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Carbonyl-Functionalized Cyclazines as Colorants and Air-Stable *n*-Type Semiconductors

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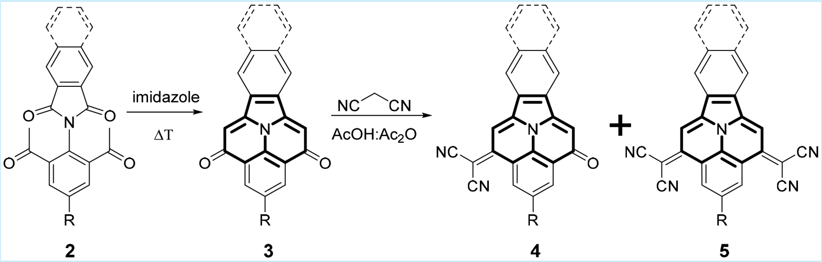
Supporting Information



ABSTRACT: A series of π-extended cycl[3,3,2]azines (**3**) bearing additional carbonyl groups were synthesized via aldol condensations. Two strong electron acceptor molecules (**4** and **5**), with low-lying LUMO energy levels of −3.99 and −3.95 eV, respectively, were obtained. Organic thin-film transistors (TFTs) based on the cyanated cyclazine derivatives **5** were fabricated by vapor deposition, exhibiting extraordinarily stable *n*-type semiconductor character under ambient condition with the highest electron mobility of 0.06 cm^2 V^{-1} s^{-1} consistently for more than 30 months.

Recently, nitrogen doping of carbon materials such as nanodiamonds and graphenes has gained increasing attention.[1,2] Cyclazines I−III, where the nitrogen is located in the center of a tricyclic conjugated π-system, represent the smallest possible cutout of N-graphenes. The term cyclazines was introduced by Boekelheide et al.; thereby, cycl[3,2,2]azine (**I**), cycl[3,3,3]azine (**II**) and cycl[3,3,2]azinium cation (**III**) (see Figure 1) are known as the most popular examples.[3−5]

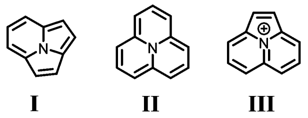
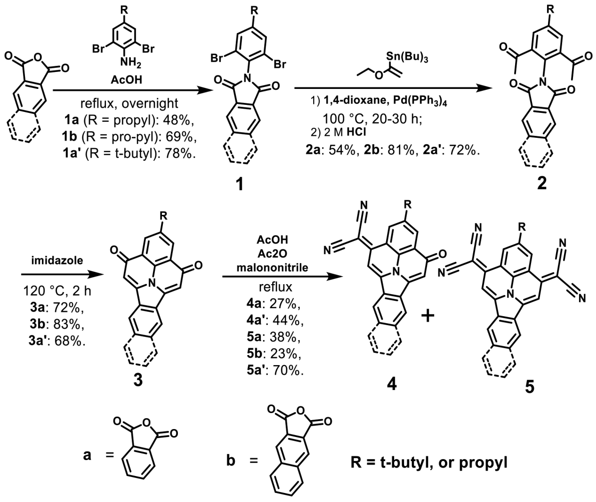


Figure 1. Structures of cyclazines.

Cyclazines can also be described as N-bridged annulenes with three different bonding situations at the N atom, yielding a pyrrolic (**I**), pyridinic (**II**), or quaternary (**III**) center. However, despite their attractive chemical, physicochemical, and magnetic properties, difficult synthetic routes to cyclazines have somehow hampered further studies.[6−9]

Herein, for the first time, we describe the synthesis and characterization of carbonyl-functionalized cyclazines. With two C═O groups as auxochromic units, *di*ketocycl[3,3,2]azine **3** (Scheme 1), like other carbonyl-based chromophores, reveals pronounced colorant properties.[10] Furthermore, the strong

Scheme 1. Synthesis of Compounds 1, 2, 3, 4, and 5



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electron acceptor **5** serves as *n*-type semiconductors in TFTs with high air stability. The title system (**3**) was synthesized using an optimized aldol condensation protocol that was recently developed in our group.[11]

Using commercially accessible phthalic anhydride (**a**) or 2,3-naphthalenedicarboxylic anhydride (**b**) as starting materials, cyclazine **3** was obtained via a three-step reaction. Considering that 2,6-diacetylaniline is not easily available and its reaction with anhydrides is accompanied by several byproducts, the initial imidization was performed between anhydrides **a**/**b** and 4-propyl-2,6-dibromoaniline in acetic acid under reflux conditions, leading to **1a** and **1b** in yields of 48% and 69%, respectively.[11] Subsequent Stille coupling was conducted in 1,2-dioxane at 100 °C for 12 h, furnishing acetyl derivative **2a**. The most critical step, the aldol condensation, was carried out using imidazole as a solvent at 120 °C for 2 h, giving **3a** in 72% yield and **3b** in 83% yield. In order to test the reactivity of the carbonyl groups in **3**, malononitrile was reacted with **3** under Knoevenagel conditions under acidic conditions. The yields of the 2-fold condensation are much improved if the reactants are well solubilized. In this case, when R is a *tert*-butyl group, **5a′** was obtained in 70% yield after purification.

The structures of all new compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS or elemental analysis (see the Supporting Information). Single crystals of **3a′** and **5a′** were obtained by slow diffusion of hexane into CH_2Cl_2 solutions. As shown in Figure 2, both **3a′** and **5a′** have a planar conjugated core structure. **3a′** possesses an almost-perfect head-to-tail parallel arrangement between two neighboring molecules, while **5a′** exhibits a slip angle of ~120°. Nevertheless, both crystals show a staircase-type assembly in the crystal structures (Figure 2, *c*-axis view of the crystals **3a′** and **5a′**). Wide-angle X-ray scattering (WAXS) of the dried powders of **4a′**, **5a′**, and **5b** (see the Supporting Information) confirmed the presence of similar packing modes.

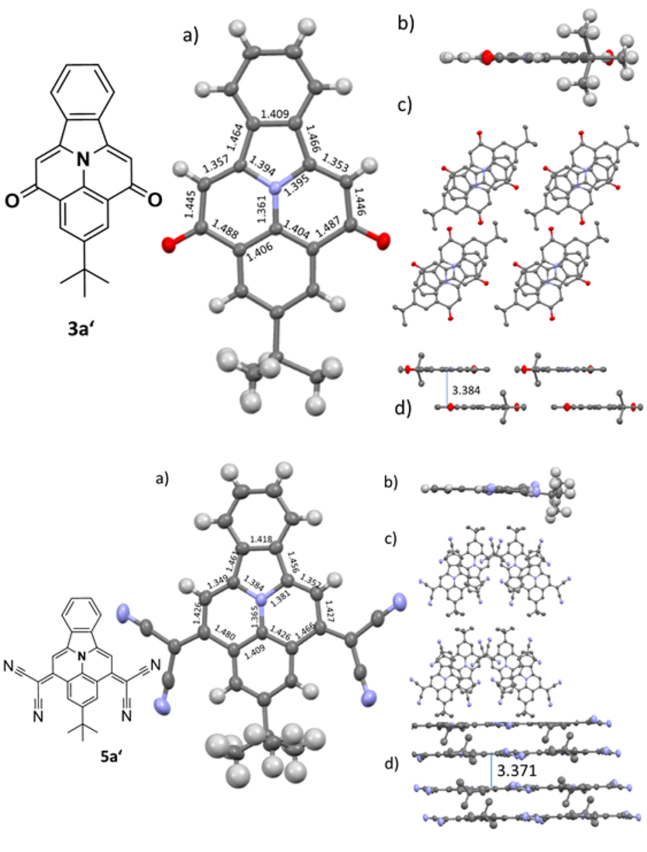

Figure 2. Crystal structures of **3a′** and **5a′**: (a) top view and (b) side view. Columnar packing diagram along (c) the *b*-axis and (d) the *c*-axis.

Cyclic voltammetry was performed on all cyclazines **3**−**5**. The redox potentials and the estimated lowest unoupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies are summarized in Table 1. All cases exhibit two reversible reduction waves (due to the two carbonyl groups), but only one oxidation wave (corresponding to the N atom) within the accessible potential range in CH_2Cl_2. The LUMO level decreases as the number of cyano substituents is increased. **3a** (no cyano), **4a** (two cyano groups), and **5a** (four cyano substituents) made via phthalic anhydride revealed LUMO levels of −3.37, −3.72, and −3.99 eV, respectively. While **3b**, **4b**, and **5b**, containing zero, two, and four cyano groups, respectively, showed LUMO levels of −3.33, −3.69, and −3.95 eV. Obviously, increasing the conjugation system from **a** (benzene) to **b** (naphthalene) has a minor effect on the molecular LUMO levels. Since the LUMO levels of cyclazines **5a** and **5b** are close to −4 eV, they appear as candidates for the fabrication of air-stable *n*-channel thin-film transistors (TFTs).

Cyclazines **3**−**5** fail to show fluorescence. Their ultraviolet−visible light (UV-vis) absorption spectra measured in CH_2Cl_2 are displayed in Figure 3. **3** is yellow with an absorption maximum at ~445 nm, **5a** and **5b** are blue with λ_{max} = 629 and 621 nm, respectively, indicating, again, only a weak influence of the core extension from benzene to naphthalene. On the other hand, in the solid state, all cyclazines **3a′**, **4a′**, and **5a′** reveal a golden metallic luster (see their powder pictures in the Supporting Information).

The TFTs based on **5a** and **5b** were fabricated in the bottom-gate, top-contact architecture, using a heavily doped silicon wafer as the substrate and gate electrode. The gate dielectric is a combination of a 100-nm-thick layer of thermally grown silicon dioxide, an 8-nm-thick layer of aluminum oxide grown by atomic layer deposition, and a self-assembled monolayer of *n*-tetradecylphosphonic acid.[14] During the semiconductor deposition, the substrate was held at a temperature of 140 °C. For the source and drain contacts, gold was deposited via thermal evaporation in vacuum and patterned using a shadow mask. The channel length is 100 μm and the channel width is 200 μm. The current−voltage measurements were performed in ambient air. The TFTs based on **5a** have an electron mobility of 0.02 cm^2/(V s) immediately after fabrication and 0.006 cm^2/(V s) after 30 months in air (Figure 4, top row). For **5b**, the electron mobility is 0.06 cm^2/(V s) both after fabrication and after 30 months in air (Figure 4, bottom row), reflecting a truly remarkable stability of the devices. Such a durability of TFTs is quite rare. Indeed, organic *n*-type materials have been intensively studied with a focus on charge carrier mobilities, while the critical factors for practical applications such as shelf life and operational lifetime have been set aside. The mobilities of most organic *n*-type semiconductor-based TFT devices often decrease after prolonged storage (literature reported stability values so far are given for 100 days at the most) in ambient atmosphere.[12] A case closely related to cyclazines are perylene tetracarboxdiimides PDI-FCN$_2$ carrying electron-withdrawing substituents whose devices display an almost 30% decrease of electron mobilities after three years.[13]

Table 1. Absorption and Electrochemical Properties of 3a–5b

	$\varepsilon_0{}^a$ ($M^{-1}cm^{-1}$)	λ_{max} (nm)	$E_{red}{}^b$ (V)	$E_{ox}{}^b$ (V)	E_g (eV)	HOMO^c (eV)	LUMO^d (eV)
3a	29 200	449	−1.43	1.26	2.69	−6.06	−3.37
4a	41 500	553	−1.08	1.18	2.26	−5.98	−3.72
5a	79 500	629	−0.81	1.12	1.93	−5.92	−3.99
3b	27 600	441	−1.47	1.16	2.63	−5.96	−3.33
4b	38 300	547	−1.11	0.96	2.07	−5.76	−3.69
5b	73 800	621	−0.85	0.97	1.82	−5.77	−3.95

^{a}Measured at λ_{max}. ^{b}Onset potentials, determined by cyclic voltammetric measurements in 0.1 M solution of Bu_4NPF_6 in CH_2Cl_2 vs Fc^+/Fc. ^{c}Estimated vs vacuum level from $E_{HOMO} = -4.80$ eV $- E_{ox}$. ^{d}Estimated vs vacuum level from $E_{LUMO} = -4.80$ eV $- E_{red}$.

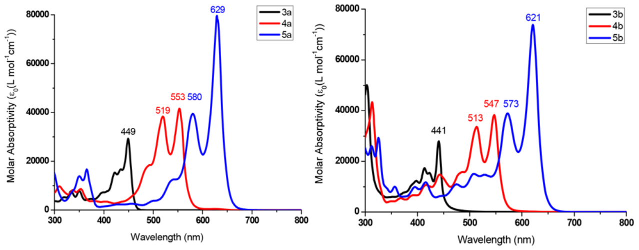

Figure 3. UV-vis absorption of **3a**, **4a**, and **5a** (left panel) and **3b**, **4b**, and **5b** (right panel) in CH_2Cl_2.

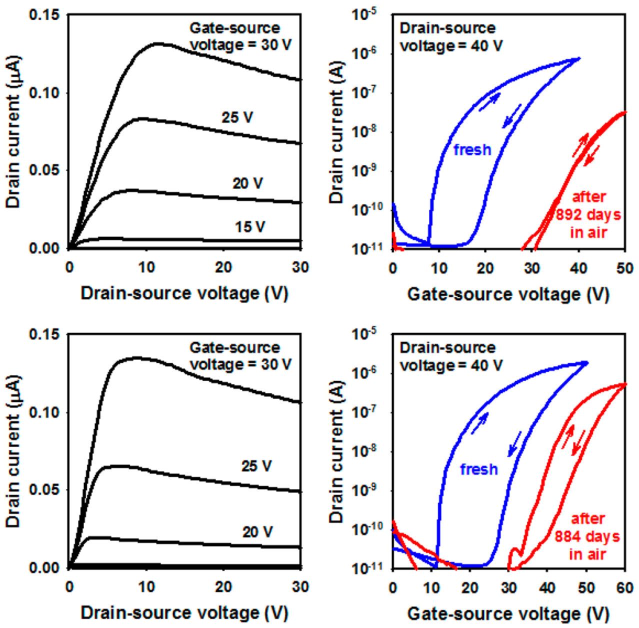

Figure 4. Measured current–voltage characteristics of *n*-channel thin-film transistors (TFTs) based on 30 nm-thick, vacuum-deposited layers of **5a** (top row) and **5b** (bottom row) as the semiconductor.

In conclusion, two cyclazine-based carbonyl chromophores **3a** and **3b** were synthesized by way of aldol condensations. The carbonyl groups of **3** were further functionalized with malononitrile to form tetracyano-substituted cyclazine derivatives **5a** and **5b** as deep blue chromophores with molar absorption coefficients close to 80 000 M^{-1} cm^{-1}. The product **5b** features high planarity, dense packing in the solid, and short interplanar distances, and it exhibits a consistent electron mobility (μ) of 0.06 $cm^2/(V\ s)$ for more than 30 months. Therefore, the new cyclazines **3**, **4**, and **5** can be used not only as colorants, but also as *n*-type semiconductors for practical applications. Further studies based on symmetric starting materials, such as pyromellitic dianhydride or 2,3,6,7-naphthalene dianhydride, are in progress.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00183.

Full experimental details and characterization data (PDF)

Accession Codes

CCDC 1817712–1817713 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Mochalin, V. N.; Shenderova, O.; Ho, D.; Gogotsi, Y. *Nat. Nanotechnol.* **2012**, *7*, 11.

(2) Narita, A.; Wang, X. Y.; Feng, X. L.; Müllen, K. *Chem. Soc. Rev.* **2015**, *44*, 6616.

(3) Boekelheide, V.; Gall, W. G. *J. Org. Chem.* **1954**, *19*, 499.

(4) Windgassen, R. J.; Saunders, W. J.; Boekelheide, V. *J. Am. Chem. Soc.* **1959**, *81*, 1459.
(5) Boekelheide, V.; Vick, G. K. *J. Am. Chem. Soc.* **1956**, *78*, 653.
(6) Farquhar, D.; Gough, T. T.; Leaver, D. *J. Chem. Soc., Perkin Trans. 1* **1976**, *3*, 341.
(7) Leupin, W.; Wirz, J. *J. Am. Chem. Soc.* **1980**, *102*, 6068.
(8) Fourmigue, M.; Eggert, H.; Bechgaard, K. *J. Org. Chem.* **1991**, *56*, 4858.
(9) Shigemitsu, Y.; Uejima, M.; Sato, T.; Tanaka, K.; Tominaga, Y. *J. Phys. Chem. A* **2012**, *116*, 9100.
(10) Zollinger, H. *Color Chemistry*, 3rd Edition; Wiley−VCH: Weinheim, Germany, 2003; pp 255−354.
(11) Jänsch, D.; Li, C.; Chen, L.; Wagner, M.; Müllen, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 2285.
(12) Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y. *J. Mater. Chem. C* **2017**, *5*, 8654.
(13) Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 15259.
(14) Hofmockel, R.; Zschieschang, U.; Kraft, U.; Rödel, R.; Hansen, N. H.; Stolte, M.; Würthner, F.; Takimiya, K.; Kern, K.; Pflaum, J.; Klauk, H. *Org. Electron.* **2013**, *14*, 3213.

