Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Fused donor-acceptor π-conjugated diazatruxenone: synthesis and electronic properties

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1. Synthesis and Characterization of compounds 3-11

10,15-Dihydro-5*H*-diindolo[1,2-*a*:1',2'-*c*]fluoren-5-one (3) and 2,2-di(1*H*-indol-3-yl)-1*H*-indene-1,3(2*H*)-dione (4): A mixture of indole (500 mg, 4.3 mmol), and indanetrione (380 mg, 2.1 mmol) in glacial acetic acid (15 mL) was heated under refluxing conditions with stirring for 18 h. The clear light yellow solution became dark red after a few minutes. The mixture was cooled to room temperature, the glacial acetic acid was evaporated by vacuum and the residue was washed with $CHCl_3$ and filtered to give **3** as a dark powder (450 mg, 60%). Compound **4** was obtained upon evaporation of the filtrate and purification of the residue by column chromatography (hexane:AcOEt 2:1) as a yellow solid (135 mg, 20%).

Compound 3: ^{1}H-NMR (300 MHz, DMSO-d_6) δ 11.95 (s, 1H, NH), 11.74 (s, 1H, NH), 9.08 (d, *J*=7.9 Hz, 1H), 8.76 (d, *J*=7.8 Hz, 1H), 8.17 (d, *J*=7.2 Hz, 1H), 7.75 (d, *J*=8.2 Hz, 1H), 7.67 (m, 1H), 7.58 (m, 3H), 7.47 (m, 1H), 7.39 (m, 1H), 7.26 (m, 2H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ 194.9, 144.6, 142.7, 141.4, 140.7, 135.7, 135.2, 134.1, 132.6, 127.7, 127.1, 126.4, 125.4, 124.4, 123.9, 122.6, 122.4, 121.7, 121.7, 121.0, 120.4, 120.0, 113.9, 113.2, 112.3, 111.7. MALDI-TOF MS m/z 358.2 (M^++1); HRMS (MALDI-TOF) calcd for $C_{25}H_{14}N_2O$: 358.1101 found: 358.1112. mp 185-186 ºC

Compound 4: ^{1}H-NMR (300 MHz, $CDCl_3$) 8.17 (s, 2H, NH), 8.09 (m, 2H), 7.91 (m, 2H), 7.46 (d, *J*=8.1 Hz, 2H), 7.32 (d, *J*=7.2 Hz, 2H), 7.15 (t, *J*=7.6 Hz, 2H), 6.99 (m, 2H), 6.95 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 199.6, 140.5, 136.7, 136.1, 125.7, 125.2, 124.1, 122.3, 121.0, 119.9, 111.8, 111.3, 59.5. ESI-MS [M+Na]+ m/z 399; HRMS (ESI +) calcd for $C_{25}H_{16}N_2O_2Na$: 399.1103 found: 399.1101. mp 180-183 ºC

7,12-dibromo-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (5): A mixture of 6-bromo-1*H*-indole (500 mg, 2.5 mmol), and indanetrione (227 mg, 1.27 mmol) in glacial acetic acid (15 mL) was heated under refluxing conditions with stirring for 18 h. The clear light yellow solution became dark red after a few minutes. The mixture was cooled to room temperature, the glacial acetic acid was evaporated by vacuum and the residue was washed with $CHCl_3$ and filtered to give **5** as a dark powder (550 mg, 83%). ^{1}H-NMR (300 MHz, Acetone-d_6) δ 11.31 (s, 1H), 11.08 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.69 (m, 2H), 7.46 (m, 2H), 7.35 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H).^{13}C-NMR (75 MHz, Acetone-d_6) δ 194.0, 144.1, 142.6, 142.0, 135.5,

134.2, 133.9, 132.8, 127.1, 125.9, 125.7, 123.2, 123.2, 122.9, 122.4, 122.0, 121.5, 121.0, 119.9, 119.5, 118.7, 114.4, 113.8, 113.5, 112.2. MALDI-TOF MS m/z 516.0 (M^+ +1); HRMS (MALDI-TOF) calcd for $C_{25}H_{12}Br_2N_2O$: 515.9292 found: 515.9302. mp >400 ºC

5,10-dimethyl-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (6): A mixture of diazatruxene (150 mg, 0.42 mmol), KOH (469 mg, 8.4 mmol), and Iodomethane (178.4 mg, 1.2 mmol) in acetone (10 mL) was stirred at room temperature in a sealed tube for 18h. The solvent was evaporated by under a stream of N_2. The mixture was partitioned between H_2O and CH_2Cl_2 and the organic phase dried over $MgSO_4$. The solvent was evaporated and the residue was purified by precipitation with CH_2Cl_2/CH_3CN to give **6** as a dark solid (102.5 mg, 63%).^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.40 (d, *J*=8.0 Hz, 1H), 8.48 (d, *J*=8.2 Hz, 1H), 7.67 (m, 2H), 7.45 (m, 6H), 7.19 (t, *J*=7.2 Hz, 1H), 4.34 (s, 3H), 4.14 (s, 3H). ^{13}C-NMR δ (75 MHz, $CDCl_3$) 194.7, 145.2, 144.7, 143.5, 139.5, 137.9, 134.8, 133.9, 128.3, 126.7, 126.5, 126.4, 125.5, 124.1, 123.6, 122.9, 122.9, 122.1, 121.7, 121.6, 120.4, 116.3, 114.2, 110.4, 108.9, 36.3, 35.6. UV (CH_2Cl_2, 25 ºC) λ_{max} 279 nm (log ε = 4.77). MALDI-TOF MS m/z 386.2 (M^+ +1); HRMS (MALDI-TOF) calcd for $C_{27}H_{18}N_2O$: 386.1414 found: 386.1417. mp 185-190 ºC

5,10-dihexyl-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (7): A mixture of diazatruxene (250 mg, 0.70 mmol), KOH (782 mg, 14 mmol), $[CH_3(CH_2)_3]_4N(HSO_4)$ (12 mg, 0.03 mmol), and 1- Iodohexane (444.3 mg, 2.1 mmol) in acetone (10 mL) was heated at 80 ºC with stirring for 18h. The mixture was cooled to room temperature, partitioned between H_2O and CH_2Cl_2 and the organic phase dried over $MgSO_4$. The solvent was evaporated and the residue was purified by precipitation with CH_2Cl_2/CH_3CN to give **5b** as a dark solid (200.5 mg, 54%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.45 (d, *J*=7.9 Hz, 1H), 8.23 (d, *J*=8.1 Hz, 1H), 7.65 (d, *J*=7.2 Hz, 1H), 7.41 (m, 8H), 7.18 (t, *J*=7.2 Hz, 1H), 4.68 (t, *J*=8.0 Hz, 2H), 4.54 (t, *J*=7.6 Hz, 2H), 2.00 (t, *J*=7.8 Hz, 2H), 1.67 (m, 2H), 1.23 (m, 12H), 0.87 (m, 3H), 0.76 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 194.8, 144.9, 144.3, 142.6, 138.9, 138.0, 134.9, 133.8, 128.4, 126.8, 126.2, 126.1, 125.6, 124.1, 123.5, 123.3, 122.9, 122.6, 120.4, 120.4, 116.7, 114.9, 111.8, 109.4, 47.2, 46.7, 31.5, 31.2, 30.1, 28.5, 26.4, 26.2, 22.5, 22.4, 14.0, 13.9. UV (CH_2Cl_2, 25 ºC) λ_{max} 280 nm (log ε = 4.92). MALDI-TOF MS m/z 526.4 (M^+ +1); HRMS (MALDI-TOF) calcd for $C_{37}H_{38}N_2O$: 526.2979 found: 526.2985. mp 110-115 ºC

5,10-didodecyl-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (8): A mixture of diazatruxene (500 mg, 1.4 mmol), KOH (1.5 g, 28 mmol), $[CH_3(CH_2)_3]_4N(HSO_4)$ (24 mg, 0.07 mmol), and 1- Iodododecane (1.2 g, 4.2 mmol) in acetone (15 mL) was heated at 80 ºC with stirring for 18h. The mixture was cooled to room temperature, it was partitioned between H_2O and CH_2Cl_2 and the organic phase dried over $MgSO_4$. The solvent was evaporated and the residue was purified by precipitation with CH_2Cl_2/CH_3CN to give **5c** as a red solid (200.5 mg, 57%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.46 (d, *J*=7.9 Hz, 1H), 8.26 (d, *J*=8.2 Hz, 1H), 7.67 (d, *J*=7.0 Hz, 1H), 7.42 (m, 8H), 7.18 (t, *J*=7.3 Hz, 1H), 4.72 (d, *J*=8.0 Hz, 2H), 4.57 (d, *J*=7.6 Hz, 2H), 2.01 (t, *J*=7.7 Hz, 2H), 1.70 (m, 2H), 1.23 (m, 36H), 0.90 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 194.7, 144.9, 144.2, 142.6, 138.9, 137.9, 134.8, 133.8, 128.3, 126.7, 126.2, 126.0, 125.6, 124.0, 123.5, 123.3, 122.8, 122.6, 122.6, 120.4, 120.3, 116.6, 114.8, 111.7, 109.4, 47.1, 46.7, 31.9, 30.2, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 29.3, 29.0, 28.6, 26.6, 26.4, 22.7, 14.2. UV (CH_2Cl_2, 25 ºC) λ_{max} 279 nm (log ε = 4.76). MALDI-TOF MS m/z 694.6 (M^++1); HRMS (MALDI-TOF) calcd for $C_{49}H_{62}N_2O$: 694.4857 found: 694.4849. mp 65-75 ºC.

7,12-dibromo-5,10-didodecyl-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (9): A mixture of **5** (400 mg, 0.77 mmol), KOH (862 mg, 15.4 mmol), $[CH_3(CH_2)_3]_4N(HSO_4)$ (13 mg, 0.03 mmol), and 1- Iodododecane (570 mg, 2 mmol) in acetone (10 mL) was heated at 80 ºC with stirring for 18h. The mixture was cooled to room temperature, partitioned between H_2O and CH_2Cl_2 and the organic phase dried over $MgSO_4$. The solvent was evaporated and the residue was purified by precipitation with CH_2Cl_2/CH_3CN to give **9** as a red solid (250 mg, 39%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.48 (d, *J* = 7.9 Hz, 1H), 8.33 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.57 (m, 3H), 7.45 (m, 1H), 7.37 (m, 2H), 7.21 (t, *J* = 7.1 Hz, 1H), 4.80 (t, *J* = 8.0 Hz, 2H), 4.65 (t, *J* = 7.6 Hz, 2H), 2.03 (m, 2H), 1.72 (m, 2H), 1.18 (m, 36H), 0.89 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 194.1, 144.7, 144.1, 143.1, 138.3, 137.6, 134.4, 133.8, 128.2, 127.0, 126.8, 124.2, 124.0, 123.5, 123.4, 122.7, 122.7, 122.6, 121.8, 121.1, 120.1, 116.0, 116.0, 114.4, 113.8, 113.8, 112.2, 47.0, 46.5, 31.9, 31.9, 30.0, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 28.9, 28.6, 26.5, 26.3, 22.7, 22.7, 14.2, 14.1. MALDI-TOF MS m/z 852.4 (M^+ +1); HRMS (MALDI-TOF) calcd for $C_{49}H_{60}Br_2N_2O$: 852.3053 found: 852.3064. UV (CH_2Cl_2, 25 ºC) λ_{max} 309 nm (log ε = 4.73). mp 90-95 ºC

