Electronic Supplementary Material (ESI) for Chemical Communications.

# Supporting information for:

*Unprecedented rearrangement of diketopyrrolopyrroles leads to structurally unique chromophores*

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## General Information.

Absorption spectra were measured with the aid of a PerkinElmer UV/Vis Lambda 35 spectrometer, fluorescence spectra with the aid of a Horiba Fluorolog. All calculations within this work were made with the aid of the Gaussian 09 package.[1] Optimization of the molecular geometry in the ground electronic state ($S_0$) and lowest excited state ($S_1$) were performed with the DFT and TD DFT B3LYP/cc-PVDZ methods. The structures and spectra of molecules in solutions were calculated within the framework of the PCM model with the use of the default options of this model implemented in the Gaussian package. The vibrational structures of the electronic spectra were calculated with a procedure included in Gaussian 09, which used the Franck–Condon factors and the Duchinsky matrix.[2]

Compounds 1,4-diketo-3,6-di(thien-3-yl)pyrrolo[3,4-c]pyrrole,[3] 1,4-diketo-3,6-di(2-*t*-butylthien-4-yl)pyrrolo[3,4-c]pyrrole,[4] 1,4-diketo-3,6-di(thien-2-yl)pyrrolo[3,4-c]pyrrole,[5] diketo-3,6-di(fur-3-yl)pyrrolo[3,4-c]pyrrole[6] and **11**,[5] were synthetized following the literature procedures.

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[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09, Revision B.01*, Gaussian Inc.: Wallingford CT, 2010.

[2] Barone, V.; Bloino, J.; Biczysko, M.; Santoro, F. *Fully Integrated Approach to Compute Vibrationally Resolved Optical Spectra: From Small Molecules to Macrosystems*. J. Chem. Theory Comput. 2009, **5**, 540−554.

[3] Grzybowski, M.; Glodkowska-Mrowka, E.; Hugues, V.; Brutkowski, W.; Blanchard-Desce, M.; Gryko, D. T.*; Chemistry - A European Journal*, **2015**, *21*, 9101-9110.

[4] Grzybowski, M.; Glodkowska-Mrowka, E.; Stoklosa, T.; Gryko, D.T. *Org. Lett.*, **2012**, *14*, 2670–2673.

[5] Pigment was obtained following the general procedure (Grzybowski, M.; Glodkowska-Mrowka, E.; Stoklosa, T.; Gryko, D.T. *Org. Lett.*, **2012**, *14*, 2670–2673) and was used without further purification.

[6] a) Data, P.; Kurowska, A.; Pluczyk, S.; Zassowski, P.; Pander, P.; Jedrysiak, R.; Czwartosz, M.; Otulakowski, L.; Suwinski, J.; Lapkowski, M.; Monkman, A. P. *J. Phys. Chem. C*, **2016**, *120*, 2070–2078; b) Naik, M.A.; Venkatramaiah, N.; Kanimozhi, C.; Patil, S.; *J. Phys. Chem. C*, **2012**, *116*, 26128–26137.

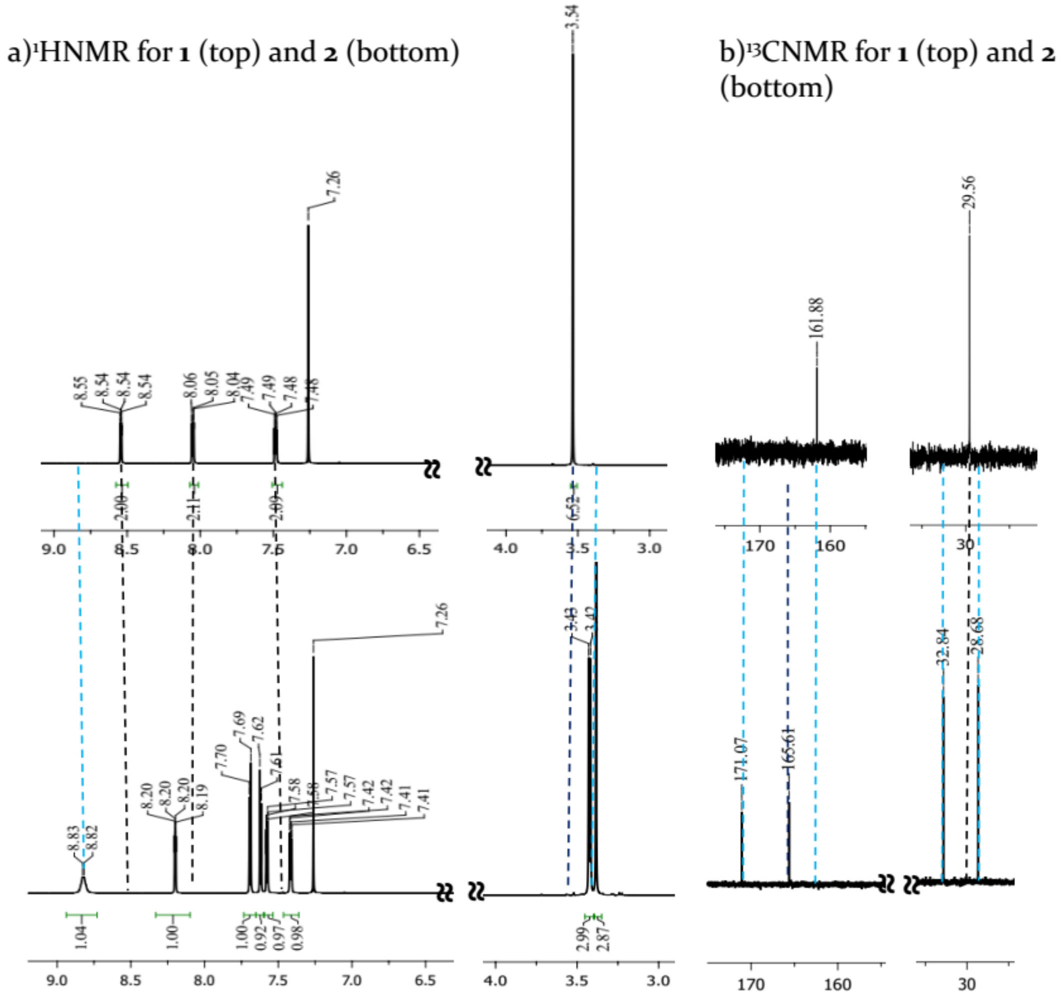


**Figure S1**. Comparison of $^{1}$H NMR and $^{13}$C NMR spectra for **1** and **2.**

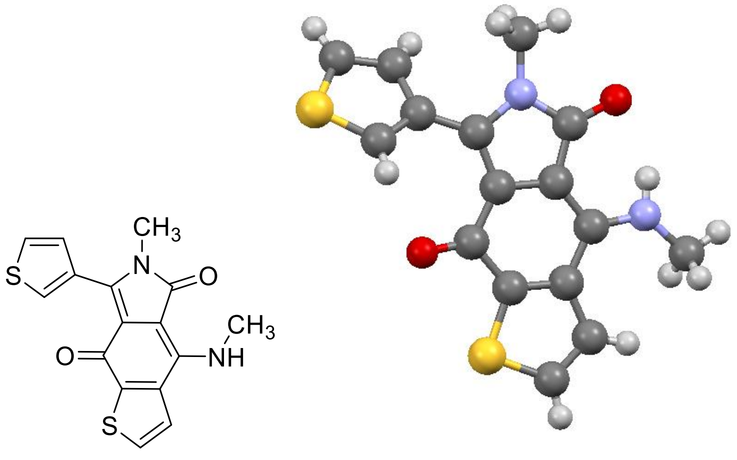


**Figure S2**. a) Structure of the product **2**; CCDC 1574216; b) X-Ray structure of **2** (crystalized from the DCM/MeOH mixture as small purple prisms), where atoms are indicated by the following colors: carbon (grey), oxygen (red), nitrogen (blue) and sulfur (yellow).

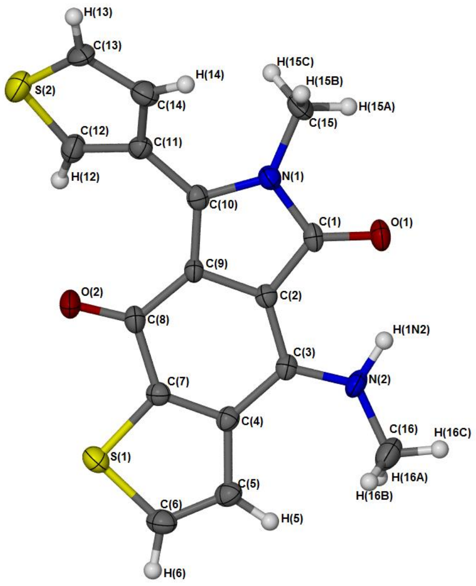


**Figure S3**. ORTEP representation drawn with 30% probability ellipsoids (the X-ray structure of dye **2**).

**Crystal data and refinement parameters**: $C_{33}H_{28}N_4O_5S_4$, $Mr = 688.8$, purple-brown, triclinic, space group $P$-1, $a$ =11.015(4), $b$ =12.958(3), $c$ = 13.124(4) Å, $\alpha$ = 66.19(1), $\beta$ =67.72(1), $\gamma$ = 70.35(1)°, $V$ = 1548.3(8) Å$^3$, $Z$ = 2, $\rho_{calc}$ = 1.48 g cm$^{-3}$, $\mu$(CuK$\alpha$) = 3.23 mm$^{-1}$, $\theta_{max}$ = 65.1°, 34388 reflections measured, 5072 unique, 472 parameters, $R$ = 0.082, $wR$ = 0.191 ($R$ = 0.143, $wR$ = 0.216 for all data), GooF = 1.03. CCDC 1574216.

**Table S1**. Influence of reaction conditions on the rearrangement of DPP **1** into dye **2**.

| Entry | Lewis acid (eq.) | Additive (eq.) | Solvent | T, ˚C | t, h | Yield,[b] % |
|---|---|---|---|---|---|---|
| 1 | $BF_3$·$Et_2O$ (3) | - | TFE | 70 | 43 | 72 |
| 2 | $BF_3$·$Et_2O$ (3) | HTIB (2) | TFE | 70 | 67 | 60 |
| 3 | $BF_3$·$Et_2O$ (3) | - | HFIP | 50 | 24 | 75 |
| 4 | $BF_3$·$Et_2O$ (3) | - | $PhCF_3$ | 100 | 24 | trace |
| 5 | $BCl_3$ (3) | - | TFE | 70 | 120 | trace |
| 6 | $BPh_3$ (3) | - | HFIP/$CHCl_3$ | 50 | 72 | 0 |
| 7 | PivOH (10) | - | - | 50 | 24 | 0 |
| 8 | TFA (3) | - | $CHCl_3$ | 60 | 24 | 0 |
| 9 | TfOH (3) | - | $CHCl_3$ | 60 | 24 | 0 |
| 10 | $Y(OTf)_3$ (1) | - | TFE | 70 | 24 | 0 |
| 11 | $Y(OTf)_3$ (1) | HTIB (2) | TFE | 70 | 24 | 0 |
| 12 | TMSOTf (1) | - | TFE | 70 | 24 | 0 |
| 13 | TMSOTf (1) | HTIB (2) | TFE | 70 | 24 | 0 |
| 14 | $POCl_3$ (10) | - | - | 80 | 24 | 0 |
| 15 | $POCl_3$ (10) | - | DCE | 80 | 24 | 0 |
| 16 | $Tf_2O$ (10) | - | - | 80 | 24 | 0 |

**Table S2**. Optical properties of the rearranged DPPs.

| Dye | solvent | $\lambda_{abs}$ [nm] | $\lambda_{em}$ [nm] | Φ [%] | t, [ns] | $k_{r,}10^7$ $s^{-1}$ |
|---|---|---|---|---|---|---|
| **2** | hexane | 566 | 581 | - | 5.49 | - |
| | toluene | 573 | 599 | 56[a] | 6.94 | 8.1 |
| | DCM | 570 | 601 | 48[a] | 8.21 | 5.9 |
| | ACN | 566 | 603 | 42[a] | 7.24 | 5.8 |
| | MeOH | 565 | 617 | 28[a] | 5.11 | 5.5 |
| **4** | hexane | 566 | 586 | 37[a] | 5.37 | 6.9 |
| | toluene | 571 | 600 | 38[a] | 6.64 | 5.7 |
| | DCM | 569 | 605 | 49[a] | 7.78 | 6.3 |
| | ACN | 562 | 605 | 38[a] | 6.97 | 5.5 |
| | MeOH | 560 | 614 | 28[a] | 5.36 | 5.2 |
| **6** | hexane | 566 | 583 | 28[a] | 4.20 | 6.7 |
| | toluene | 573 | 597 | 47[a] | 5.67 | 8.3 |
| | DCM | 571 | 602 | 47[a] | 6.45 | 7.3 |
| | ACN | 568 | 605 | 38[a] | 6.08 | 6.3 |
| | MeOH | 568 | 615 | 25[a] | 4.26 | 5.9 |
| **8** | hexane | 581 | 604 | 21[a] | 2.80 | 7.5 |
| | toluene | 586 | 617 | 25[a] | 3.16 | 7.9 |
| | DCM | 582 | 619 | 15[a] | 2.25 | 6.7 |
| | ACN | 575 | 615 | 13[a] | 2.00 | 6.5 |
| | MeOH | 575 | 625 | 3.2[a] | 0.62 | 5.2 |
| **10** | toluene | 549 | 567 | 12[b] | 2.70 | 4.4 |
| | DCM | 549 | 573 | 13[b] | 2.33 | 5.6 |
| | ACN | 543 | 577 | 11[b] | 2.11 | 5.2 |
| | MeOH | 547 | 605 | 9.7[b] | 2.35 | 4.1 |
| **14** | hexane | 600 | 609 | 29[c] | 2.98 | 9.7 |
| | toluene | 608 | 623 | 29[c] | 2.89 | 10.0 |
| | DCM | 606 | 624 | 20[c] | 2.24 | 8.9 |
| | ACN | 601 | 622 | 19[c] | 2.16 | 8.8 |
| | MeOH | 602 | 635 | 3.4[c] | 0.64 | 5.3 |
| **16** | toluene | 545 | 580 | 59[b] | 6.10 | 9.7 |
| | DCM | 541 | 582 | 57[b] | 7.25 | 7.9 |
| | ACN | 429 | 581 | 46[b] | 6.49 | 7.1 |
| | MeOH | 513 | 589 | 38[b] | 5.72 | 6.6 |

[a]Calculated in respect to Rh 101 in MeOH. [b]Calculated in respect to Rh 6G in EtOH. [c]Calculated in respect to SRh101 in EtOH.

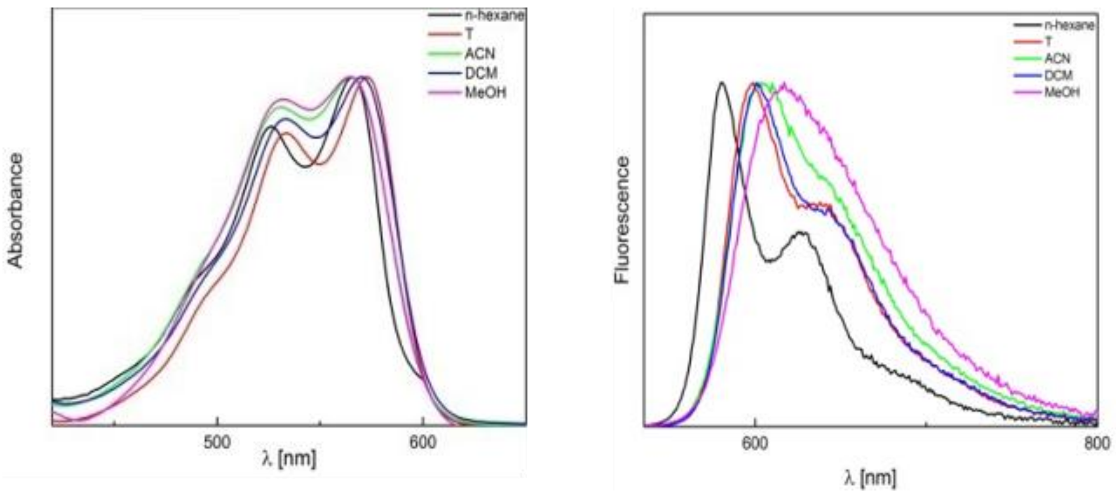


**Figure S4**. Absorption and fluorescence spectra of **2** in various solvents.

**Table S3**. Wavenumbers (u) , wavelengths (λ) and oscillator strengths (f) for the $S_0 \rightarrow S_i$ transitions calculated by TDDFT B3LYP/cc-pVDZ method for **2** in a DCM solution.

| i | u[cm$^{-1}$], | λ [nm] | *f* |
|---|---|---|---|
| 1 | 17143 | 583.3 | 0.4046 |
| 2 | 24391 | 410.0 | 0.0073 |
| 3 | 26028 | 384.2 | 0.0445 |
| 4 | 28887 | 346.2 | 0.0143 |
| 5 | 30406 | 328.9 | 0.0182 |
| 6 | 30765 | 325.0 | 0.0924 |
| 7 | 30973 | 322.9 | 0.1110 |
| 8 | 31795 | 314.5 | 0.2025 |
| 9 | 32690 | 305.9 | 0.2532 |
| 10 | 33934 | 294.7 | 0.1321 |
| 11 | 36174 | 276.4 | 0.0105 |
| 12 | 41343 | 241.9 | 0.0388 |
| 13 | 42556 | 235.0 | 0.0187 |
| 14 | 42970 | 232.7 | 0.0041 |
| 15 | 43157 | 231.7 | 0.0846 |
| 16 | 43545 | 229.6 | 0.2602 |
| 17 | 43670 | 229.0 | 0.4049 |
| 18 | 44701 | 223.7 | 0.1871 |
| 19 | 44847 | 223.0 | 0.1097 |
| 20 | 45567 | 219.5 | 0.0907 |
| 21 | 46009 | 217.3 | 0.0082 |
| 22 | 46447 | 215.3 | 0.0154 |
| 23 | 46788 | 213.7 | 0.0203 |
| 24 | 46974 | 212.9 | 0.0024 |
| 25 | 47193 | 211.9 | 0.0458 |

**Table S4**. The coordinates [in Å] and frequencies [in $\text{cm}^{-1}$] calculated with the B3LYP/cc-pVDZ and TD B3LYP/cc-pVDZ for the optimized structures of **2**.

