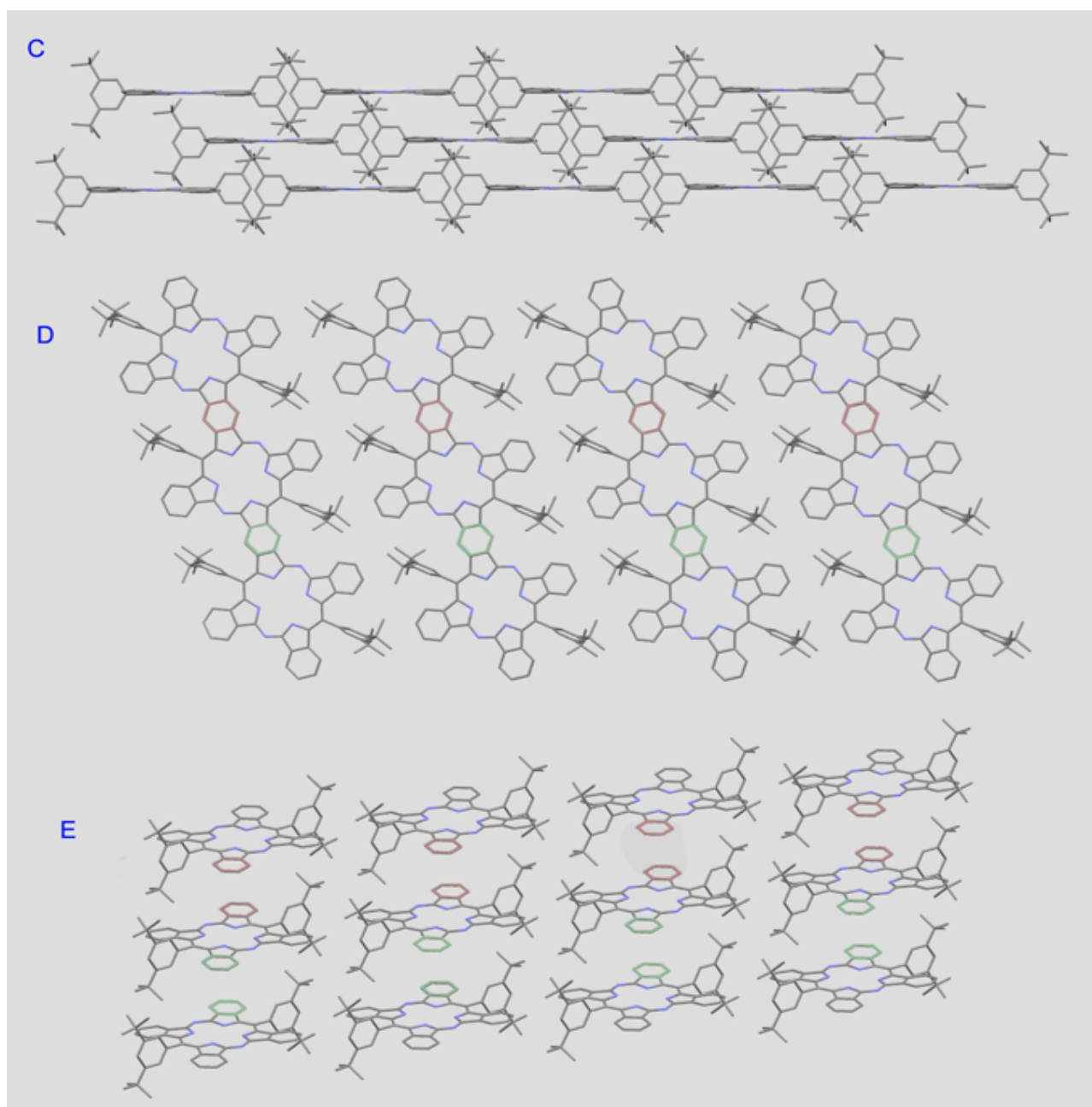


Figure 3. Arrangement of Ar_2TBDAP (3) molecules in crystal, part 2. The belts located at stacking distance. C. View from aside; D. View from atop, stacked benzo-rings are highlighted in pink and green; E. The same view at an angle.

Distortion analysis

The degree and main mode of distortion obtained by applying Shelnutt's normal-coordinate structural decomposition.²