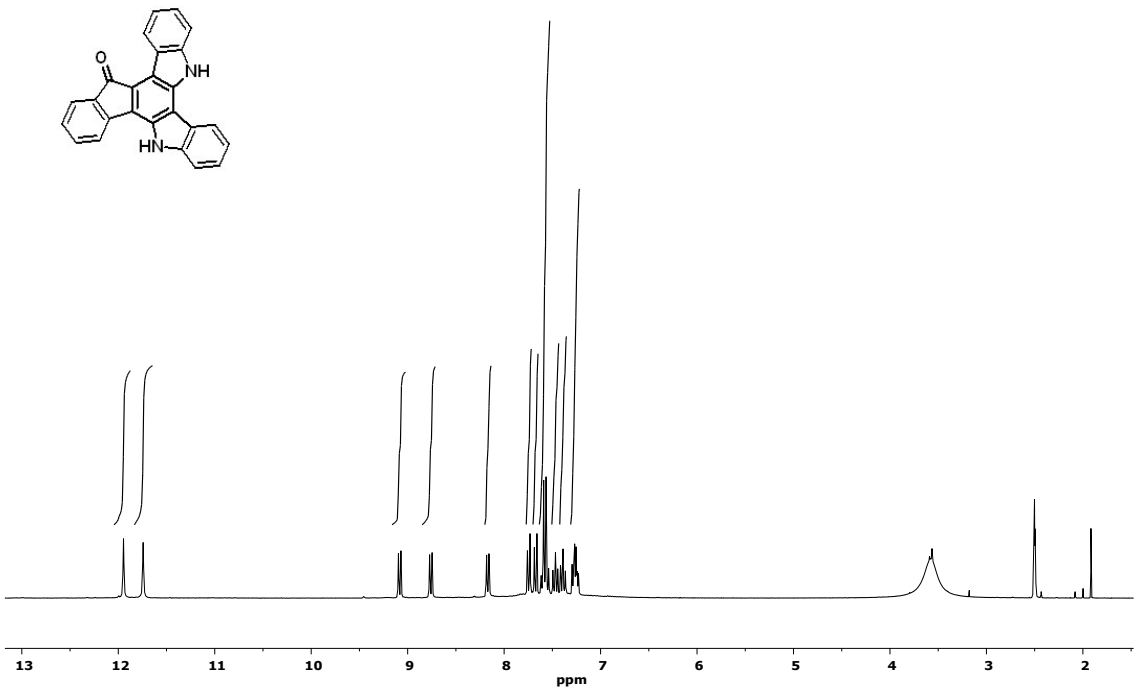
5,10-didodecyl-7,12-bis(4-methoxyphenyl)-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (10): A solution **9** (100 mg, 0.11 mmol), (4-methoxyphenyl)boronic acid (54 mg, 0.35 mmol) and $Pd(PPh_3)_4$ (41 mg, 0.03 mmol) in 9 mL of tetrahydrofuran was carefully degassed over 15 minutes. Then, 1 mL of 2 M aqueous K_2CO_3 was added. The mixture was heated at 150 ºC for 2 hours in a microwave. The mixture was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$ and the solvent was evaporated in vacuum. The residue was purified by column chromatography (hexane/CH_2Cl_2 1:1) to give **10** as a purpura solid (35 mg, 32%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.46 (d, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 7.77-7.70 (m, 4H), 7.67 (m, 2H), 7.58 (s, 1H), 7.53 (m, 3H), 7.44 (t, *J* = 6.9 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.13-7.04 (m, 4H), 4.76 (t, *J* = 8.0 Hz, 2H), 4.62 (t, *J* = 7.5 Hz, 2H), 3.93 (s, 3H). 3.92 (s, 3H), 2.05 (m, 2H), 1.74 (m, 2H), 1.42-1.40 (m, 36H), 0.87 (m, 6H) . ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13C NMR (75 MHz, CDCl3) δ 194.6, 159.3, 159.1, 144.9, 144.7, 143.1, 139.1, 139.0, 138.8, 138.2, 134.9, 134.7, 133.7, 133.7, 128.6, 128.5, 127.9, 126.7, 125.8, 123.9, 123.7, 122.6, 122.4, 122.0, 121.5, 119.6, 119.6, 116.5, 114.6, 114.4, 114.2, 109.3, 107.3, 55.4, 47.1, 46.5, 31.9, 31.9, 30.2, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.2, 28.3, 28.6, 26.6, 26.4, 22.7, 14.2. MALDI-TOF MS m/z 906.6 (M^+); HRMS (MALDI-TOF) calcd for $C_{63}H_{74}N_2O_3$: 906.5694. found: 906.5687. UV (CH_2Cl_2, 25 ºC) λ_{max} (log ε = 3.84). mp 100-105 ºC

5,10-didodecyl-7,12-bis(4-nitrophenyl)-5*H*-indeno[1,2-*a*]indolo[3,2-*c*]carbazol-15(10*H*)-one (11): A solution of **9** (100 mg, 0.11 mmol), (4-nitrophenyl)boronic acid (59 mg, 0.35 mmol) and $Pd(PPh_3)_4$ (34 mg, 0.03 mmol) in 9 mL of tetrahydrofuran was carefully degassed over 15 minutes. Then, 1 mL of 2 M aqueous K_2CO_3 was added. The mixture was heated at 150 ºC for 2 hours in a microwave. The mixture was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$ and the solvent was evaporated in vacuum. The residue was purified by column chromatography (hexane/CH_2Cl_2 1:3) to give **11** as a purpura solid (33 mg, 32%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.42 (d, *J* = 8.6 Hz, 1H), 8.39 (d, *J* = 8.4 Hz, 2H), 8.28 (d, *J* = 8.3 Hz, 2H), 8.20 (d, *J* = 8.30 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.68 (s, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.57-7.40 (m, 5H), 7.19 (t, *J* = 7.1 Hz, 1H), 4.61 (m, 4H), 1.94 (m, 2H), 1.73 (m, 2H), 1.37-0.97 (m, 36H), 0.86 (m, 6H) . ^{13}C-NMR (75 MHz, $CDCl_3$) δ 194.5, 148.3, 147.4, 147.1, 146.1, 144.5, 144.5, 142.9, 139.5, 138.8, 136.6, 134.6, 134.0, 128.9, 128.0, 127.9, 127.2, 126.3, 124.3, 124.1, 124.0, 123.7, 123.1, 122.8, 120.0, 119.9, 116.1, 114.1, 110.3, 108.0, 47.2,

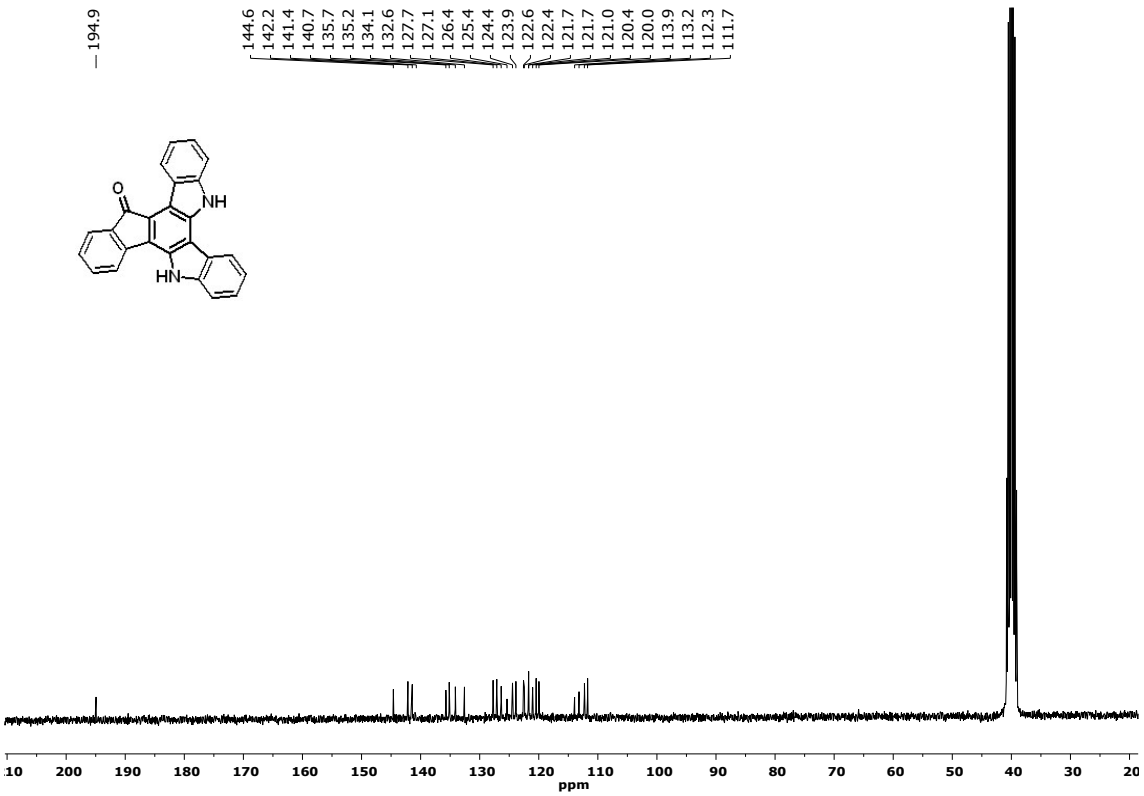
46.6, 31.9, 31.9, 30.2, 29.7, 29.6, 29.4, 29.4, 29.3, 29.3, 29.2, 28.9, 28.6, 26.6, 26.4, 22.7, 14.1. MALDI-TOF MS m/z 936.6 (M^+); HRMS (MALDI-TOF) calcd for $C_{61}H_{68}N_4O_5$: 936.5192 found: 936.5184. UV (CH_2Cl_2, 25 ºC) λ_{max} 282 nm (log ε = 4.67). mp 165-170 ºC