| | $S_0$ | | | $S_1$ | | |
|---|---|---|---|---|---|---|
| atom | x | y | z | x | y | z |
| S | -2.5600 | -2.9759 | 0.0567 | -2.5515 | -2.9934 | 0.0793 |
| S | 4.6310 | -1.7504 | -0.1378 | 4.5915 | -1.7627 | -0.2871 |
| O | -0.5338 | 3.5368 | -0.0995 | -0.5483 | 3.5463 | -0.0821 |
| O | 0.3440 | -2.3681 | -0.1946 | 0.3968 | -2.3298 | 0.1171 |
| N | 1.2595 | 2.0249 | -0.0612 | 1.2600 | 2.0584 | 0.0062 |
| N | -2.9647 | 2.1257 | -0.0009 | -2.9445 | 2.1180 | -0.0351 |
| C | -0.1118 | 2.3705 | -0.0740 | -0.0969 | 2.3884 | -0.0394 |
| C | -0.8247 | 1.1221 | -0.0660 | -0.8121 | 1.1208 | -0.0297 |
| C | -2.2159 | 0.9965 | -0.0105 | -2.2378 | 0.9707 | -0.0175 |
| C | -2.7278 | -0.3714 | 0.0401 | -2.7426 | -0.3712 | 0.0103 |
| C | -4.0747 | -0.8707 | 0.1068 | -4.0844 | -0.8839 | 0.0112 |
| H | -4.9694 | -0.2558 | 0.1384 | -4.9851 | -0.2757 | -0.0123 |
| C | -4.1292 | -2.2394 | 0.1264 | -4.1363 | -2.2506 | 0.0438 |
| H | -5.0214 | -2.8606 | 0.1784 | -5.0275 | -2.8749 | 0.0510 |
| C | -1.7971 | -1.4169 | 0.0127 | -1.7825 | -1.4251 | 0.0397 |
| C | -0.3259 | -1.3274 | -0.0877 | -0.3375 | -1.3185 | 0.0611 |
| C | 0.1366 | 0.0511 | -0.0806 | 0.1338 | 0.0728 | -0.0003 |
| C | 1.4211 | 0.6392 | -0.0537 | 1.4325 | 0.6624 | 0.0093 |
| C | 2.7367 | 0.0130 | 0.0251 | 2.7280 | 0.0261 | 0.0171 |
| C | 2.9870 | -1.2924 | -0.3744 | 2.9572 | -1.2546 | -0.4907 |
| H | 2.2505 | -2.0042 | -0.7397 | 2.2160 | -1.9244 | -0.9184 |
| C | 5.0244 | -0.1920 | 0.5288 | 5.0180 | -0.2556 | 0.4805 |
| H | 6.0324 | 0.0224 | 0.8770 | 6.0313 | -0.0879 | 0.8393 |
| C | 3.9360 | 0.6310 | 0.5520 | 3.9482 | 0.5852 | 0.5659 |
| C | 2.2549 | 3.0719 | -0.2223 | 2.2650 | 3.0962 | -0.1463 |
| H | 1.7171 | 3.9605 | -0.5788 | 1.7403 | 4.0027 | -0.4754 |
| H | 3.0206 | 2.7758 | -0.9518 | 3.0154 | 2.8038 | -0.8943 |
| H | 2.7418 | 3.3319 | 0.7313 | 2.7730 | 3.3208 | 0.8053 |
| C | -4.4009 | 2.2610 | 0.0984 | -4.3809 | 2.2784 | -0.0263 |
| H | -4.9265 | 1.8063 | -0.7592 | -4.8488 | 1.8201 | -0.9145 |
| H | -4.6408 | 3.3326 | 0.1058 | -4.6088 | 3.3521 | -0.0307 |
| H | -4.8021 | 1.8206 | 1.0276 | -4.8341 | 1.8301 | 0.8741 |
| H | -2.3972 | 2.9777 | -0.0413 | -2.3512 | 2.9600 | -0.0631 |
| H | 3.9822 | 1.6320 | 0.9709 | 4.0122 | 1.5542 | 1.0546 |

| | S$_0$ | | S$_1$ | | | S$_0$ | | S$_1$ | |
|---|---|---|---|---|---|---|---|---|---|
| no | freq [cm$^{-1}$] | IR act | freq [cm$^{-1}$] | IR act | no | freq [cm$^{-1}$] | IR act | freq [cm$^{-1}$] | IR act |
| 1 | 37.4 | 2.29 | 36.0 | 2.16 | 49 | 928.0 | 37.17 | 925.8 | 33.10 |
| 2 | 43.2 | 0.86 | 49.9 | 0.92 | 50 | 946.0 | 29.42 | 944.2 | 16.80 |
| 3 | 58.8 | 0.17 | 60.5 | 1.87 | 51 | 1019.2 | 22.19 | 974.9 | 55.27 |
| 4 | 71.2 | 3.42 | 81.0 | 1.37 | 52 | 1068.1 | 3.44 | 1043.5 | 89.22 |
| 5 | 100.2 | 1.11 | 85.3 | 2.50 | 53 | 1081.3 | 9.84 | 1064.0 | 6.65 |
| 6 | 120.4 | 1.31 | 114.3 | 1.57 | 54 | 1102.5 | 18.84 | 1098.6 | 9.24 |
| 7 | 139.1 | 0.30 | 148.8 | 1.45 | 55 | 1118.2 | 8.61 | 1101.2 | 3.48 |
| 8 | 155.2 | 1.53 | 158.3 | 0.23 | 56 | 1131.2 | 0.50 | 1120.7 | 0.30 |
| 9 | 183.8 | 0.35 | 184.8 | 0.16 | 57 | 1133.0 | 1.05 | 1124.0 | 7.84 |
| 10 | 198.1 | 2.79 | 192.7 | 3.27 | 58 | 1143.9 | 62.71 | 1133.0 | 0.88 |
| 11 | 218.0 | 0.20 | 211.3 | 0.19 | 59 | 1184.2 | 0.70 | 1179.9 | 4.07 |
| 12 | 228.7 | 0.22 | 216.7 | 0.52 | 60 | 1203.9 | 30.18 | 1207.8 | 20.84 |
| 13 | 241.9 | 2.60 | 231.2 | 2.05 | 61 | 1235.2 | 1.29 | 1225.8 | 17.51 |
| 14 | 257.0 | 1.48 | 248.4 | 3.39 | 62 | 1239.4 | 13.67 | 1236.3 | 42.18 |
| 15 | 266.1 | 0.18 | 260.4 | 1.88 | 63 | 1275.4 | 77.17 | 1261.4 | 64.13 |
| 16 | 286.8 | 1.11 | 276.9 | 6.25 | 64 | 1306.4 | 76.70 | 1300.6 | 109.78 |
| 17 | 291.5 | 10.98 | 289.8 | 3.70 | 65 | 1375.0 | 124.72 | 1352.6 | 98.50 |
| 18 | 297.4 | 1.89 | 293.4 | 1.05 | 66 | 1380.3 | 119.51 | 1368.6 | 1.07 |
| 19 | 334.4 | 4.23 | 327.1 | 0.58 | 67 | 1390.8 | 77.24 | 1379.5 | 56.25 |
| 20 | 363.7 | 6.75 | 362.5 | 2.74 | 68 | 1404.4 | 10.16 | 1404.5 | 23.90 |
| 21 | 401.6 | 4.32 | 372.5 | 4.95 | 69 | 1434.5 | 25.91 | 1414.6 | 53.17 |
| 22 | 420.3 | 0.35 | 400.0 | 3.12 | 70 | 1439.4 | 131.45 | 1429.6 | 9.68 |
| 23 | 462.7 | 6.26 | 445.6 | 0.95 | 71 | 1454.0 | 75.81 | 1435.8 | 101.39 |
| 24 | 464.8 | 1.15 | 456.9 | 10.12 | 72 | 1459.8 | 51.31 | 1447.0 | 83.84 |
| 25 | 478.4 | 0.88 | 457.3 | 1.58 | 73 | 1460.8 | 6.92 | 1454.2 | 8.84 |
| 26 | 498.0 | 21.41 | 492.1 | 32.71 | 74 | 1476.6 | 27.66 | 1471.0 | 4.95 |
| 27 | 531.5 | 0.53 | 523.3 | 4.25 | 75 | 1486.4 | 16.40 | 1477.5 | 12.62 |
| 28 | 572.8 | 6.84 | 557.2 | 7.40 | 76 | 1490.0 | 35.62 | 1483.8 | 13.20 |
| 29 | 620.9 | 4.62 | 598.3 | 7.98 | 77 | 1502.5 | 54.98 | 1500.3 | 245.07 |
| 30 | 628.3 | 1.80 | 622.3 | 2.87 | 78 | 1532.5 | 178.63 | 1507.2 | 38.66 |
| 31 | 681.8 | 25.09 | 650.8 | 46.47 | 79 | 1542.6 | 233.27 | 1527.1 | 51.17 |
| 32 | 687.8 | 0.85 | 668.3 | 8.35 | 80 | 1553.1 | 11.00 | 1538.8 | 43.82 |
| 33 | 694.0 | 21.17 | 675.4 | 24.95 | 81 | 1563.8 | 2.69 | 1553.9 | 5.42 |
| 34 | 703.0 | 23.06 | 677.9 | 12.82 | 82 | 1657.7 | 452.07 | 1582.1 | 190.01 |
| 35 | 707.5 | 1.50 | 701.1 | 12.06 | 83 | 1670.4 | 360.52 | 1632.5 | 497.55 |
| 36 | 710.1 | 7.03 | 711.4 | 3.60 | 84 | 1723.9 | 399.70 | 1696.3 | 439.05 |
| 37 | 720.4 | 21.67 | 716.7 | 11.29 | 85 | 3008.8 | 104.21 | 3015.1 | 67.09 |
| 38 | 753.0 | 6.28 | 733.3 | 2.29 | 86 | 3037.2 | 61.93 | 3036.8 | 59.86 |
| 39 | 774.8 | 51.82 | 763.3 | 73.72 | 87 | 3065.5 | 26.61 | 3075.2 | 16.25 |
| 40 | 795.9 | 16.17 | 779.5 | 13.11 | 88 | 3113.6 | 12.67 | 3110.9 | 13.57 |
| 41 | 814.2 | 25.80 | 793.2 | 24.26 | 89 | 3130.2 | 16.03 | 3139.4 | 14.11 |
| 42 | 819.5 | 13.51 | 797.8 | 22.64 | 90 | 3152.0 | 1.74 | 3151.2 | 1.80 |
| 43 | 832.3 | 20.71 | 802.3 | 16.36 | 91 | 3240.2 | 0.82 | 3236.4 | 6.27 |
| 44 | 847.9 | 5.61 | 832.4 | 4.48 | 92 | 3244.3 | 18.97 | 3238.0 | 4.81 |
| 45 | 858.8 | 42.03 | 854.0 | 69.85 | 93 | 3245.6 | 17.14 | 3255.3 | 6.56 |
| 46 | 889.8 | 15.46 | 882.8 | 7.01 | 94 | 3264.5 | 4.82 | 3256.0 | 4.81 |
| 47 | 894.2 | 5.57 | 883.4 | 1.35 | 95 | 3264.8 | 2.72 | 3257.6 | 7.92 |
| 48 | 897.5 | 0.29 | 888.8 | 1.37 | 96 | 3397.1 | 53.40 | 3297.6 | 157.98 |

**Table S5**. Wavelengths (λ) and oscillator strengths (f) for absorption and fluorescence of **2** in the investigated solvents (characterized by the dielectric constants ε). μ($S_0$) and μ($S_1$) are the calculated dipole moments in $S_0$ and $S_1$ states.

| **2** | ε | $\lambda_{abs}$ [nm] | f | $\lambda_{flu}$ [nm] | *f* | μ($S_0$) [D] | μ($S_1$) [D] |
|---|---|---|---|---|---|---|---|
| isolated | | 535.9 | 0.258 | 613.9 | 0.217 | 3.00 | 4.43 |
| n-Hexane | 1.88 | 554.6 | 0.321 | 637.2 | 0.279 | 3.47 | 5.13 |
| Toluene | 2.37 | 560.6 | 0.340 | 645.1 | 0.298 | 3.63 | 5.37 |
| DCM | 8.93 | 583.3 | 0.405 | 676.5 | 0.365 | 4.23 | 6.29 |
| Methanol | 32.81 | 591.4 | 0.424 | 688.3 | 0.387 | 4.45 | 6.65 |
| ACN | 35.69 | 591.7 | 0.425 | 688.7 | 0.388 | 4.46 | 6.66 |

## Study of fluorescence spectra.

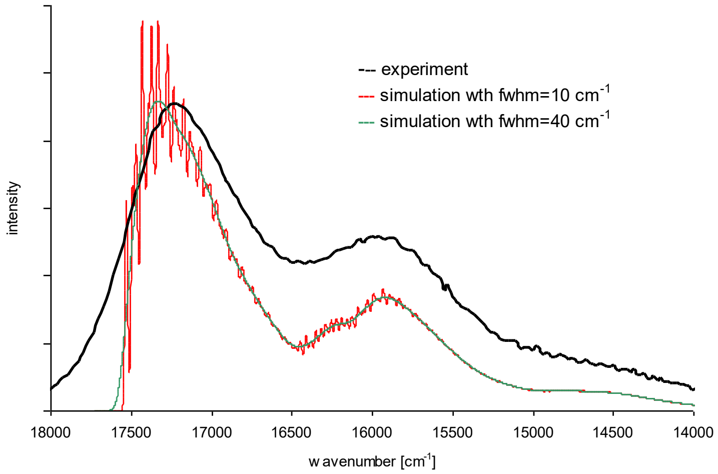


**Figure S5**. Fluorescence spectrum of **2** in *n*-hexane and its simulations (with two different half-widths). FC factors for the $S_1 \rightarrow S_0$ transition are given in form of the vertical solid lines.

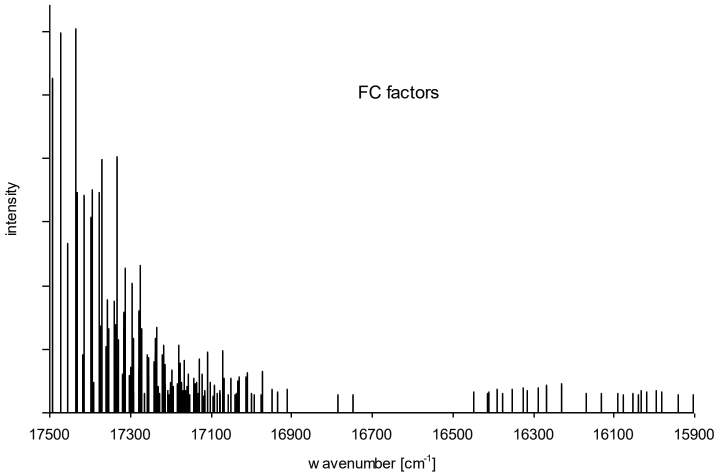


**Figure S6.** Franck-Condon factors for the $S_1 \rightarrow S_0$ transition in **2.**

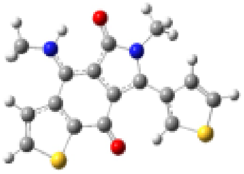
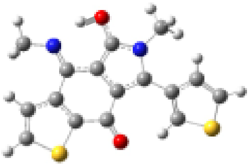
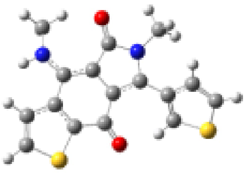
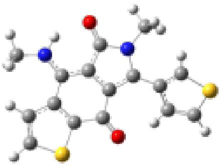
## Conformational Study

The compound **2**, which served as a model for these studies, has a complicated structure (Table S1). It may exist in the form of four conformational isomers, including the normal conformer (A), isomeric forms with intramolecular proton transfer (N…HO, B), and with an inverted *N*-methylamino group (allowing for hydrogen bonding, C) as well as the conformer with thiophene ring rotated around the single bond (D).

The characteristic feature of the prepared the rearranged DPPs is the relatively small Stokes shift between the maxima of the lowest energy absorption and the fluorescence band. They vary between ~500 and ~1500cm$^{-1}$, which clearly indicates that they exist as single conformers. We verified such a conclusion by the DFT and TDDFT/B3LYP/cc-pVDZ calculations performed with the optimization of the molecular structures.

According to the obtained data, the conformer A is the most stable as it has the lowest energy in the electronic ground $S_0$ and in the lowest of the excited $S_1$ states. Thus, for energetic reasons we may eliminate conformational isomers with intramolecular proton transfer (B) and with an inverted *N*-methylamino group (C) from further considerations. It is noteworthy that the form D may be only weakly populated at room temperature. Thus, we consider that the normal conformer A is the only one which contributes to the experimentally observed spectrum of **2**.

**Table S6.** Energies of conformational isomers for **2**$^{a}$**.**

| Conformer | Isomeric form | E($S_0$)$^{b}$ | E($S_1$)$^{b}$ |
|---|---|---|---|
| **A** |  | 0 | 0 |
| **B** |  | 4487 | 4183 |
| **C** |  | 1849 | 2466 |
| **D** |  | 258 | 266 |

$^{a}$Optimized in the electronic ground $S_0$ and in the lowest excited $S_1$ states with respect to form **A**. $^{b}$Energies are given in cm$^{-1}$

### Cyclic Voltammetry

The position of heteroatom and presence of EDG have minimal influence of the redox potentials (**2** *versus* **8**, and **2** *versus* **6**) with the effect of heteroatom's origin even less pronounced (**2** *versus* **10**). Half-wave potentials ($E_{red}$1/2) varied in the range of -1.28 – -0.93V. The most negative one belongs to dye **16**, bearing dimethoxyphenyl substituent what is in line with the influence of electron-donating groups on the electrochemical properties. Compound **14**, possessing additional conjugated rings, displays the highest $E_{red}$ 1/2 among the tested molecules.

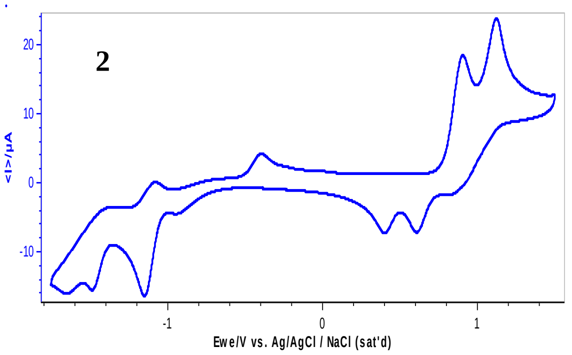
It is worth underlining that all tested compounds undergo multistep irreversible redox processes if voltammograms are measured at the broad range of the potentials.

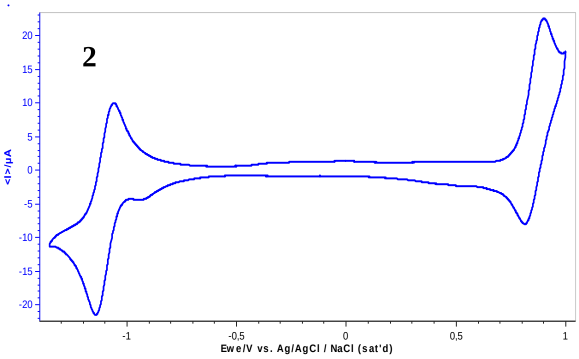
**Table S7.** Redox potentials of the rearranged DPPs in dichloromethane.

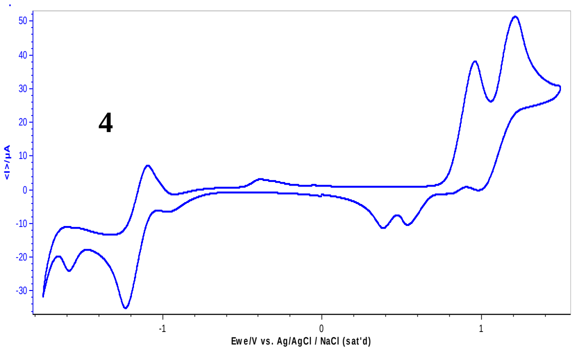
| Dye | $E_{ox}^{pa}$,V | $E_{ox}^{pc}$, V | $E_{ox}^{onset}$, V | IP, eV | $E_{red}^{pa}$, V | $E_{red}^{pc}$, V | $E_{red}$1/2, V | $E_{red}^{onset}$, V | EA, eV |
|---|---|---|---|---|---|---|---|---|---|
| **2** | 0.90 | 0.81 | 0.78 | -5.1 | -1.06 | -1.15 | -1.10 | -1.02 | -3.3 |
| **4** | 0.96 | 0.81 | 0.78 | -5.1 | -1.08 | -1.23 | -1.15 | -1.06 | -3.3 |
| **6** | 0.86 | 0.75 | 0.74 | -5.1 | -1.12 | -1.22 | -1.17 | -1.07 | -3.3 |
| **8** | 0.92 | 0.80 | 0.78 | -5.1 | -1.07 | -1.16 | -1.15 | -1.03 | -3.3 |
| **10** | 0.94 | - | 0.82 | -5.2 | -1.08 | -1.20 | - | -1.05 | -3.3 |
| **14** | 0.89 | 0.79 | 0.74 | -5.1 | -0.89 | -0.97 | -0.93 | -0.81 | -3.5 |
| **16** | 0.80 | 0.69 | 0.67 | -5.0 | -1.24 | -1.33 | -1.28 | -1.19 | -3.2 |

[a]Measurement conditions: electrolite ($NBu_4ClO_4$, c= 0.1M); $DCM_{dry}$, potential sweep rate: 100 $mVs^{-1}$, working electrode: glassy carbon (GC); auxiliary electrode: Pt wire; reference electrode: Ag/AgCl; all measurements were conducted at room temperature

The ionic potential and electron affinity values were estimated from the onset potentials of the first oxidation and reduction events, respectively. The ionic potential and electron affinity were calculated according to the following equations: $IP(eV) = -[E_{ox}^{onset} - E^{1/2}(Fc/Fc^{+}) + 4.8]$ and $EA(eV) = -[E_{red}^{onset} - E^{1/2}(Fc/Fc^{+}) + 4.8]$


2
<I>/µA
20
10
0
-10
-1
0
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)