Supporting Information

Carbonyl-Functionalized Cyclazines as Colorants and Air-Stable n-Type Semiconductors

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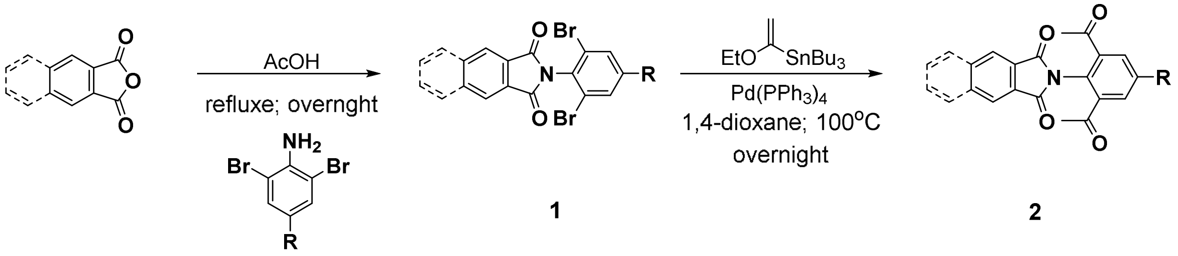
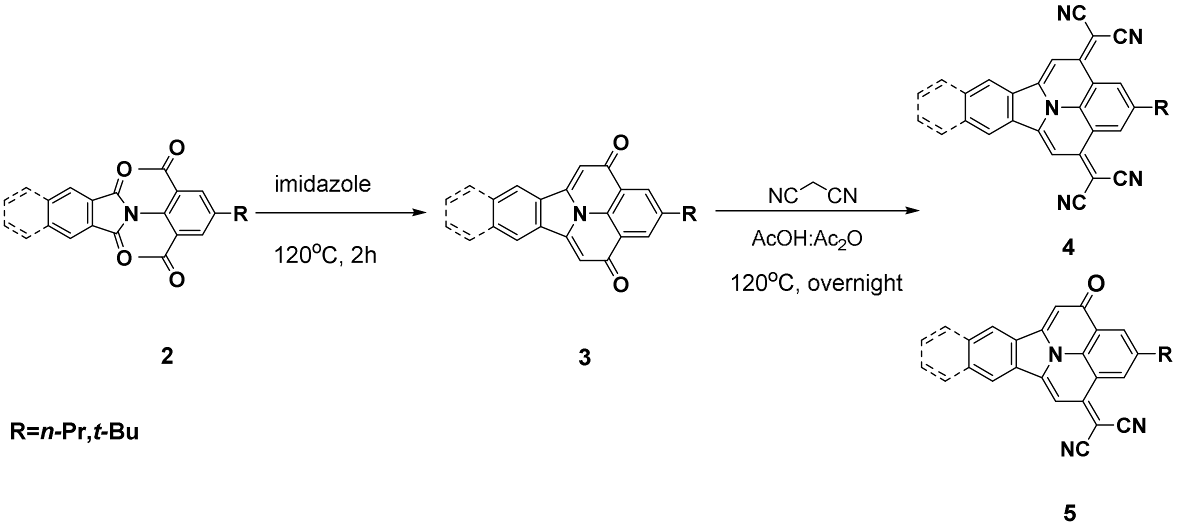
1. General Methods

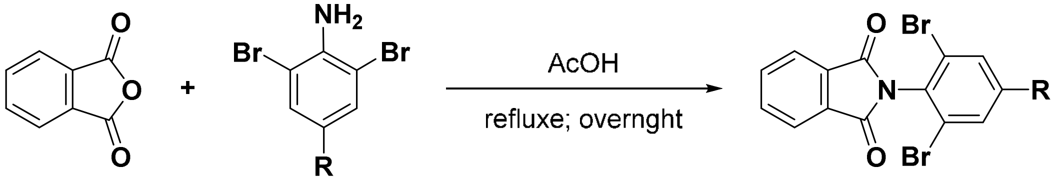
All the raw materials used were purchased from Sigma–Aldrich, Fluka, Fisher Scientific, VWR and Acros and unless otherwise stated were used without further purification. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AVANCE 300, Bruker AVANCE 500 and Bruker AVANCE 700 spectrometer in the listed deuterated solvents. Elemental analysis of solid samples was carried out on a Foss Heraeus Vario EL. FD mass spectra were recorded with a VG Instruments ZAB 2-SE-FPD. Solution UV-Vis absorption and emission spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrophotometer and J&MTIDAS spectrofluorometer in dichloromethane in a conventional quartz cell (light pass 10 mm). CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a dichloromethane solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature. A Pt wire, a silver wire, and a glassy carbon electrode were used as the counter electrode, the reference electrode, and the working electrode, respectively. Powder X-ray diffraction (XRD) measurements were conducted with a STOE STADI P transmission diffractometer with Ge(111) single crystal monochromator. Doffractopm üatterms were recorded with a DECTRIS solid-state strip detector MYTHEN 1K in an omega-2-theta scan type using a step size of 2.1° and a counting time of 20 s per step.

2. Experimental Section

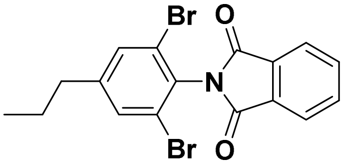




General method: Compound 1:

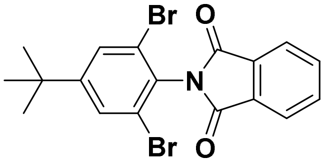


A mixture of phthalic anhydride (1.48g, 10.00mmol) and 2,6-dibromo-aniline (12.00 mmol) was dissolved in 20ml of acetic acid and refluxed. The reaction is monitored by TLC (petroleum ether/ethyl acetate, 5/1) and upon completion the solvent was evaporated under reduced pressure, the residue was recrystallized from MeOH to give the desired product as colorless well-defined crystalls.



2-(2,6-dibromo-4-propylphenyl)isoindoline-1,3-dione (1a)

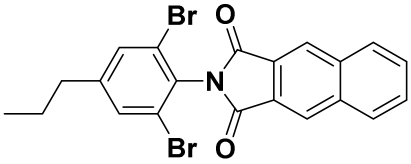
Yield: 1.80 g (43%). ^{1}**H NMR** (300 MHz, CD_2Cl_2, 298K): δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.67 (m, 2H), 2.63 (m, 2H), 7.55 (s, 2H), 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.98 (dd, *J* = 5.5, 3.1 Hz, 2H). ^{13}**C NMR** (75 MHz, CD_2Cl_2, 298K): δ 14.06 (1C, CH_3), 24.60 (1C, CH_2), 37.73 (1C, CH_2), 124.51, 124.99, 132.37, 133.03, 135.24, 148.61, 166.32 (2C, C=O). **Elemental analysis** calcd (%) for $C_{17}H_{13}Br_2NO_2$: C 48.26, H 3.10, N 3.31; found: C 48.27, H 3.04, N 3.30. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{17}H_{13}Br_2NO_2$: 423.10; found: 423.6 (100) $[M]^+$. **Melting Point**: 200-201 °C.



2-(2,6-dibromo-4-(tert-butyl)phenyl)isoindoline-1,3-dione (1a')

Yield: 3.40 g (78%). ^{1}**H NMR** (300 MHz, $CDCl_3$, 298K) δ 1.34 (s, 9H), 7.67 (s, 2H), 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 8.00 (dd, *J* = 5.5, 3.1 Hz, 2H). ^{13}**C NMR** (75 MHz, $CDCl_3$, 298K) δ 31.14 (3C, CH_3), 35.35 (1C, C-CH_3), 124.26, 124.64, 129.99, 131.97, 134.69, 156.20, 165.97 (2C, C=O). **Elemental analysis**

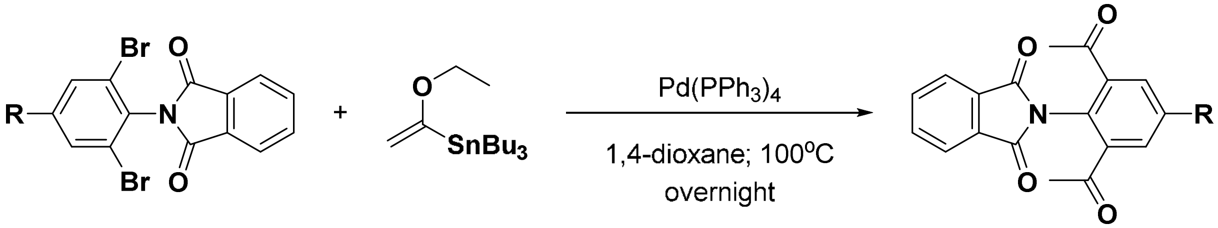
calcd (%) for $C_{18}H_{15}Br_2NO_2$: C 49.46, H 3.46, N 3.20; found: C 49.73, H 3.52, N 3.09. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{18}H_{15}Br_2NO_2$: 437.13; found: 437.2 (100) $[M]^+$. **Melting Point**: 228-229 °C.



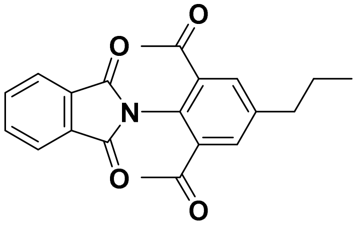
2-(2,6-dibromo-4-propylphenyl)-1H-benzo[f]isoindole-1,3(2H)-dione (1b)

Yield: 3.23 g (69%). **^{1}H NMR** (300 MHz, CD_2Cl_2, 298K): δ 1.00 (t, *J* = 7.3 Hz, 3H), 1.70 (m, 2H), 2.64 (m, 2H), 7.57 (s, 2H), 7.77 (dd, *J* = 6.3, 3.3 Hz, 2H), 8.15 (dd, *J* = 6.2, 3.3 Hz, 2H), 8.49 (s, 2H). **^{13}C NMR** (75 MHz, CD_2Cl_2, 298K): δ 14.08 (1C, CH_3), 24.61 (1C, CH_2), 37.74 (1C, CH_2), 124.83, 126.18, 127.93, 129.40, 130.12, 130.92, 133.03, 136.27, 148.59, 166.06 (2C, C=O). **Elemental analysis** calcd (%) for $C_{21}H_{15}Br_2NO_2$: C 53.31, H 3.20, N 2.96; found: C 53.40, H 3.42, N 3.09. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{21}H_{15}Br_2NO_2$: 473.16; found: 473.2 (100) $[M]^+$. **Melting Point**: 218-219 °C.

General method: Compound 2:

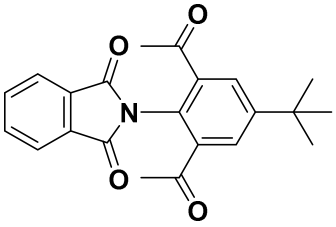


A solution of 2-(2,6-dibromo-4-(substituted)phenyl)isoindoline-1,3-dione (5.0 mmol), $Pd(PPh_3)_4$ (347 mg, 0.03 mmol), a in 1,4-dioxane (80 mL) was stirred (10 min) under a positive flow of argon. To the yellow solution was added tributyl(1-ethoxy-1-ethenyl)stannane (4.23 ml, 12.5 mmol) dissolved in 1,4-dioxane (10 mL). The solution was heated at reflux (20-30h) whereupon a dark brown solution was formed. The progress of the reaction was monitored to completion using TLC (hexane/ DCM). The reaction mixture was cooled to ambient temperature, 50 ml 1N HCl were added and stirred for 5h at r.t. The reaction mixture was extracted with DCM and dried under $MgSO_4$ and solvent was evaporated until dryness. The crude product was purified by recrystallization from MeOH-DCM to give product as colorless crystals.



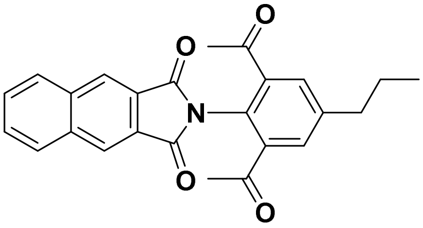
2-(2,6-diacetyl-4-propylphenyl)isoindoline-1,3-dione (2a)

Yield 0.95 g (54%). **^{1}H NMR** (300 MHz, CD_2Cl_2, 298K) δ 1.03 (t, *J* = 7.3 Hz, 3H), 1.75 (h, *J* = 7.3 Hz, 2H), 2.77 (m, 2H), 7.75 (s, 2H), 7.80 (m, 2H), 7.89 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K) δ 14.13 (1C, CH_3), 24.93 (1C, CH_2), 29.37 (2C, CH_3), 38.14 (1C, CH_3), 124.20, 124.29, 124.80, 132.25, 132.75, 134.97, 138.86, 145.11, 168.12 (2C, C=O), 199.67 (2C, C=O). **Elemental analysis** calcd (%) for $C_{21}H_{19}NO_4$: C 72.19, H 5.48, N 4.01; found: C 71.98, H 5.31, N 3.87. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{21}H_{19}NO_4$: 349.39; found: 349.9 (100) $[M]^+$. **Melting Point**: 230-231 °C (with color changing).



2-(2,6-diacetyl-4-(tert-butyl)phenyl)isoindoline-1,3-dione (2a')

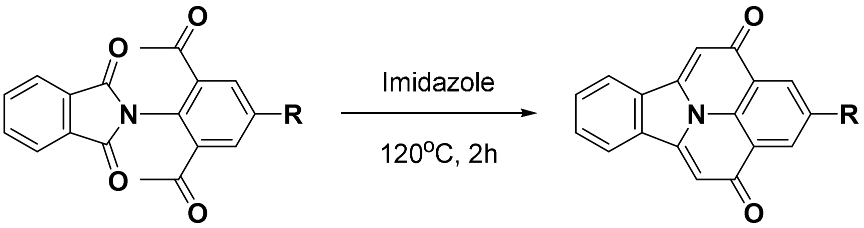
Yield 1.31 g (72%). **^{1}H NMR** (300 MHz, $CDCl_3$, 298K) δ 1.42 (s, 9H), 2.55 (s, 6H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.88-7.92 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K) δ 29.09 (2C, CH_3), 31.26 (3C, CH_3), 35.21 (1C, C-CH_3), 124.02, 124.32, 128.85, 132.37, 134.44, 138.28, 152.67, 167.84 (2C, C=O), 199.36 (2C, C=O). **Elemental analysis** calcd (%) for $C_{22}H_{21}NO_4$: C 72.71, H 5.82, N 3.85; found: C 72.87, H 5.80, N 3.84. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{22}H_{21}NO_4$: 363.41; found: 362.90 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 292 nm (3600 $M^{-1}cm^{-1}$). **Melting Point**: 266-267 °C (with color changing).



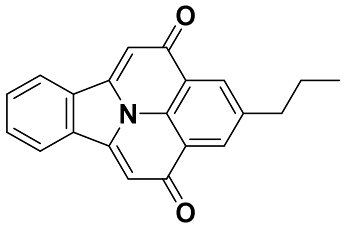
2-(2,6-diacetyl-4-propylphenyl)-1H-benzo[f]isoindole-1,3(2H)-dione (2b)

Yield 1.70 g (81%). **^{1}H NMR** (300 MHz, CD_2Cl_2, 298K) δ 1.03 (t, *J* = 7.3 Hz, 3H), 1.75 (h, *J* = 7.3 Hz, 2H), 2.77 (m, 2H), 7.75 (s, 2H), 7.80 (m, 2H), 7.89 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K) δ 14.14 (1C, CH_3), 24.94 (1C, CH_2), 29.36 (2C, CH_3), 38.15 (1C, CH_3), 125.02, 125.78, 128.33, 129.91, 130.85, 132.22, 136.22, 138.76, 145.11, 167.84 (2C, C=O), 199.68 (2C, C=O). **Elemental analysis** calcd (%) for $C_{25}H_{21}NO_4$: C 75.17, H 5.30, N 3.51; found: C 75.47, H 5.50, N 3.24. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{25}H_{21}NO_4$: 399.45; found: 399.80 (100). **Melting Point**: 250-251 °C (with color changing).