3. 3 Copy of representative NMR spectra of compounds 3-11

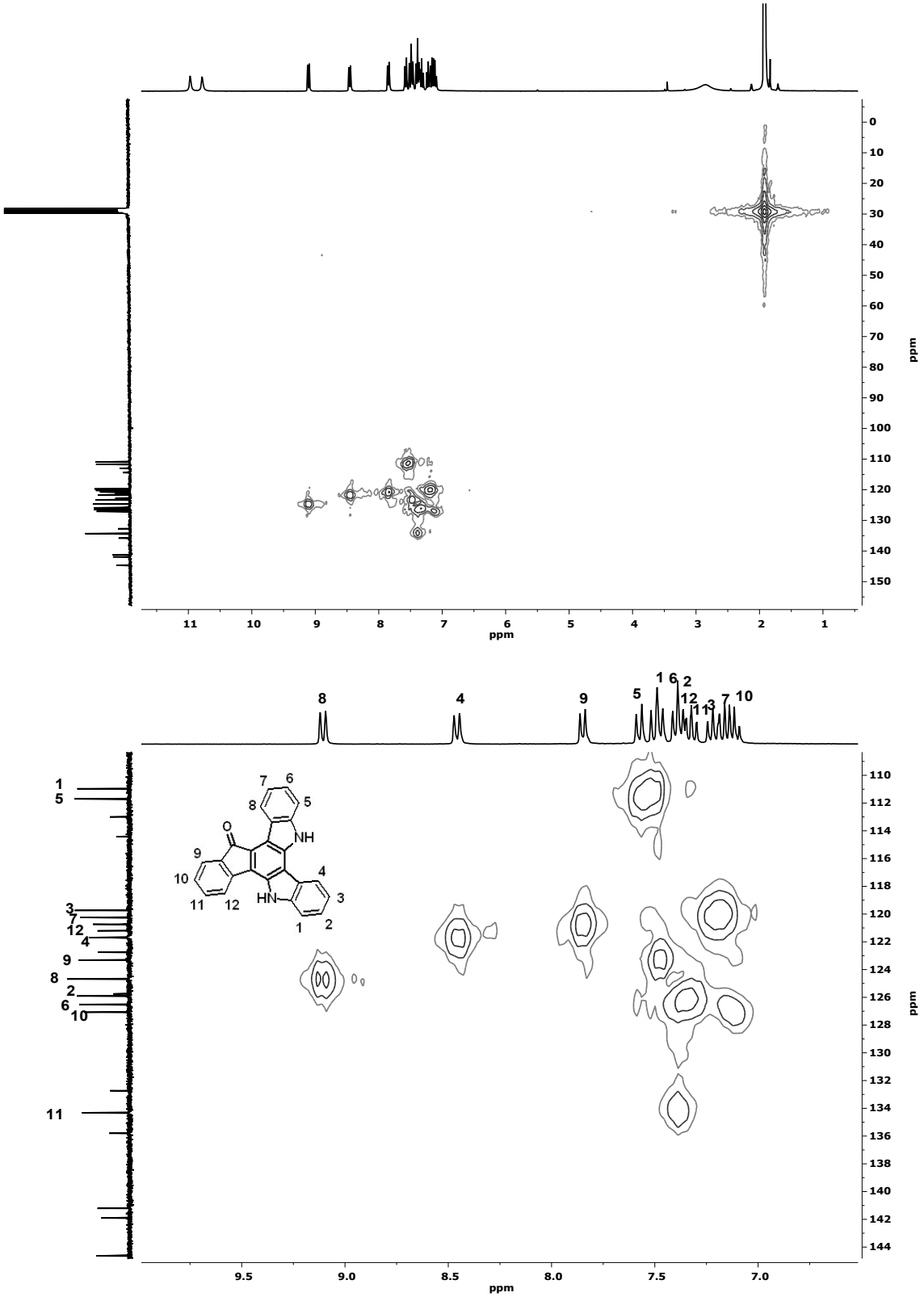
Copy of ^{1}H NMR spectrum (300 MHz, DMSO-*d*6) of compound 3



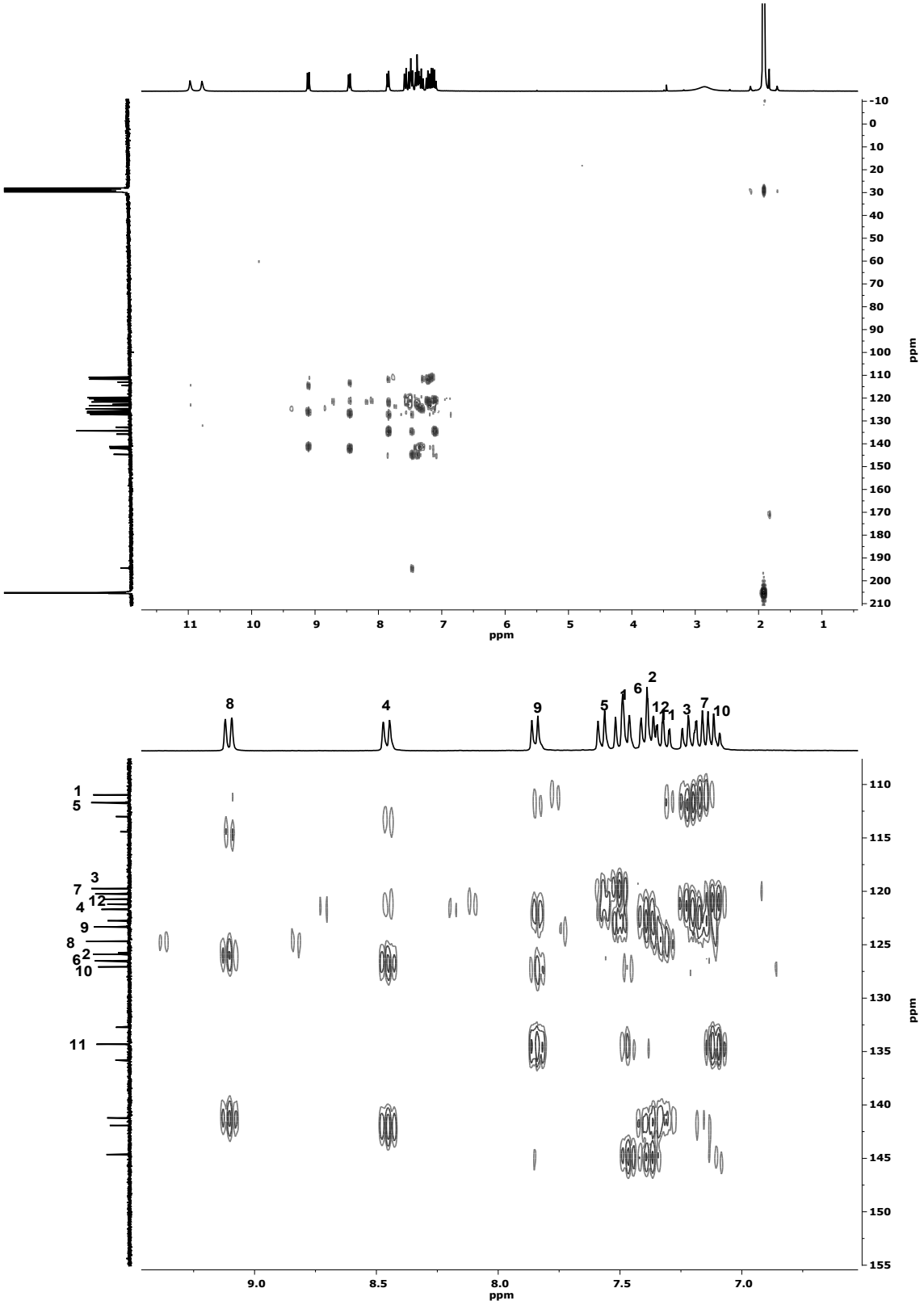
Copy of ^{13}C NMR spectrum (75 MHz, DMSO-*d*6) of compound 3



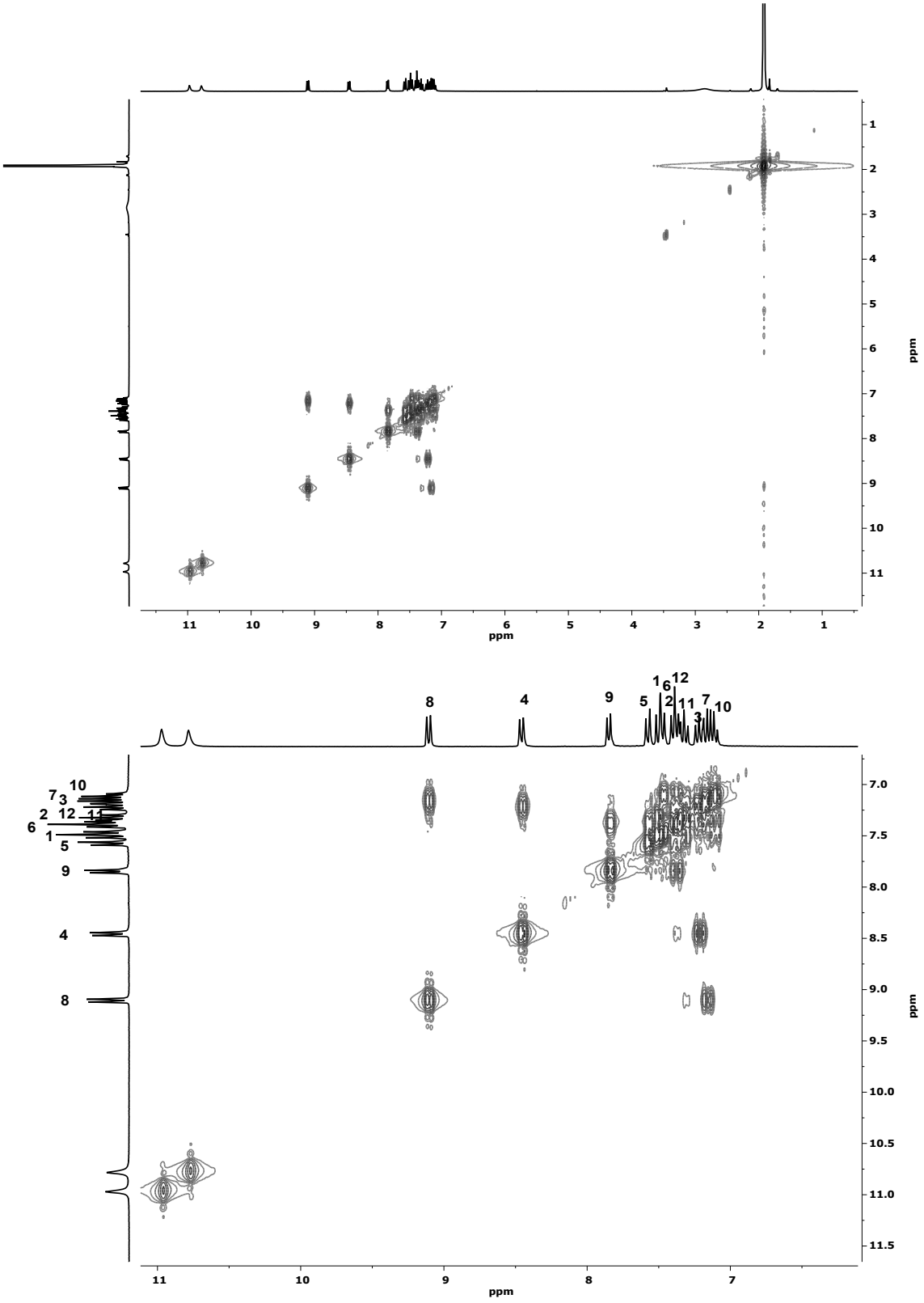
Copy of HMQC spectrum (300 MHz, CD_3COCD_3) of compound 3