2
<I>/µA
20
15
10
5
0
-5
-10
-15
-20
-1
-0,5
0
0,5
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)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<I>/µA
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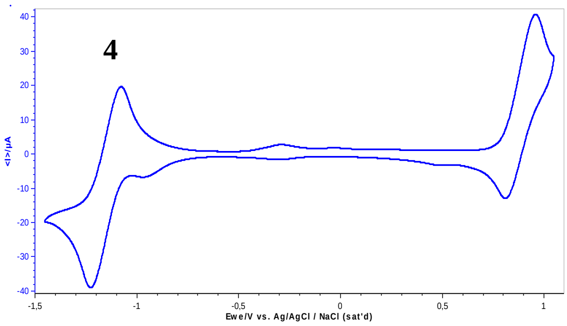
40
30
20
10
0
-10
-20
-30
-1
0
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)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<I>/µA
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30
20
10
0
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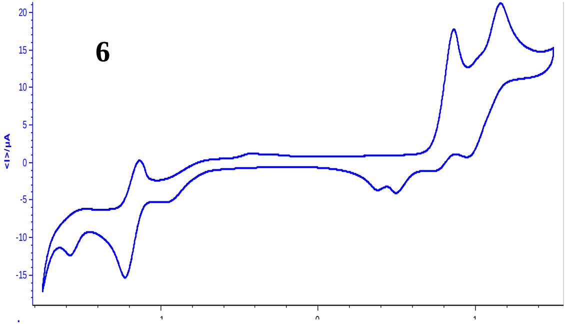
-30
-40
-1,5
-1
-0,5
0
0,5
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)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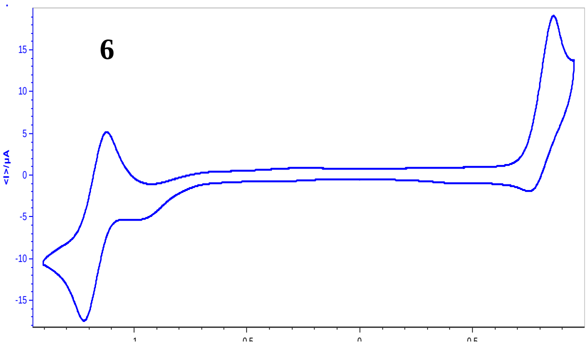
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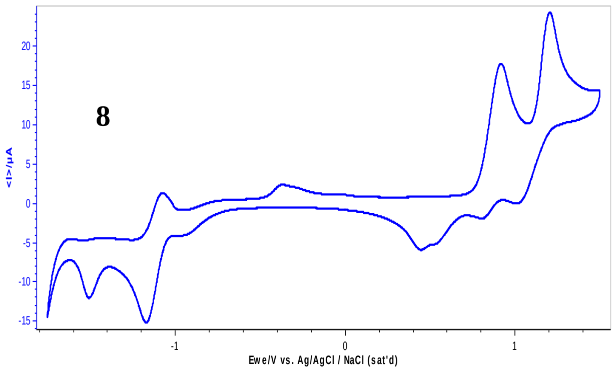
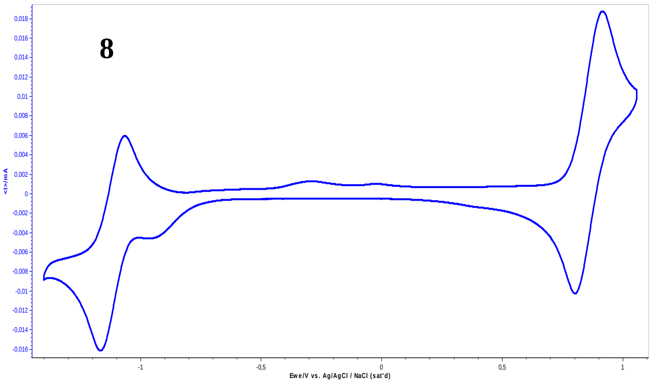
15
10
5
0
-5
-10
-15


8
<I>/µA
20
15
10
5
0
-5
-10
-15
-1
0
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)


8
<I>/mA
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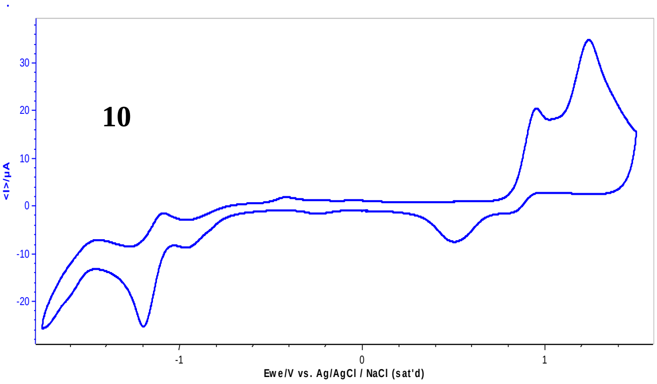
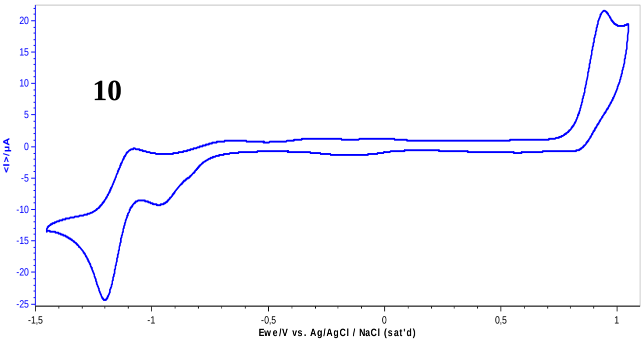
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
-0.004
-0.006
-0.008
-0.01
-0.012
-0.014
-0.016
-1
-0.5
0
0.5
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)


10
<I>/µA
30
20
10
0
-10
-20
-1
0
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)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<I>/µA
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-15
-20
-25
-1,5
-1
-0,5
0
0,5
1
Ewe/V vs. Ag/AgCl / NaCl (sat'd)

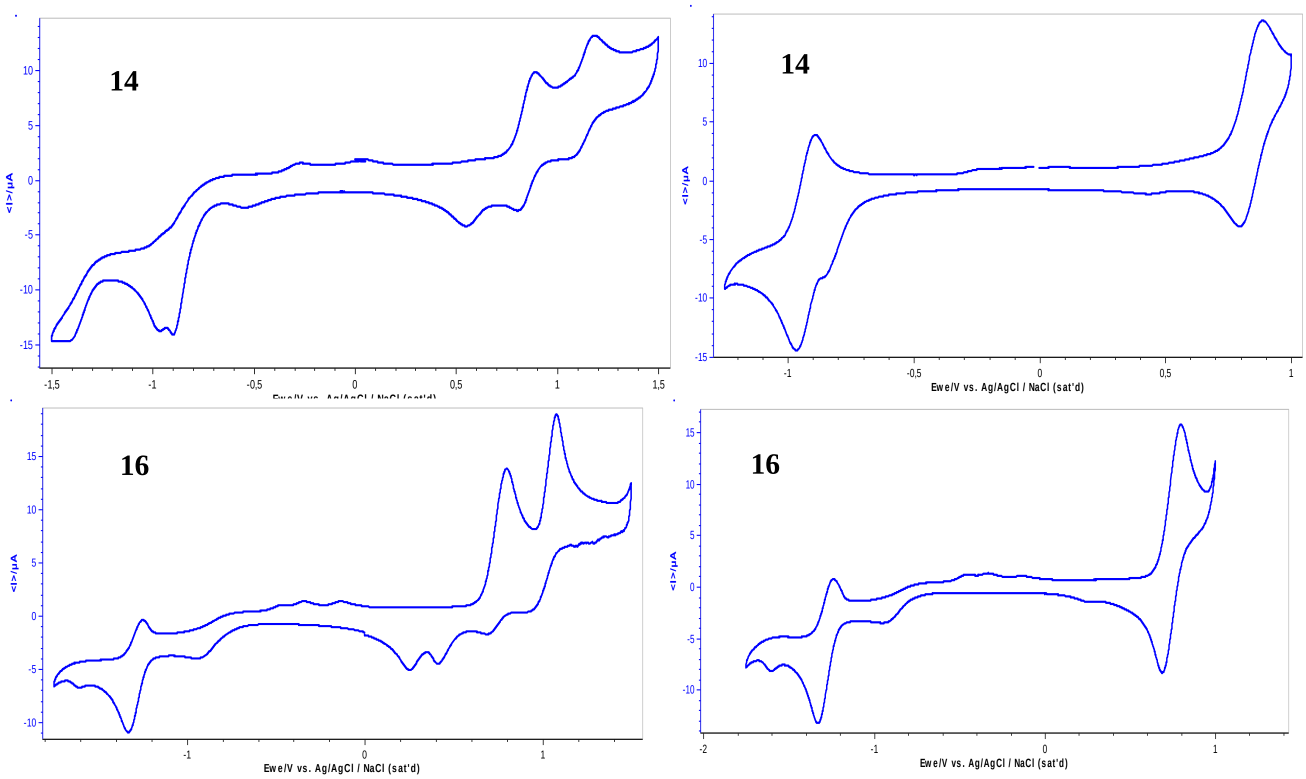


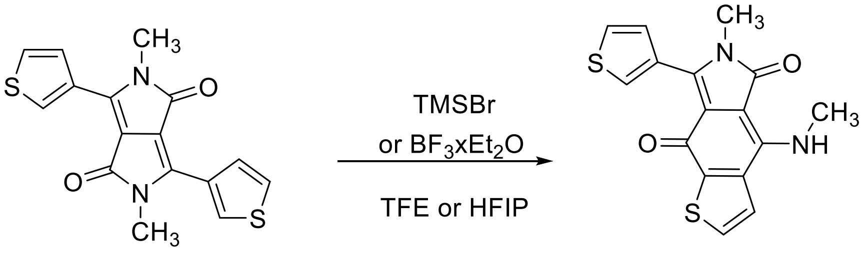
**Figure S7.** Voltammogrames for the rearranged DPPs.

## General procedure for synthesis of *N,N*-dialkylated diketopyrrolopyrroles.

Unless otherwise noted, the mixture of parent pigment (1 mmol, 1 eq.), corresponding base (10 mmol, 10 eq.) and tetra-*n*-butylammonium hydrogen sulfate (TBAHS, 5%mol) in dry DMF (30 ml) were reacted at elevated temperature for 30 min. Subsequently alkylated agent (10 mmol, 10 eq.) was added in one portion. Reaction was conducted for additional 17 h. Expected product was precipitated from the cold reaction mixture, filtered off and recrystallized from DCM/hexanes mixture.

## General procedure for the synthesis of the rearranged DPPs

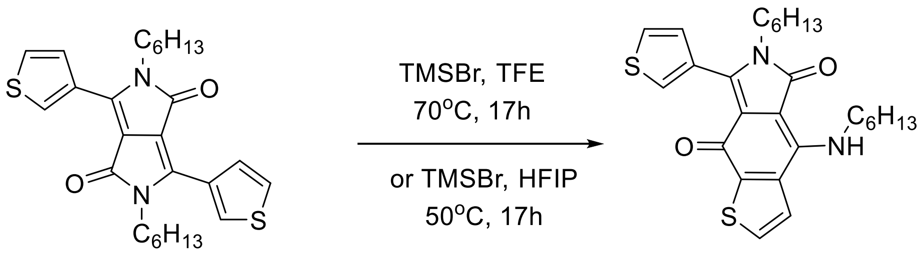
Corresponding *N,N*-dialkylated DPP (0.15 mmol, 1 eq.) was dissolved in 1 ml of polifluorinated alcohol at the Ace Pressure Tube. Subsequently, TMSBr (0.15 mmol, 1 eq.) was added and reaction was conducted for 17 h. at elevated temperature. Next, obtained mixture was evaporated with Celite and purified by means of dry vacuum column chromatography (DCVC).



1 2

**2,5-Dimethyl-1,4-diketo-3,6-di(thien-3-yl)pyrrolo[3,4-c]pyrrole (1)** was obtained from 1,4-diketo-3,6-di(thien-3-yl)pyrrolo[3,4-c]pyrrole (300 mg, 1 mmol)[3] in the presence of TBAHS (17 mg, 0.05 mmol), $K_2CO_3$(1.38 g, 10 mmol) and $Me_2SO_4$ (0.95 ml, 10 mmol) in $DMF_{dry}$ (30 ml). Reaction was conducted for 17h at 120°C, leading to 295 mg (90%) of the expected product.
$^1H$ NMR ($CDCl_3$) δ (ppm): 8.55 (dd, 2H, $J_1$ = 3.0 Hz, $J_2$ = 1.3 Hz), 8.10 (dd, 2H, $J_1$ = 5.4 Hz, $J_2$ = 1.3 Hz), 7.49 (dd, 2H, $J_1$ = 5.0 Hz, $J_2$ = 3.0 Hz), 3.54 (s, 6H); $^{13}C$ NMR ($CDCl_3$) δ (ppm): 161.9, 141.8, 130.5, 129.9, 127.9, 126.5, 110.0, 107.8, 29.6; HRMS: (ESI) calcld. for $C_{16}H_{13}N_2O_2S_2$ $[M+H^+]$ 329.0418, found: 329.0409.

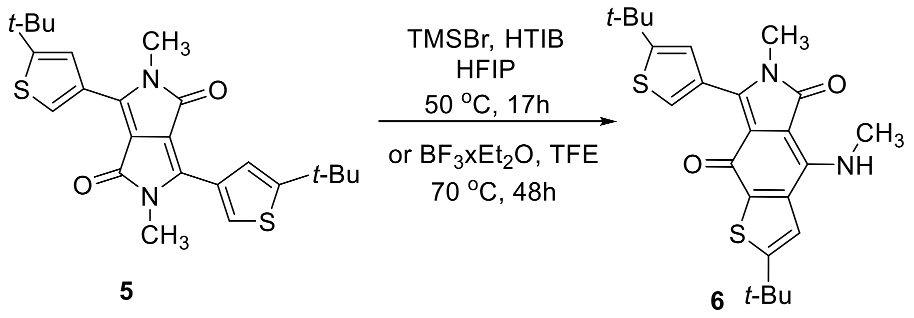
**6-methyl-4-(methylamino)-7-(thiophen-3-yl)-5H-thieno[2,3-f]isoindole-5,8(6H)-dione** (**2**) was obtained from 2,5-dimethyl-1,4-diketo-3,6-di(thien-3-yl)pirolo[3,4-c]pirole (**1**, 50 mg, 0.15 mmol) dissolved at TFE (1 ml) in the presence of TMSBr (20 µl, 0.15 mmol). Reaction was conducted for 17h at 70 °C evaporated with Celite and purified by means of DCVC (0.2% MeOH w DCM). Desired product was crystallized from DCM/hexanes, affording 37.5 mg (75%) of the desired product.
Alternatively, in the presence of TMSBr (20 µl, 0.15 mmol) and HFIP (1ml) at 50°C, leading to 36.5 mg (73%) of **2**.
Alternatively, in the presence of $BF_3xEt_2O$ (37 µl, 0.3 mmol) and TFE (1ml) at 70°C, leading to 36.0 mg (72%) of **2**.
$^1H$ NMR ($CDCl_3$) δ (ppm): 8.78 (bq, 1H, $J$ = 5.0 Hz), 8.19 (dd, 1H, $J_1$ = 3.0 Hz, $J_2$ = 1.3Hz), 7.66 (d, 1H, $J$ = 5.3 Hz), 7.59 (d, 1H, $J$ = 5.4 Hz), 7.57 (dd, 1H, $J_1$ = 5.0 Hz, $J_2$ = 1.3 Hz), 7.40 (dd, 1H, $J_1$ = 5.0 Hz, $J_2$ = 3.0 Hz), 3.43 (d, 3H, $J$ = 6.0 Hz), 3.38 (s, 3H); $^{13}C$ NMR ($CDCl_3$) δ (ppm): 171.1, 165.6, 151.0, 146.9, 141.3, 135.1, 131.7, 130.3, 129.0, 128.7, 126.4, 124.8, 110.9, 99.9, 32.8, 28.7; HRMS: (ESI) calcld. for $C_{16}H_{13}N_2O_2S_2$ $[M+H^+]$ 329.0418, found: 329.0409.



3 4

**2,5-Di-*n*-hexyl-1,4-diketo-3,6-di(thien-3-yl)pyrrolo[3,4-c]pyrrole** (**3**) was obtained from 1,4-diketo-3,6-di(thien-3-yl)pyrrolo[3,4-c]pyrrole (300 mg, 1 mmol)[3] in the presence of TBAHS (17 mg, 0.05 mmol), $K_2CO_3$(1.38 g, 10 mmol) and *n*-$C_6H_{13}Br$ (1.40 ml, 10 mmol) in $DMF_{dry}$ (30 ml). Reaction was conducted for 17h at 120°C, evaporated with Celite, filtered through the pad of silica (DCM:hexanes = 1:1) and recrystallized from DCM/hexanes, leading to 305 mg (65%) of the expected product.
$^1H$ NMR ($CDCl_3$) δ (ppm): 8.53 (dd, 2H, $J_1$ = 2.7 Hz, $J_2$ = 1.2 Hz), 7.91 (dd, 2H, $J_1$ = 5.0 Hz, $J_2$ = 1.0 Hz), 7.47 (dd, 2H, $J_1$ = 5.0 Hz, $J_2$ = 3.0 Hz), 3.94-3.90 (m, 4H), 1.75-1.67 (m, 4H), 1.41-1.34 (m, 4H), 1.33-1.27 (m, 8H), 0.90-0.87 (m, 6H); $^{13}C$ NMR ($CDCl_3$) δ (ppm): 162.0, 141.6, 130.3, 129.7, 127.5, 126.5, 108.3, 42.1, 31.4, 29.7, 26.5, 22.5, 13.9; HRMS: (ESI) calcld. for $C_{26}H_{33}N_2O_2S_2$ $[M+H^+]$ 469.1983, found: 469.1978.
**6-hexyl-4-(hexylamino)-7-(thiophen-3-yl)-5H-thieno[2,3-f]isoindole-5,8(6H)-dione (4)** was obtained from z 2,5-di-*n*-hexyl-1,4-diketo-3,6-di(thien-3-yl)pyrrolo[3,4-c]pyrrole (**3**, 66 mg, 0.15 mmol) dissolved at HFIP (1 ml) in the presence of TMSBr (20 μl, 0.15 mmol). Reaction was conducted for 17h at 50 °C, evaporated with Celite and purified by means of DCVC (0.5%MeOH w DCM). Desired product was crystallized from hexanes affording 50 mg (75%) of the desired product.
Alternatively, in the presence of TMSBr (20 μl, 0.15 mmol) and TFE (1ml) at 70°C, leading to 39.3 mg (60%) of **4**.

$^1H$ NMR ($CDCl_3$) δ (ppm): 8.85 (bt, 1H, $J$ = 4.7 Hz), 7.98 (dd, 1H, $J_1$ = 3.0 Hz, $J_2$ = 1.2 Hz), 7.63 (bs, 2H), 7.46-7.41 (m, 2H), 3.83-3.78 (m, 4H), 1.88-1.80 (m, 2H), 1.40-1.33 (m, 4H), 1.28-1.20 (m, 10H), 0.94-0.90 (m, 3H), 0.86-0.81 (m, 3H); $^{13}C$ NMR ($CDCl_3$) δ (ppm): 171.3, 165.7, 151.0, 146.2, 141.0, 135.3, 131.7, 129.2, 128.9, 128.3, 126.5, 125.2, 111.3, 99.9, 45.9, 41.2, 31.4, 31.2, 30.2, 29.5, 26.5, 26.4, 22.48, 22.46, 13.99, 13.94; HRMS: (ESI) calcld. for $C_{26}H_{33}N_2O_2S_2$ $[M+H^+]$ 469.1983, found 469.1978.



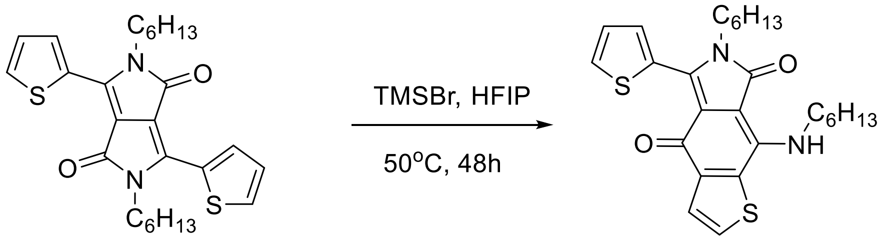
5 6

**2,5-Dimethyl-1,4-diketo-3,6-di(2-*t*-butylthien-4-yl)pyrrolo[3,4-c]pyrrole (5)** was obtained from 1,4-diketo-3,6-di(2-*t*-butylthien-4-yl)pyrrolo[3,4-c]pyrrole[4] (412 mg, 1 mmol) in the presence of TBAHS (17 mg, 0.05 mmol), $K_2CO_3$(1.38 g, 10 mmol) and $Me_2SO_4$ (0.95 ml, 10 mmol) in $DMF_{dry}$ (30 ml). Reaction was conducted for 17h at 120°C, evaporated with Celite and filtered through the pad of silica (DCM). Desired product was recrystallized from DCM/hexanes, leading to 308 mg (70%) of the expected product.

$^1$H NMR ($CDCl_3$) δ (ppm): 8.17 (d, 2H, *J* = 1.7 Hz), 7.93 (d, 2H, *J* = 1.7 Hz), 3.52 (s, 6H), 1.46 (s, 18H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 161.9, 158.4, 141.9, 129.4, 127.3, 122.8, 107.6, 34.7, 32.4, 29.6; HRMS: (ESI) calcld. for $C_{24}H_{28}N_2O_2S_2Na$ [M+Na$^+$] 463.1490, found 463.1483.

**2-(tert-butyl)-7-(5-(tert-butyl)thiophen-3-yl)-6-methyl-4-(methylamino)-5H-thieno[2,3-f]isoindole-5,8(6H)-dione (6)** was obtained from 2,5-dimethyl-1,4-diketo-3,6-di(2-*t*-butylthien-4-yl)pyrrolo[3,4-c]pyrrole (**5**, 69.5 mg, 0.15 mmol) dissolved in HFIP (1 ml) in the presence of TMSBr (20 μl, 0.15 mmol) and HTIB (3 mg, 5 %mol). Reaction was conducted for 17h at 50°C, evaporated with Celite and purified by means of DCVC (MeOH:DCM = 2:98). Desired product was crystallized from hexanes, leading to 42.1 mg (60%) of **7**.
Alternatively, in the presence of TMSBr (20 μl, 0.15 mmol) in TFE (1 ml), leading to 18.1 mg (26%) of **7**.