General method: Compound 3:

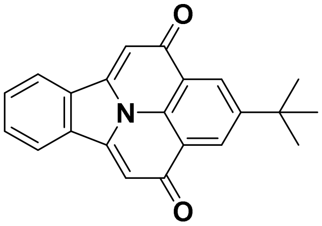


The N-(2,6-diacetyl-4-(substituted)phenyl)phthalimide (200mg) and imidazole (2-3 g) was stirred at 120°C in 50ml *Schlenk tube* for 2h. The reaction mixture was cooled to ambient temperature, and then 20 ml of water were added and stirred for 30 min at r.t. The yellow suspension was filtrated and washed several times with small portions of water and MeOH. The crude product could be purified by the short column chromatography (CH_2Cl_2) or by recrystallization from CH_2Cl_2 – hexane mixture to give product as yellow needles.



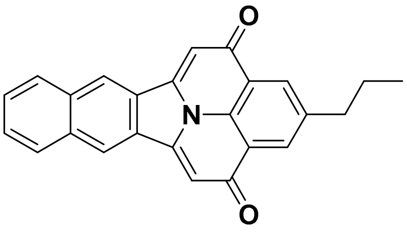
2-propylbenzo[1,2]indolizino[6,5,4,3-ija]quinoline-4,11-dione (3a)

Yield 129mg (72%) ^{1}**H NMR** (300 MHz, CD_2Cl_2, 298K) δ 0.98 (t, *J* = 7.3 Hz, 3H), 1.74 (m, 2H), 2.79 (m, 2H), 6.68 (s, 2H), 7.62 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.84 (dd, *J* = 5.7, 3.1 Hz, 2H), 8.26 (s, 2H). ^{13}**C NMR** (75 MHz, CD_2Cl_2, 298K) δ 13.96 (1C, CH_3), 25.10 (1C, CH_2), 38.25 (1C, CH_2), 107.40 (2C, CH), 123.82, 124.87, 132.70, 133.72, 134.38, 141.44, 146.16, 179.86 (2C, C=O). **Elemental analysis** calcd (%) for $C_{21}H_{15}NO_2$: C 80.49, H 4.83, N 4.47; found: 80.51, H 4.84, N 4.40 **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{21}H_{15}NO_2$:313.36; found: 313.5 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 450, 435 and 422 nm (27290, 16080 and 14440 $M^{-1}cm^{-1}$). **Melting Point**: >350 °C.



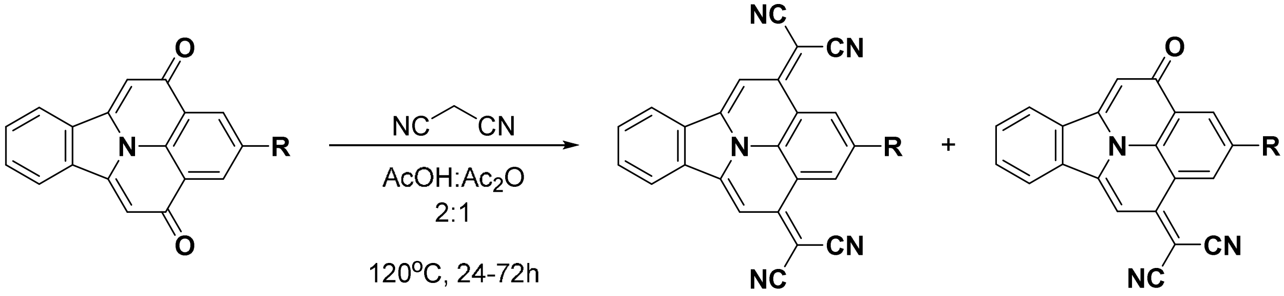
2-(tert-butyl)benzo[1,2]indolizino[6,5,4,3-ija]quinoline-4,11-dione (3a')

Yield 124mg (68%) ^{1}**H NMR** (300 MHz, CD_2Cl_2, 298K) δ 1.45 (s, 9H), 6.71 (s, 2H), 7.64 (dd, *J* = 5.7, 3.1 Hz, 2H), 7.87 (dd, J = 5.6, 3.1 Hz, 2H), 8.52 (s, 2H). ^{13}**C NMR** (75 MHz, CD_2Cl_2, 298K) δ 31.44 (3C, CH_3), 35.66 (1C, C-CH_3), 107.21 (2C, CH), 123.63, 124.46, 129.67, 132.49, 133.54, 133.92, 145.92, 149.78, 179.75 (2C, C=O). **Elemental analysis** calcd (%) for $C_{22}H_{17}NO_2$: C 80.71, H 5.23, N 4.28; found: C 80.82, H 5.03, N 4.28 **FD mass spectrum** (8 kV): *m/z* (%):calcd for $C_{22}H_{17}NO_2$: 327.38; found: 328.4 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 449, 422 nm (29300, 15250 $M^{-1}cm^{-1}$). Structure proven by XRD (CCDC1817713, Unit Cell Parameters: a 10.9591(10) b 6.7680(5) c 11.0796(10) P21/m). **Melting Point**: >350 °C.

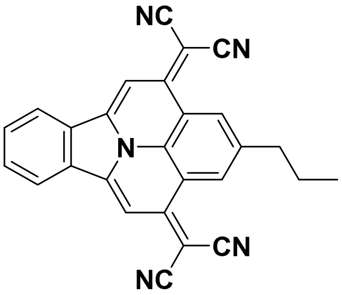


2-propylnaphtho[2',3':1,2]indolizino[6,5,4,3-ija]quinoline-4,13-dione (3b)

Yield 160mg (83%) **^{1}H NMR** (300 MHz, $C_2D_2Cl_4$, 298K) δ 0.99 (t, *J* = 7.3 Hz, 3H), 1.75 (dq, *J* = 14.6, 7.3 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 6.86 (s, 2H), 7.66 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.98 (dd, *J* = 6.2, 3.3 Hz, 2H), 8.27 (s, 2H), 8.30 (s, 2H). **^{13}C NMR** (75 MHz, $C_2D_2Cl_4$, 298K) δ 13.65 (1C, CH_3), 24.36 (1C, CH_2), 37.61 (1C, CH_2), 106.31 (2C, CH), 123.92, 124.36, 128.81, 129.06, 129.40, 131.99, 134.38, 141.12, 145.42, 179.13 (2C, C=O). **Elemental analysis** calcd (%) for $C_{25}H_{17}NO_2$: C 82.63, H 4.72, N 3.85; found: C 82.83, H 4.84, N 3.70 **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{25}H_{17}NO_2$:363.42; found: 363.50 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 440 nm (25600 $M^{-1}cm^{-1}$). **Melting Point**: >350 °C.

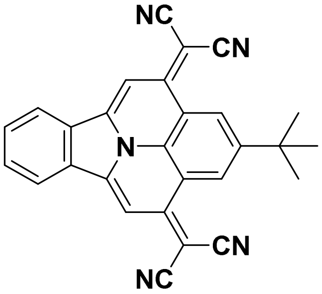


Diketone **3** (100mg) and malononitrile (300 mg, 4.54 mmol) were added to a mixture of acetic acid and acetic anhydride (2:1) and the mixture was stirred at 120°C for the indicated time. The reaction was monitored by TLC (CH_2Cl_2) and amount ratio of **4** and **5** was controlled by addition of malononitrile. Then solvents were evaporated until dryness. The crude mixture of products was separated by the flesh column chromatography (CH_2Cl_2/Ac_2O 20:1) and product **4** obtained as flat crystals with a blue-goldis color and product **5** as as flat crystals with a red-goldish color.



2,2'-(2-propylbenzo[1,2]indolizino[6,5,4,3-ija]quinoline-4,11-diylidene)dimalononitrile (5a)

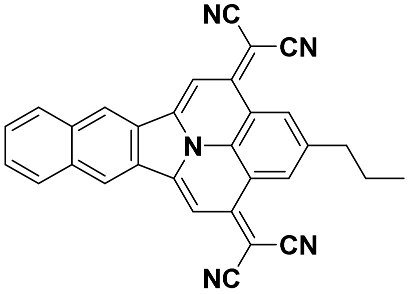
Yield 50mg (38%). **^{1}H NMR** (500 MHz, $C_2D_2Cl_4$, 353K) δ 1.10 (t, *J* = 7.3 Hz, 3H), 1.88 (q, *J* = 7.3 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 7.57 (s, 2H), 7.79 (dd, *J* = 5.4, 2.9 Hz, 2H), 8.06 (dd, *J* = 5.3, 3.0 Hz, 2H), 9.23 (s, 2H). **^{13}C NMR** (126 MHz, $C_2D_2Cl_4$, 353K) δ 13.35 (1C, CH_3), 23.47 (1C, CH_2), 37.83 (1C, CH_2), 68.25 (2C, $C(CN)_2$), 105.74 (2C, CH), 115.14, 116.28, 119.77, 123.24 (2C, CH), 129.24, 131.28, 132.21 (2C, CH), 132.87 (2C, CH), 140.13, 142.24, 151.18 (2C, $C=C(CN)_2$). **HRMS**: *m/z* (%): calcd for $C_{27}H_{15}N_5$: 409.1327 (100); found: 409.1306 (100) $[M]^+$. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{27}H_{15}N_5$: 409.45; found: 409.8 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 630, 580 nm (81120, 39980 $M^{-1}cm^{-1}$). **Melting Point**: >350 °C.



2,2'-(2-(tert-butyl)benzo[1,2]indolizino[6,5,4,3-ija]quinoline-4,11-diylidene)dimalononitrile (5a')

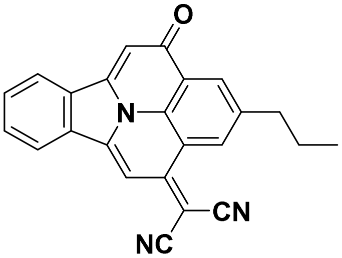
Yield 91mg (70%). **^{1}H NMR** (300 MHz, $C_2D_2Cl_4$, 383K) δ 1.58 (s, 9H), 7.59 (s, 2H), 7.80 (dd, *J* = 5.7, 3.0 Hz, 2H), 8.07 (dd, *J* = 5.6, 3.0 Hz, 2H), 9.51 (s, 2H). **^{13}C NMR** (126 MHz, $C_2D_2Cl_4$, 383K) δ 30.90 (1C, $C(CH_3)_3$), 36.29 (3C, CH_3), 68.46 (2C, $C(CN)_2$), 105.65 (2C, CH), 114.99, 116.33, 119.59, 123.16, 128.87, 129.85, 131.40, 132.73, 140.04, 151.59 (2C, $C=C(CN)_2$). **HRMS**: *m/z* (%): calcd for $C_{28}H_{17}N_5$: 423.1484 (100); found: 423.1464 (100) $[M]^+$. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{28}H_{17}N_5$: 423.15; found: 423.20 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 629, 580 nm (79700, 39420 $M^{-1}cm^{-1}$).

Structure proven by XRD (CCDC1817712, Unit Cell Parameters: a 7.1712(5) b 34.461(3) c 10.3979(6) P21/n). **Melting Point**: >350 °C.



2,2'-(2-propylnaphtho[2',3':1,2]indolizino[6,5,4,3-ijа]quinoline-4,13-diylidene)dimalononitrile (5b)

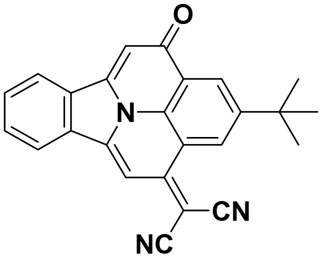
Yield 30 mg (23%). ^{1}**H NMR** (700 MHz, $C_2D_2Cl_4$, 373K) δ 1.13 (t, *J* = 7.3 Hz, 3H), 1.92 (d, *J* = 22.2 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 7.71 (s, 2H), 7.80 (dd, *J* = 5.6, 3.0 2H), 8.20 (dd, *J* = 5.6, 3.1 H 2H), 8.57 (s, 2H), 9.30 (s, 2H). ^{13}**C NMR** spectrum of **5b** could not be recorded due to its low solubility. **HRMS**: *m/z* (%): calcd for $C_{31}H_{17}N_5$: 459.5120 (100); found: 459.5152 (100) $[M]^+$. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{31}H_{17}N_5$: 459.51; found: 459.80 (100) $[M]^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 621, 573 nm (73800, 38800 $M^{-1}cm^{-1}$). **Melting Point**: >350 °C.



2-(11-oxo-2-propylbenzo[1,2]indolizino[6,5,4,3-ija]quinolin-4(11H)-ylidene)malononitrile (4a)

Yield 30 mg (27 %). ^{1}**H NMR** (300 MHz, $C_2D_2Cl_4$, 298K) δ 1.01 (t, *J* = 7.3 Hz, 3H), 1.78 (q, *J* = 7.4 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H), 6.85 (s, 1H), 7.42 (s, 1H), 7.71 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.89 (m, 1H), 7.98 (m, 1H), 8.36 (s, 1H), 9.13 (s, 1H). ^{13}**C NMR** (75 MHz, $C_2D_2Cl_4$, 298K) δ 13.62 (1C, CH_3), 24.04 (1C, CH_2), 37.72 (1C, CH_2), 65.35 (1C, $C(CN)_2$), 104.52 (1C, CH), 108.22 (1C, CH), 116.01, 117.07, 119.43, 123.31, 123.42, 124.09, 131.17, 131.70, 132.54, 132.65, 132.80, 133.67, 140.88, 141.67, 145.30, 152.25, 178.49 (1C, $C=C(CN)_2$), 190.98 (1C, C=O). **HRMS**: *m/z* (%): calcd for $C_{24}H_{15}N_3O$: 361.4040 (100);

found: 361.4026 (100) [M]$^+$. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{24}H_{15}N_3O$: 361.40; found: 361.8 (100) [M]$^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 554, 520 nm (42100, 38800 $M^{-1}cm^{-1}$). **Melting Point**: >350 °C.

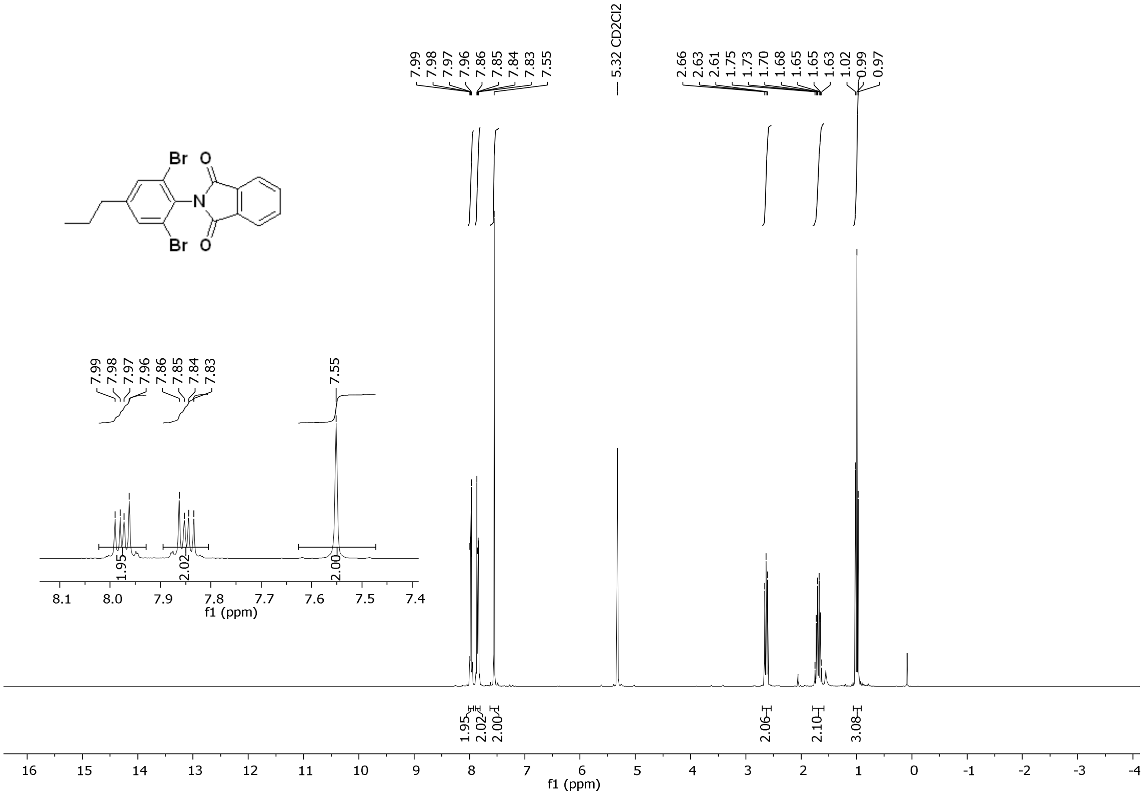


2-(2-(tert-butyl)-11-oxobenzo[1,2]indolizino[6,5,4,3-ija]quinolin-4(11H)-ylidene)malononitrile (4a')