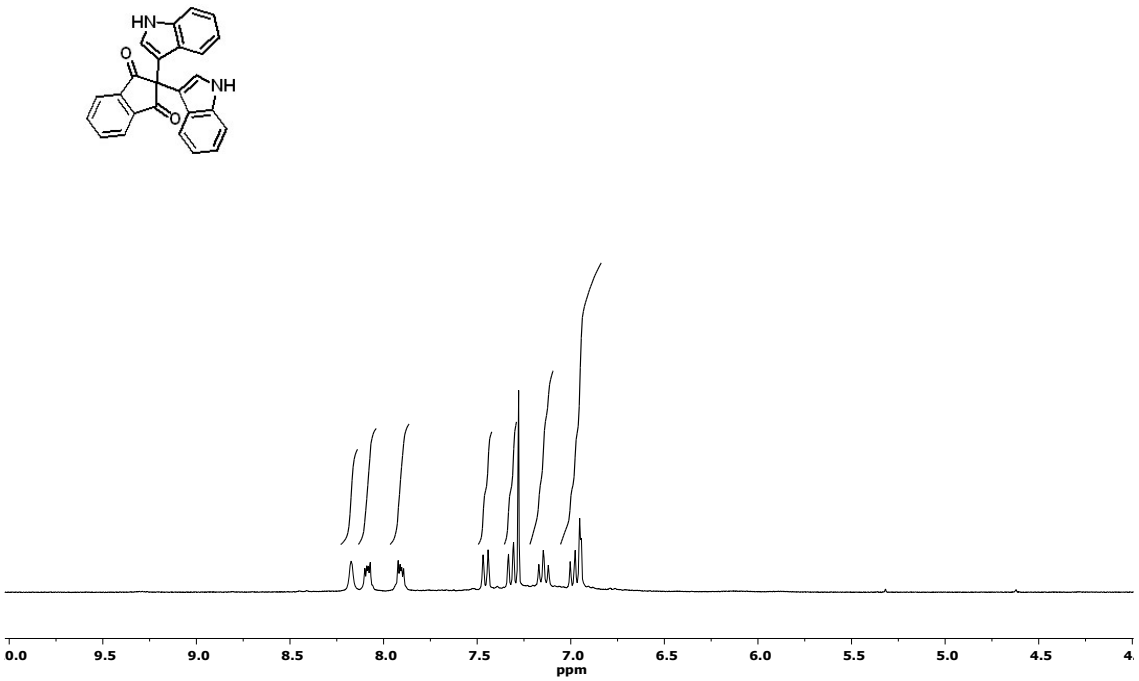
Copy of HMBC spectrum (300 MHz, CD_3COCD_3) of compound 3



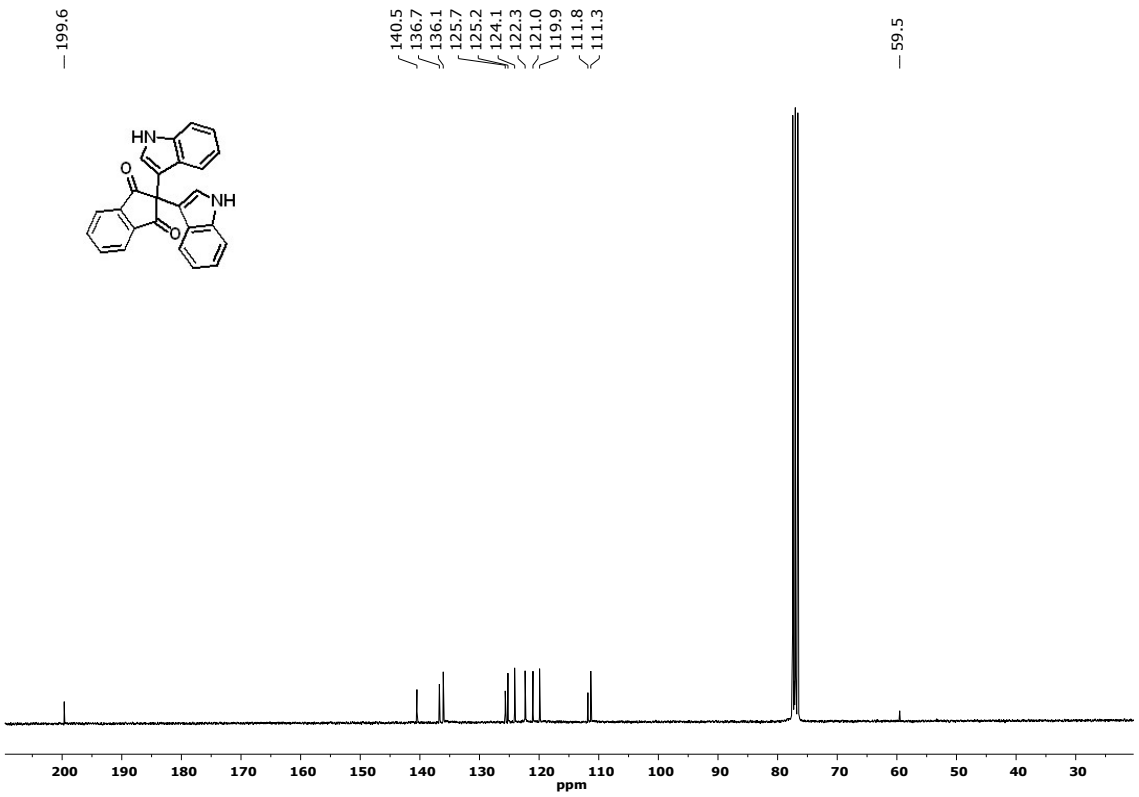
Copy of COSY spectrum (300 MHz, CD_3COCD_3) of compound 3



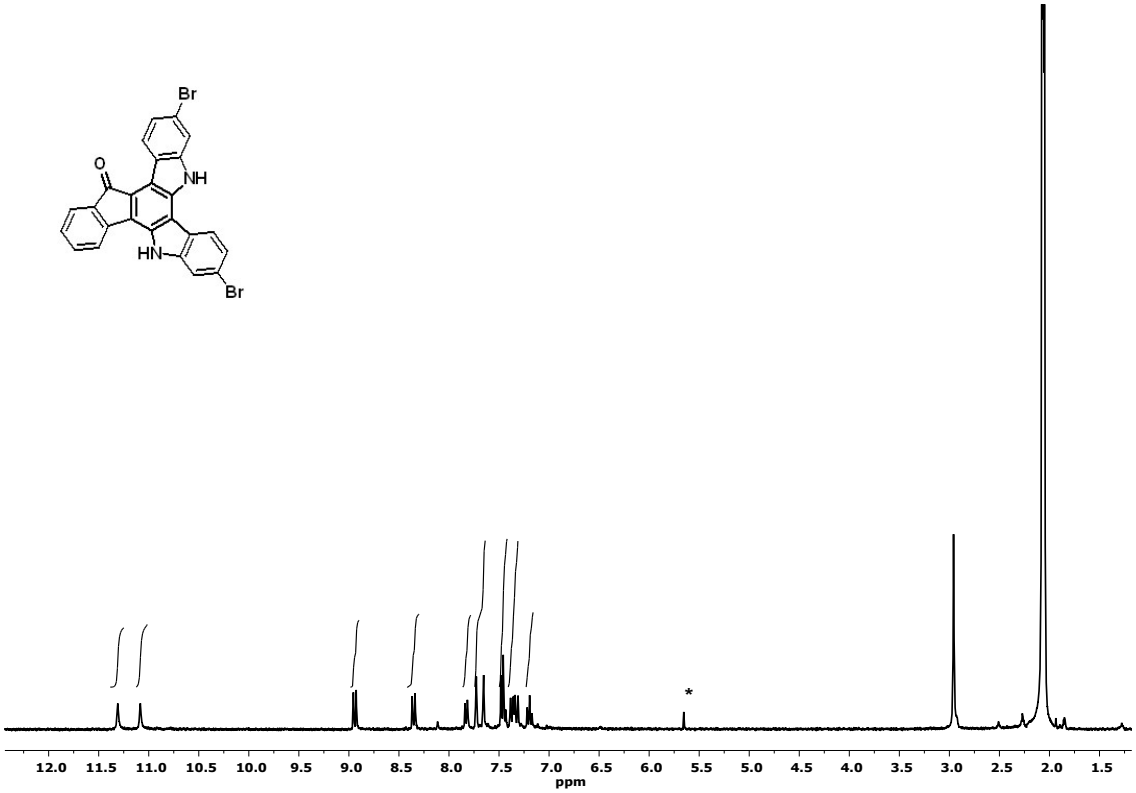
Copy of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound 4



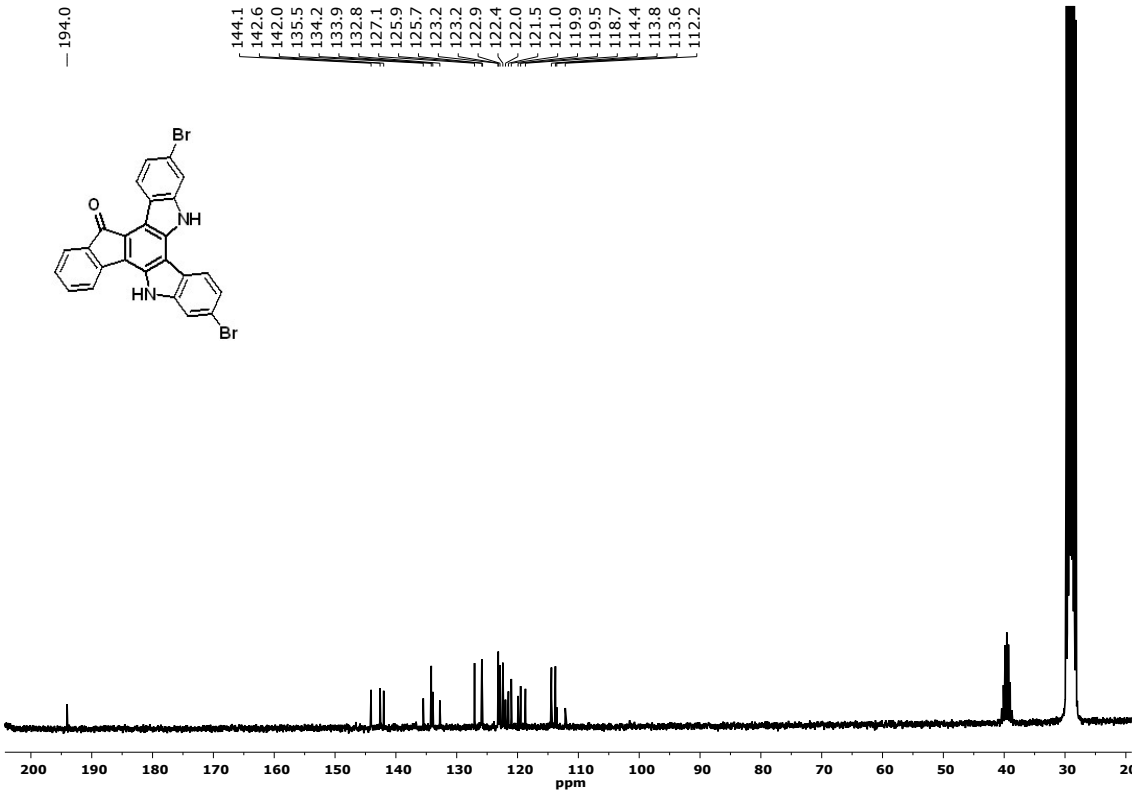
Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 4