NSD result generated from file andr4.pdb at Thu Mar 13 20:51:40 MSK 2014

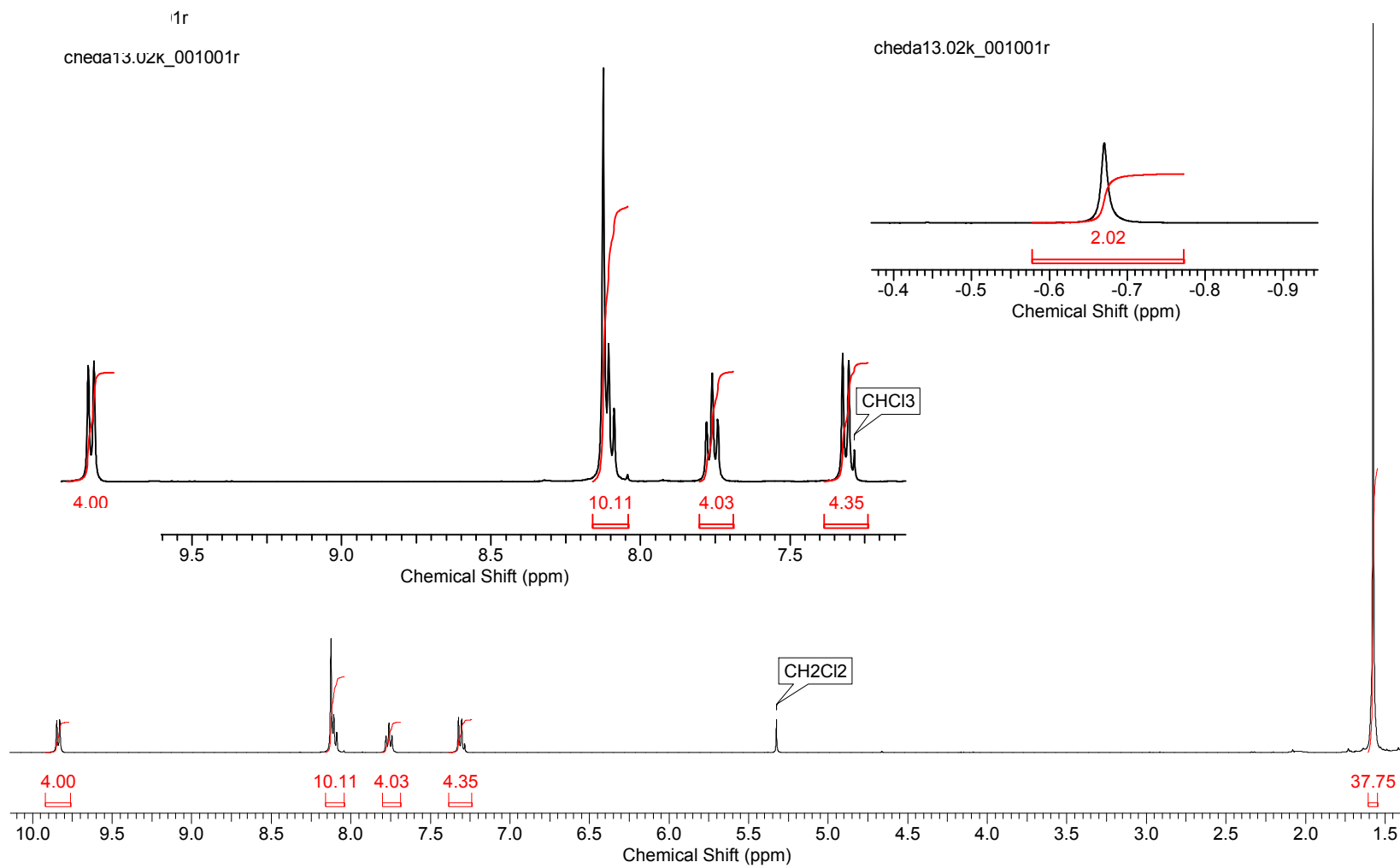
Summary of the NSD (in Å):

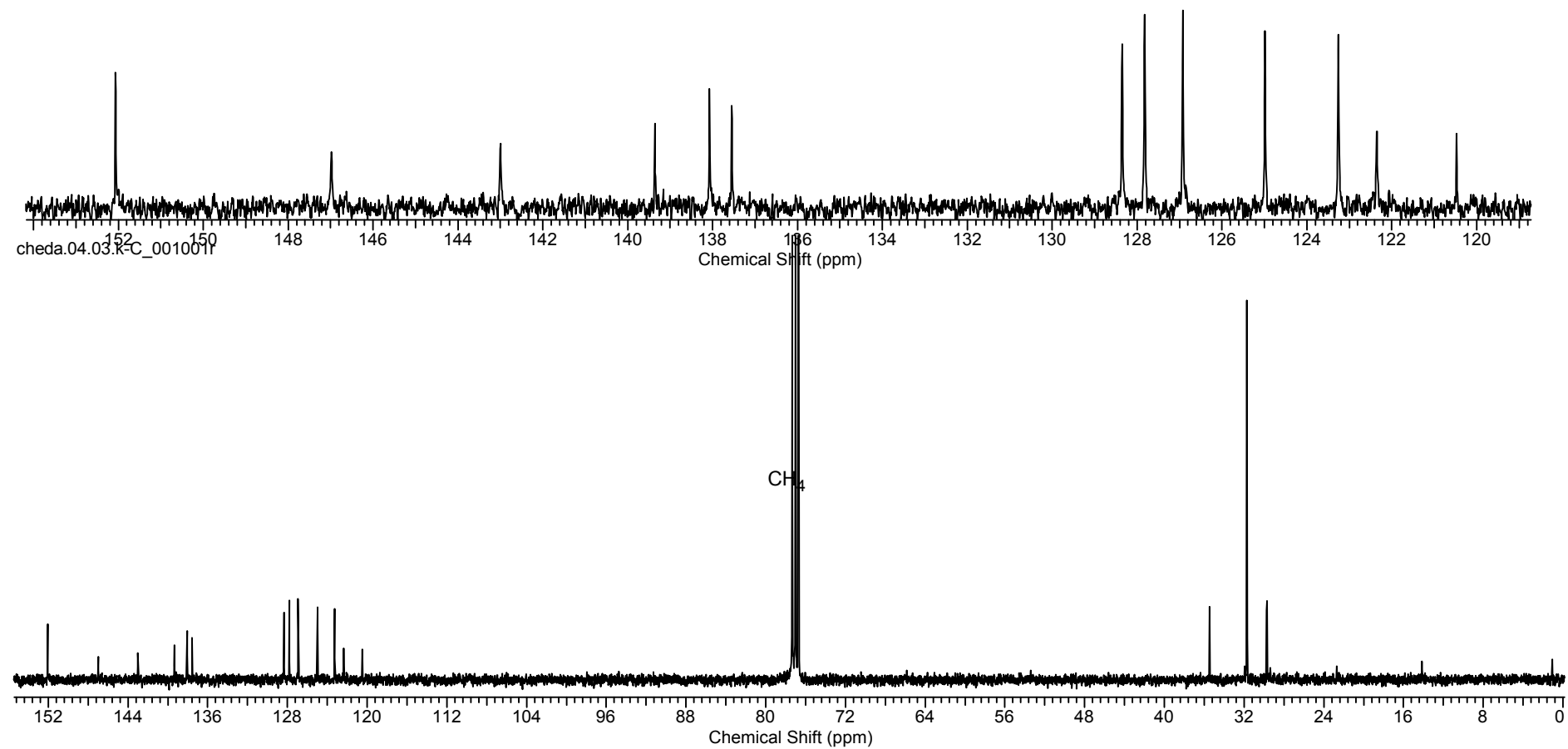
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min.	0,3463	0,0509	0,3391	-0,0171	-0,0003	-0,0001	0,0673	0,0070
ext.	0,4329	0,0251	0,3409	-0,0174	-0,0003	-0,0001	0,0673	0,0068
			0,2587	-0,0165	0,0007	-0,0006	-0,0032	-0,0170
comp.	0,4526	0,0000	0,4324	0,0276	0,0012	0,0012	0,1289	0,0234
basis	Doop	doop	B2u	B1u	A2u	Eg (x)	Eg (y)	A1u
min.	0,2227	0,0109	-0,0000	0,0001	-0,0000	0,1573	-0,1576	0,0001