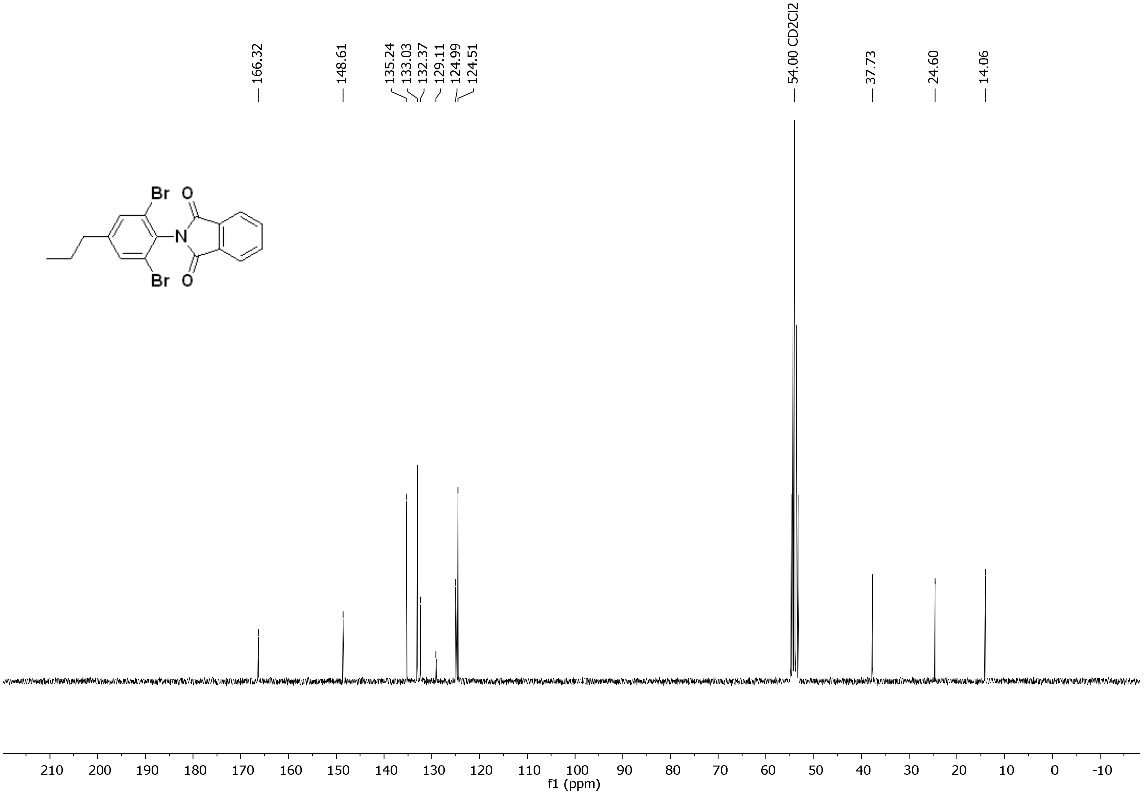
Yield 50 mg (44 %). **^{1}H NMR** (300 MHz, $C_2D_2Cl_4$, 298K) δ 1.47 (s, 9H), 6.85 (s, 1H), 7.41 (s, 1H), 7.71 (dd, *J* = 5.7, 3.1 Hz, 3H), 7.89 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.98 (dd, *J* = 5.9, 2.7 Hz, 1H), 8.58 (d, *J* = 1.9 Hz, 1H), 9.38 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (75 MHz, $C_2D_2Cl_4$, 298K) δ 31.06, 35.76, 65.32, 69.33, 73.78, 104.51, 108.26, 114.85, 116.04, 117.23, 119.22, 123.34, 123.44, 123.91, 129.29, 130.94, 131.18, 132.55, 132.63, 132.78, 145.19, 150.42. **HRMS**: *m/z* (%): calcd for $C_{25}H_{17}N_3O$: 375.4310 (100); found: 375.4336 (100) [M]$^+$. **FD mass spectrum** (8 kV): *m/z* (%): calcd for $C_{25}H_{17}N_3O$: 375.43; found: 375.5 (100) [M]$^+$. **UV-Vis (CH_2Cl_2):** λ_{max} = 553, 520 nm (41500, 38400 $M^{-1}cm^{-1}$). **Melting Point**: >350 °C.

3. ^{1}H NMR and ^{13}C NMR Spectra

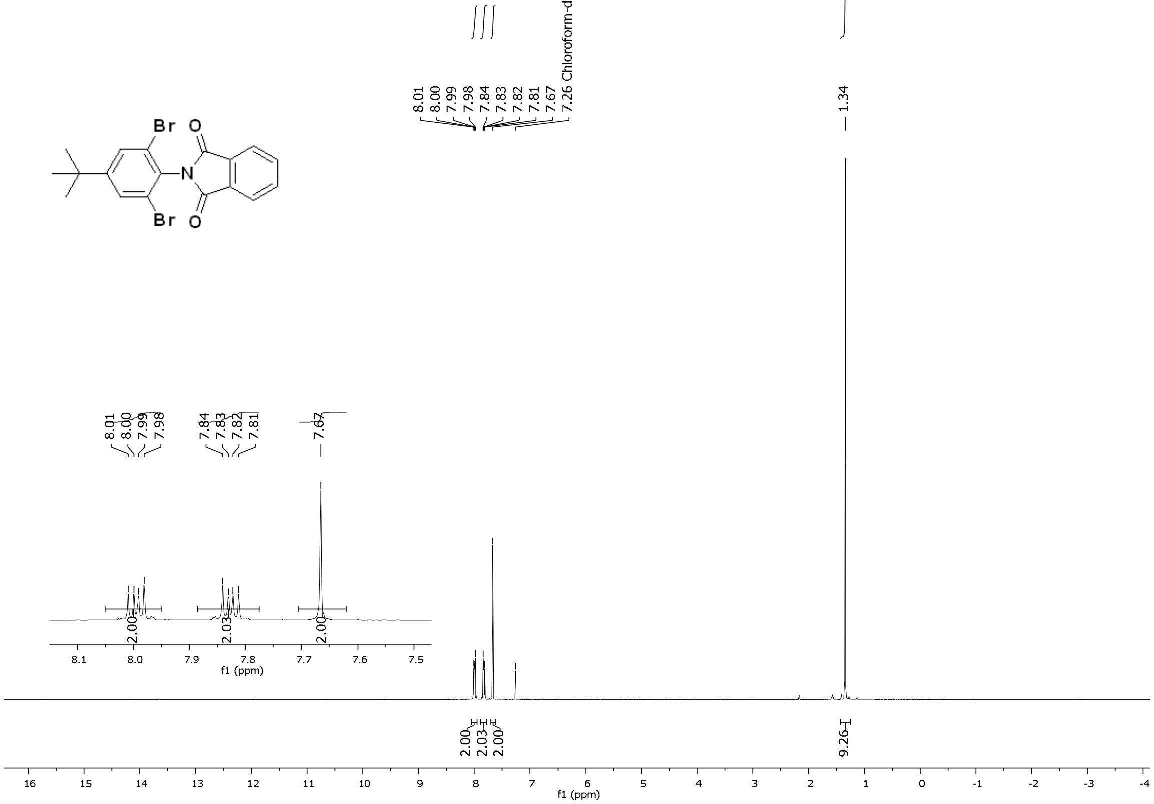
^{1}H NMR spectrum of **1a** (300 MHz, CD_2Cl_2, 298K)



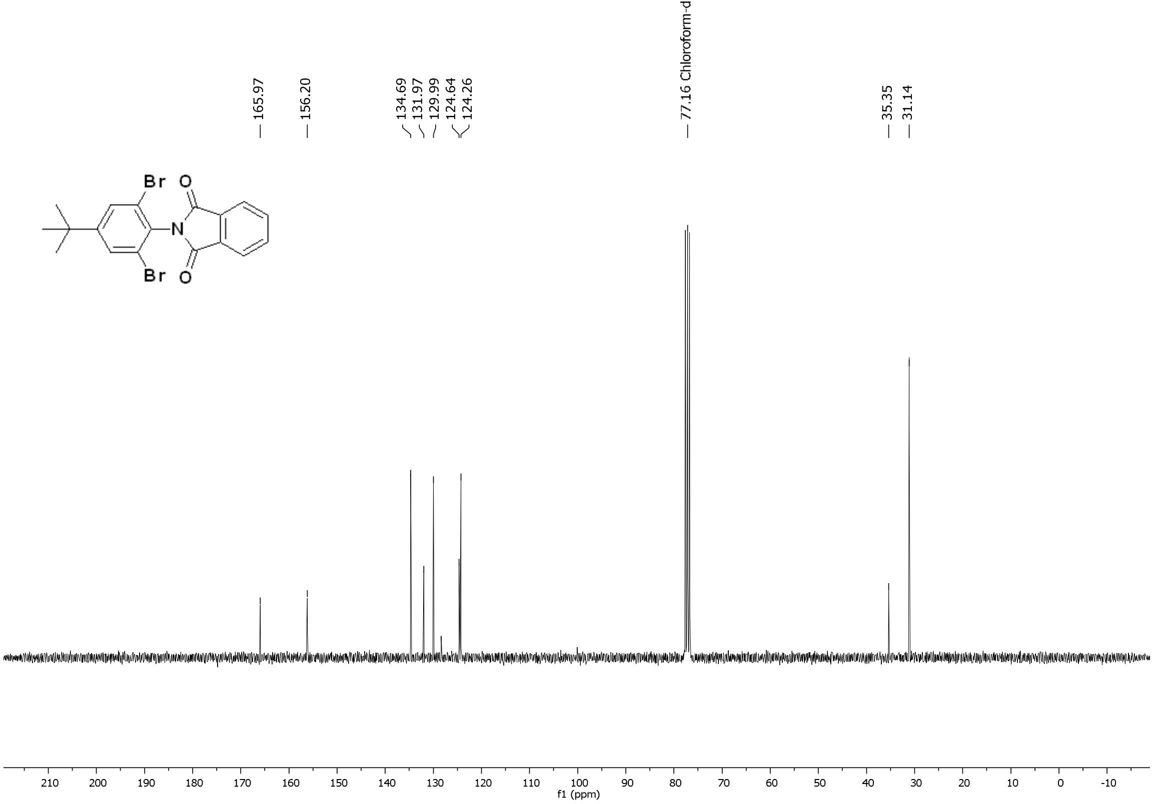
^{13}C NMR spectrum of **1a** (75 MHz, CD_2Cl_2, 298K)



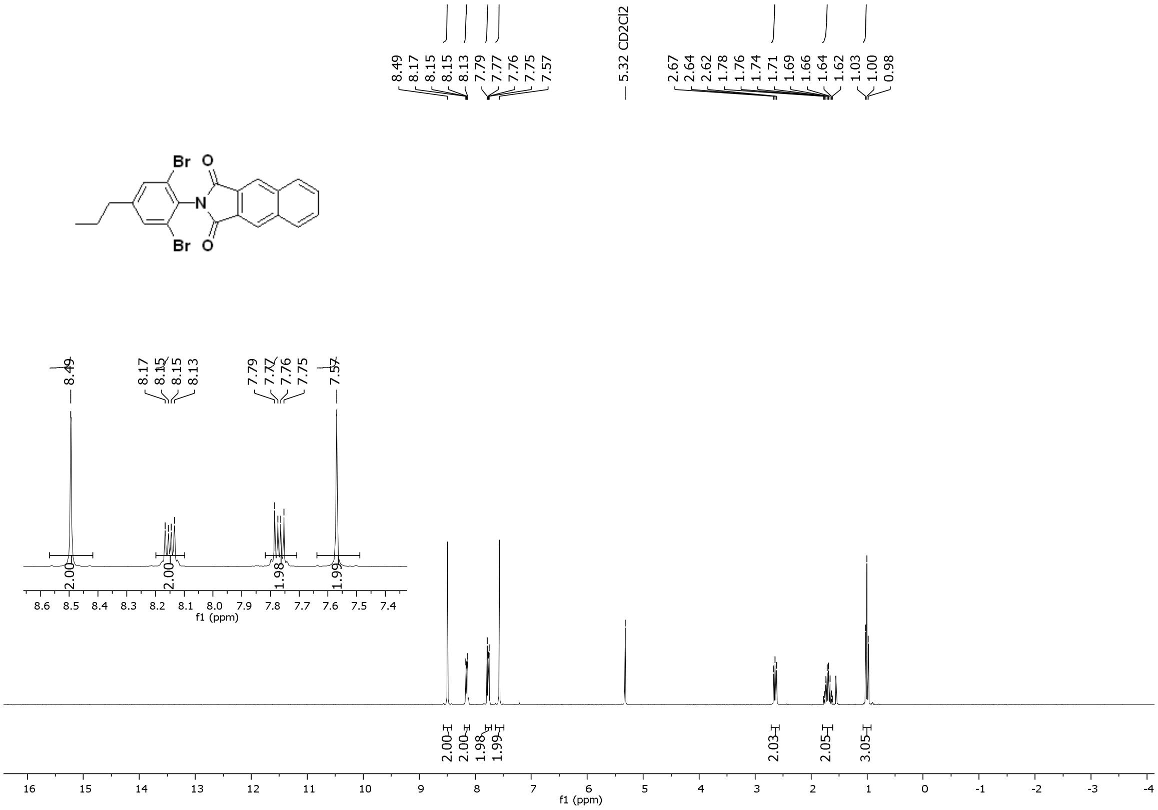
^{1}H NMR spectrum of **1a’** (300 MHz, $CDCl_3$, 298K)



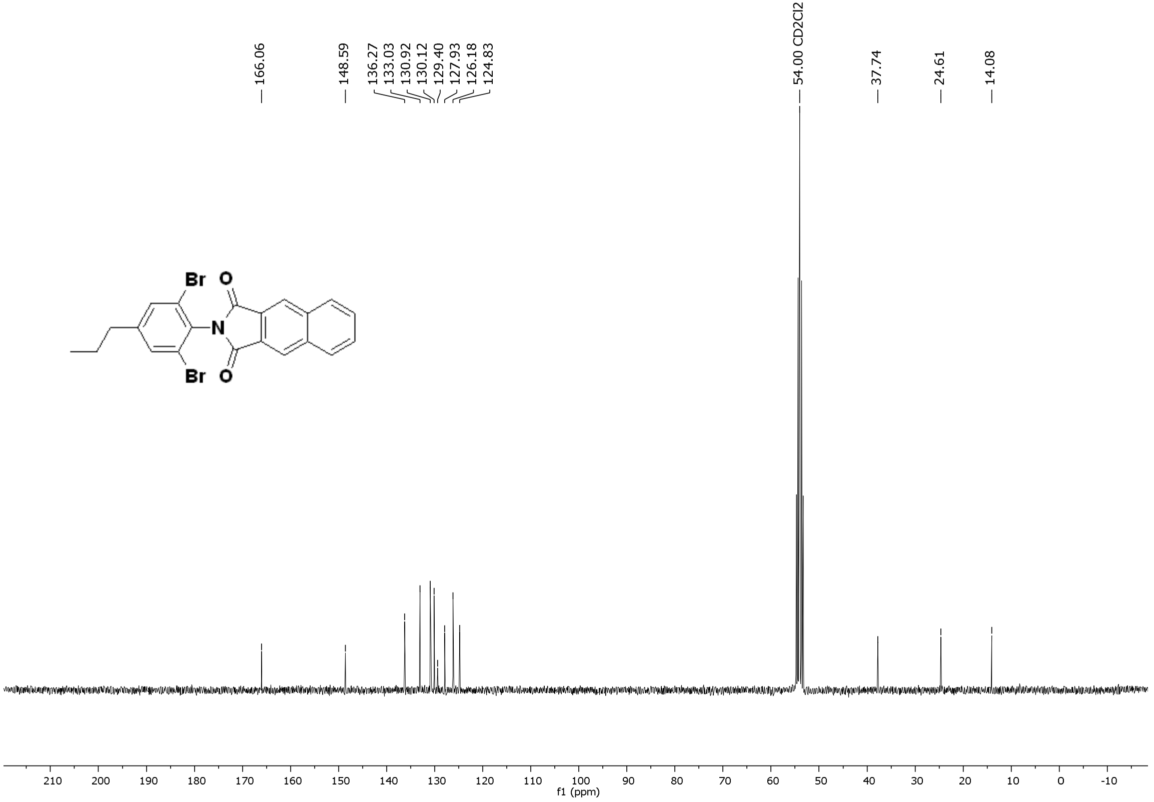
^{13}C NMR spectrum of **1a’** (75 MHz, $CDCl_3$, 298K)