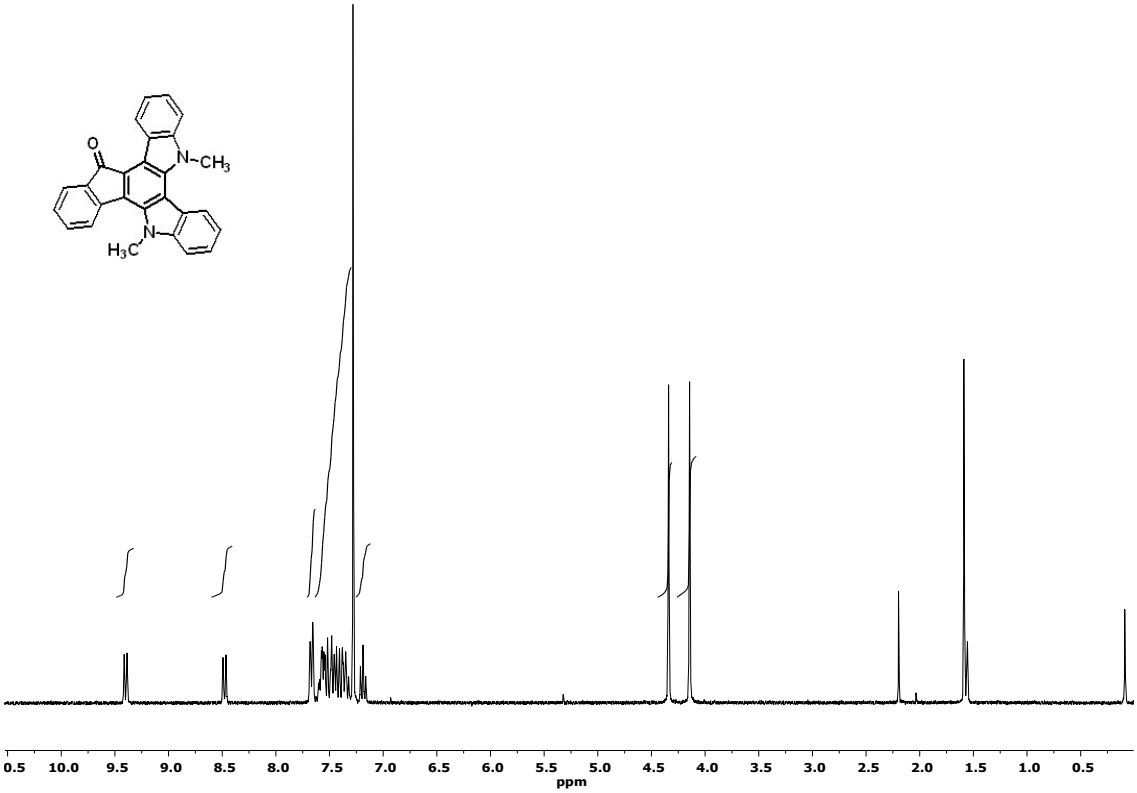
Copy of ^{1}H NMR spectrum (300 MHz, Acetone-*d*6) of compound 5



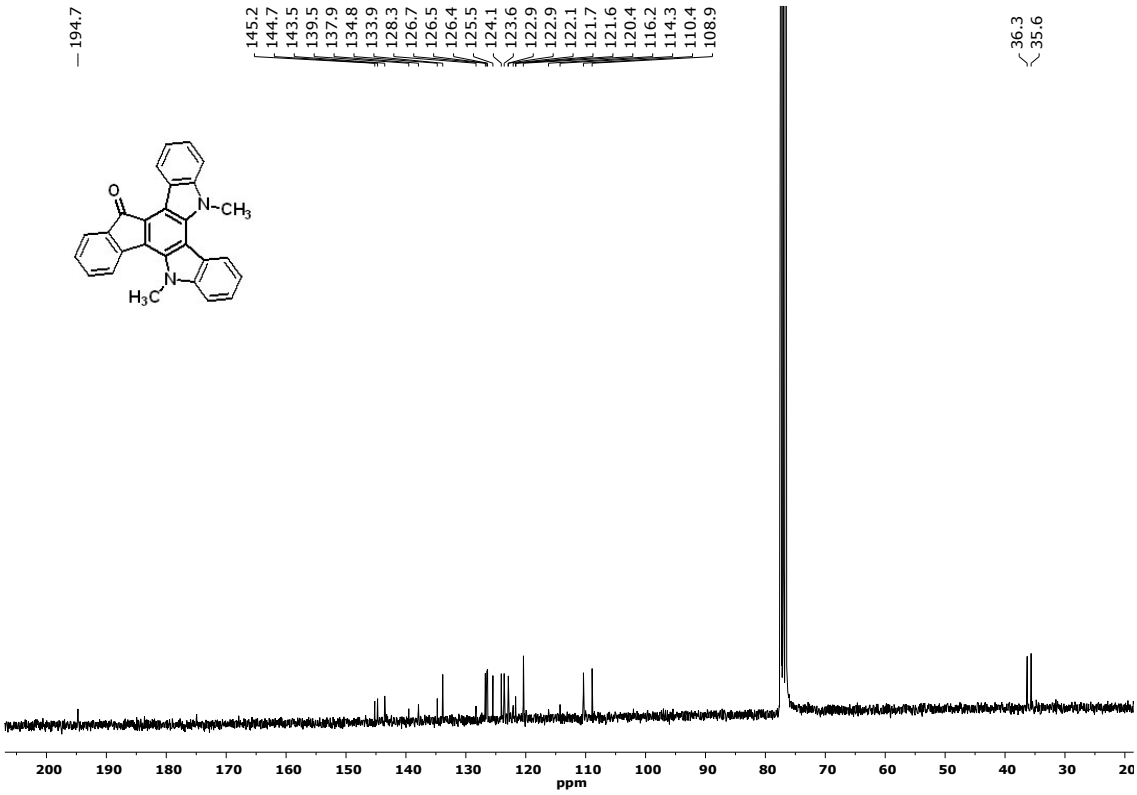
Copy of ^{13}C NMR spectrum (75 MHz, Acetone-*d*6) of compound 5



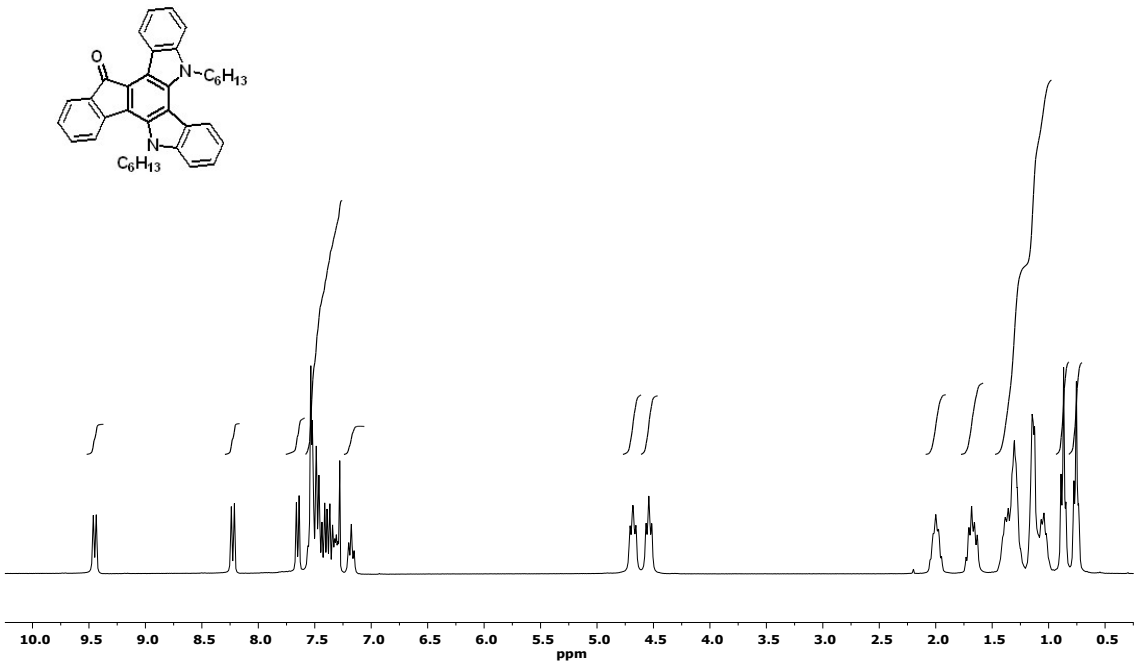
Copy of ^{1}H NMR spectrum (300 MHz, CD_3Cl) of compound 6



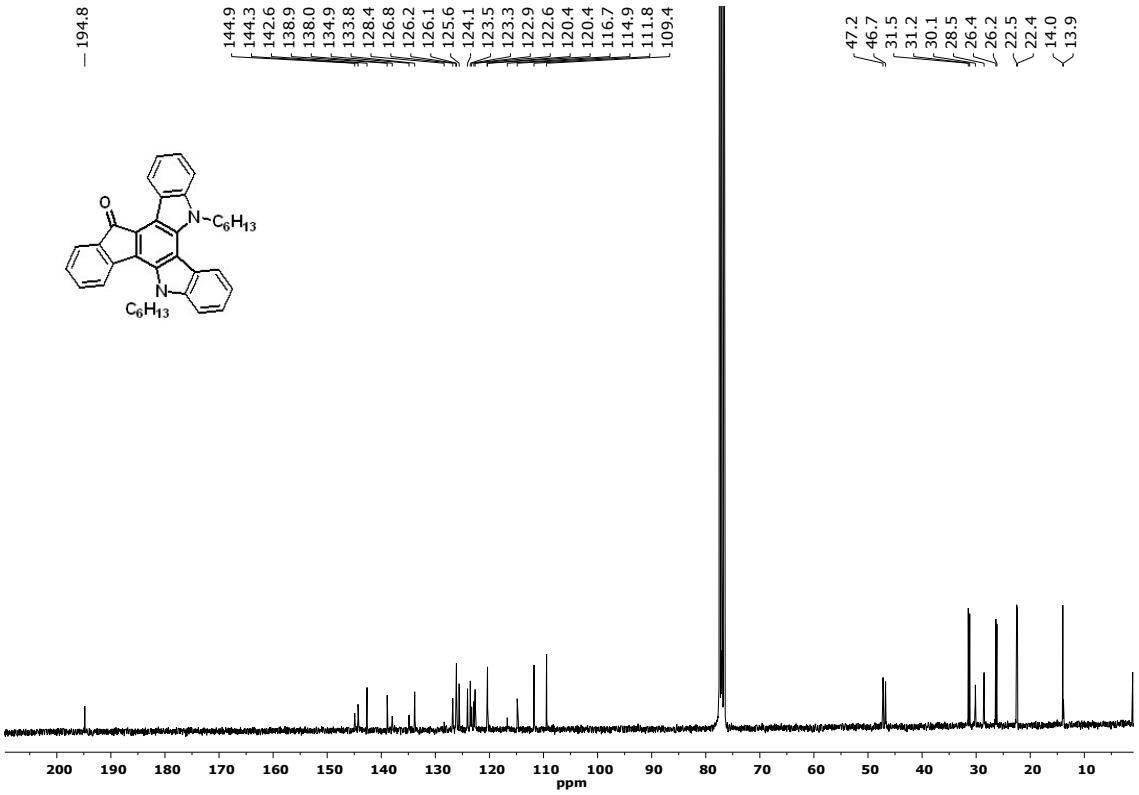
Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 6