$^1$H NMR ($CDCl_3$) δ (ppm): 8.81 (bq, 1H, *J* = 4.7 Hz), 7.99 (d, 1H, *J* = 1.1 Hz), 7.39 (s, 1H), 7.27 (d, 1H, *J* = 1.2 Hz), 3.44 (d, 3H, *J* = 5.7 Hz), 3.37 (s, 3H), 1.439 (s, 9H), 1.435 (s, 9H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 171.2, 165.8, 164.4, 156.6, 148.4, 146.9, 141.6, 134.9, 128.3, 127.9, 122.8, 120.6, 110.7, 99.9, 35.2, 34.6, 32.9, 32.5, 32.2, 28.8; HRMS: (ESI) calcld. for $C_{24}H_{29}N_2O_2S_2$ [M+H$^+$] 441.1670, found 441.1670.



**7**

**8**

**2,5-Di-*n*-hexyl-1,4-diketo-3,6-di(thien-2-yl)pyrrolo[3,4-c]pyrrole** (**7**) obtained from 1,4-diketo-3,6-di(thien-2-yl)pyrrolo[3,4-c]pyrrole (300 mg, 1 mmol)[5] in the presence of TBAHS (17 mg, 0.05 mmol), $K_2CO_3$ (1.38 g, 10 mmol) i *n*-$C_6H_{13}Br$ (1.40 ml, 10 mmol) in $DMF_{dry}$ (30 ml). Reaction was conducted for 17h at 120°C, evaporated with Celite, filtered through the pad of silica (DCM:hexanes = 1:1) and recrystallized from DCM/hexanes, leading to 370 mg (79%) of the expected product. Spectral properties concur with the published data.[7]

**6-hexyl-8-(hexylamino)-5-(thiophen-2-yl)-4H-thieno[2,3-f]isoindole-4,7(6H)-dione** (**8**) was obtained from 2,5-*n*-hexyl-1,4-diketo-3,6-di(thien-2-yl)pyrrolo[3,4-c]pyrrole (**7**, 164 mg, 0.35 mmol) dissolved in HFIP (3 ml) in the presence of TMSBr (46 μl, 0.35 mmol). Reaction was conducted for 48h at 50°C, evaporated with Celite and purified by means of DCVC (EtOAc:hexanes = 1:9). Desired product was recrystallized from pentane, affording 52.5 mg (32%) of **8**.
$^1$H NMR ($CDCl_3$) δ (ppm): 8.85 (bs, 1H), 7.92 (dd, 1H, $J_1$ = 3.7 Hz, $J_2$ = 1.1 Hz), 7.79 (d, 1H, *J* = 5.3 Hz), 7.57 (dd, 1H, $J_1$= 5.0 Hz, $J_2$ = 1.1 Hz), 7.53 (d, 1H, *J* = 5.3 Hz), 7.21 (dd, 1H, $J_1$ = 5.0 Hz, $J_2$ = 3.7 Hz), 3.93-3.88 (m, 2H), 3.82-3.77 (m, 2H), 1.86-1.80 (m, 2H), 1.66-1.57 (m, 2H), 1.56-1.49 (m, 2H), 1.39-1.21 (m, 10H), 0.94-0.90 (m, 3H), 0.87-0.83 (m, 3H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 172.2, 165.5, 147.5, 145.6, 137.9, 135.1, 132.3, 129.7, 129.4, 129.1, 127.4, 127.3, 112.5, 99.2, 45.4, 41.4, 31.4, 31.3, 30.2, 29.6, 26.5, 26.4, 22.48, 22.47, 13.99, 13.95; HRMS: (ESI) calcld. for $C_{26}H_{33}N_2O_2S_2$ [M+H$^+$] 469.1983, found 469.1981.

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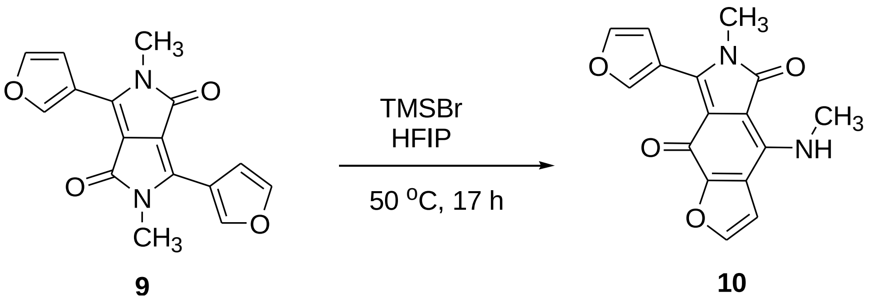
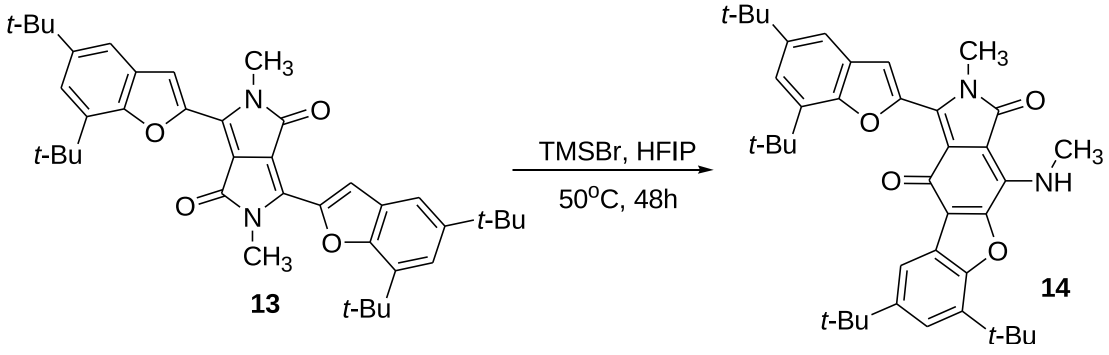


**9** **10**

**2,5-Dimethyl-1,4-diketo-3,6-di(fur-3-yl)pyrrolo[3,4-c]pyrrole (9)** was obtained from 1,4-diketo-3,6-di(fur-3-yl)pyrrolo[3,4-c]pyrrole[6] (120 mg, 0.44 mmol) in the presence of $K_2CO_3$ (608 mg, 4.4 mmol) and MeOTs (820 mg, 4.4 mmol) in $DMF_{dry}$ (25 ml). Reaction was conducted at 120°C for 2h. Next, water (200 ml) was added to the cold reaction mixture and precipitate was filtered off. Obtained product was recrystallized from DCM/hexanes to afford 79.5mg (61%) of the expected product **9**.
$^1$H NMR ($CDCl_3$) δ (ppm): 8.56 (s, 2H), 7.59-7.58 (m, 2H), 7.49-7.48 (m, 2H), 3.49 (s, 6H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 161.4, 145.6, 143.9, 139.4, 116.5, 110.0, 109.8, 107.2, 28.9; HRMS: (ESI) calcld. for $C_{16}H_{12}N_2O_4Na$ [M+Na$^+$] 319.0695, found 319.0686.

**7-(Furan-3-yl)-6-methyl-4-(methylamino)-5H-furo[2,3-f]isoindole-5,8(6H)-dione (10)** was obtained from 2,5-dimethyl-1,4-diketo-3,6-di(fur-3-yl)pyrrolo[3,4-c]pyrrole (**9**, 44.5 mg, 0.15 mmol) dissolved in HFIP (1 ml) in the presence of TMSBr (20 µl, 0.15 mmol). Reaction was conducted at 50°C for 17h, evaporated with Celite and purified by means of DCVC (0.1% MeOH w DCM). Desired product was recrystallized from DCM/hexanes, affording 8 mg (18%) of **10**.

$^1$H NMR ($CDCl_3$) δ (ppm): 8.90-8.89 (m, 1H), 8.47 (bq, 1H, $J$ = 5.2 Hz), 7.67 (d, 1H, $J$ = 2.0 Hz), 7.57-7.55 (m, 1H), 7.04 (dd, 1H, $J_1$ = 5.0 Hz, $J_2$ = 1.3 Hz), 6.93 (d, 1H, $J$ = 2.0 Hz), 3.43 (s, 3H), 3.35 (d, 3H, $J$ = 5.8 Hz); $^{13}$C NMR ($CDCl_3$) δ (ppm): 165.8, 165.3, 155.9, 148.4, 146.6, 145.7, 142.8, 139.2, 122.8, 114.8, 112.2, 110.2, 109.2, 97.9, 31.8, 28.8; HRMS: (EI) calcld. for $C_{16}H_{12}N_2O_4$ [M$^+$]$^\cdot$296.0797, found 296.0800.



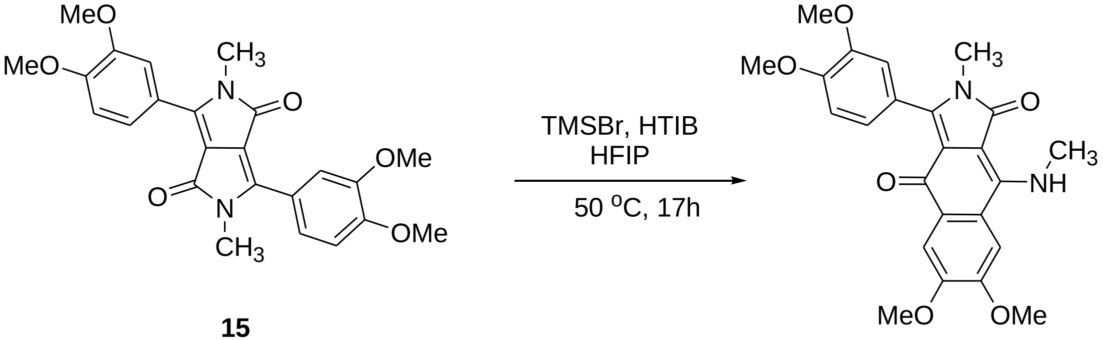
**13** **14**

**2,5-Dimethyl-1,4-diketo-3,6-di(5,7-di-*t*-butylbenzofur-3-yl)pyrrolo[3,4-c]pyrrole (13)** was obtained from 1,4-diketo-3,6-di(5,7-di-*t*-butylbenzofur-3-yl)pyrrolo[3,4-c]pyrrole (356.0 mg, 0.6 mmol)[5] in the presence of $K_2CO_3$ (1.83 g, 6.0 mmol) TBAHS (10 mg, 0.03 mmol) and $Me_2SO_4$ (1.33 ml, 3 mmol) in $DMF_{dry}$ (20 ml). Reaction was conducted at 120°C for 1h. Next, water (200 ml) was added to the cold reaction mixture and precipitate was filtered off. Obtained product was recrystallized from Toluene/MeOH to afford 362.0mg (97%) of the expected product **13**.
$^1$H NMR ($CDCl_3$) δ (ppm): 8.70 (s, 2H), 7.57 (s, 2H), 7.41 (s, 2H), 3.82 (s, 6H), 1.56 (s, 12H), 1.40 (s, 12H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 160.9, 152.5, 147.2, 144.9, 134.6, 134.1, 128.4, 122.7, 116.8, 116.6, 108.2, 35.0, 34.4, 31.7, 30.0, 29.8; HRMS: (EI) calcld. for $C_{40}H_{48}N_2O_4$ [M$^+$] 620.3614, found 620.3615.

**16,8-Di-*tert*-butyl-1-(5,7-di-*tert*-butylbenzofuran-2-yl)-2-methyl-4-(methylamino)-2H-benzofuro[2,3-*f*]isoindole-3,10-dione (14)** was obtained from 2,5-dimethyl-1,4-diketo-3,6-di(5,7-di-*t*-

butylbenzofur-3-yl)pyrrolo[3,4-c]pyrrole (**13**, 100 mg, 0.16 mmol) dissolved in HFIP (1 ml) in the presence of TMSBr (42 µl, 0.32 mmol). Reaction was conducted at 50°C for 3 days, evaporated with Celite and purified by means of DCVC (0.1% MeOH w DCM). Desired product was recrystallized from hexanes, affording 30.3 mg (30%) of **14**.

$^1$H NMR ($CDCl_3$) δ (ppm): 9.35 (s, 1H), 8.49 (bq, 1H, *J* = 5.7 Hz), 8.39 (d, 1H, *J* = 2.1 Hz), 7.65 (d, 1H, *J* = 1.8 Hz), 7.46 (d, 1H, *J* = 2.0 Hz), 7.39 (d, 1H, *J* = 1.8 Hz), 3.82 (s, 3H), 3.69 (d, 3H, *J* = 6.0 Hz), 1.56 (s, 9H), 1.55 (s, 9H), 1.44 (s, 9H), 1.40 (s, 9H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 173.4, 165.4, 153.0, 152.1, 150.8, 148.3, 146.6, 145.4, 140.2, 135.0, 133.9, 133.7, 128.5, 126.2, 124.7, 122.3, 122.1, 117.5, 116.9, 116.8, 113.3, 103.3, 35.2, 34.9, 34.4, 34.3, 32.7, 31.93, 31.86, 31.76, 31.70, 31.6, 30.4, 30.0, 29.89, 29.88 , 22.6, 14.1; HRMS: (ESI) calcld. for $C_{40}H_{48}N_2O_4$ $[M+H^+]$ 621.3692, found 621.3703.



**15**

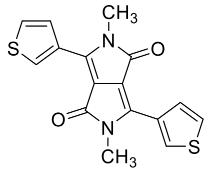
**16**

**2,5-Dimethyl-1,4-diketo-3,6-di(3,4-dimethoxyphenyl)pyrrolo[3,4-c]pyrrole (13)** was obtained from 1,4-diketo-3,6-di(3,4-dimethoxyphenyl)pyrrolo[3,4-c]pyrrole (163.2, 0.4 mmol)[5] in the presence of $K_2CO_3$ (552 mg, 4.0 mmol) and MeOTs (744 mg, 4.0 mmol) in $DMF_{dry}$ (25 ml). Reaction was conducted at 120°C for 17 h. Next, water (200 ml) was added to the cold reaction mixture and precipitate was filtered off. Obtained product was purified by means of DCVC (2% MeOH w DCM) and recrystallized from DCM/hexanes to afford 87 mg (50%) of the expected product **13**.

$^1$H NMR ($CDCl_3$) δ (ppm): 7.65 (d, 2H, *J* = 2.2 Hz), 7.37 (dd, 2H, $J_1$ = 8.3 Hz, $J_2$ = 2.2 Hz), 6.87 (d, 2H, *J* = 8.3 Hz), 4.00 (s, 6H), 3.37 (s, 6H), 3.37 (s, 6H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 162.7, 151.3, 148.6, 147.8, 122.4, 120.6, 116.5, 112.8, 110.4, 108.2, 56.1, 55.9, 29.7; HRMS: (ESI) calcld. for $C_{24}H_{24}N_2O_6Na$ $[M+Na^+]$ 459.1532, found 459.1527.

**3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-methyl-9-(methylamino)-1H-benzo[f]isoindole-1,4(2H)-dione 16** was obtained from 2,5-dimethyl-1,4-diketo-3,6-di(3,4-dimethoxyphenyl)pyrrolo[3,4-c]pyrrole (**15**, 65.0 mg, 0.15 mmol) dissolved in HFIP (1 ml) in the presence of TMSBr (40µl, 0.30 mmol) and HTIB (3 mg, 5 %mol). Reaction was conducted at 50°C for 17h, evaporated with Celite and purified by means of DCVC (0.2% MeOH w DCM). Desired product was recrystallized from DCM/hexanes, affording 43.0 mg (66%) of **16**.

$^1$H NMR ($CDCl_3$) δ (ppm): 8.80 (bs, 1H), 7.86 (s, 1H), 7.55 (s, 1H), 7.28 (dd, 1H, $J_1$ = 8.2 Hz, $J_2$ = 1.8 Hz), 7.22 (d, 1H, *J* = 1.8 Hz), 6.99 (d, 1H, *J* = 8.4 Hz), 3.99 (s, 3H), 3.95 (m, 9H), 3.50 (s, 3H), 3.27 (s, 3H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 174.9, 165.8, 151.1, 151.0, 150.4, 150.2, 148.4, 144.2, 133.4, 125.0, 123.4, 121.6, 113.1, 110.6, 110.2, 109.7, 109.4, 100.8, 56.2, 56.11, 56.07, 55.9, 34.5, 28.2; HRMS: (ESI) calcld. for $C_{24}H_{25}N_2O_6$ $[M+H^+]$ 437.1713, found. 437.1706.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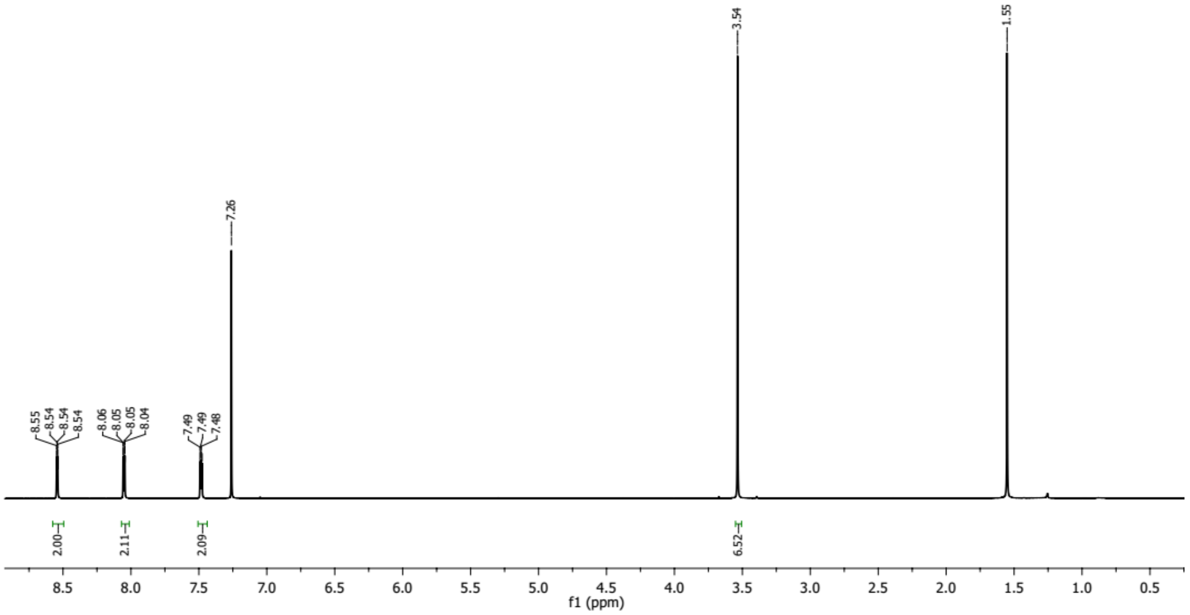
S
O
N
CH3
S