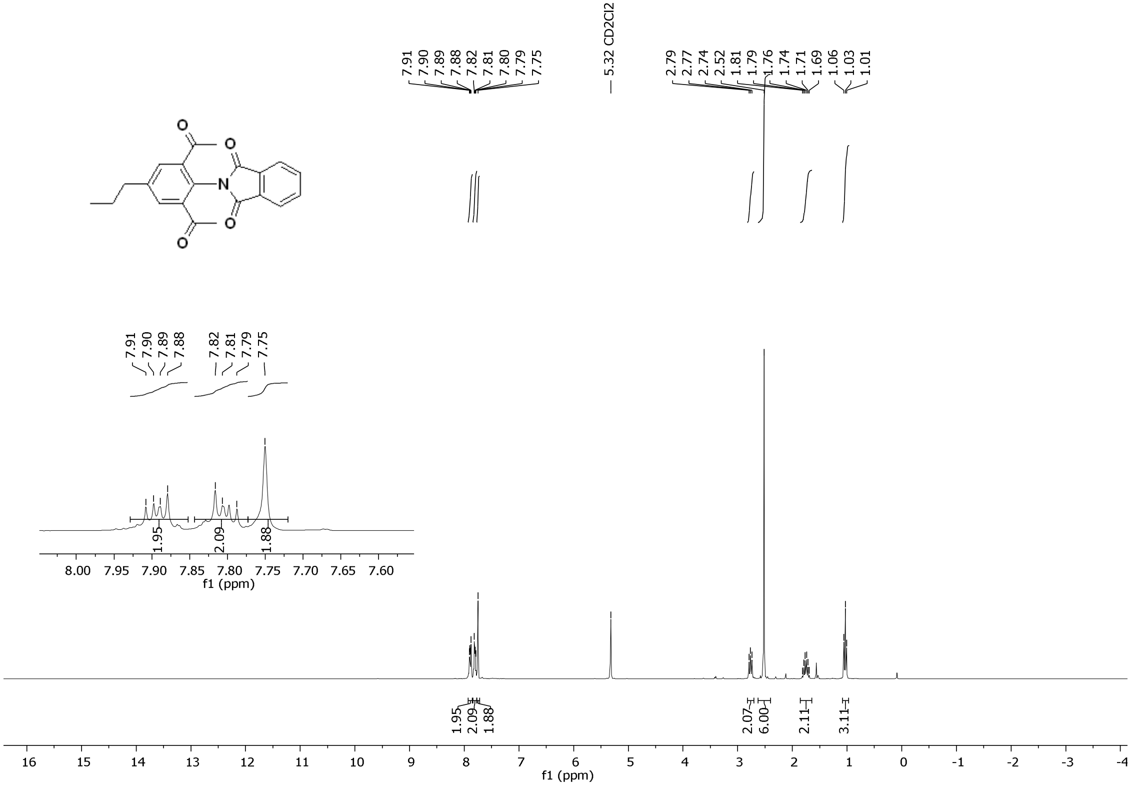
^{1}H NMR spectrum of **1b** (300 MHz, CD_2Cl_2, 298K)



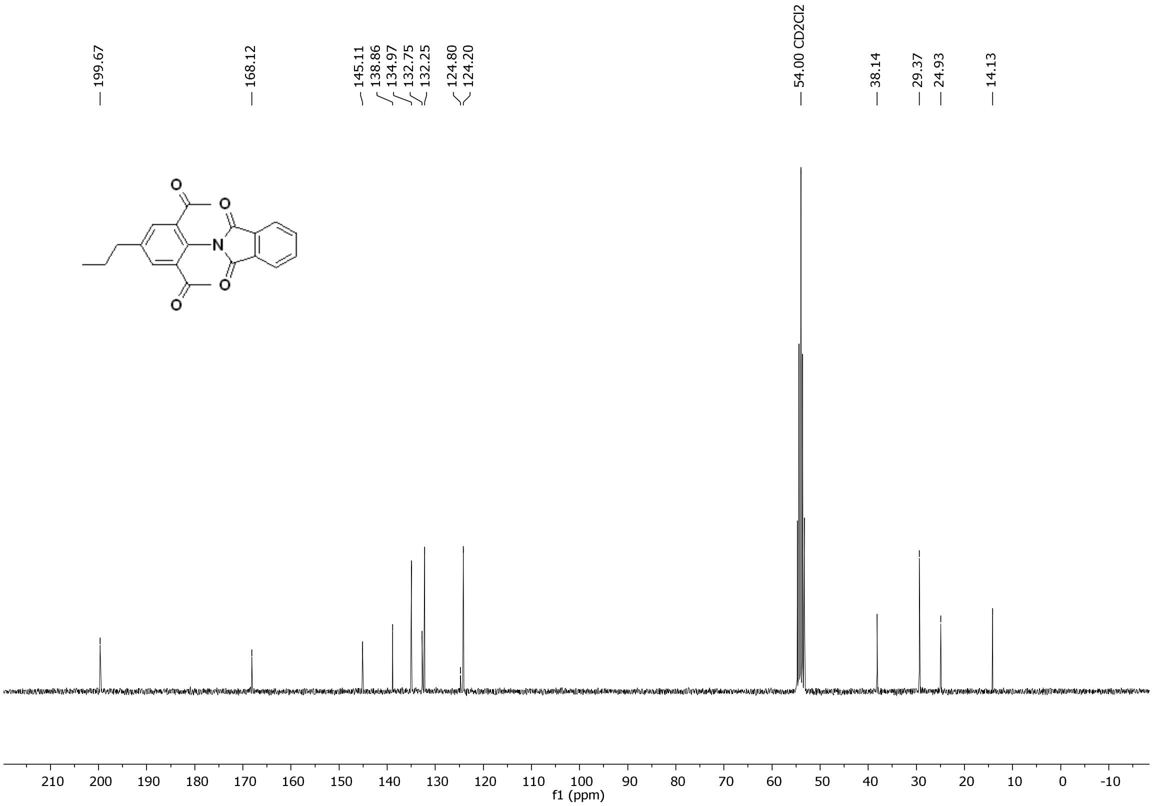
^{13}C NMR spectrum of **1b** (75 MHz, CD_2Cl_2, 298K)



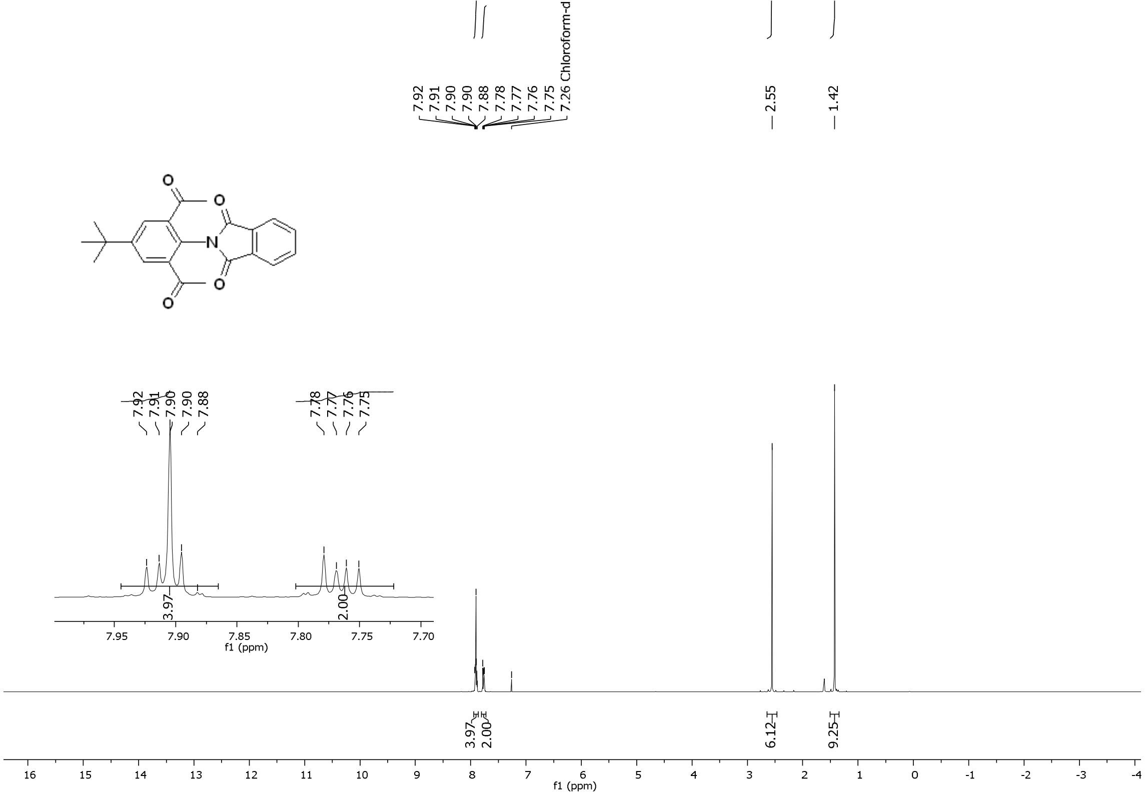
^{1}H NMR spectrum of **2a** (300 MHz, CD_2Cl_2, 298K)



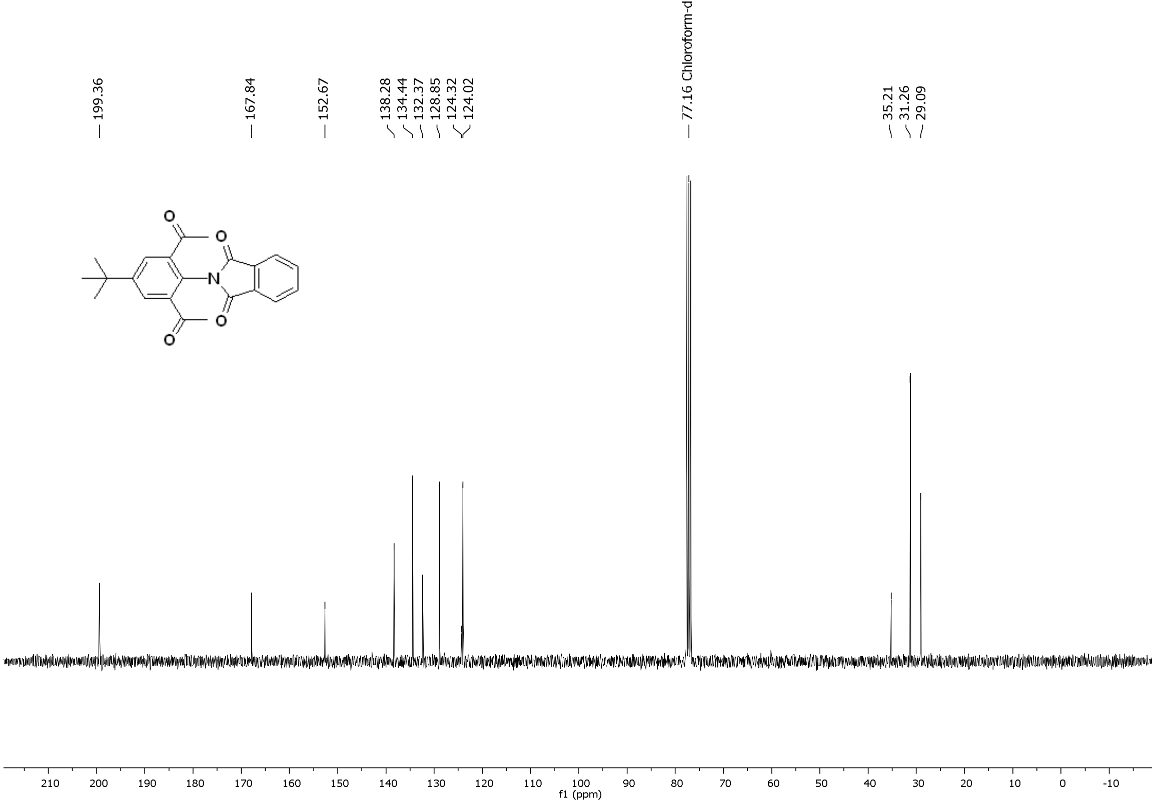
^{13}C NMR spectrum of **2a** (75 MHz, CD_2Cl_2, 298K)



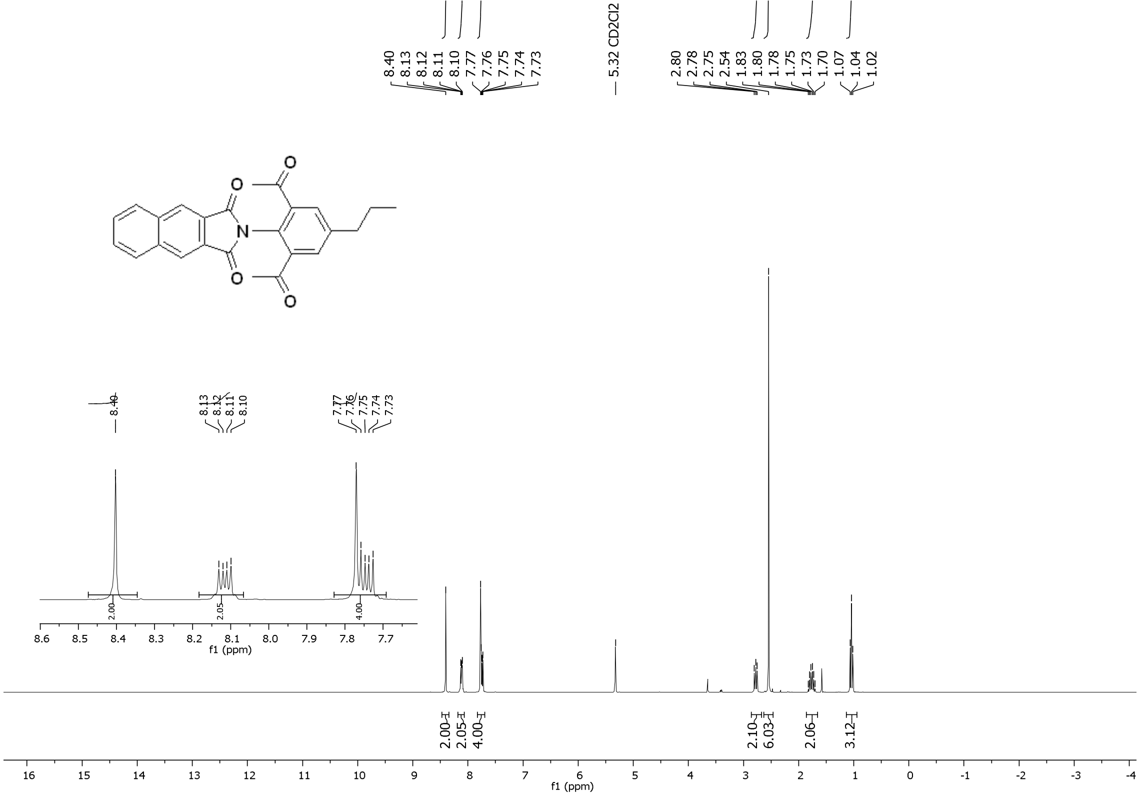
^{1}H NMR spectrum of **2a’** (300 MHz, CDCl$_3$, 298K)