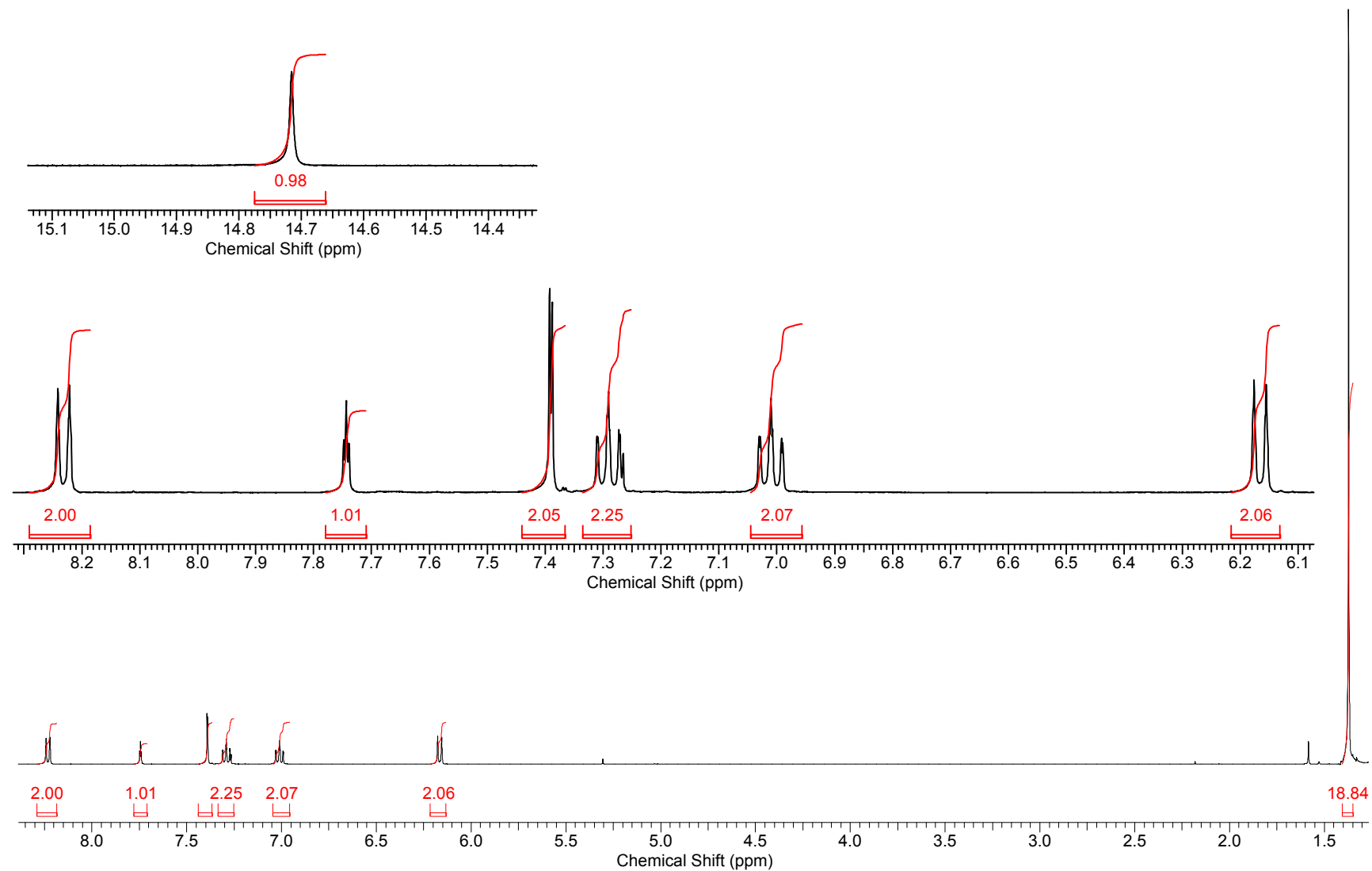
ext.	0,2301	0,0068	-0,0000	0,0001	-0,0000	0,1594	-0,1571	0,0001
			0,0000	-0,0001	0,0001	0,0563	0,0131	-0,0000
comp.	0,2337	0,0000	0,0001	0,0002	0,0001	0,1684	0,1621	0,0001