**1**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1.55
2.00
2.11
2.09
6.52
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
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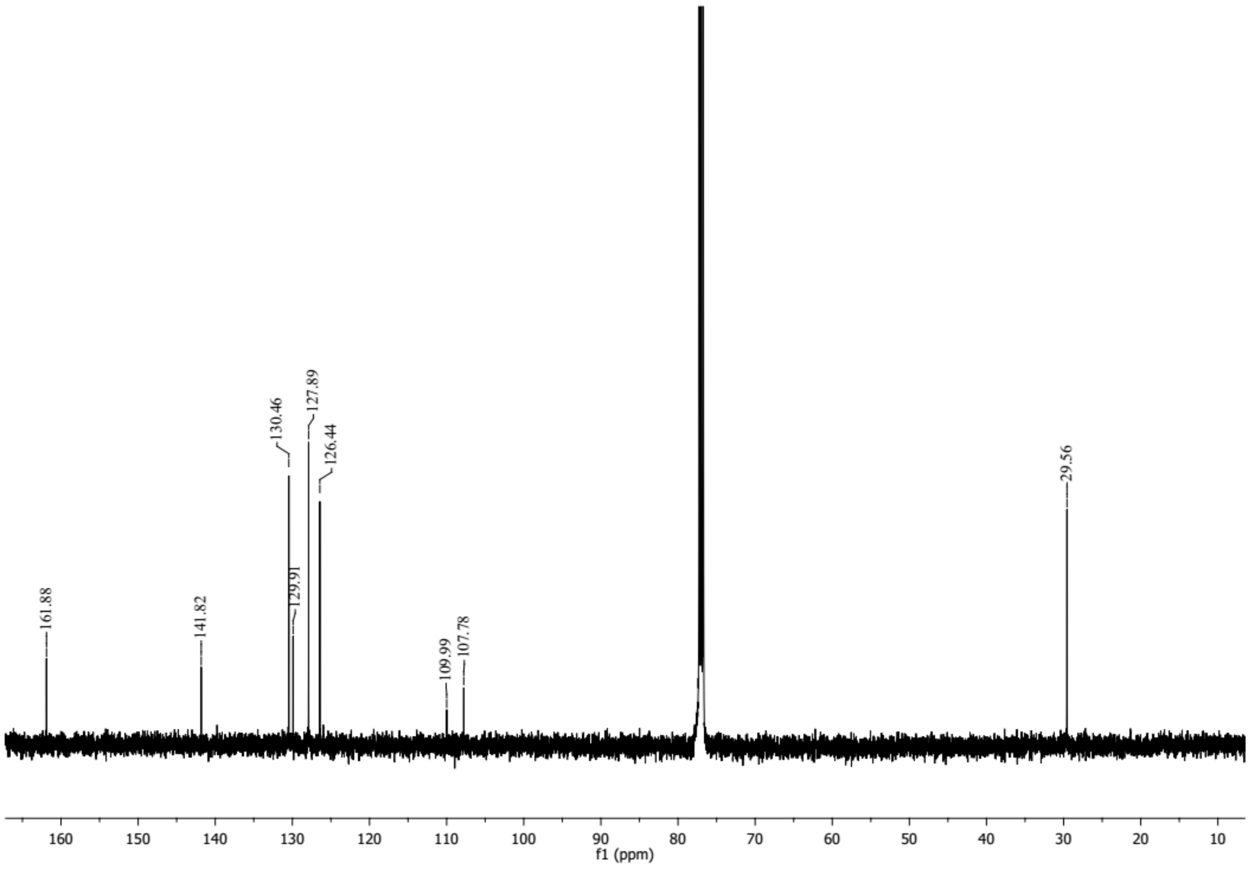
f1 (ppm)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140
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120
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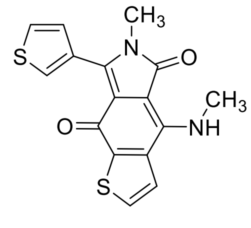
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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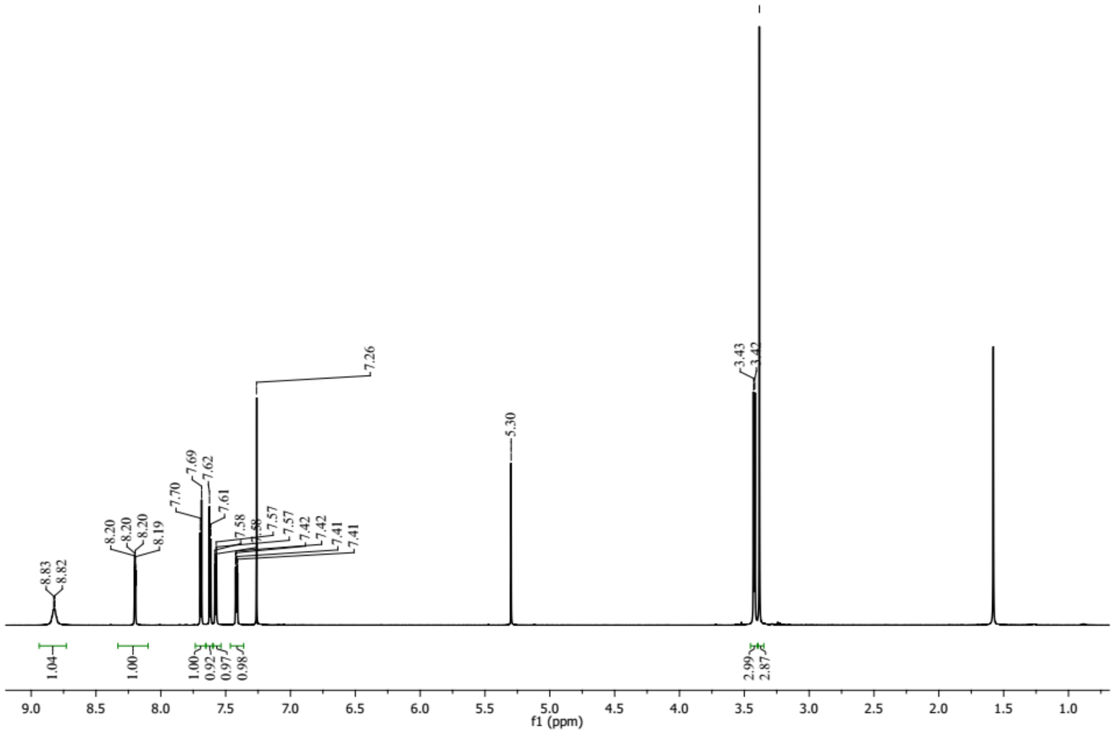
S
NH
CH3
O
S

**2**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7.57
7.42
7.42
7.41
7.41
7.26
5.30
3.43
3.42
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1.00
1.00
0.92
0.97
0.98
2.99
2.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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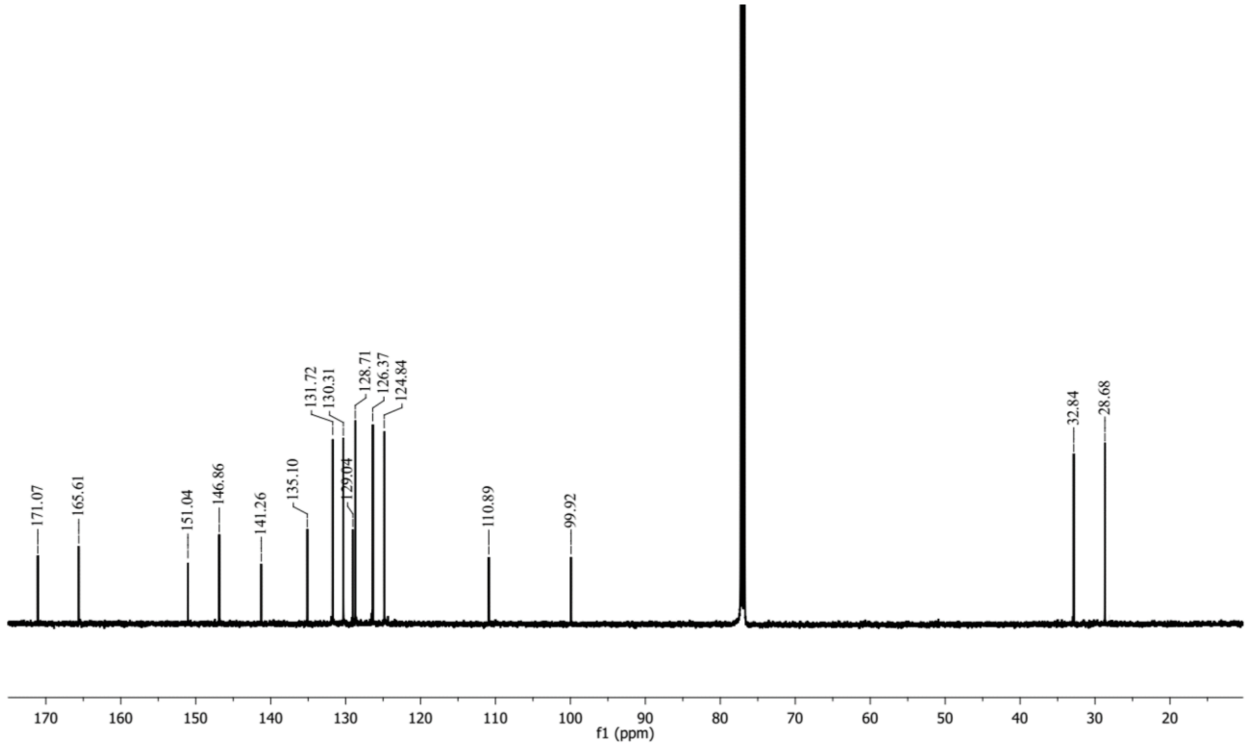
1.0
f1 (ppm)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120
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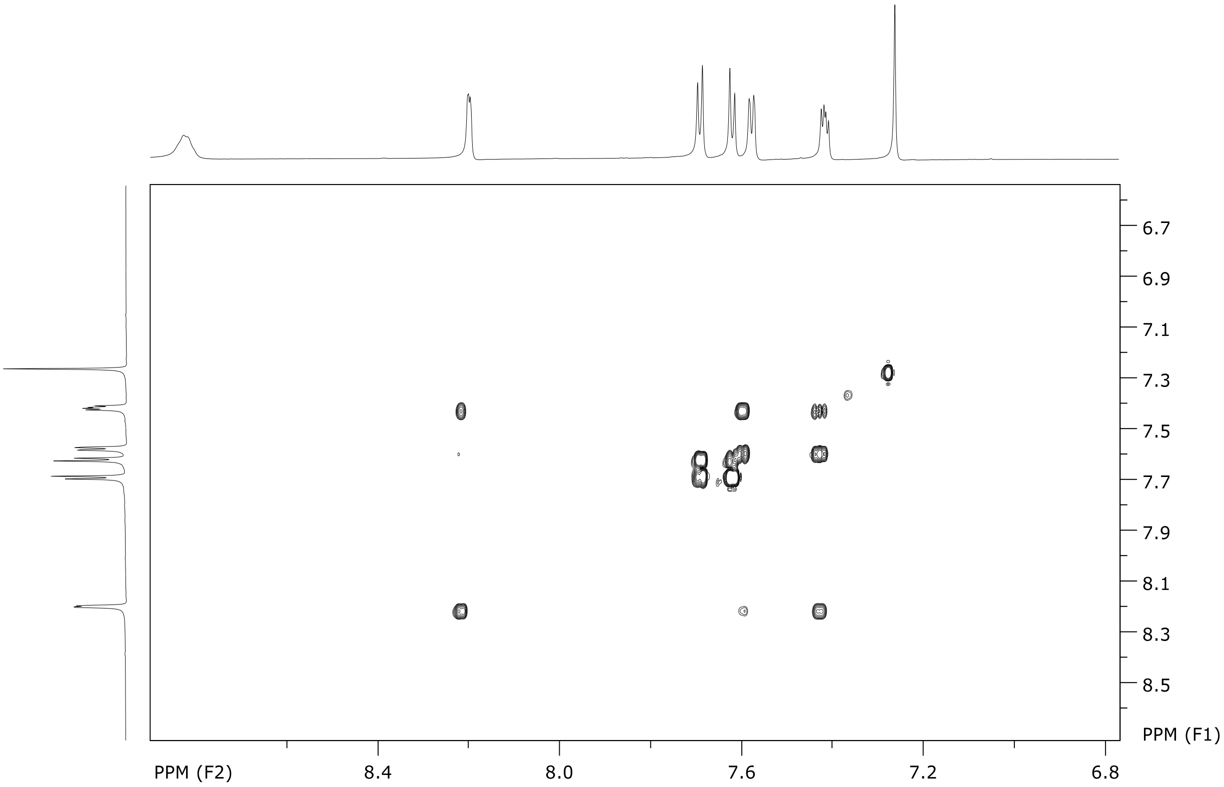
60
50
40
30
20
f1 (ppm)

COSY for **2**



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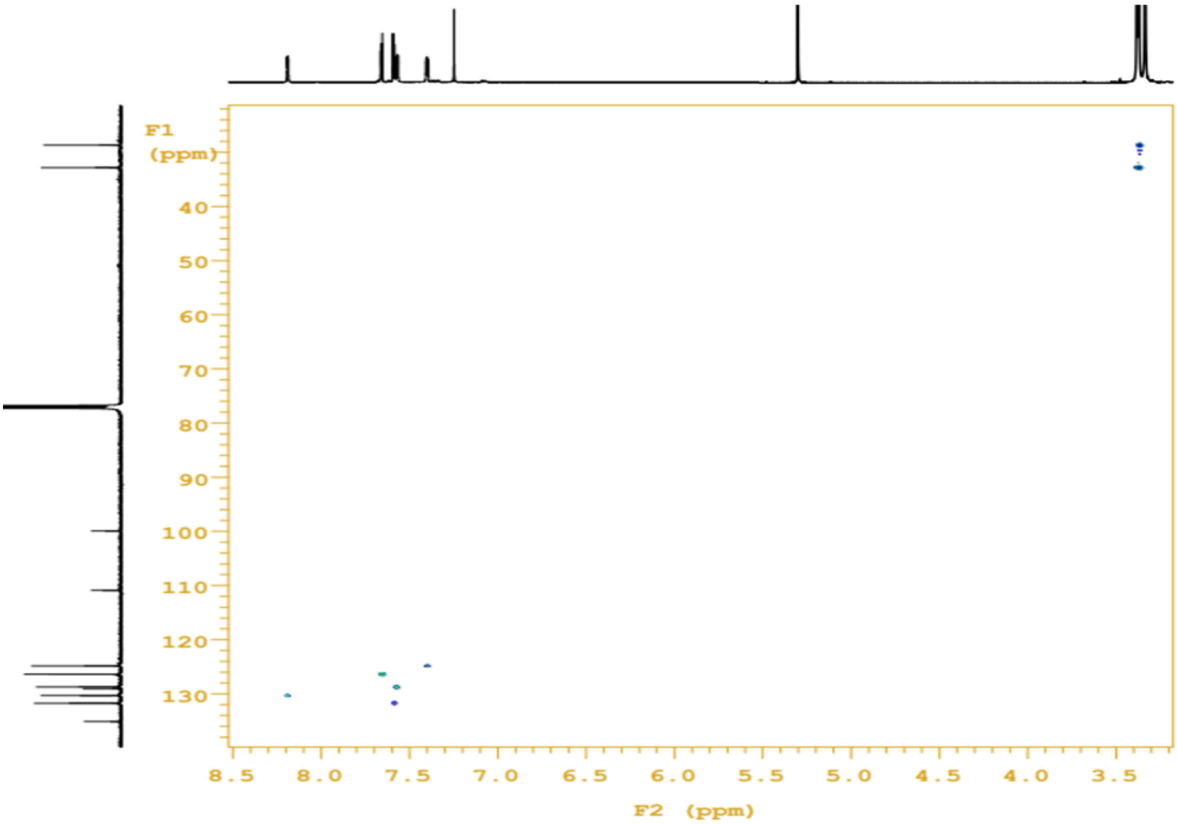

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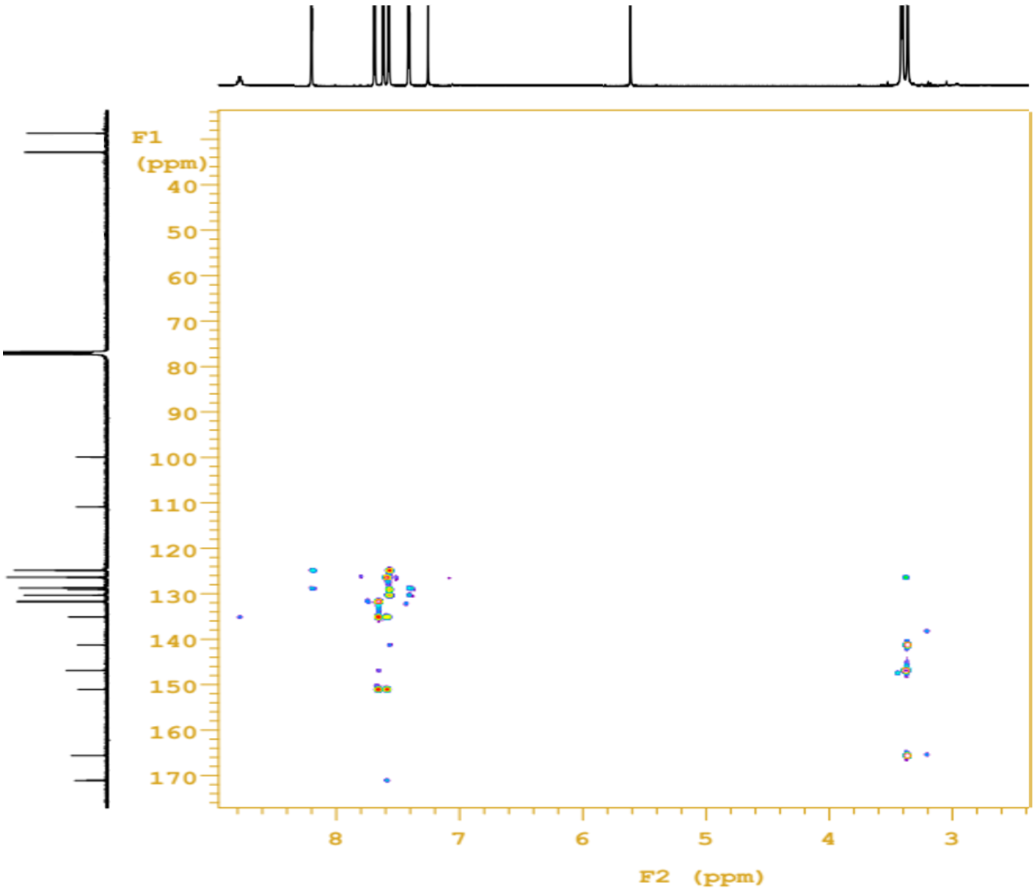

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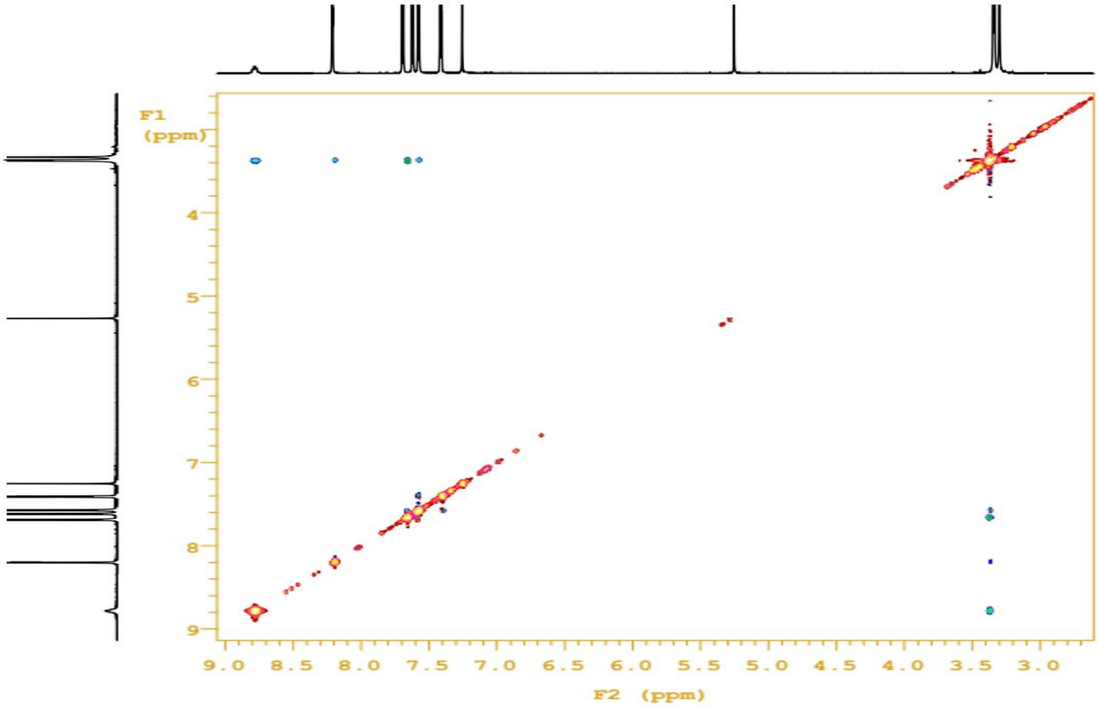

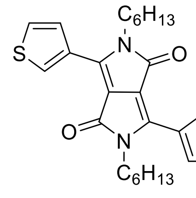
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O
N
C6H13
S