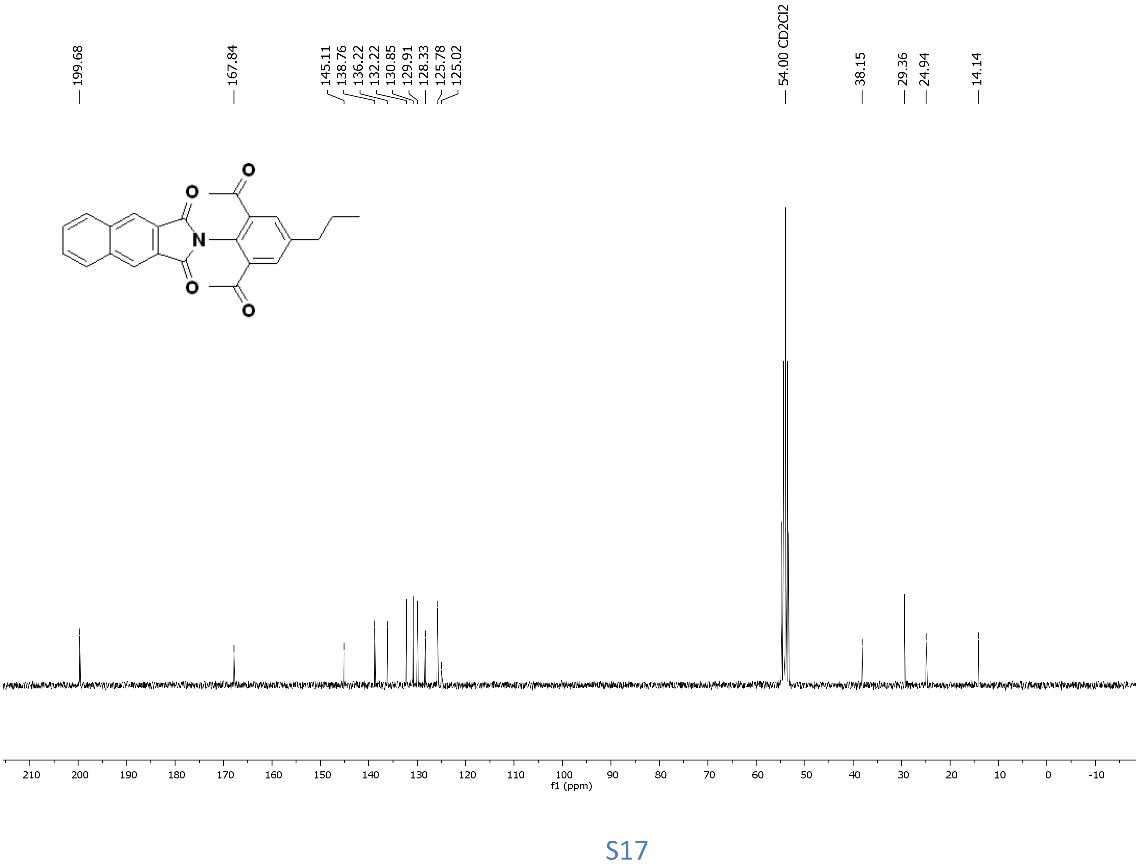
^{13}C NMR spectrum of **1a’** (75 MHz, CDCl$_3$, 298K)



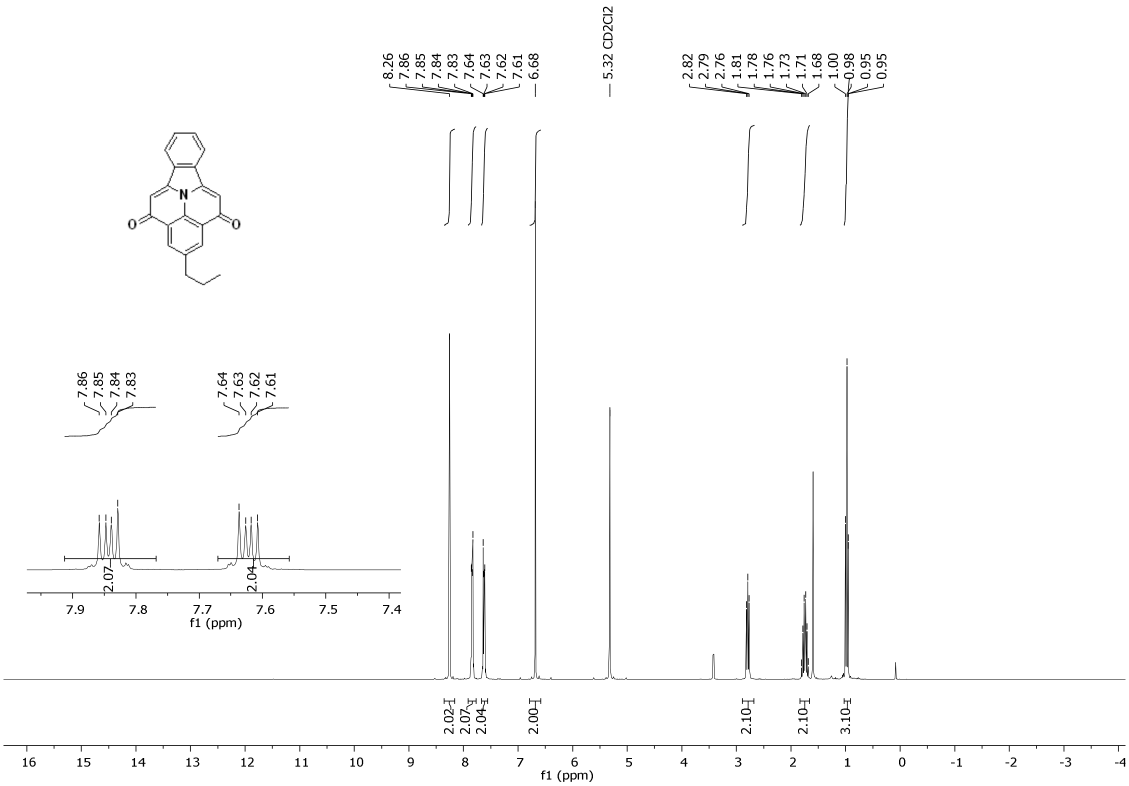
^{1}H NMR spectrum of **2b** (300 MHz, CD_2Cl_2, 298K)



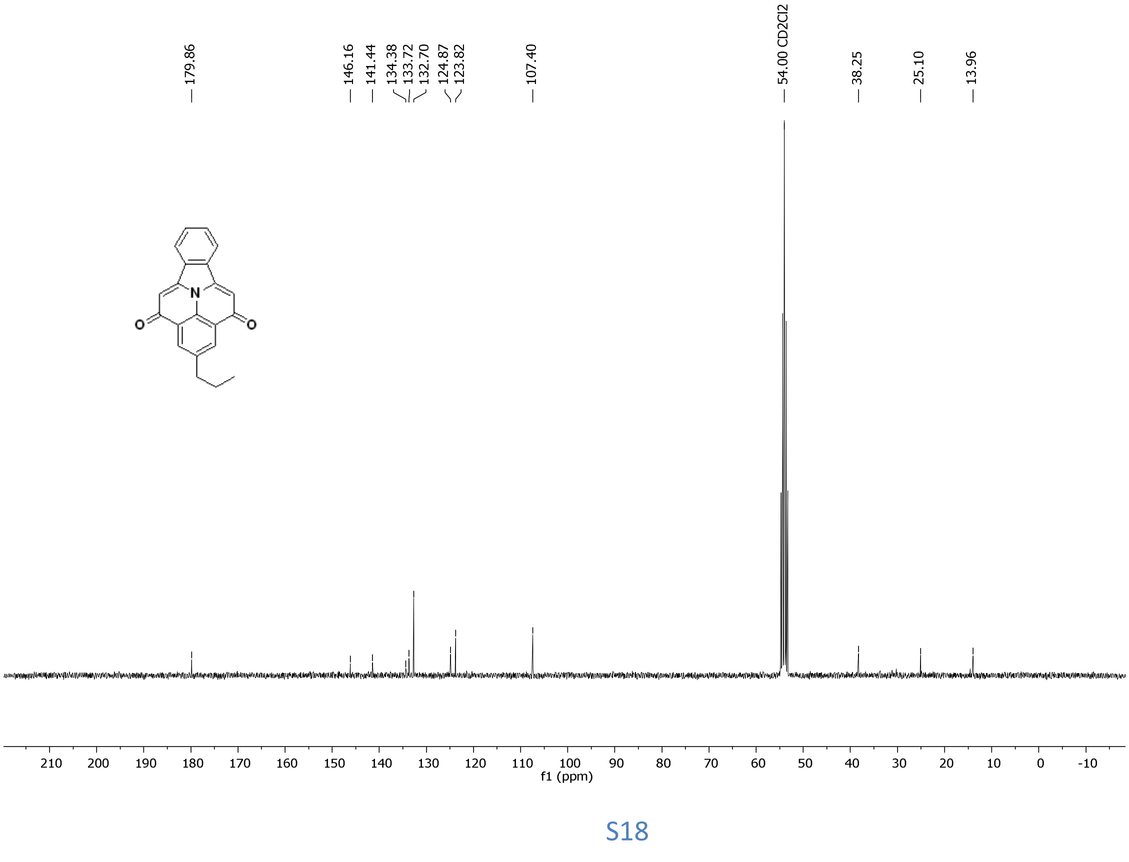
^{13}C NMR spectrum of **2b** (75 MHz, CD_2Cl_2, 298K)



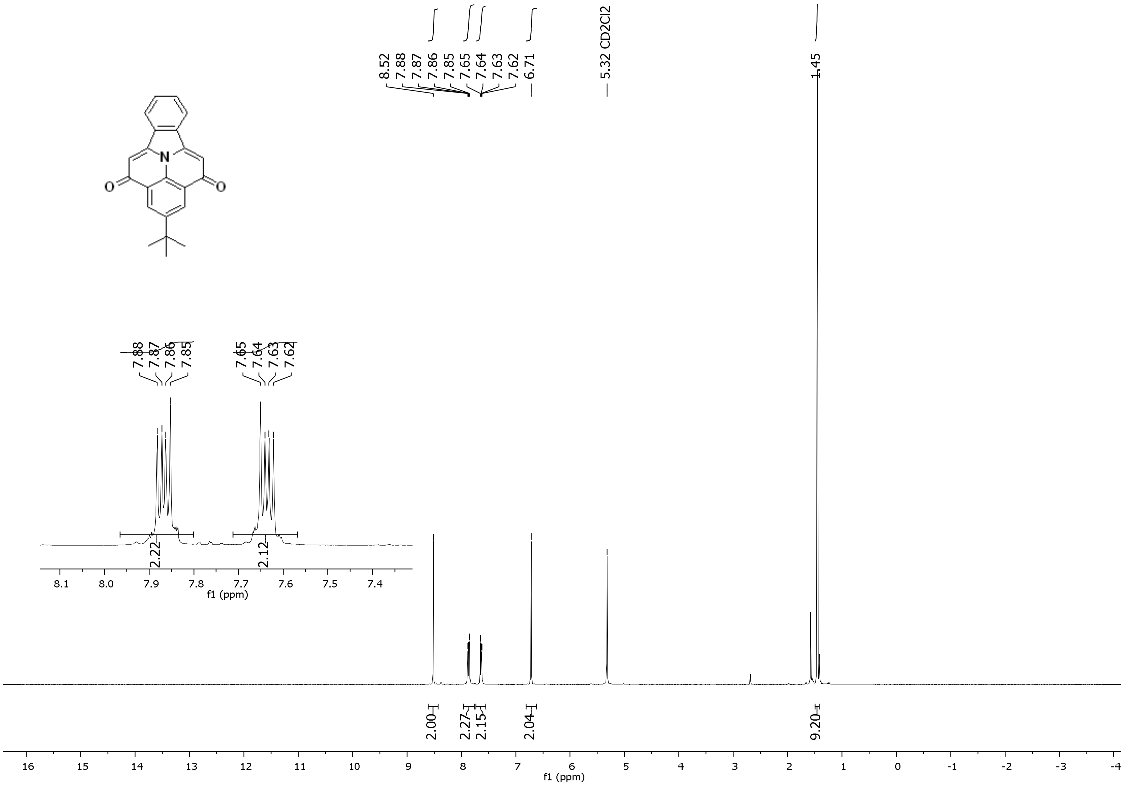
^{1}H NMR spectrum of **3a** (300 MHz, CD$_2$Cl$_2$, 298K)



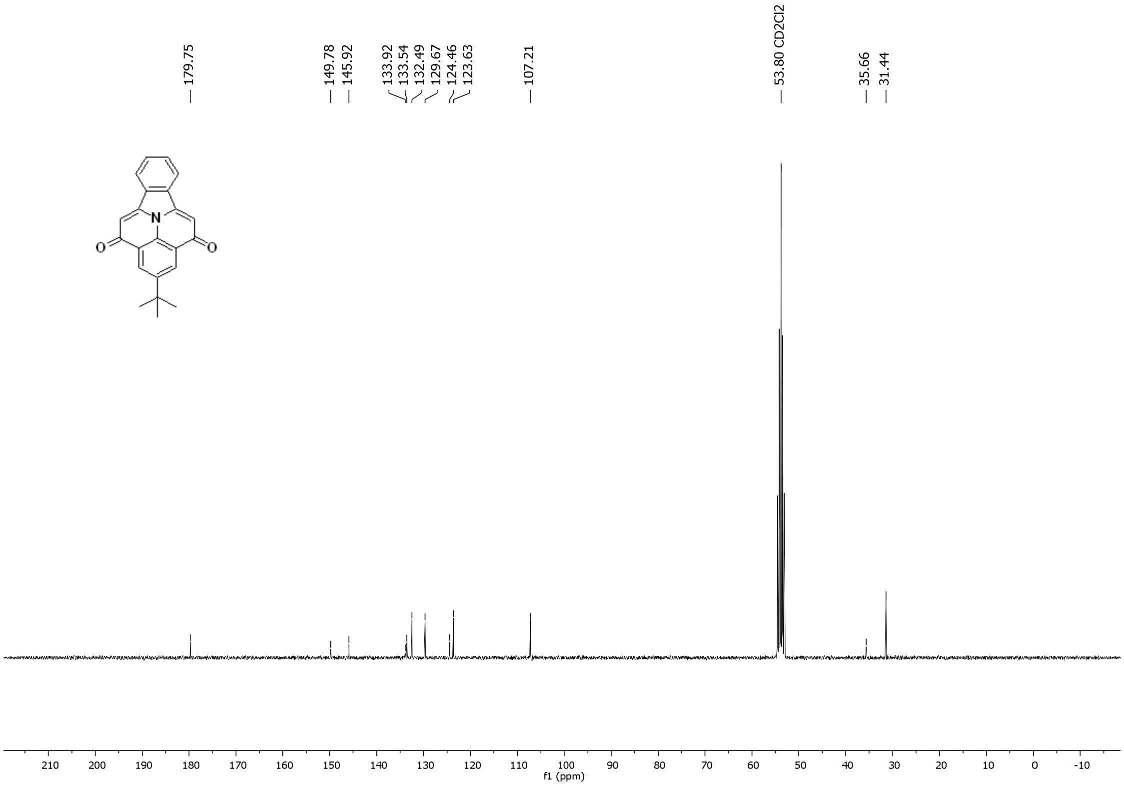
^{13}C NMR spectrum of **3a** (75 MHz, CD$_2$Cl$_2$, 298K)



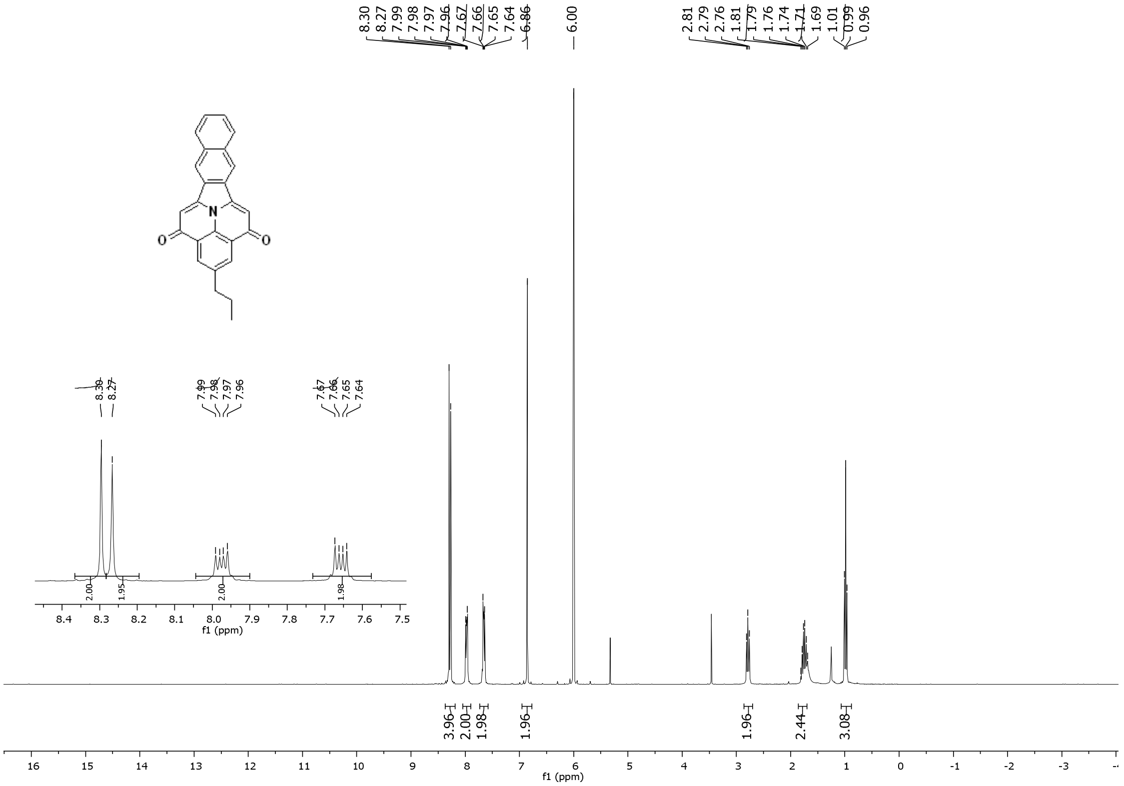
^{1}H NMR spectrum of **3a’** (300 MHz, $CDCl_3$, 298K)