NMR Spectra

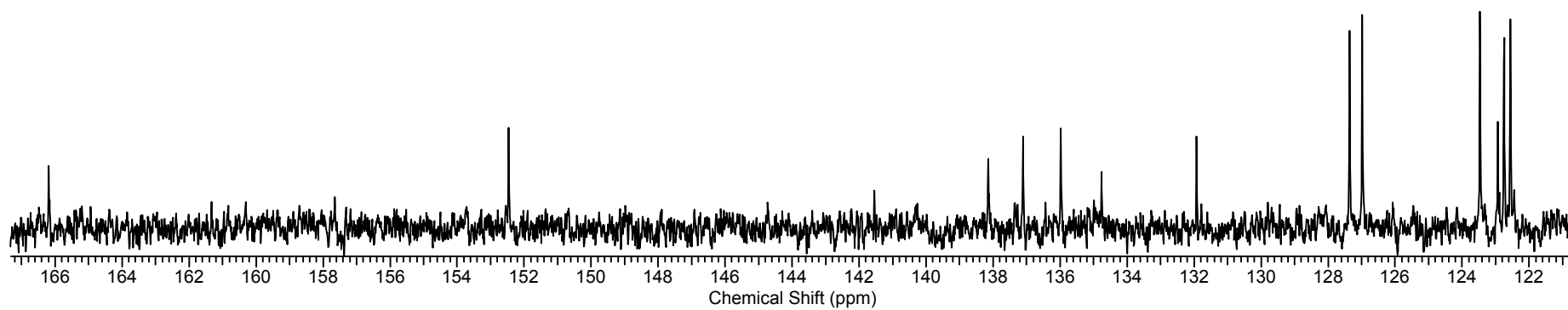
^1H NMR of TBDAP (3a) in CDCl_3



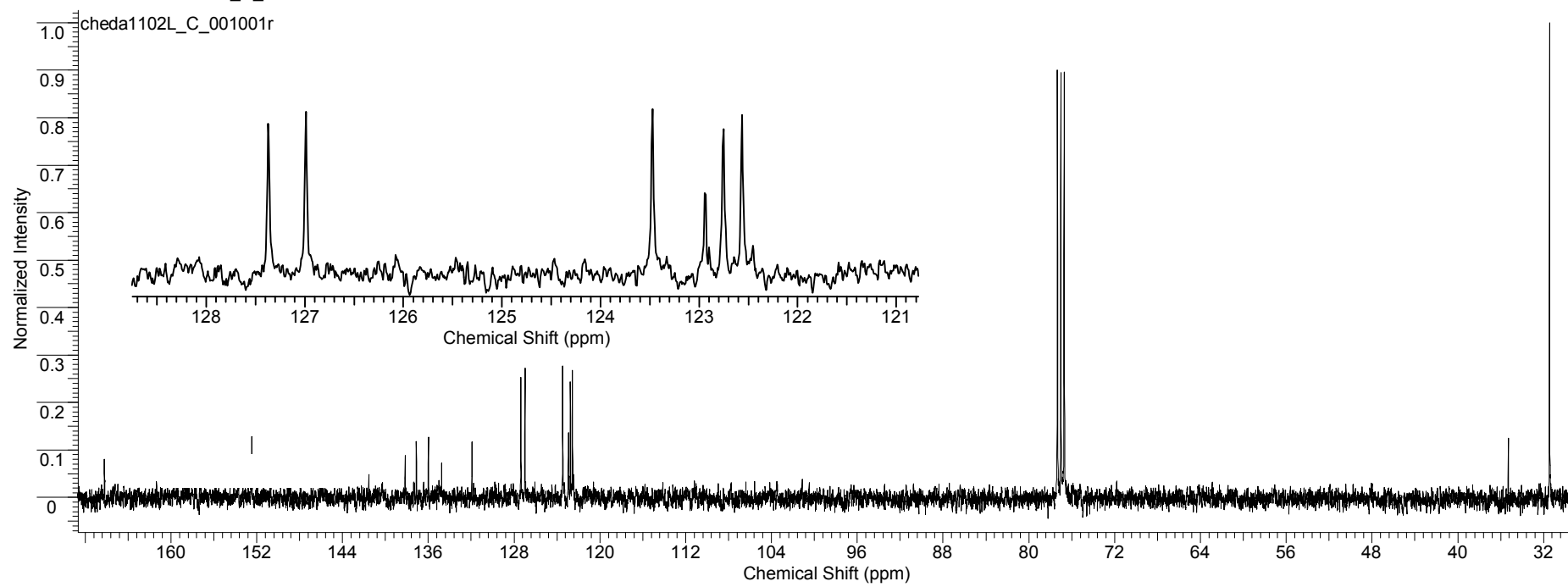
¹³C NMR of TBDAP (3a) in CDCl₃

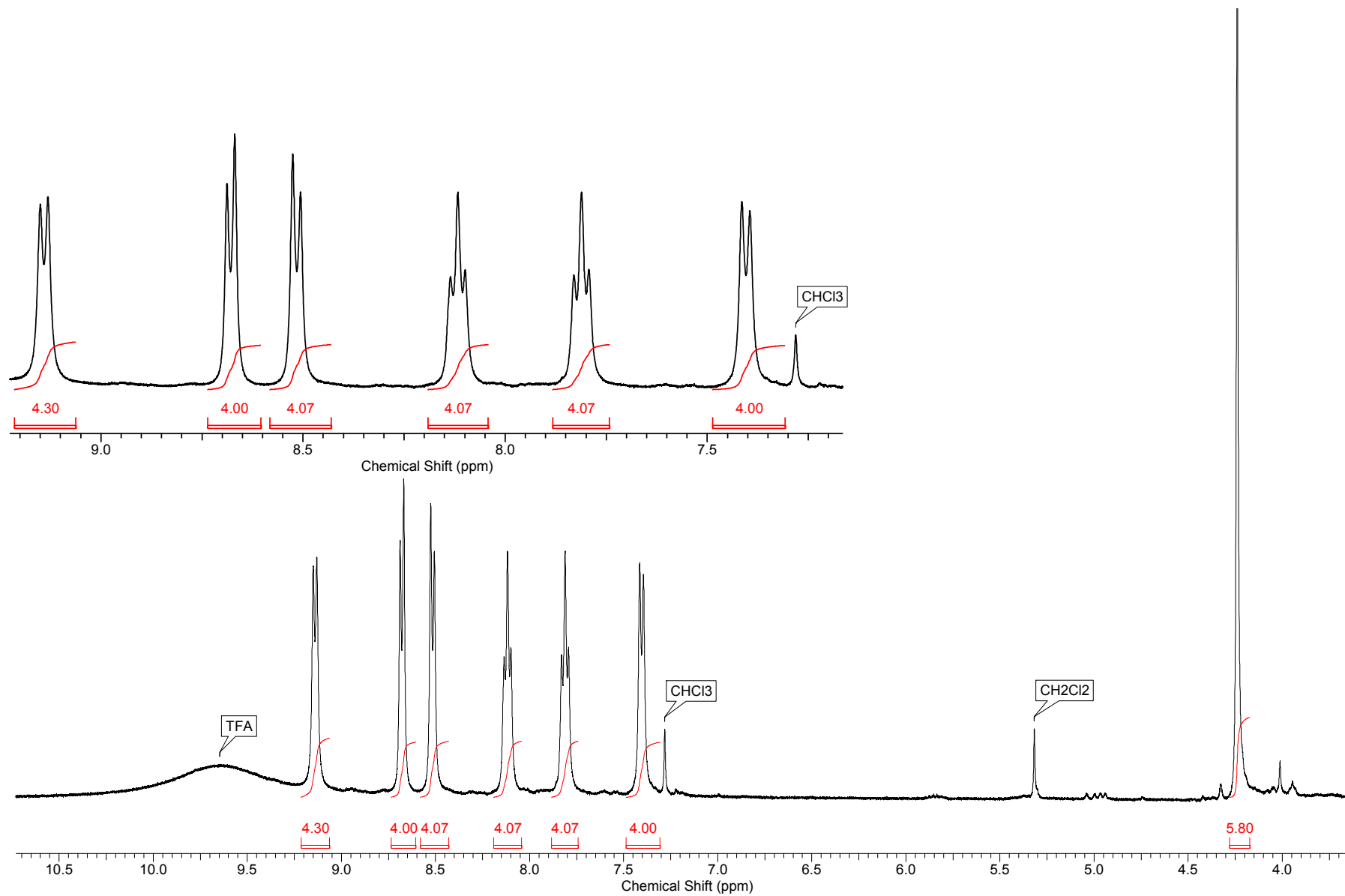
^1H and ^{13}C NMR of diazide (2) in CDCl_3 