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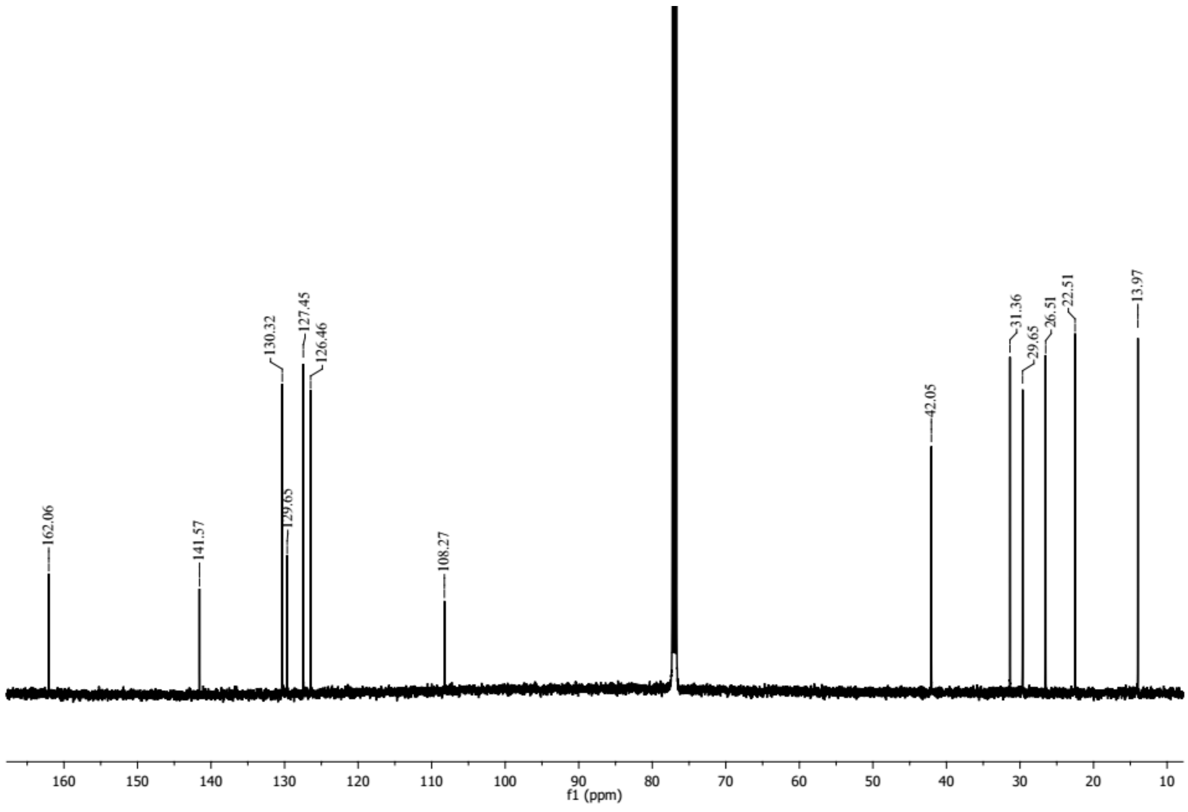
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140
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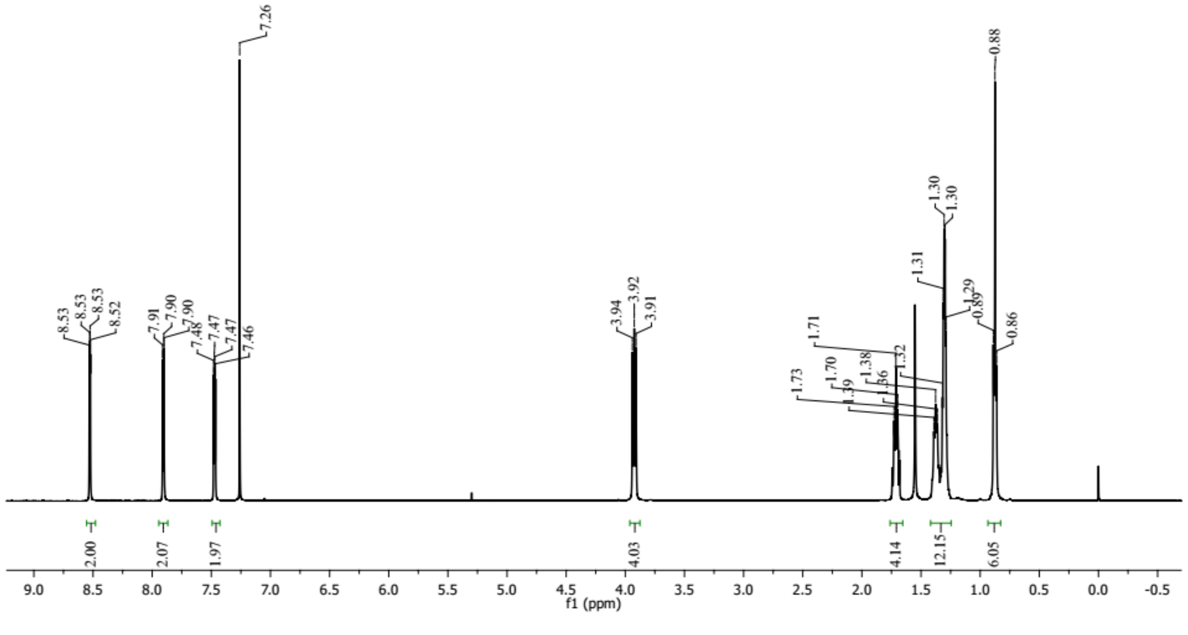
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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3.91
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1.70
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1.36
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1.30
1.29
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7.5
7.0
6.5
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5.0
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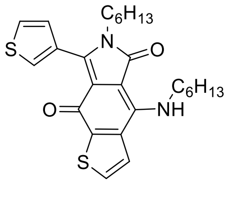
f1 (ppm)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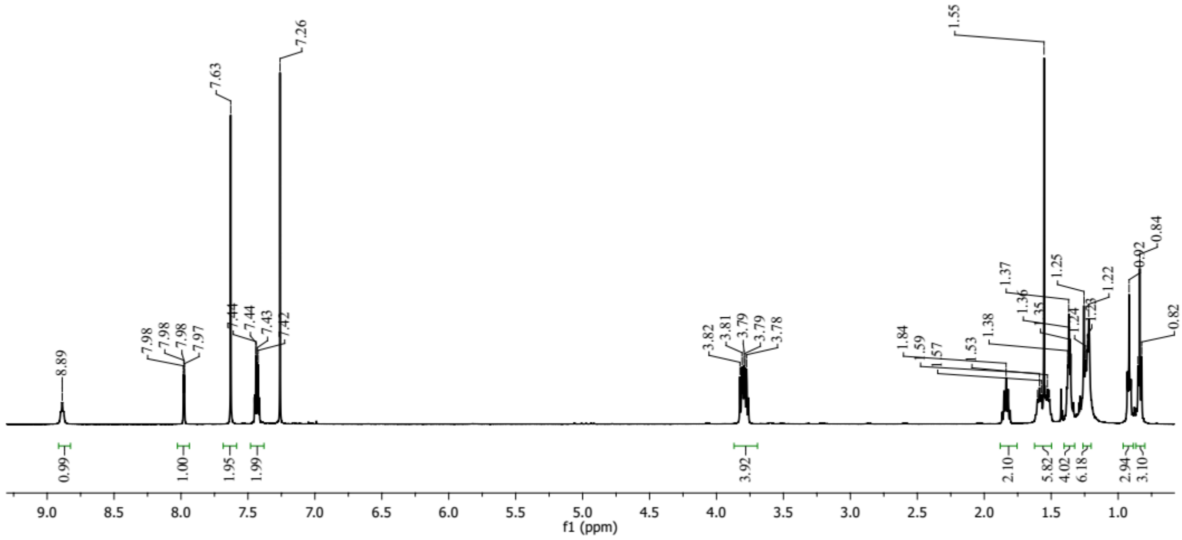
S
C6H13
NH
O
S

**4**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1.53
1.38
1.37
1.36
1.35
1.55
1.25
1.24
1.23
1.22
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0.84
0.82
0.99
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1.95
1.99
3.92
2.10
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4.02
6.18
2.94
3.10
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8.5
8.0
7.5
7.0
6.5
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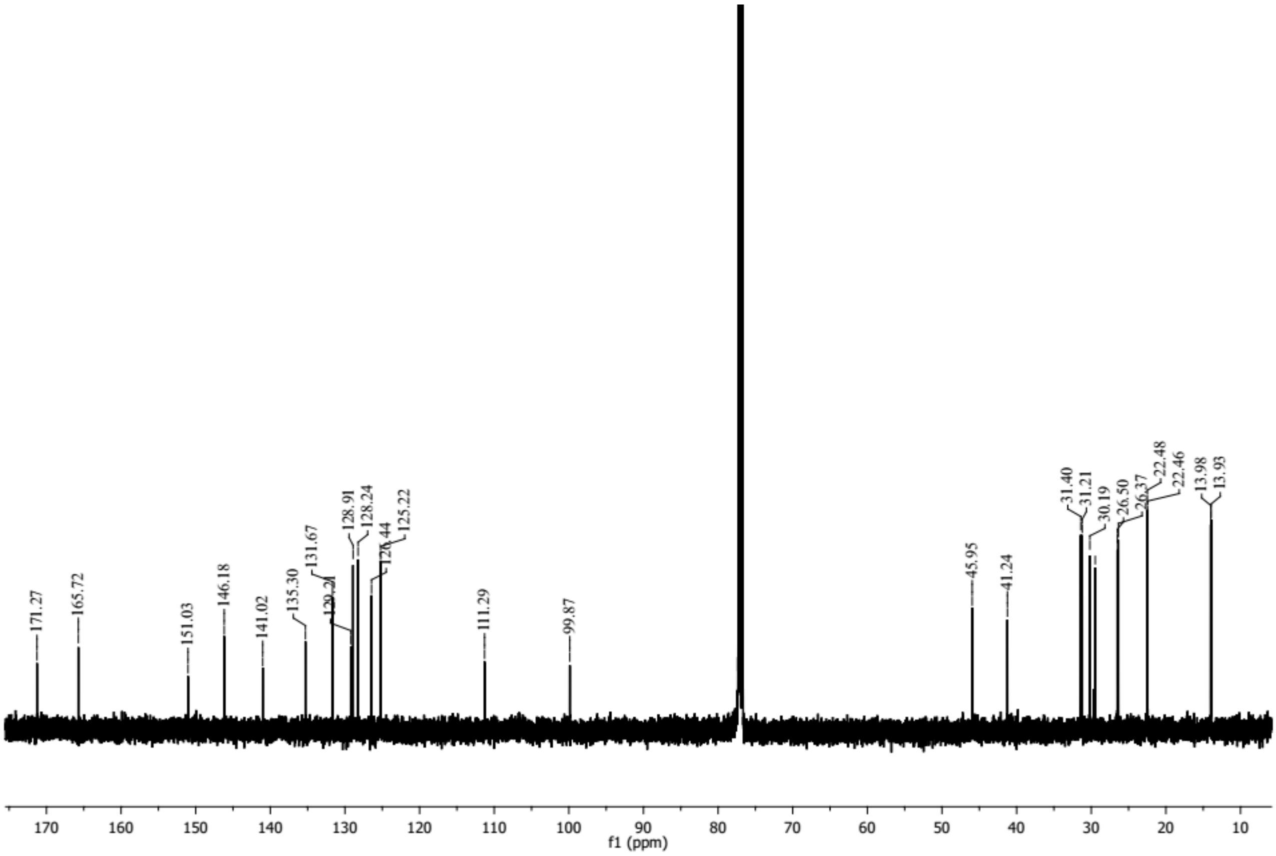
f1 (ppm)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129.21
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128.24
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111.29
99.87
45.95
41.24
31.40
31.21
30.19
26.50
26.37
22.48
22.46
13.98
13.93
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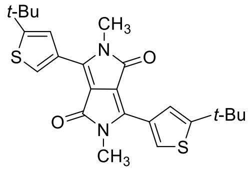
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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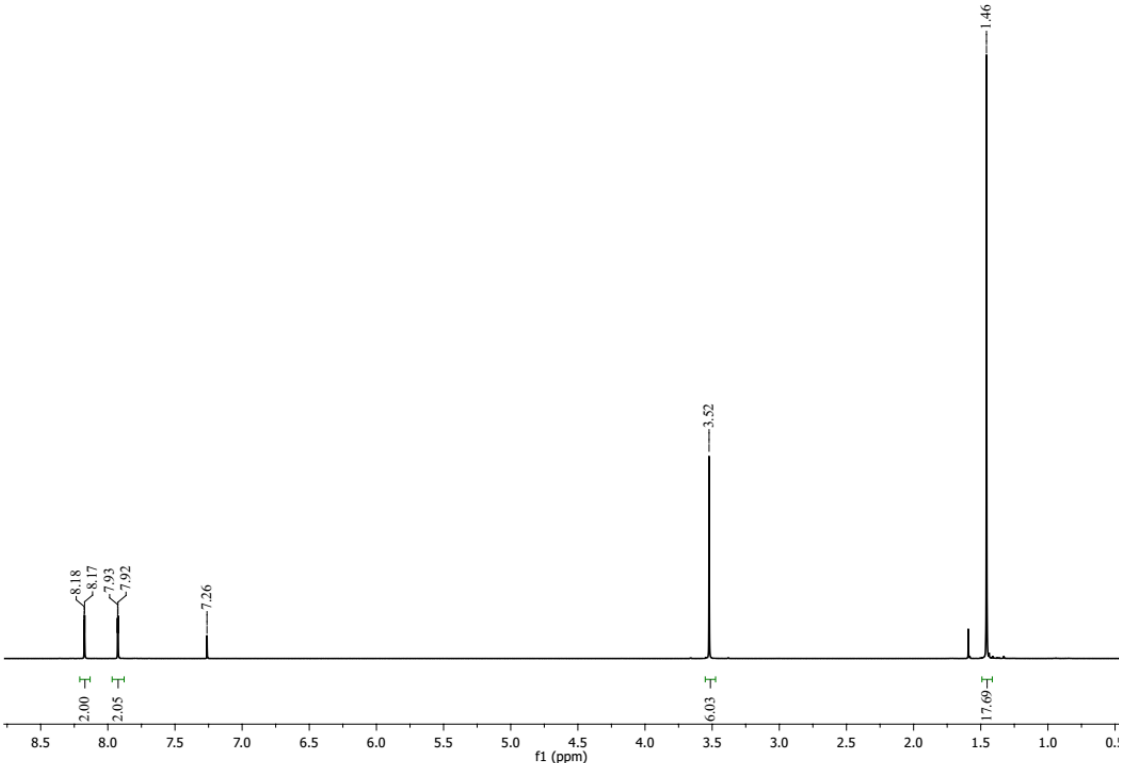
S
O
N
CH3
t-Bu
S

**5**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7.5
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6.5
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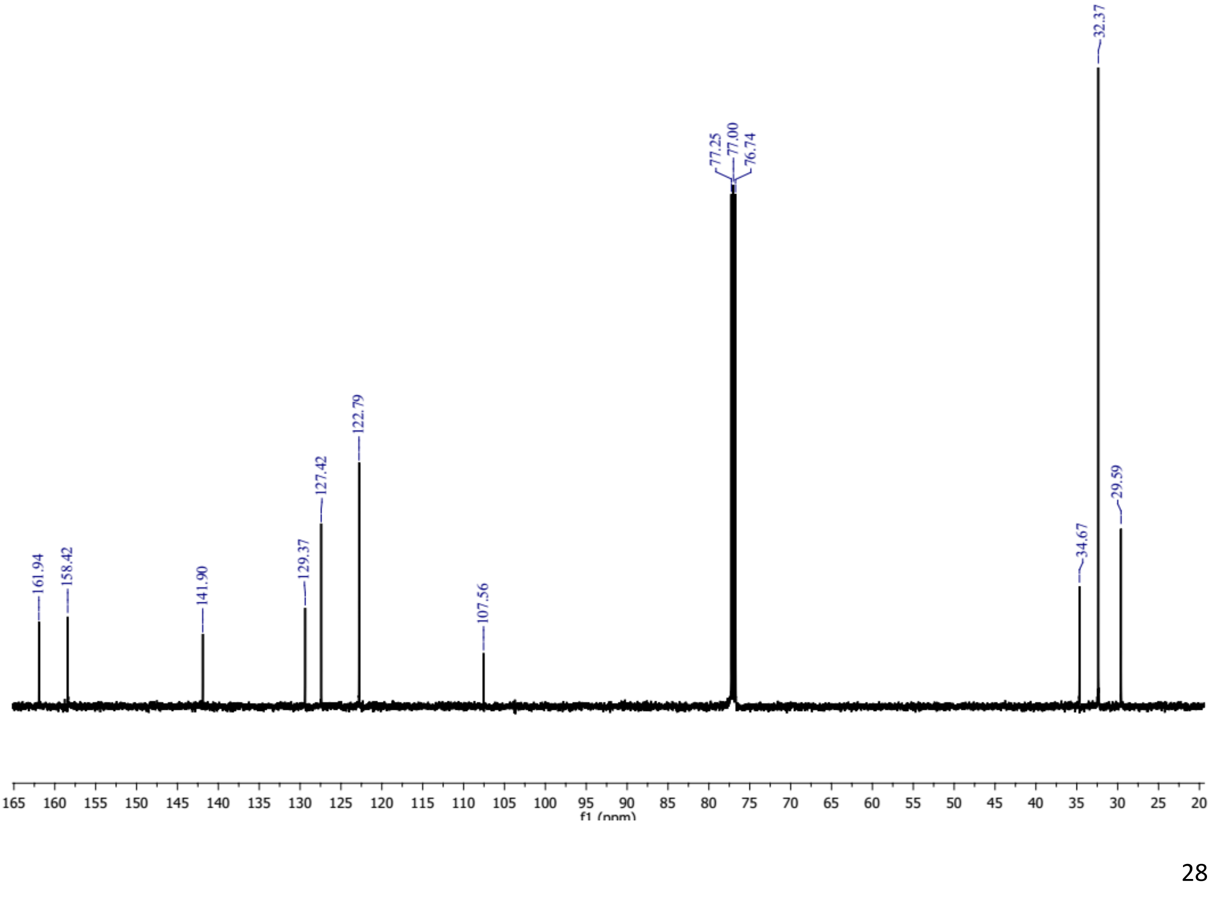
f1 (ppm)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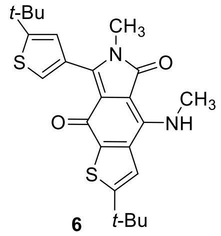
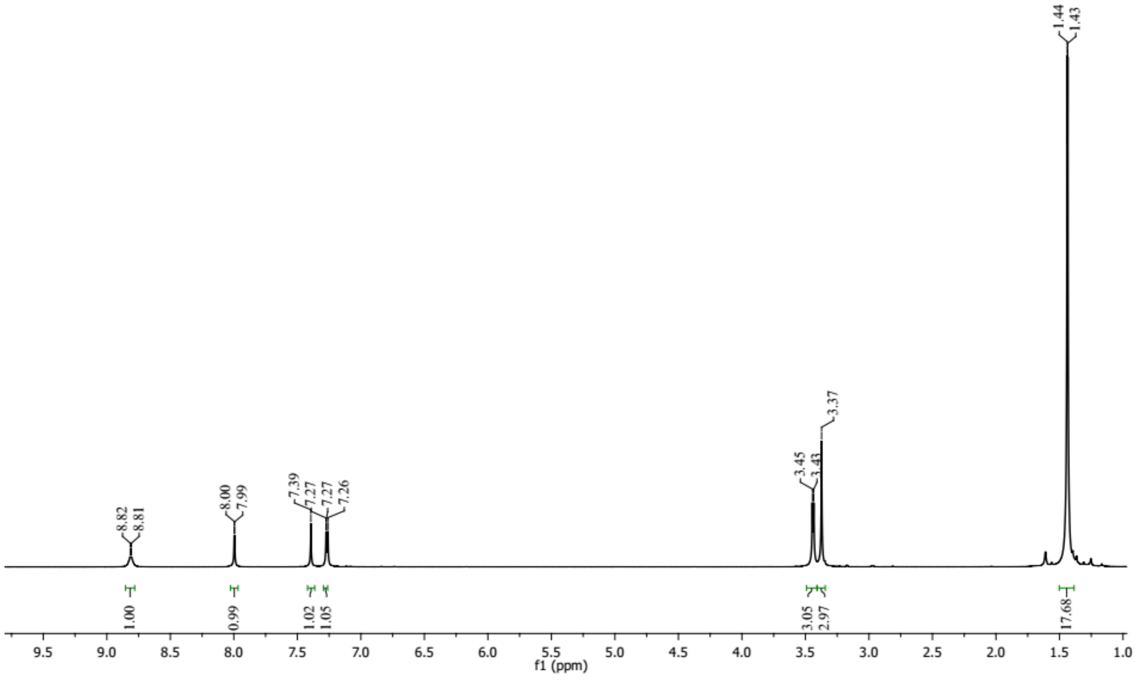
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