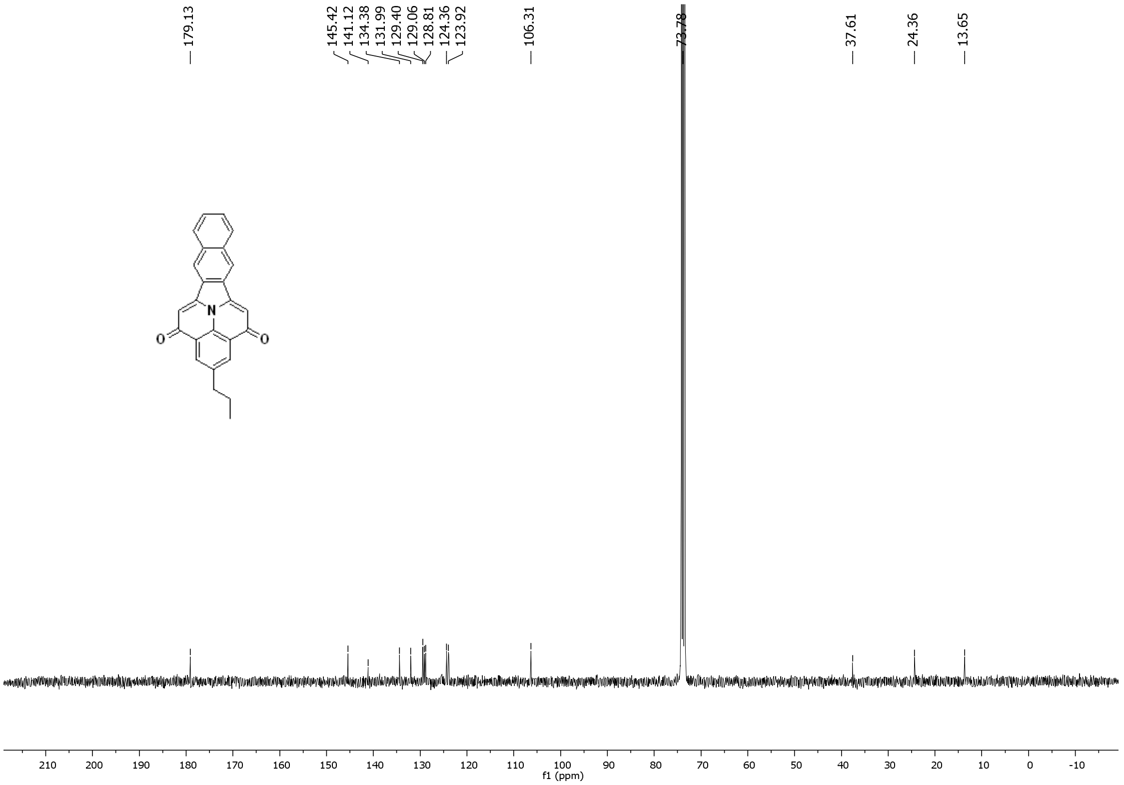
^{13}C NMR spectrum of **3a’** (75 MHz, CD_2Cl_2, 298K)



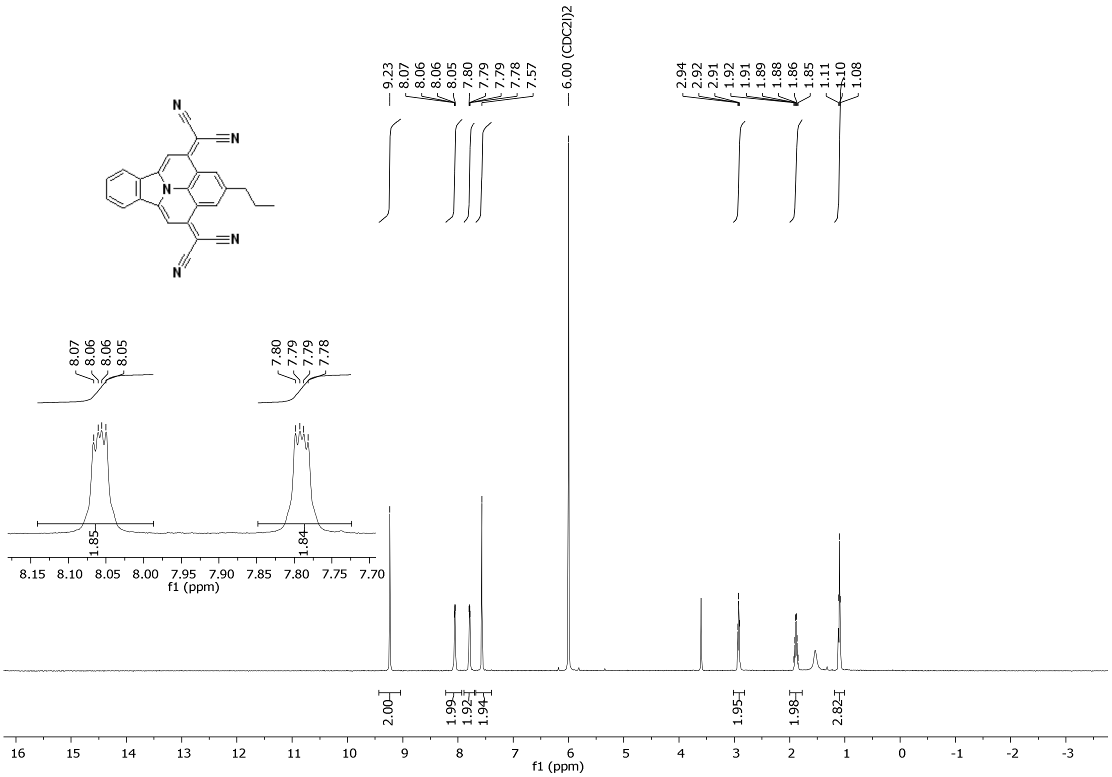
^{1}H NMR spectrum of **3b** (300 MHz, CD_2Cl_2, 298K)



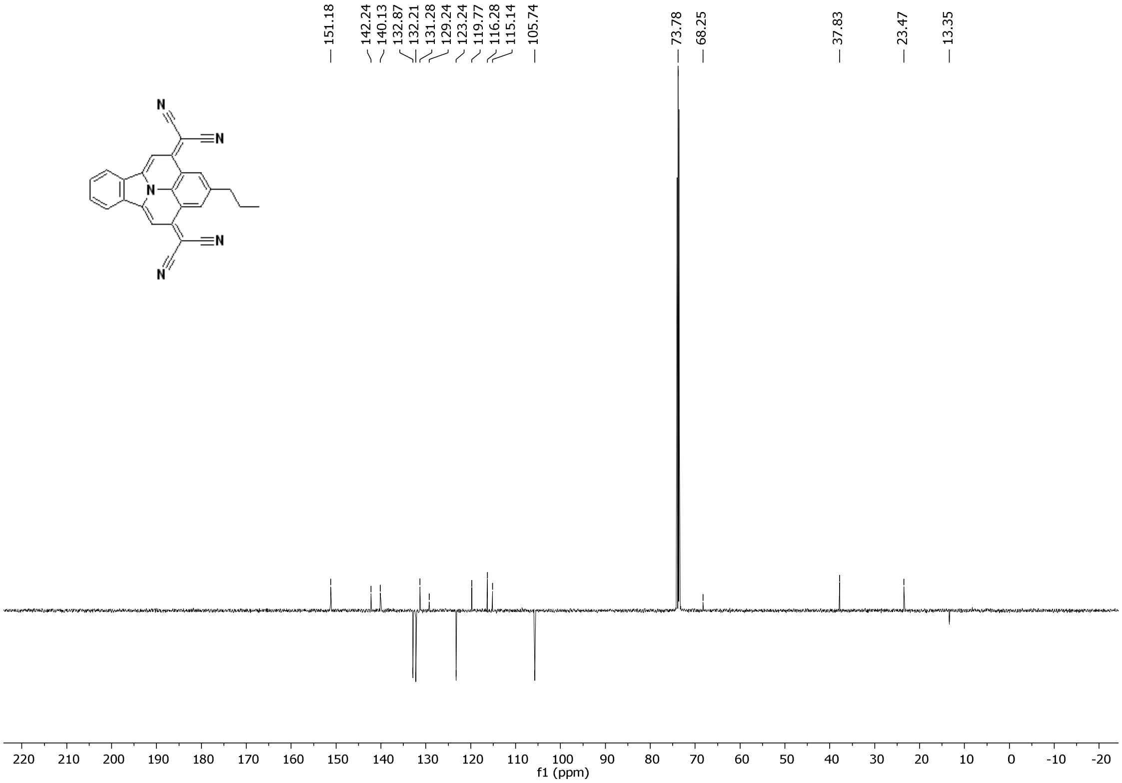
^{13}C NMR spectrum of **3b** (75 MHz, CD_2Cl_2, 298K)



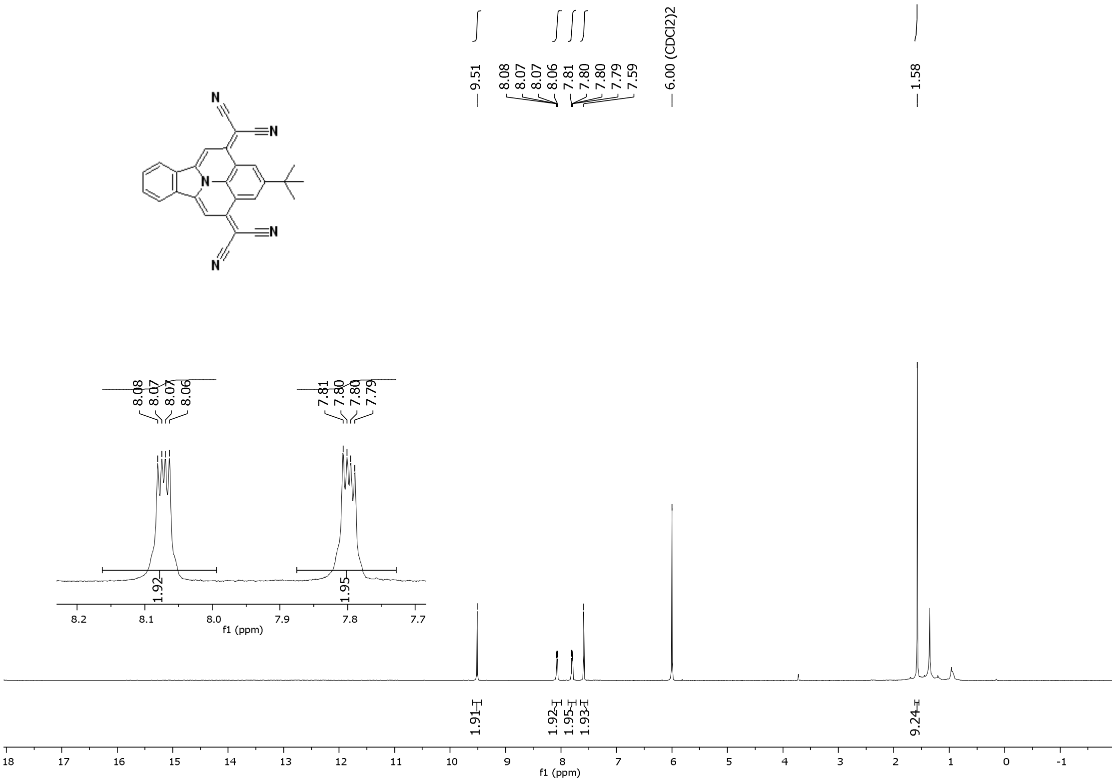
^{1}H NMR spectrum of **5a** (500 MHz, $C_2D_2Cl_4$, 353K)



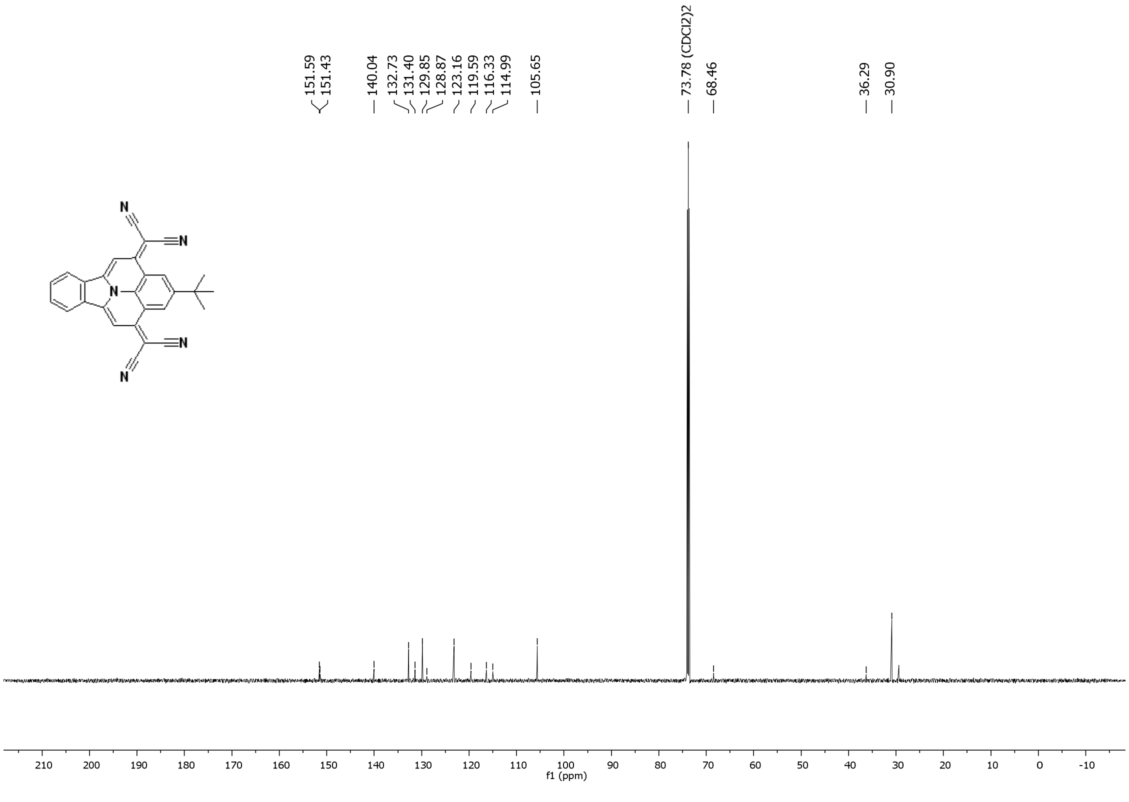
^{13}C NMR_dept spectrum of **5a** (126 MHz, $C_2D_2Cl_4$, 353K)