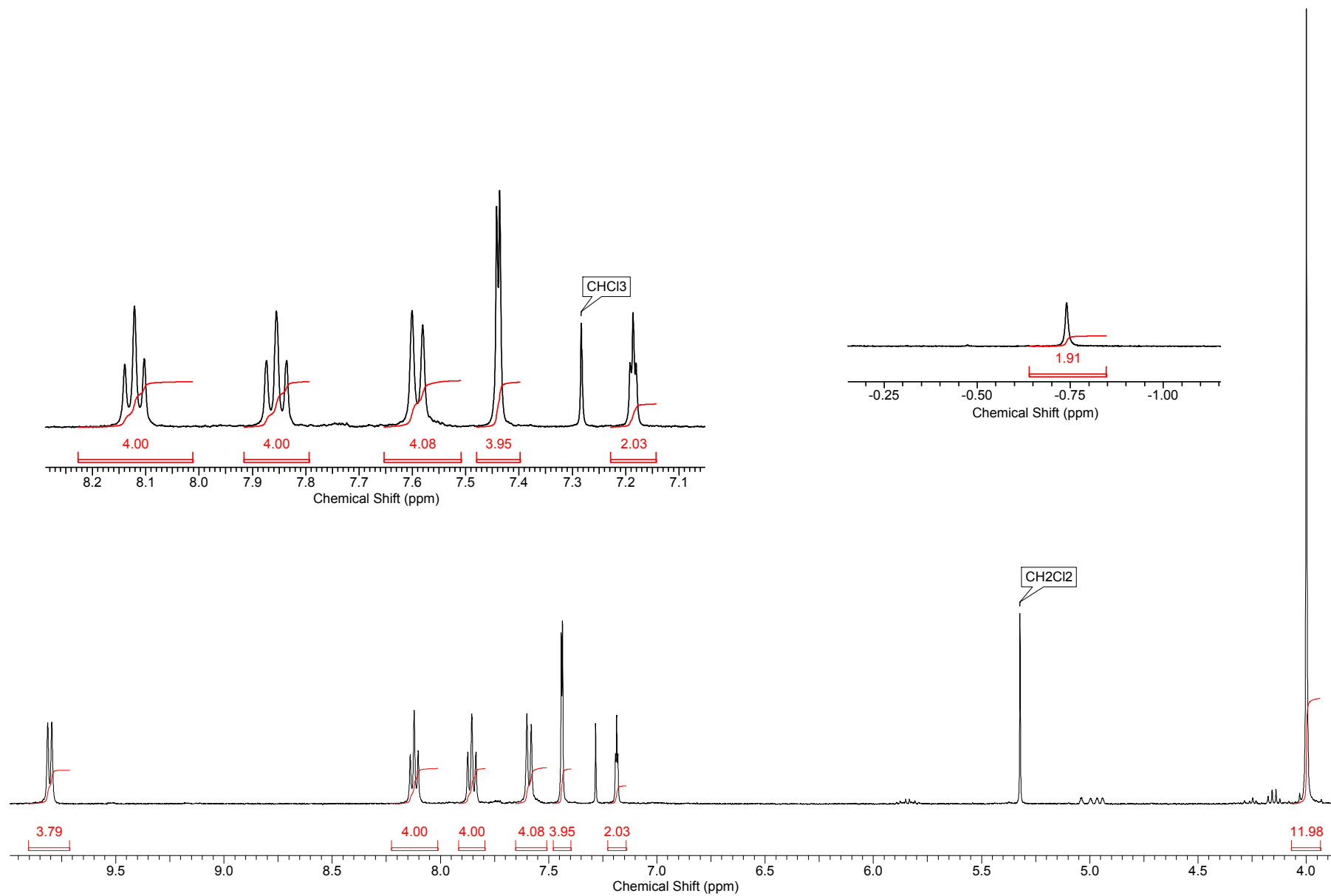
cheda1102L_C_001001r



cheda1102L_C_001001r

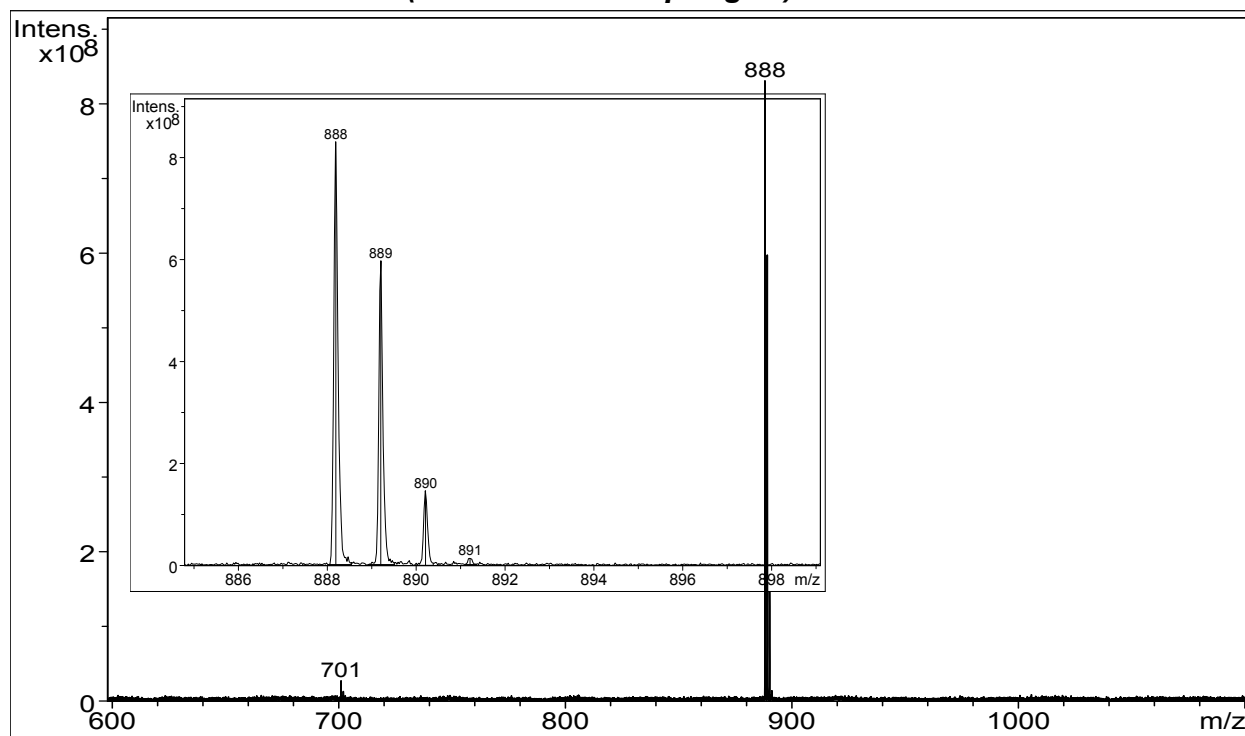
 $^{13}\text{C}_{13}$

^1H NMR of TBDAP 3b in CDCl_3 with a drop of TFA