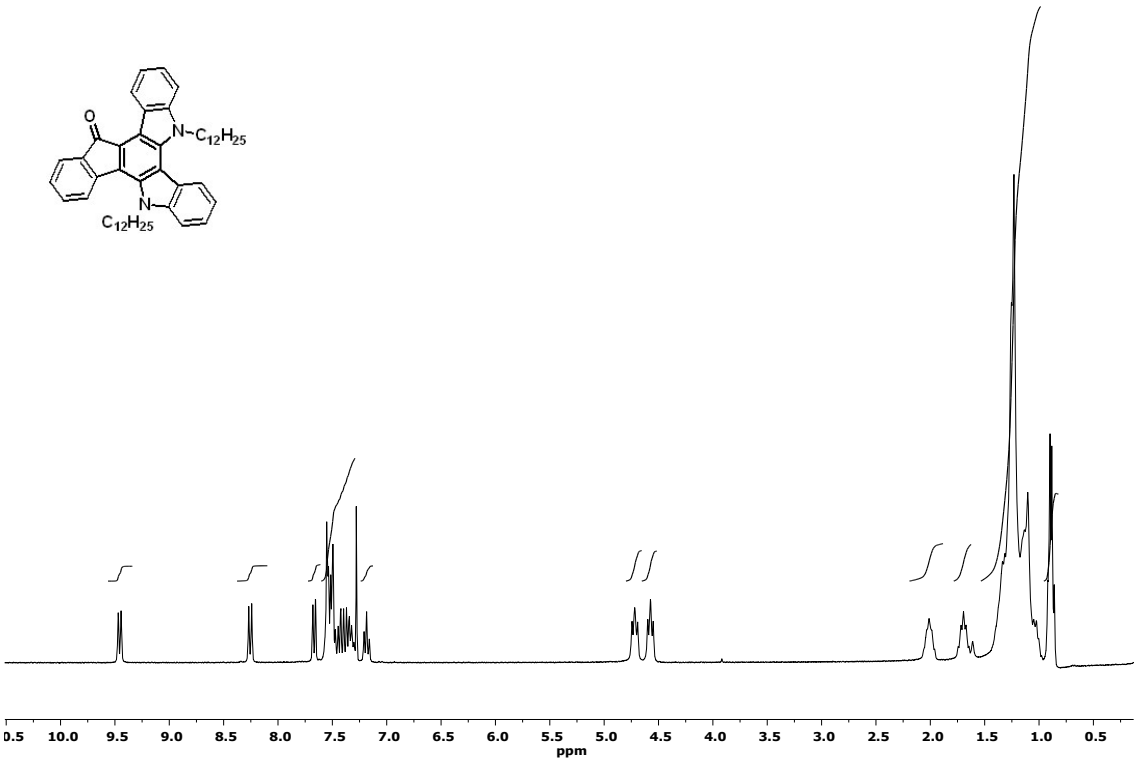
Copy of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound 7



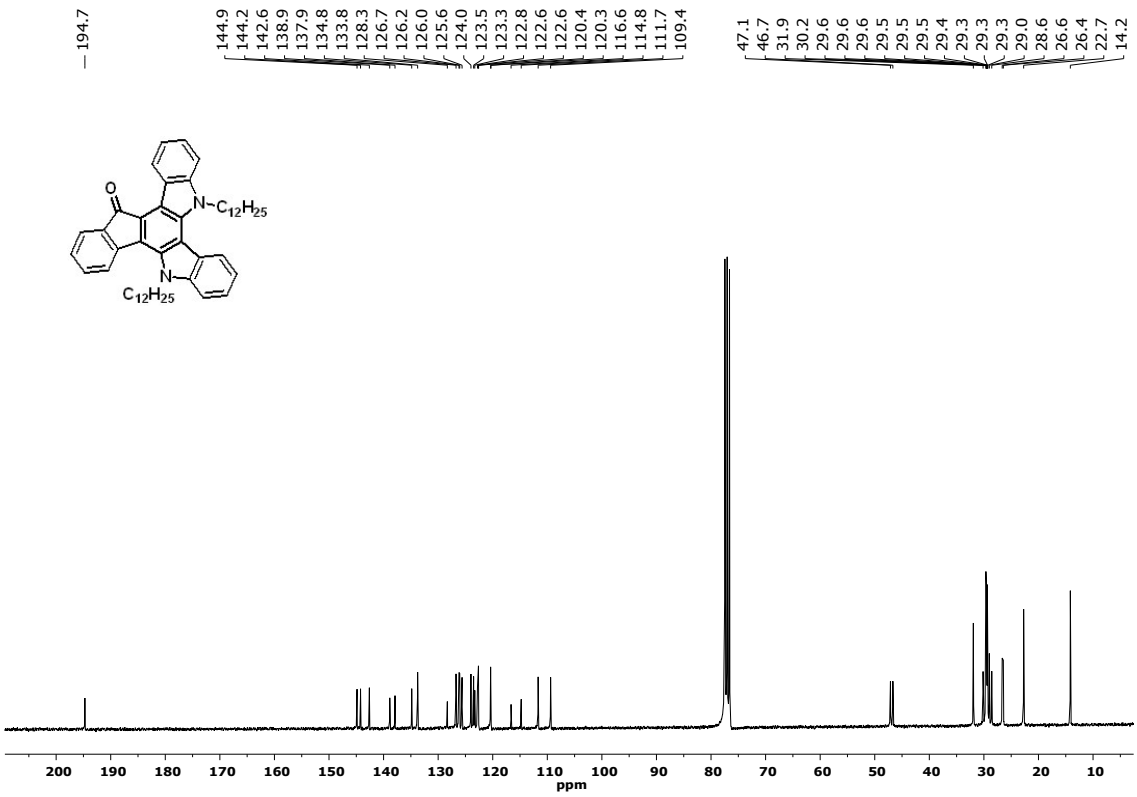
Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 7



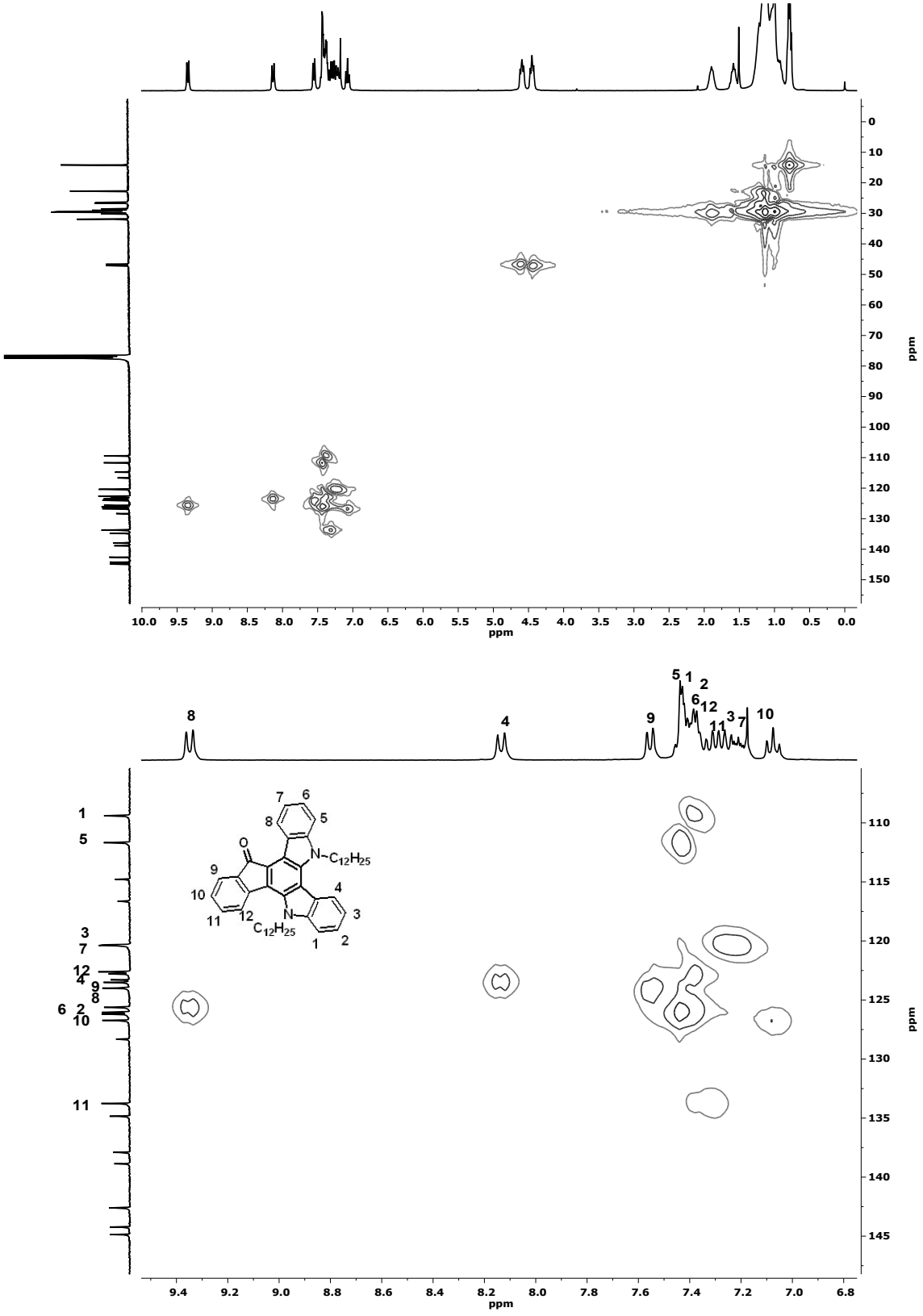
Copy of ^{1}H NMR spectrum (300 MHz, CD_3Cl) of compound 8



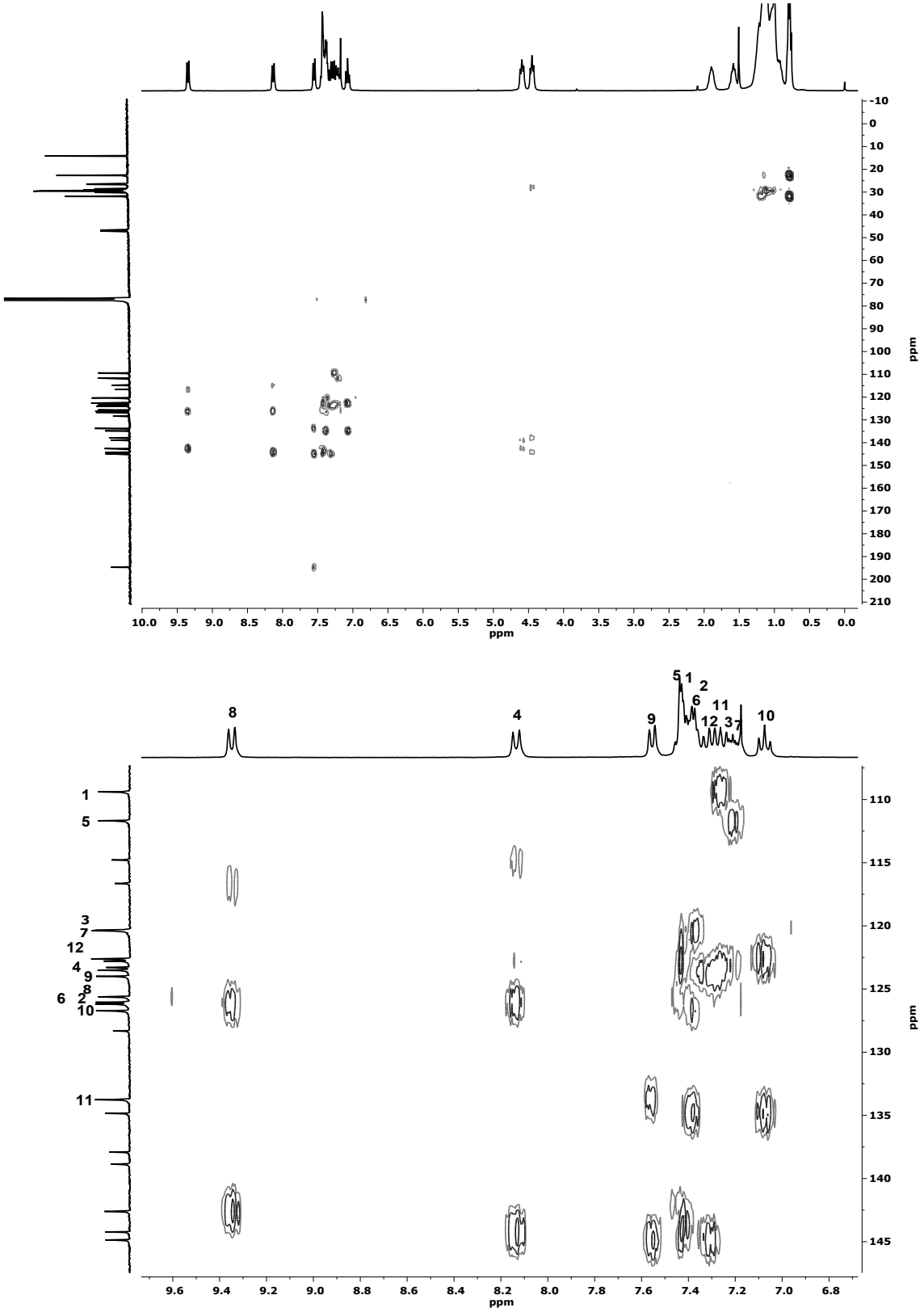
Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 8