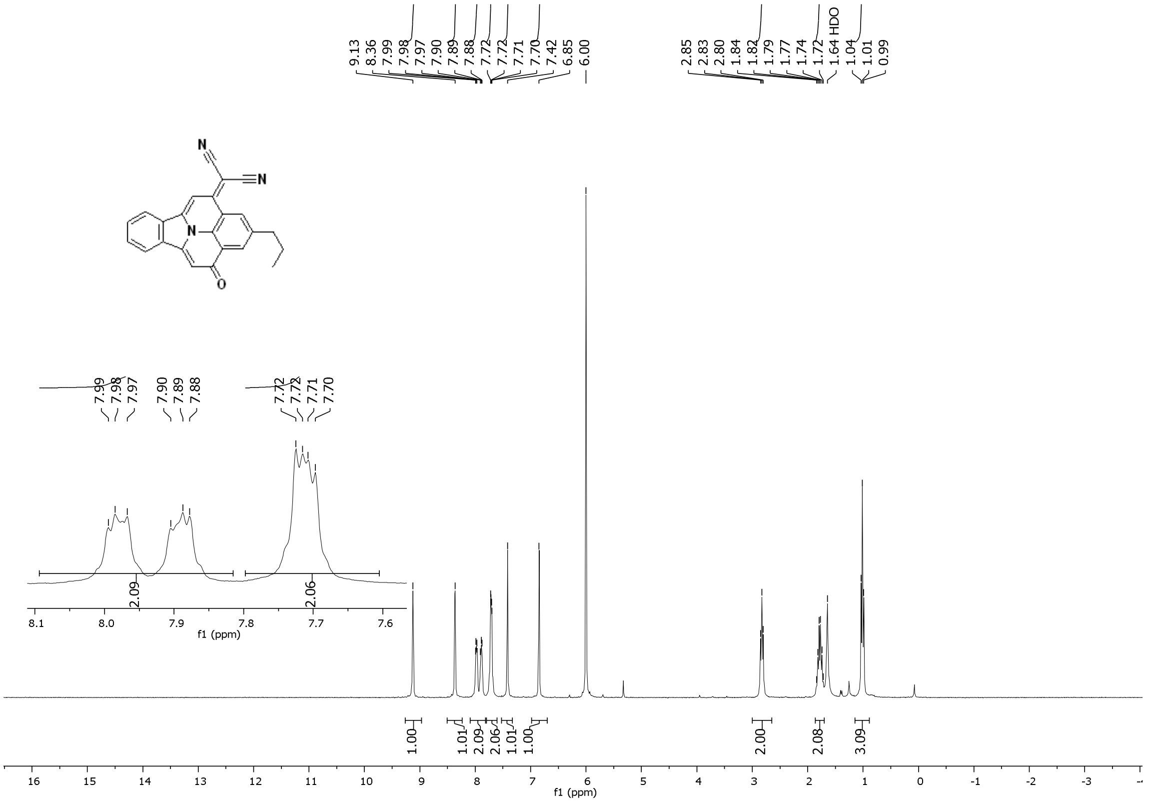
^{1}H NMR spectrum of **5a’** (500 MHz, $(CDCl_2)_2$, 383K)



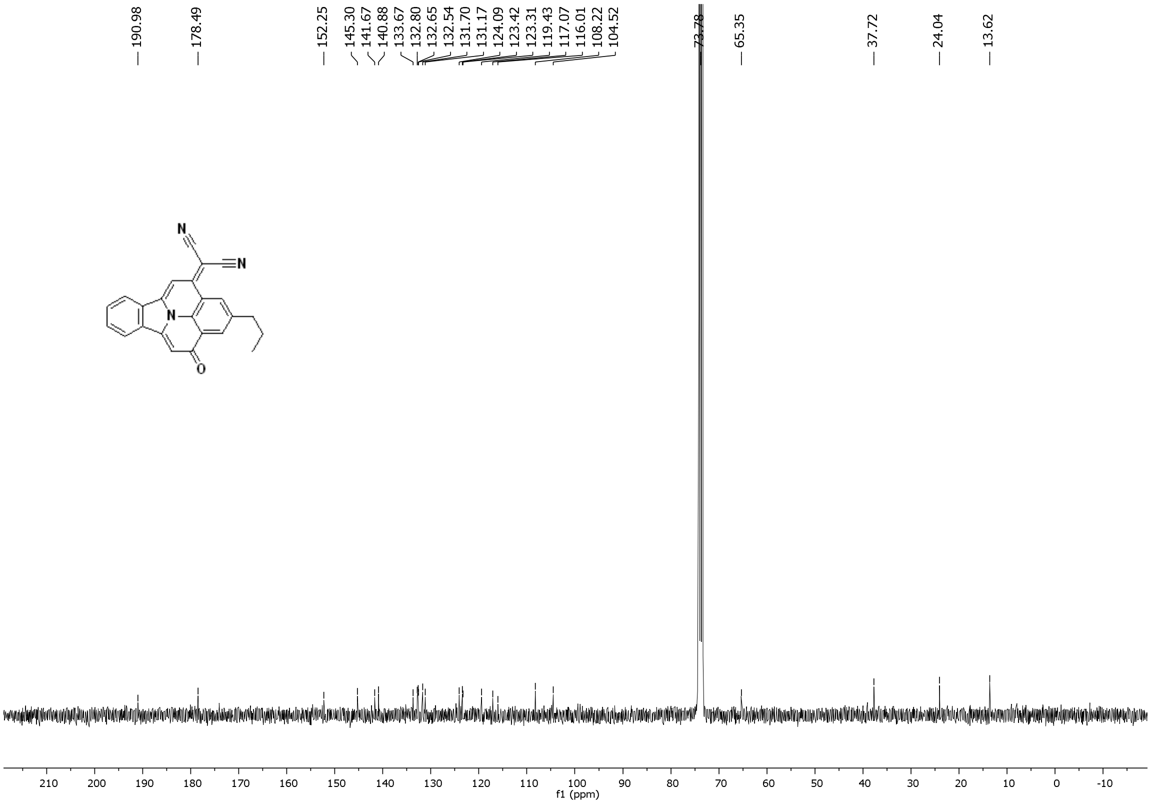
^{13}C NMR spectrum of **5a’** (126 MHz, CD_2Cl_2, 383K)



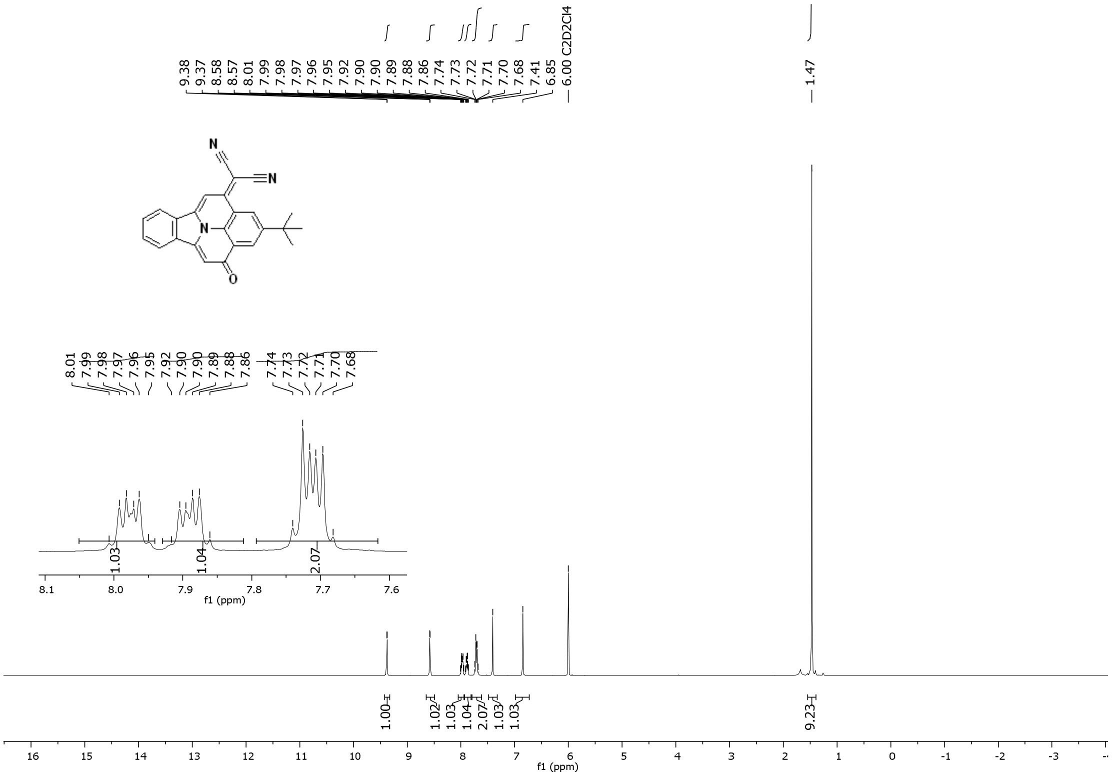
^{1}H NMR spectrum of **4a** (300 MHz, $C_2D_2Cl_4$, 298K)



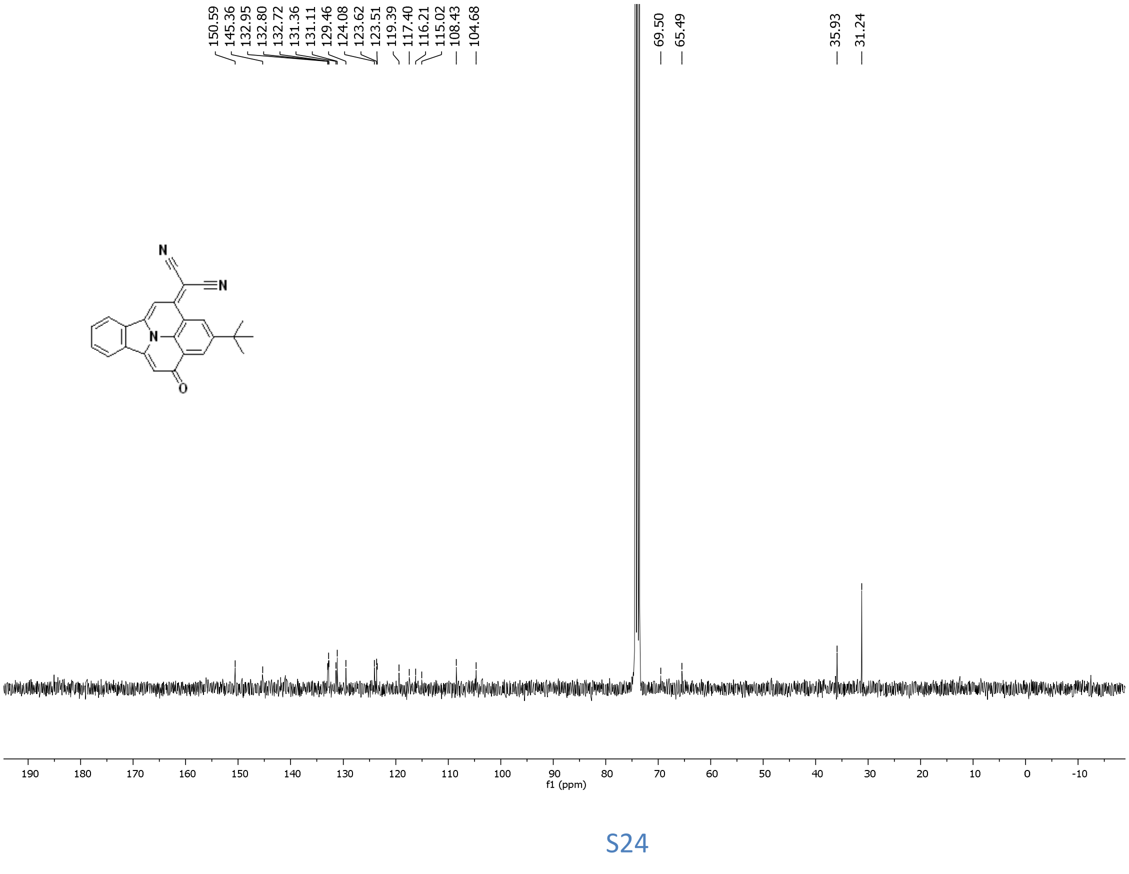
^{13}C NMR spectrum of **4a** (75 MHz, $C_2D_2Cl_4$, 298K)



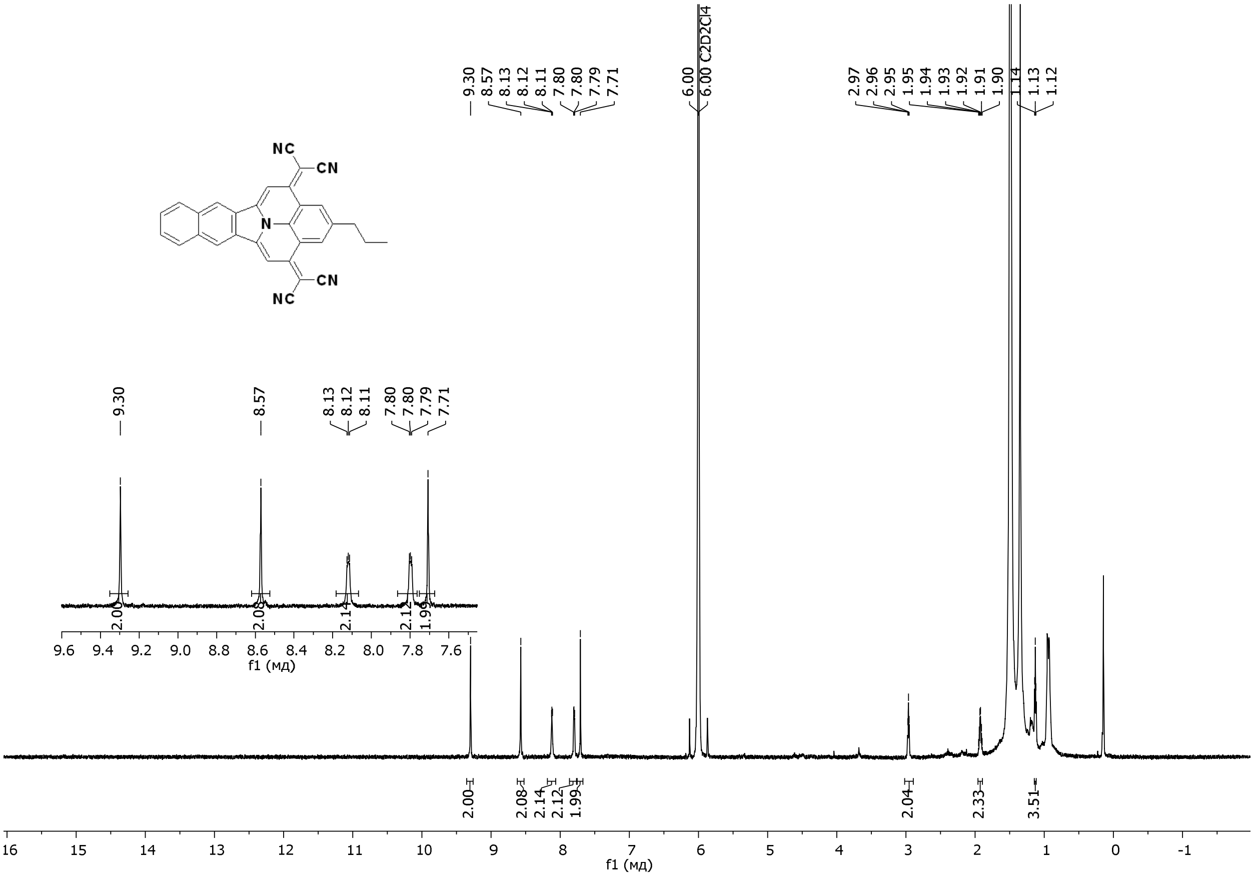
^{1}H NMR spectrum of **4a’** (300 MHz, $C_2D_2Cl_4$, 298K)



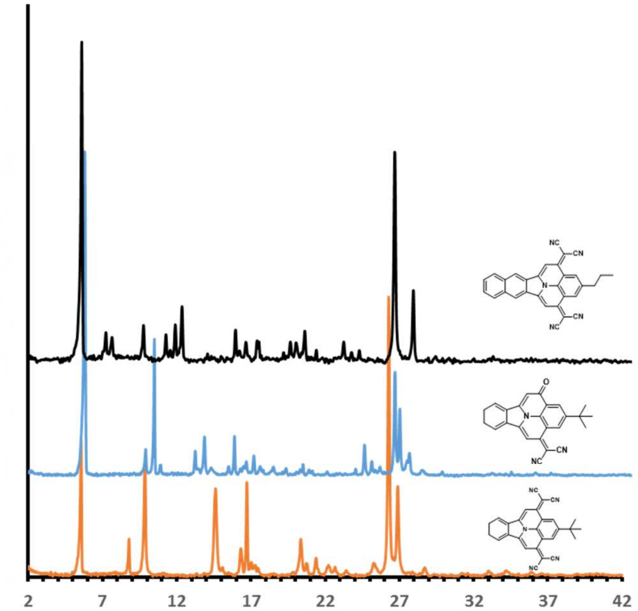
^{13}C NMR spectrum of **4a’** (75 MHz, $C_2D_2Cl_4$, 298K)



^{1}H NMR spectrum of **5b** (300 MHz, $C_2D_2Cl_4$, 373K)



4. XRD Patterns of **5b**, **4a’** and **5a’**



5. Compounds **3a’**, **4a’** and **5a’** in the Solid State