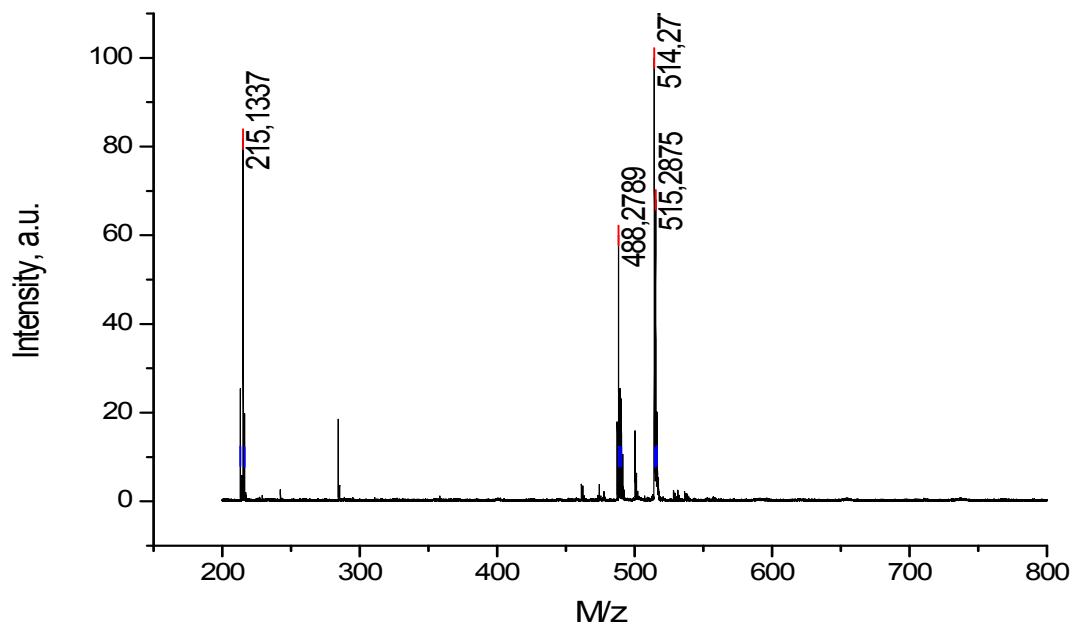
^1H NMR of TBDAP 3c in CDCl_3 

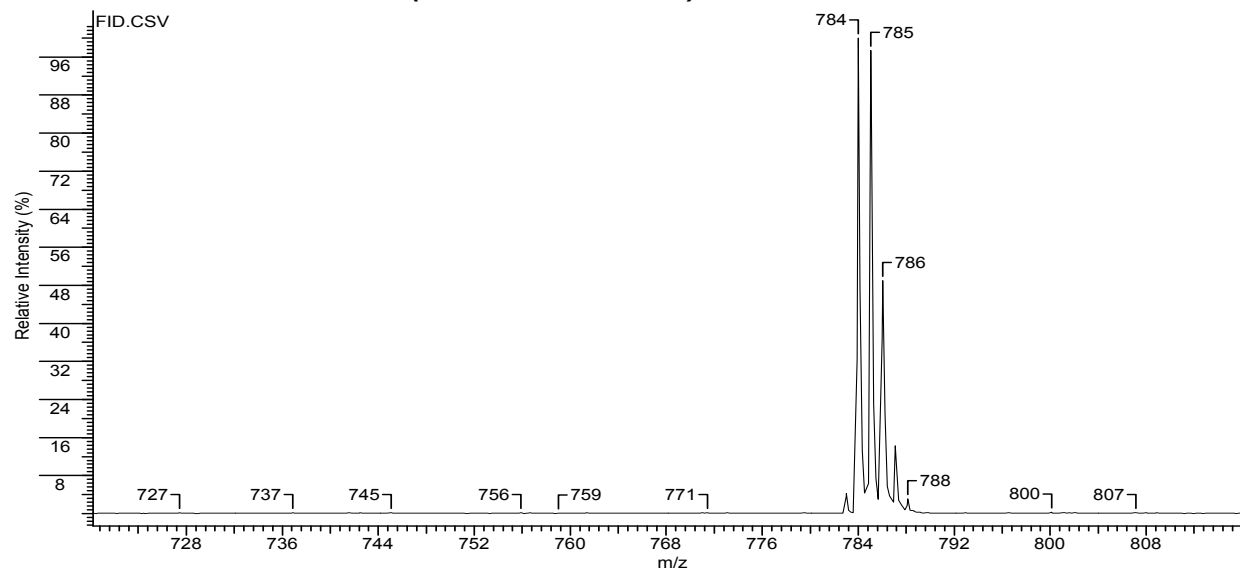
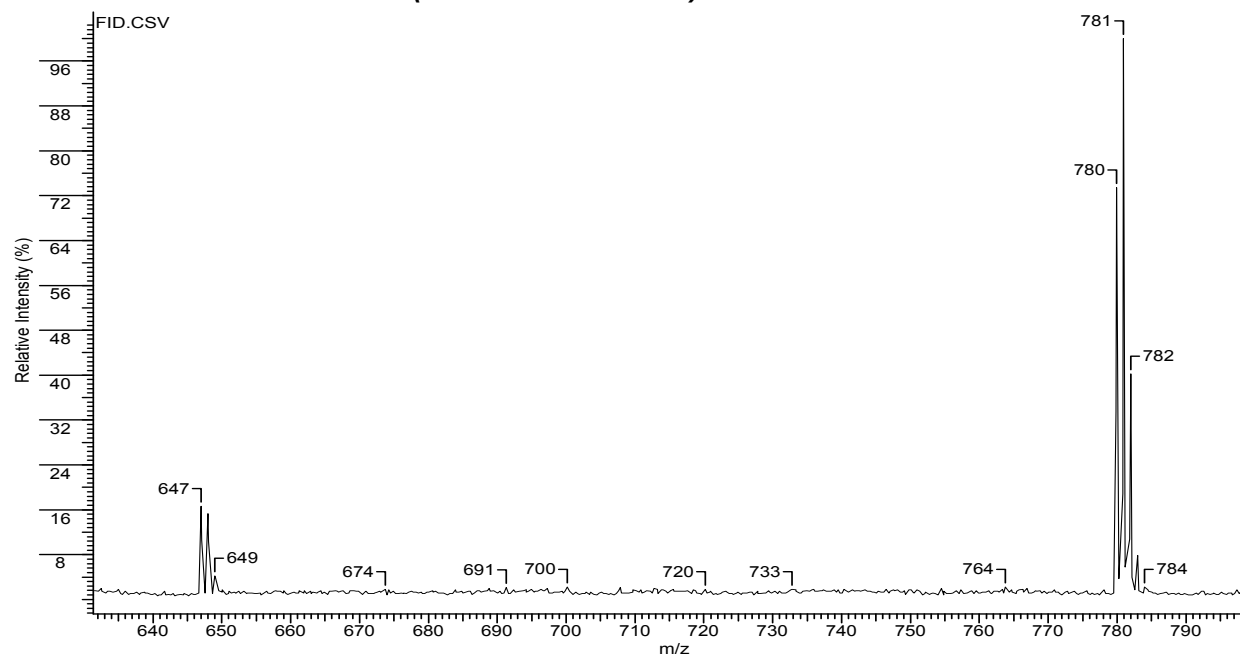
MALDI-TOF Spectra

MALDI-TOF of TBDAP 3a. (matrix: Proton Sponge®)



MALDI-TOF for diazide (2) (matrix – dithranol)



MALDI-TOF for TBDAP 3c (matrix – dithranol)**MALDI-TOF for TBDAP 3b (matrix – dithranol)**