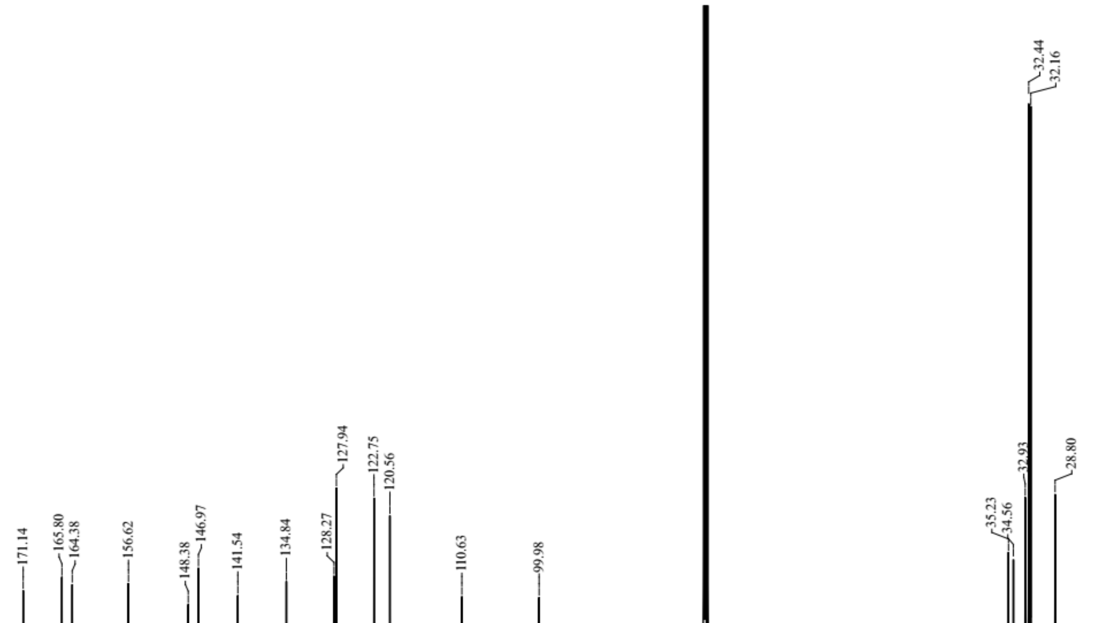


t-Bu
CH3
N
O
S
CH3
NH
O
S
t-Bu

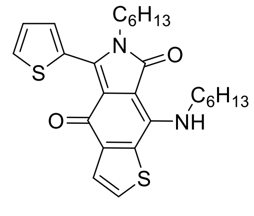
**6**



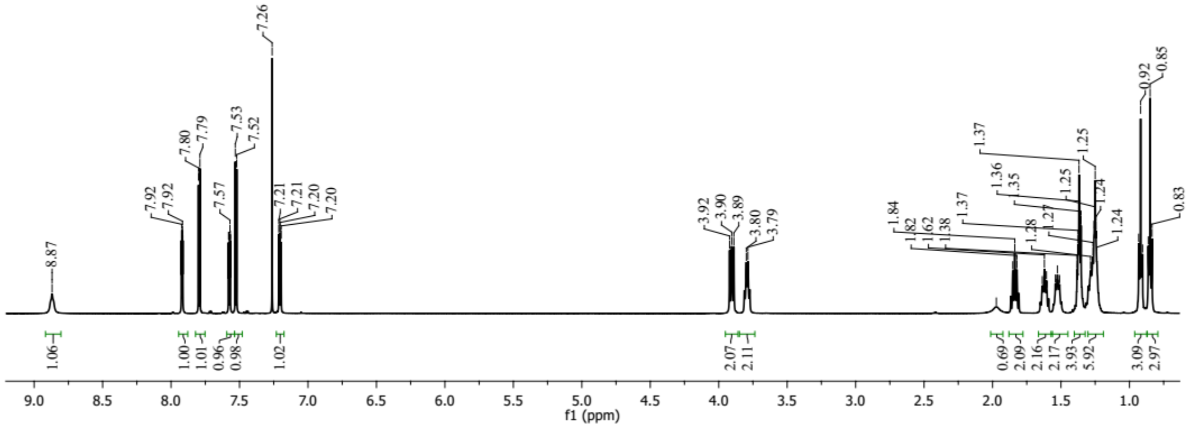
8.82
8.81
8.00
7.99
7.39
7.27
7.27
7.26
3.45
3.43
3.37
1.44
1.43
1.00
0.99
1.02
1.05
3.05
2.97
17.68
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

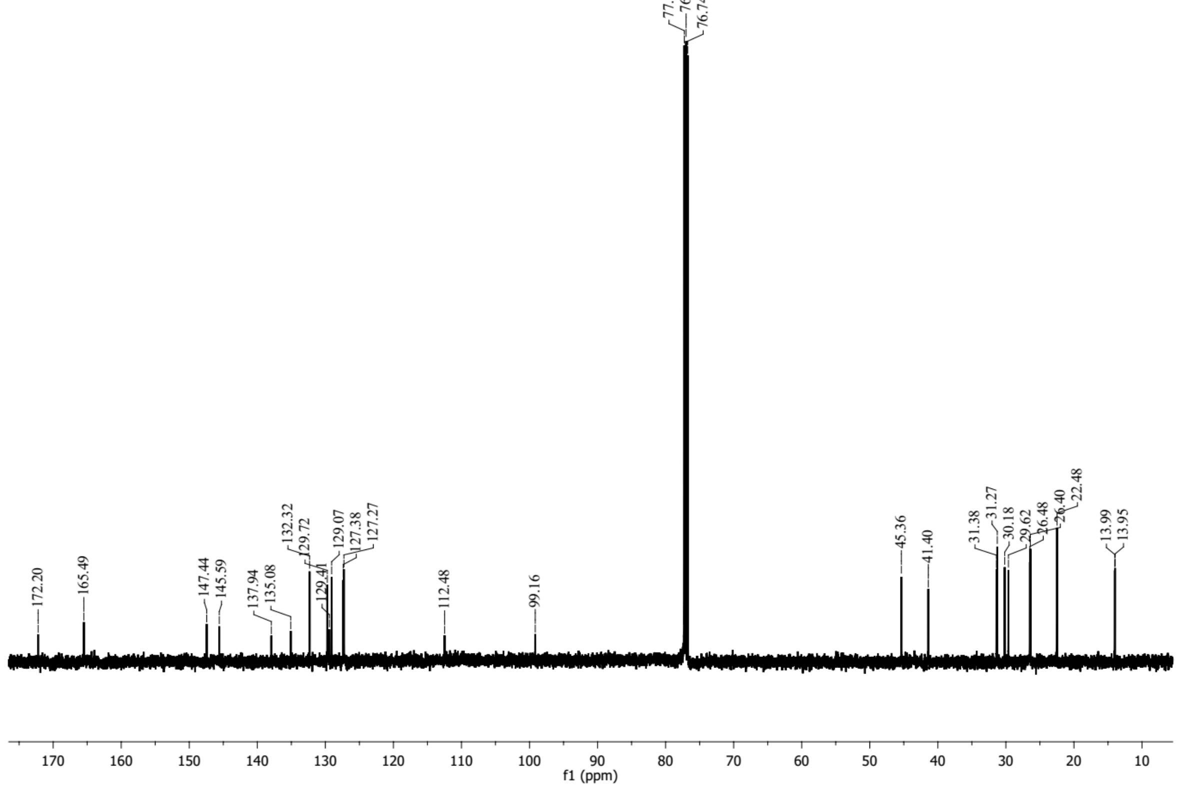


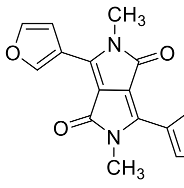
171.14
165.80
164.38
156.62
148.38
146.97
141.54
134.84
128.27
127.94
122.75
120.56
110.63
99.98
35.23
34.56
32.93
32.44
32.16
28.80
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)


C6H13
N
O
S
C6H13
NH
O
S

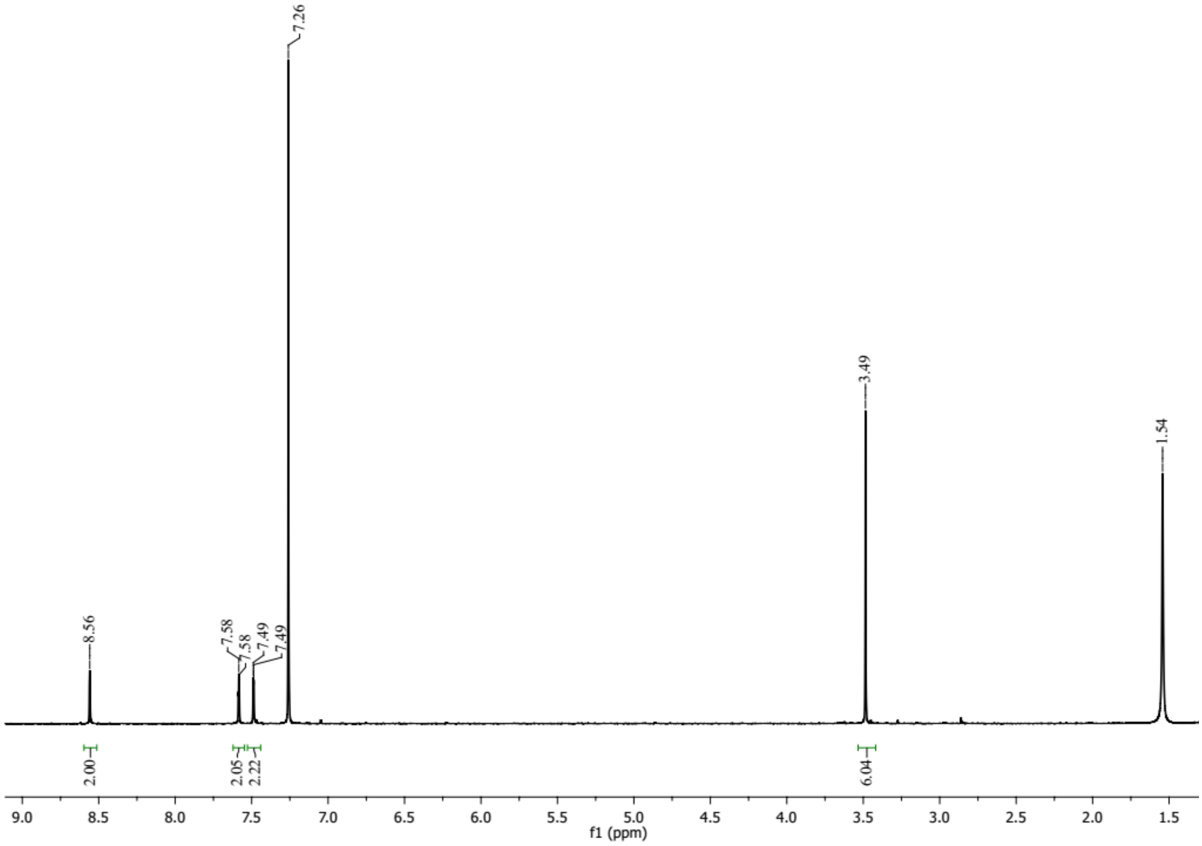
**8**

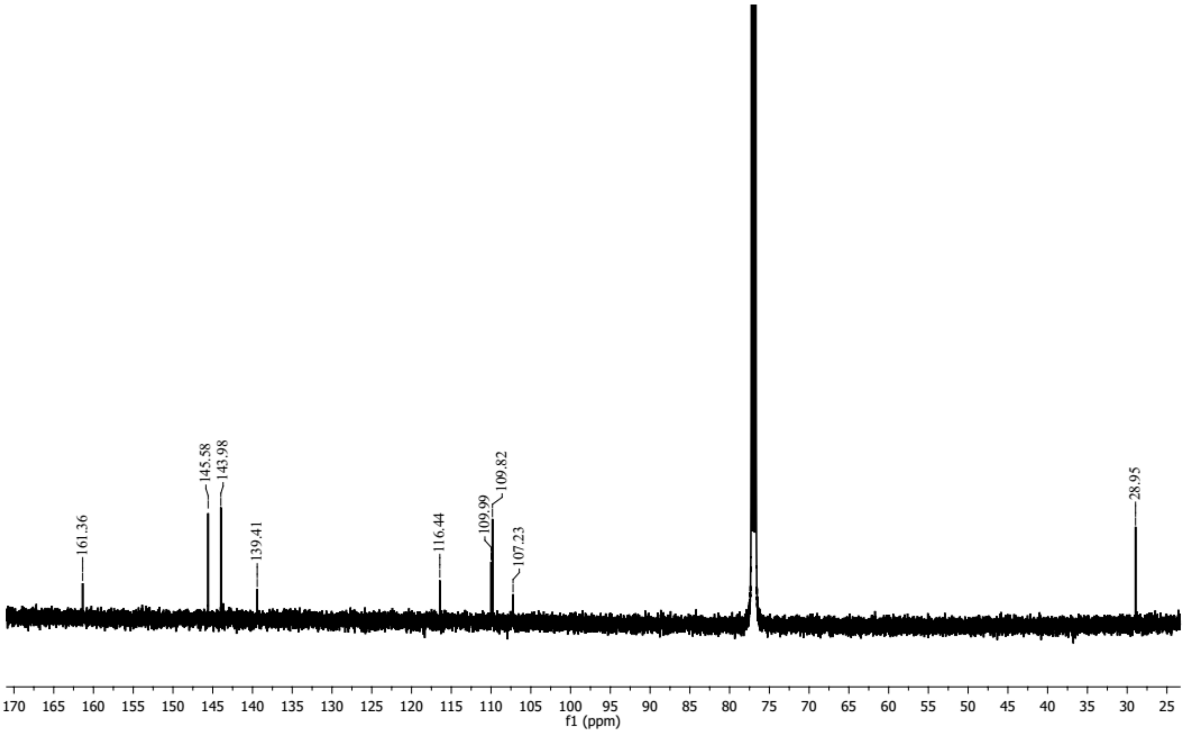

8.87
7.92
7.92
7.80
7.79
7.57
7.53
7.52
7.26
7.21
7.21
7.20
7.20
3.92
3.90
3.89
3.80
3.79
1.84
1.82
1.62
1.38
1.37
1.28
1.37
1.36
1.35
1.27
1.25
1.25
1.24
1.24
0.92
0.85
0.83
1.06
1.00
1.01
0.96
0.98
1.02
2.07
2.11
0.69
2.09
2.16
2.17
3.93
5.92
3.09
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

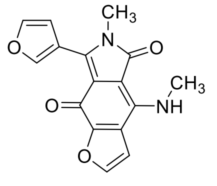

77.25
76.99
76.74
172.20
165.49
147.44
145.59
137.94
135.08
132.32
129.72
129.41
129.07
127.38
127.27
112.48
99.16
45.36
41.40
31.38
31.27
30.18
29.62
26.48
26.40
22.48
13.99
13.95
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


CH3
N
O
O
O
N
CH3
O

**9**

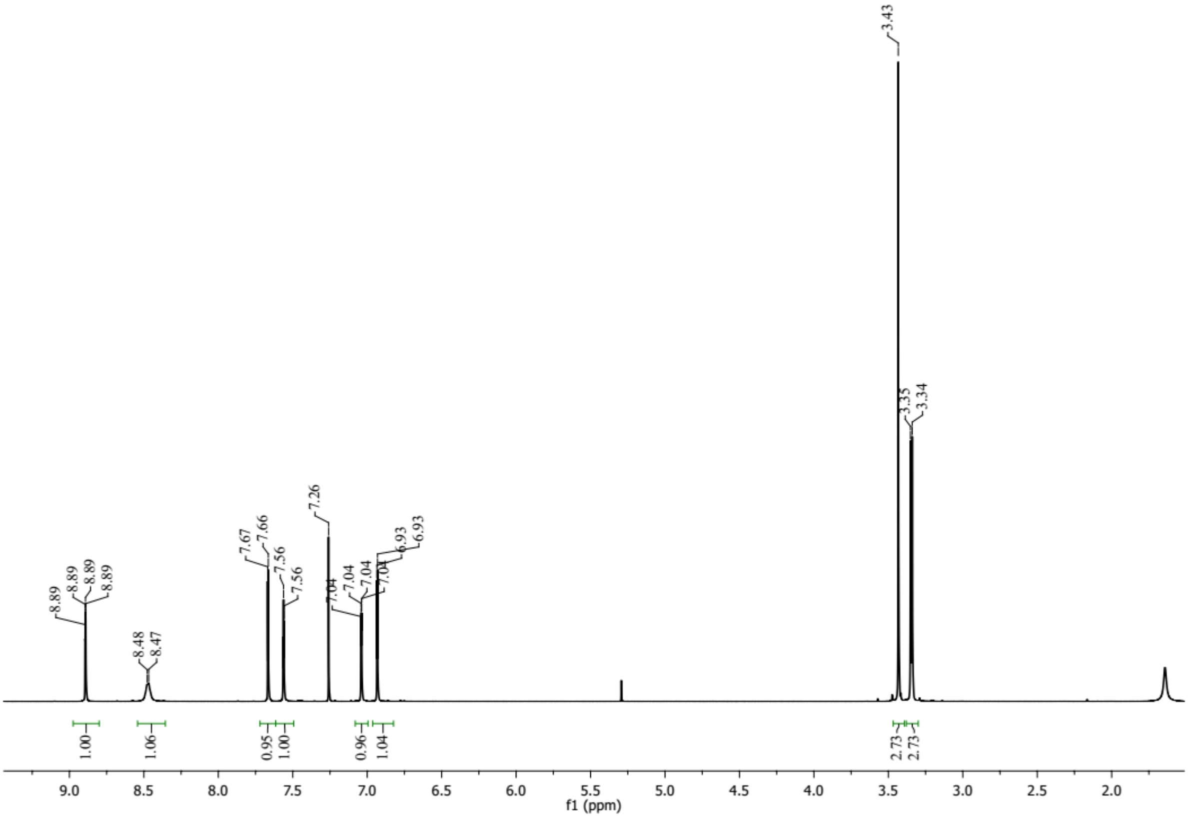

7.26
8.56
7.58
7.58
7.49
7.49
3.49
1.54
2.00
2.05
2.22
6.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


161.36
145.58
143.98
139.41
116.44
109.99
109.82
107.23
28.95
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

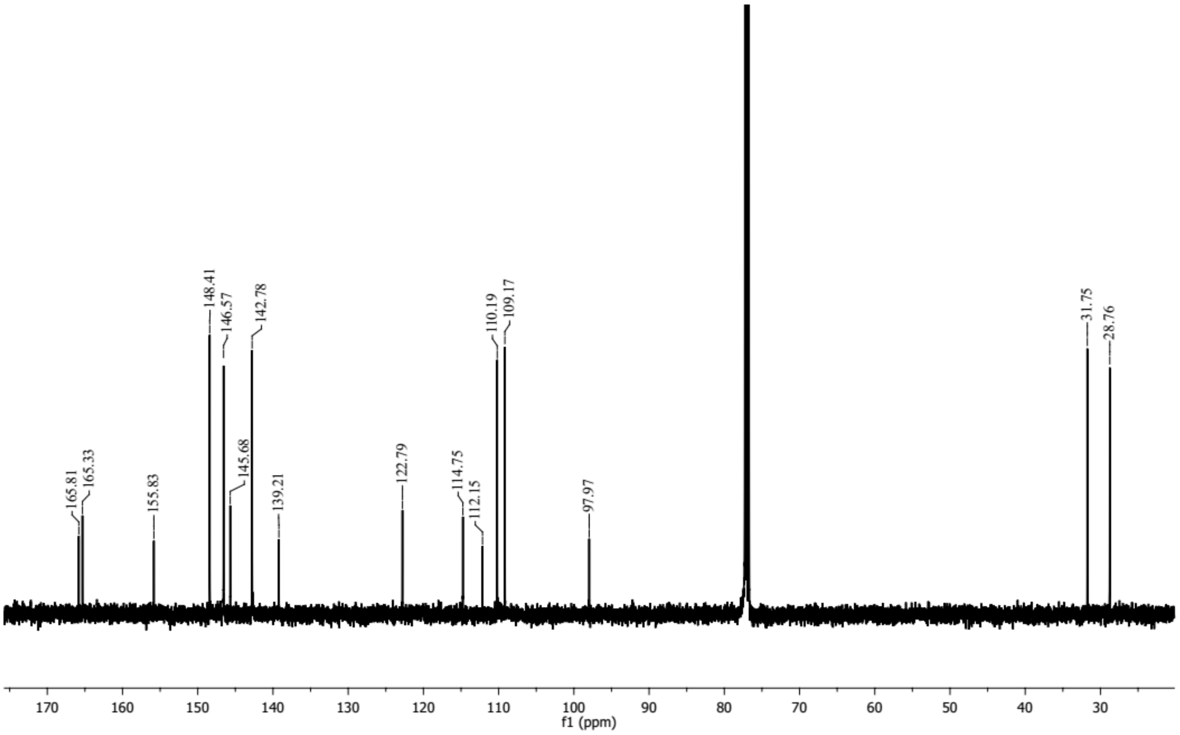


O
N
CH3
O
O
NH
CH3
O

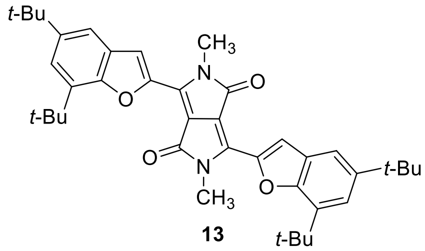
**10**



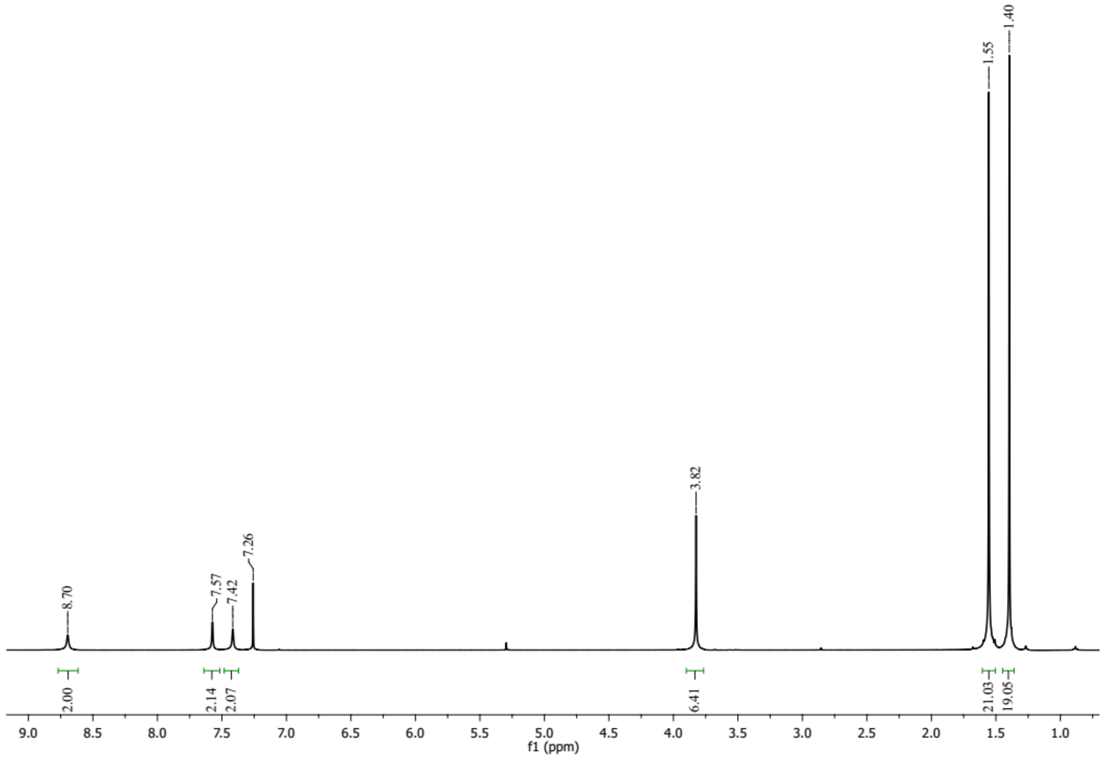
8.89
8.89
8.89
8.89
8.48
8.47
7.67
7.66
7.56
7.56
7.26
7.04
7.04
7.04
7.04
6.93
6.93
3.43
3.35
3.34
1.00
1.06
0.95
1.00
0.96
1.04
2.73
2.73
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