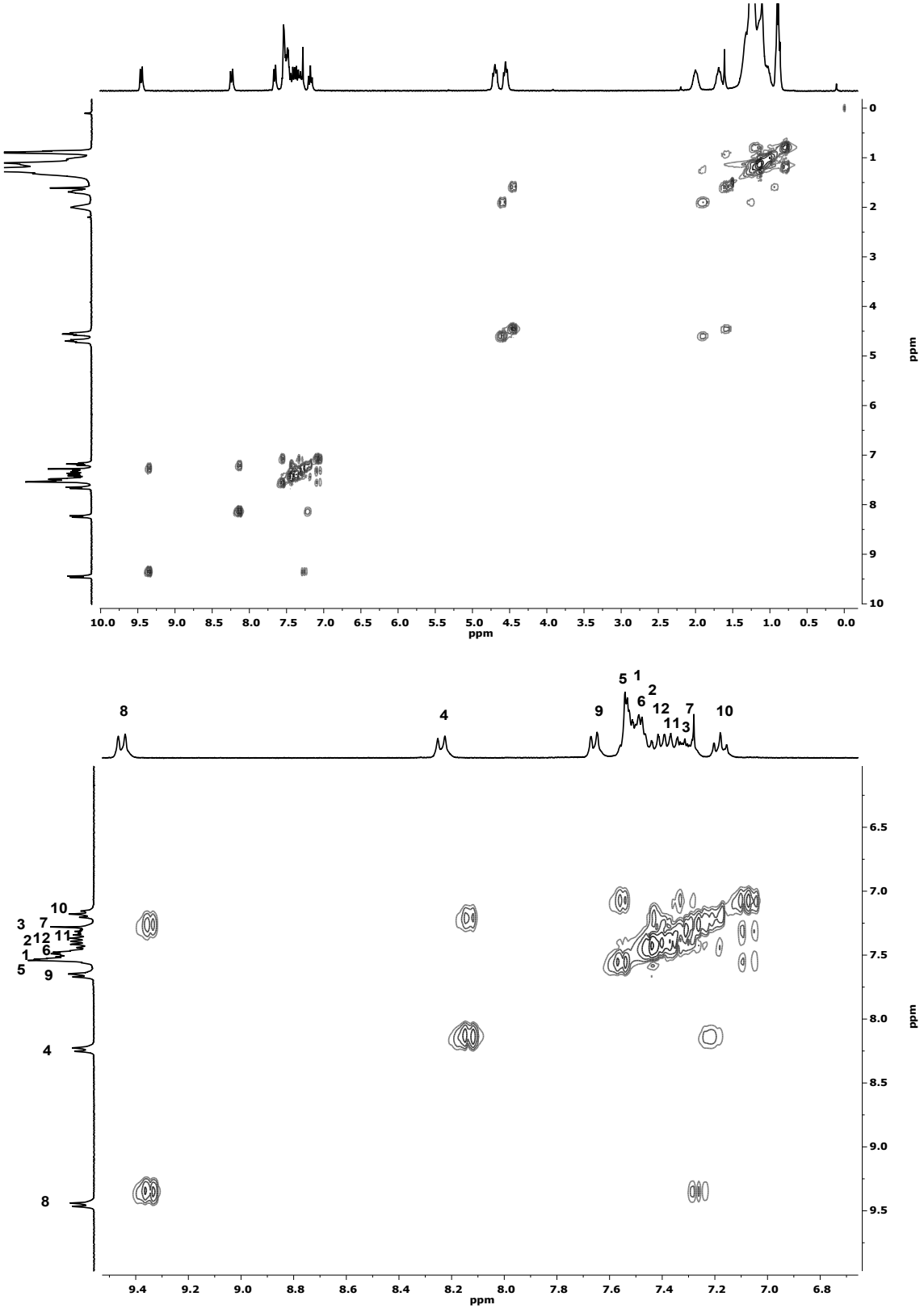
Copy of HMQC spectrum (300 MHz, $CDCl_3$) of compound 8



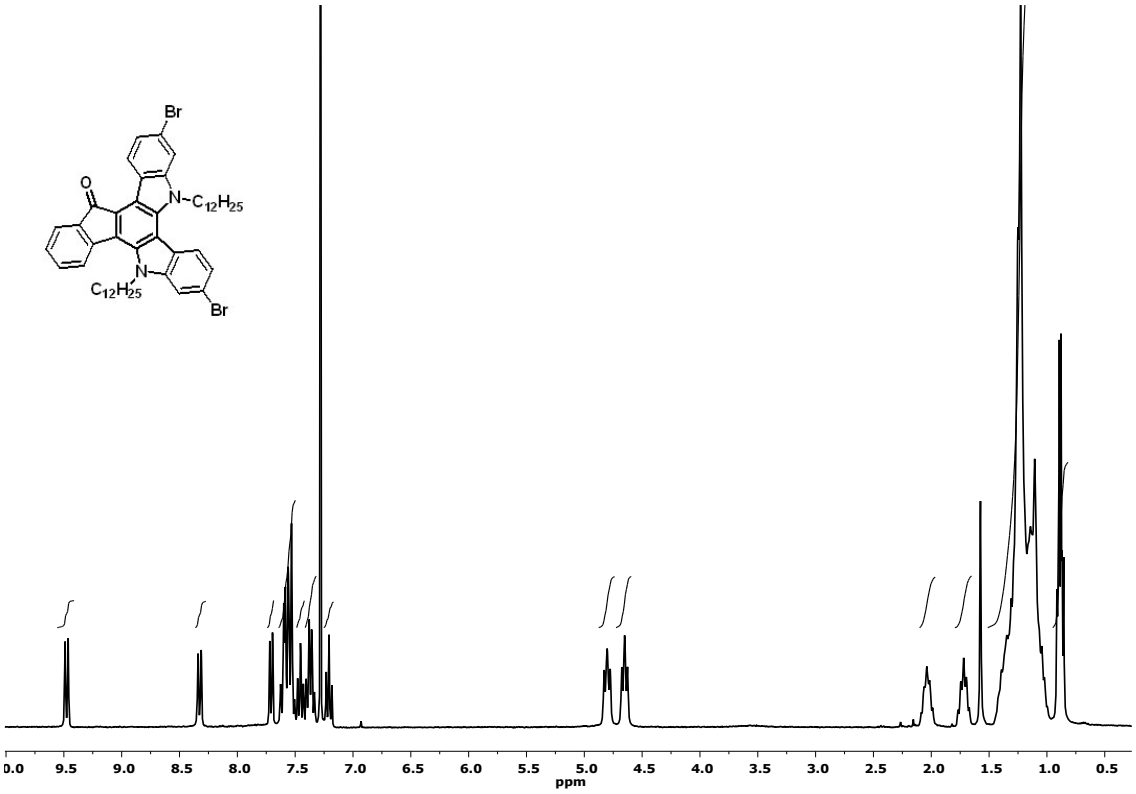
Copy of HMBC spectrum (300 MHz, $CDCl_3$) of compound 8



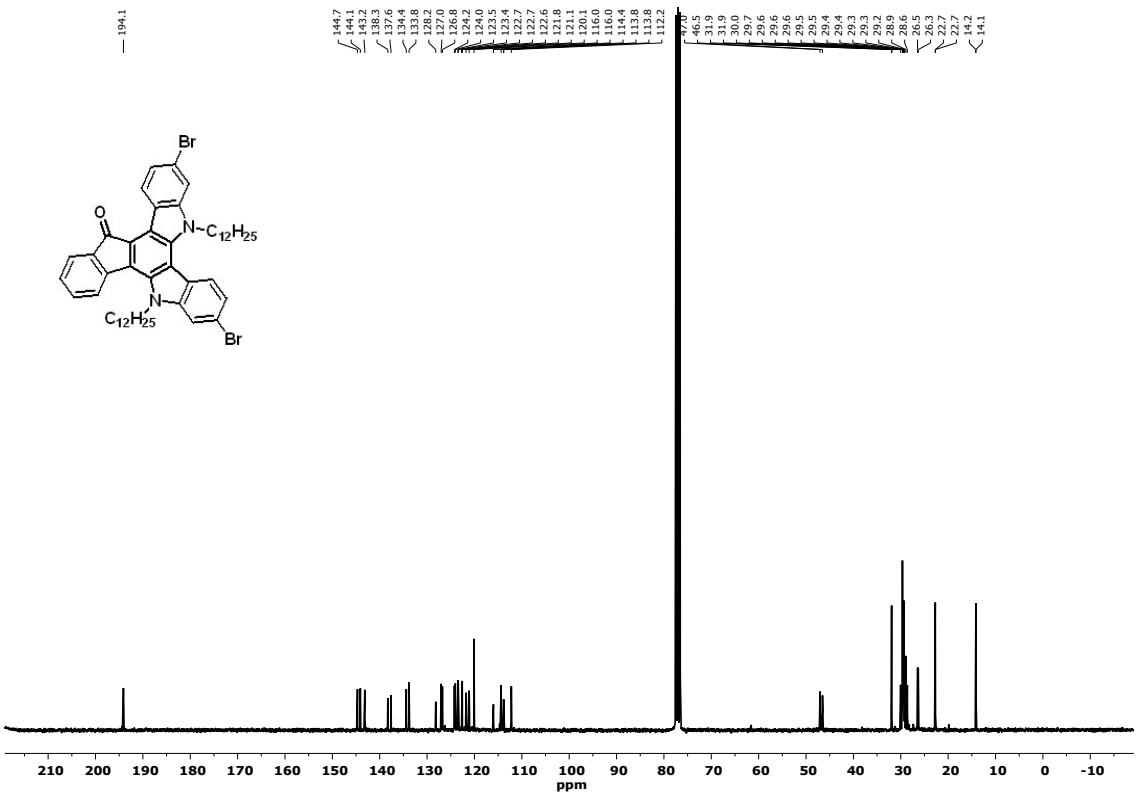
Copy of COSY spectrum (300 MHz, $CDCl_3$) of compound 8