Electronic absorption and emission spectra

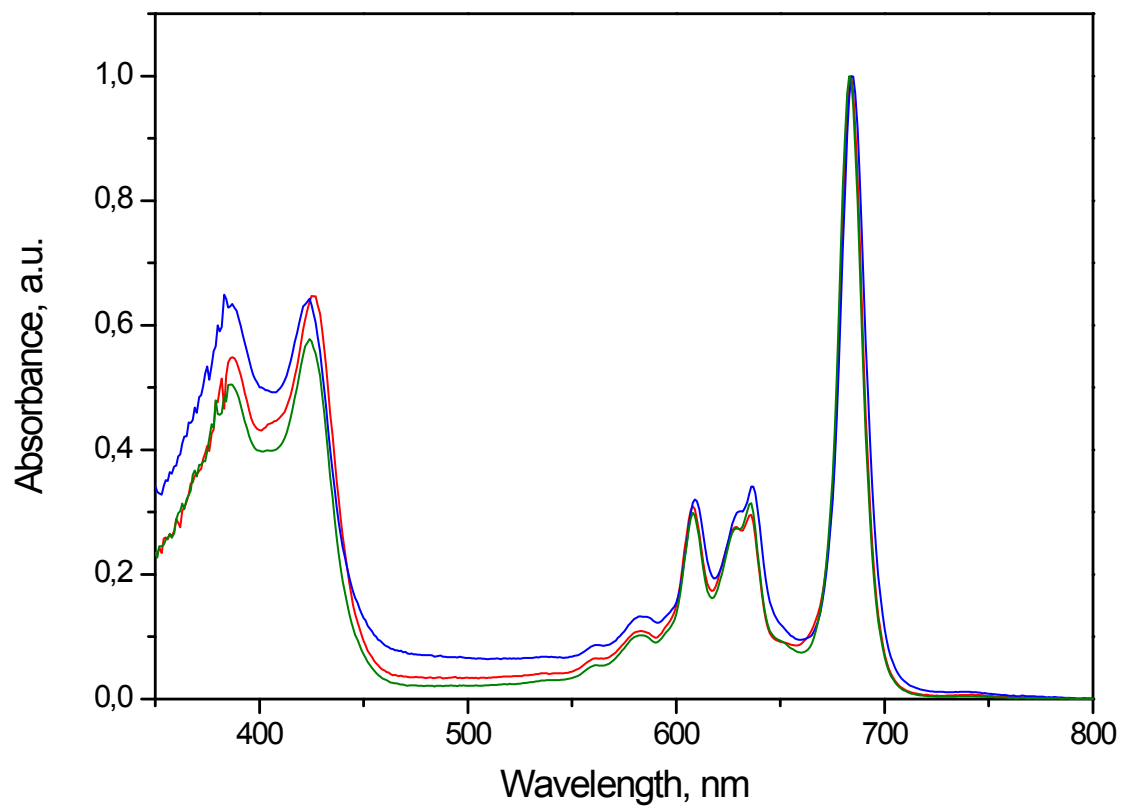


Figure 4. Electronic absorption spectra (normalized) of TBDAP derivatives 3a (red line), 3b (blue line), 3c (green line) in DCM solutions.

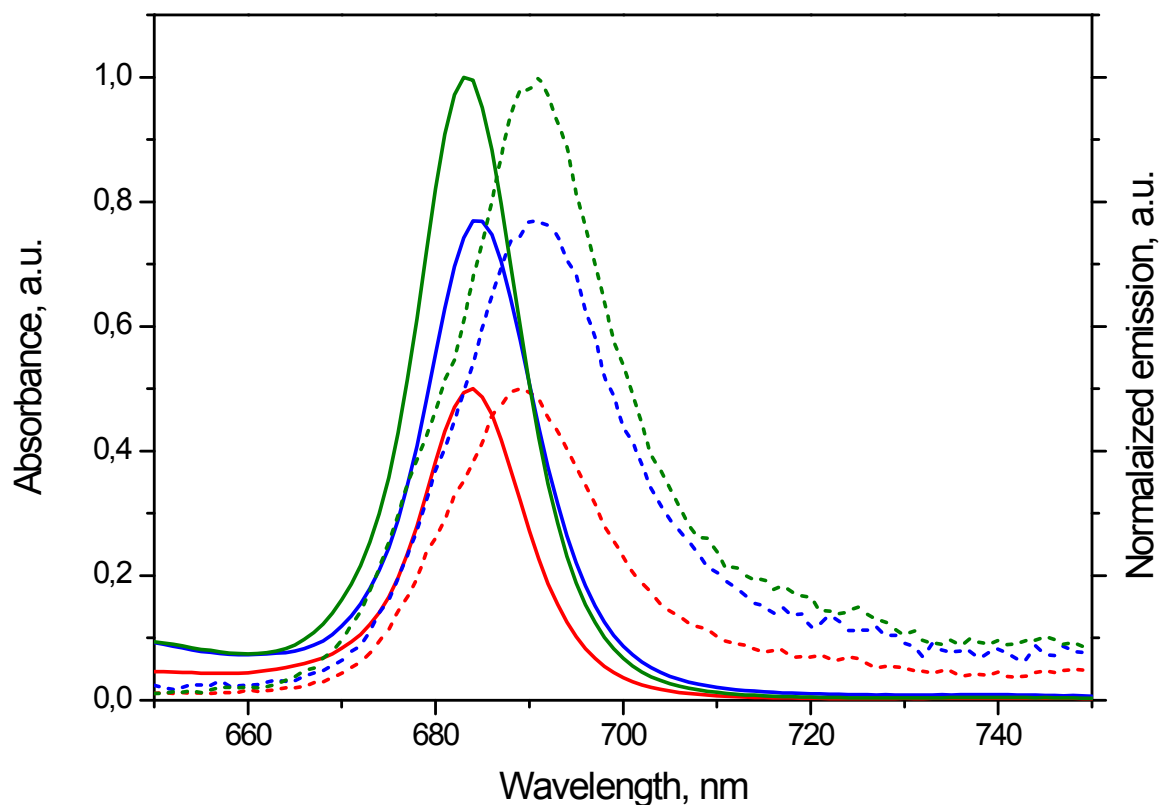


Figure 5. Electronic absorption (Q-band, solid lines) and emission (dashed lines) spectra of TBDAP derivatives 3a (red lines), 3b (blue lines), 3c (green lines) in DCM solutions. EA and emission spectra of the same compound are normalized, the spectra of different compounds are scaled in order to allow for optimal visualization of band shape.

References

- ¹ M. A. Filatov, A. Y. Lebedev, S. N. Mukhin, S. A. Vinogradov and A. V. Cheprakov, *J. Am. Chem. Soc.*, 2010, **132**, 9552.
- ² (a) Jentzen, W.; Song, X.-Z.; Shelnut, J. A. *J. Phys. Chem. B*, **1997**, *101*, 1684; (b) Jentzen, W.; Ma, J.G.; Shelnut, J.A. *Biophys. J.* **1998**, *74*, 753; (c) NSD software is accessible on-line via <http://jasheln.unm.edu/jasheln/content/nsd/NSDengine/start.htm>