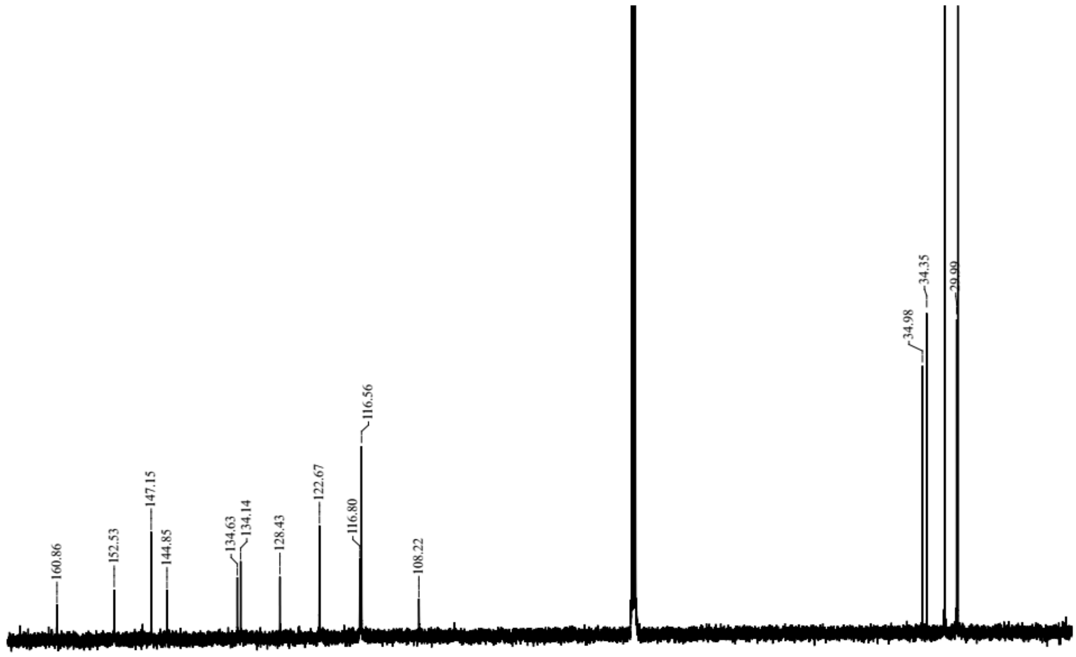


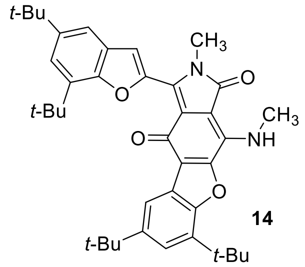
165.81
165.33
155.83
148.41
146.57
145.68
142.78
139.21
122.79
114.75
112.15
110.19
109.17
97.97
31.75
28.76
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


t-Bu
CH3
N
O
O
t-Bu
O
N
CH3
O
t-Bu
t-Bu

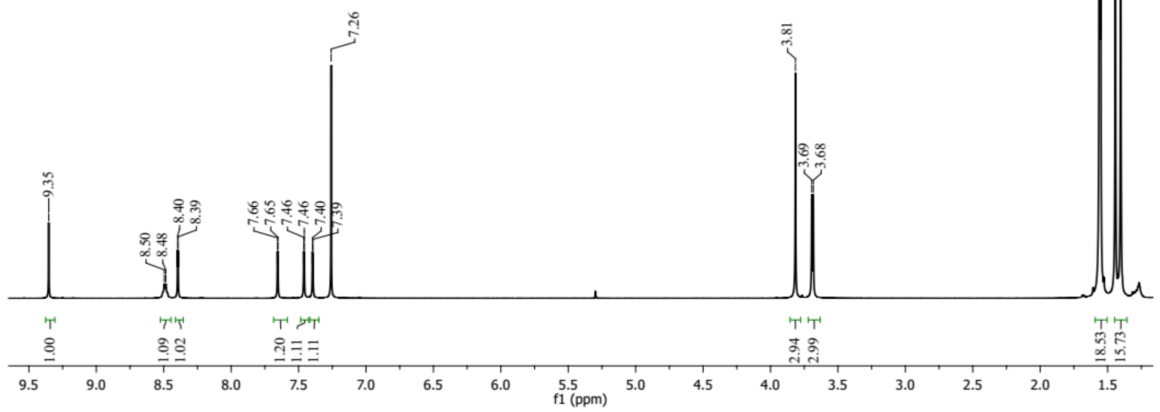
**13**

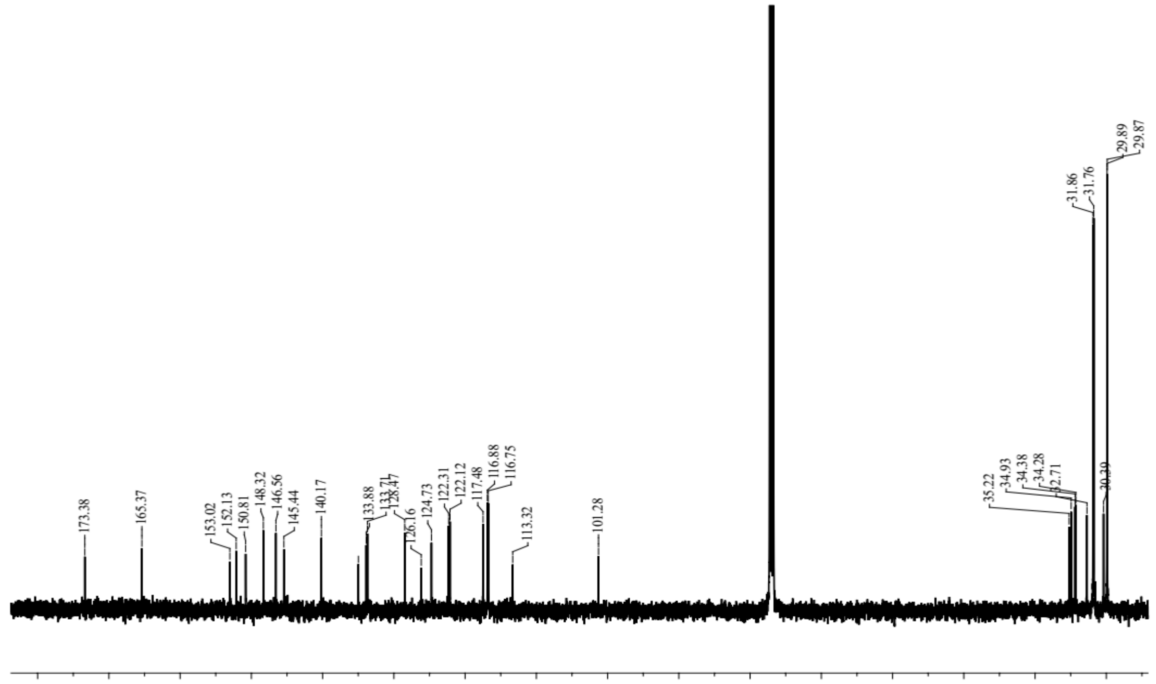

8.70
7.57
7.42
7.26
3.82
1.55
1.40
2.00
2.14
2.07
6.41
21.03
19.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

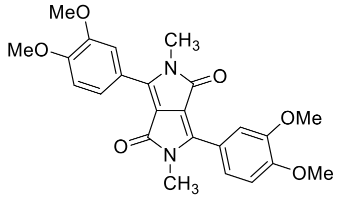

160.86
152.53
147.15
144.85
134.63
134.14
128.43
122.67
116.80
116.56
108.22
34.98
34.35
29.99
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


t-Bu
CH3
N
O
t-Bu
O
CH3
NH
O
O
t-Bu
t-Bu

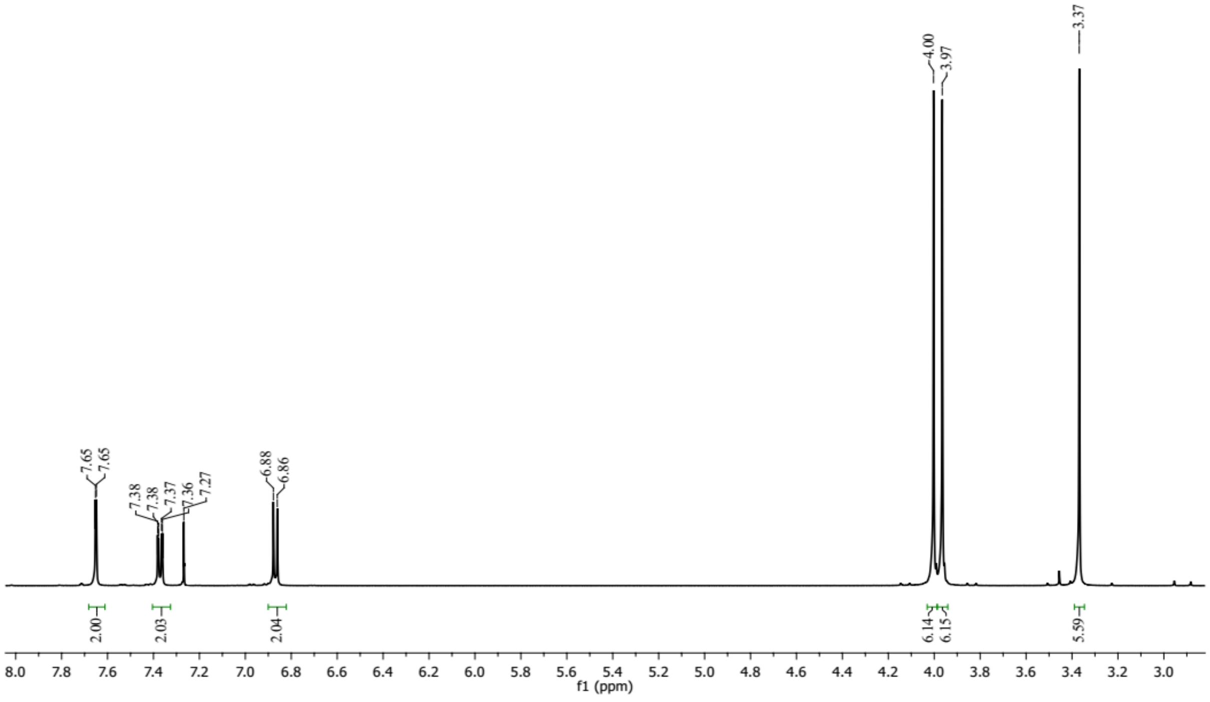
**14**

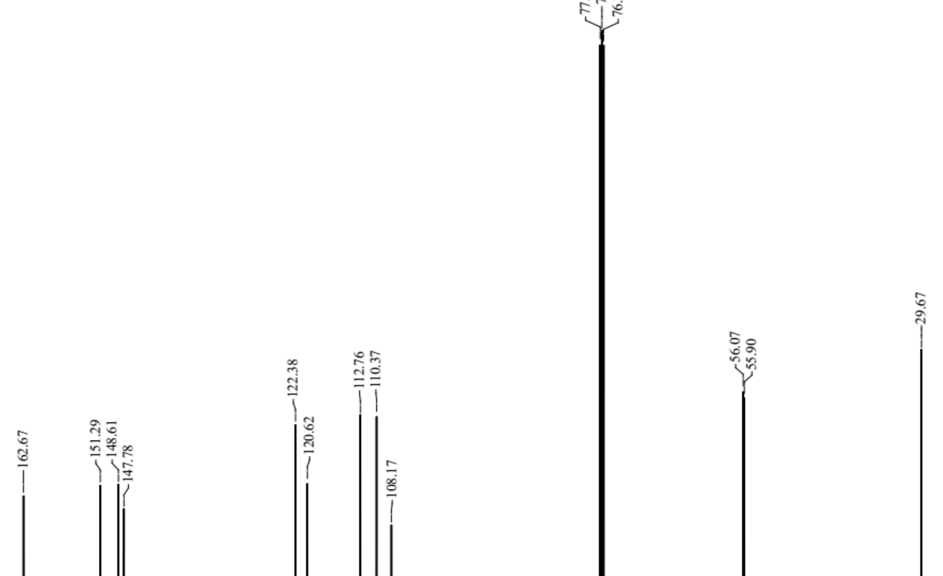

9.35
8.50
8.48
8.40
8.39
7.66
7.65
7.46
7.46
7.40
7.39
7.26
3.81
3.69
3.68
1.00
1.09
1.02
1.20
1.11
1.11
2.94
2.99
18.53
15.73
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

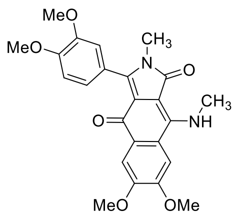

173.38
165.37
153.02
152.13
150.81
148.32
146.56
145.44
140.17
133.88
133.71
128.47
126.16
124.73
122.31
122.12
117.48
116.88
116.75
113.32
101.28
35.22
34.93
34.38
34.28
32.71
31.86
31.76
30.39
29.89
29.87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


MeO
MeO
CH3
N
O
OMe
O
N
OMe
CH3

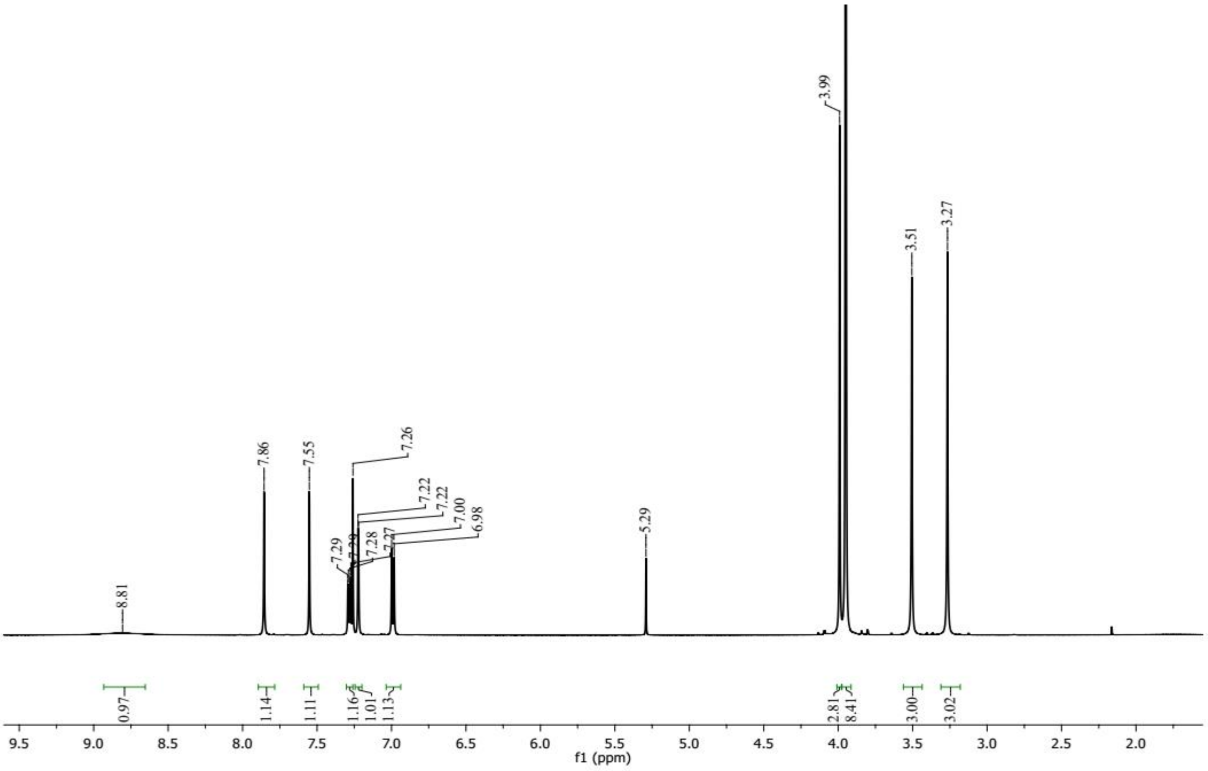
**15**

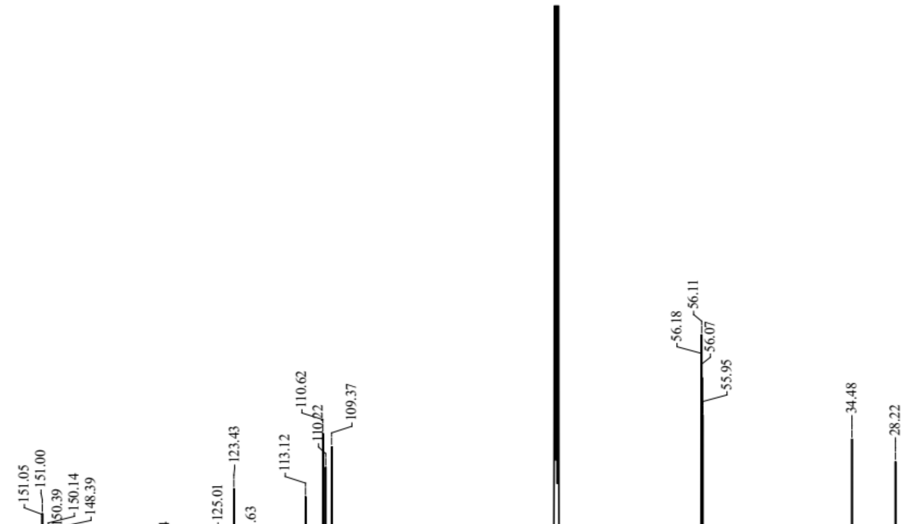

7.65
7.65
7.38
7.38
7.37
7.36
7.27
6.88
6.86
4.00
3.97
3.37
2.00
2.03
2.04
6.14
6.15
5.59
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
f1 (ppm)


162.67
151.29
148.61
147.78
122.38
120.62
112.76
110.37
108.17
77.25
77.00
76.74
56.07
55.90
29.67
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


MeO
MeO
CH3
N
O
O
NH
CH3
MeO
OMe

**16**


8.81
7.86
7.55
7.29
7.28
7.27
7.26
7.22
7.22
7.00
6.98
5.29
3.99
3.51
3.27
0.97
1.14
1.11
1.16
1.01
1.13
2.81
8.41
3.00
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


174.93
165.79
151.05
151.00
150.39
150.14
148.39
144.13
133.34
125.01
123.43
121.63
113.12
110.62
110.22
109.66
109.37
100.79
56.18
56.11
56.07
55.95
34.48
28.22
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)