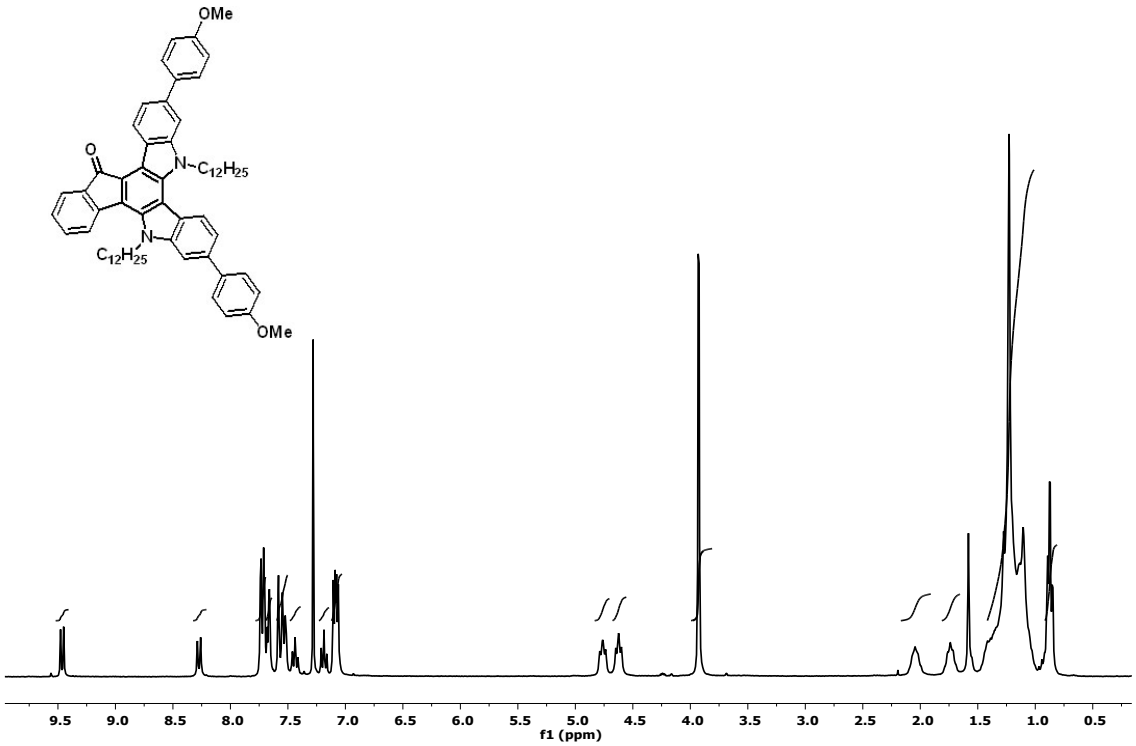
Copy of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound 9



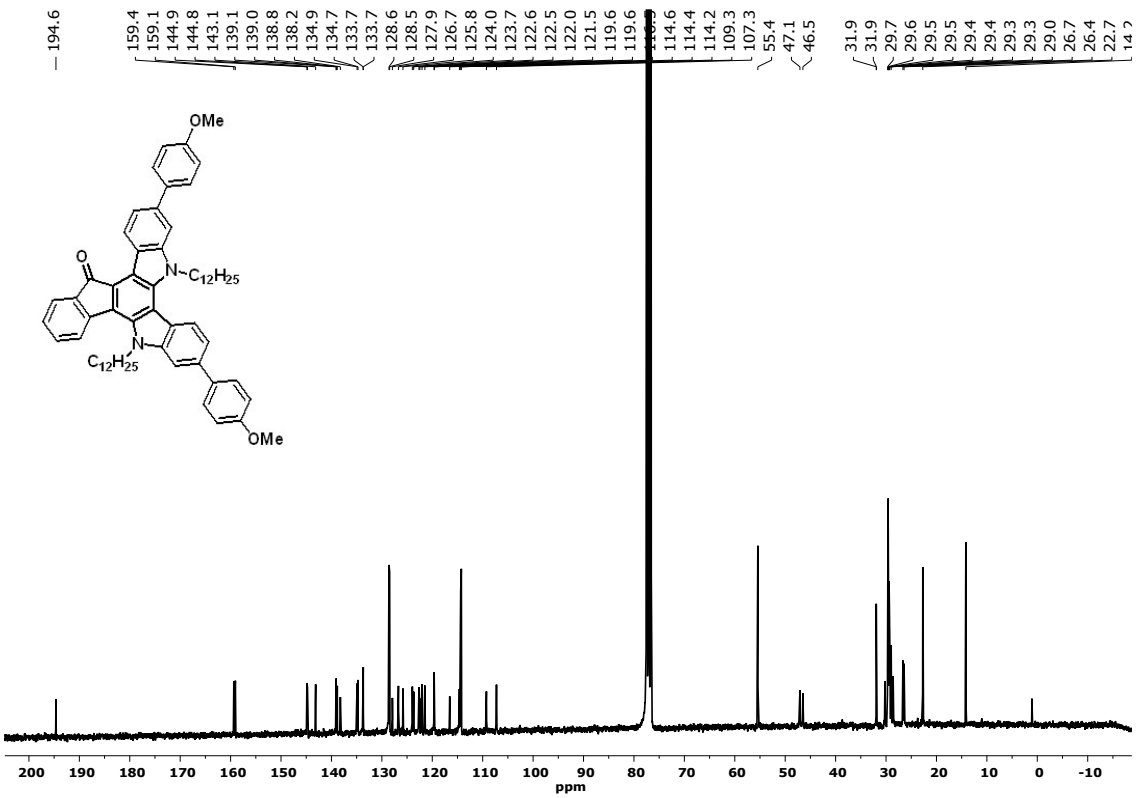
Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 9



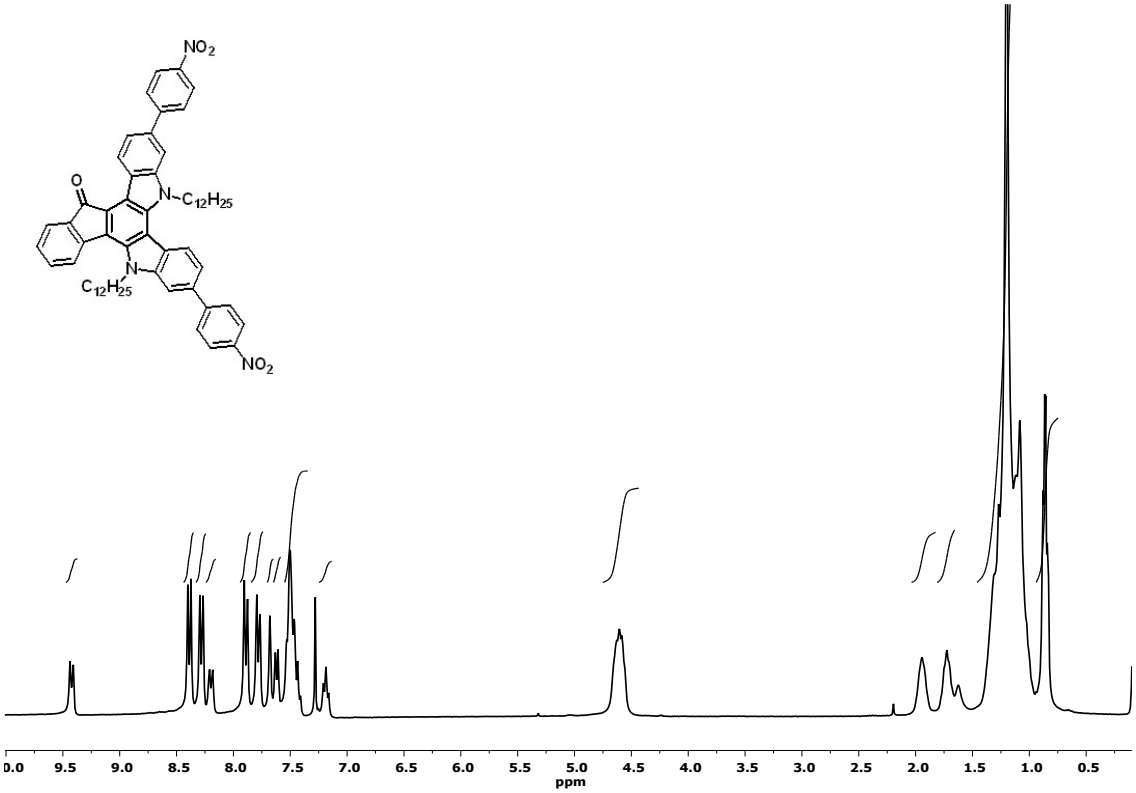
Copy of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound 10



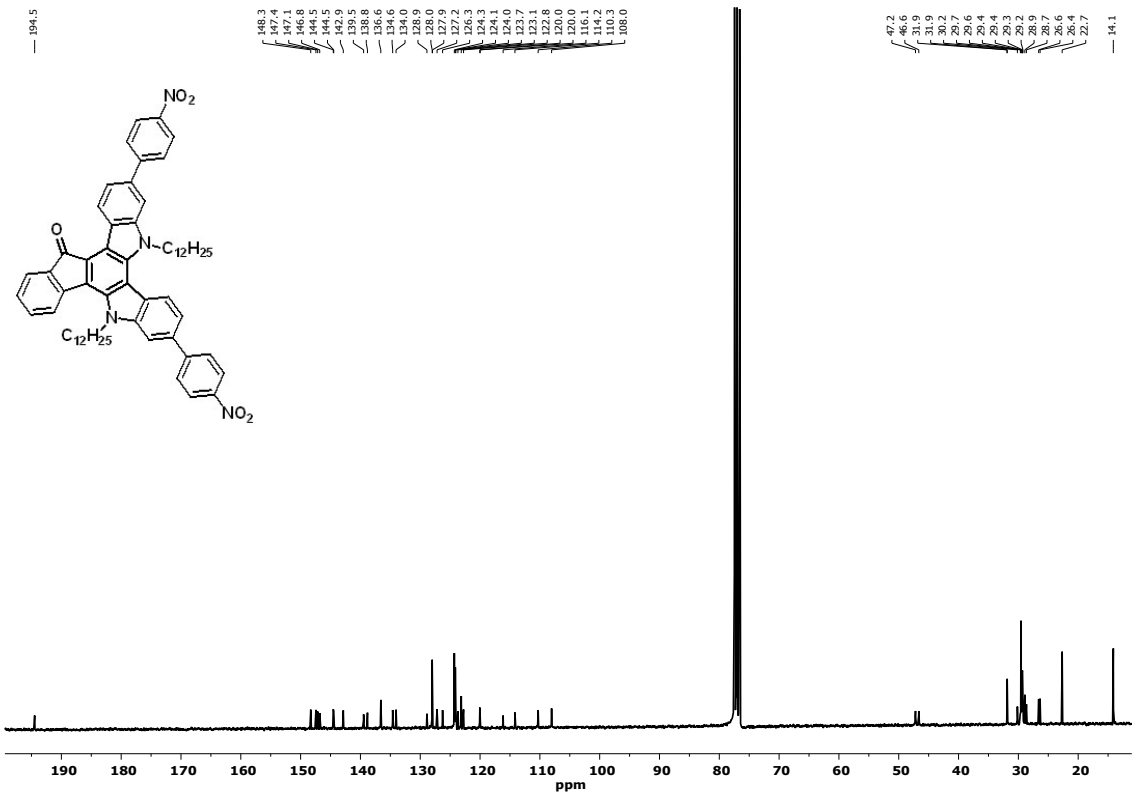
Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 10



Copy of ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound 11



Copy of ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound 11



4. Solvent variation of the ^{1}H NMR spectra of compound 3

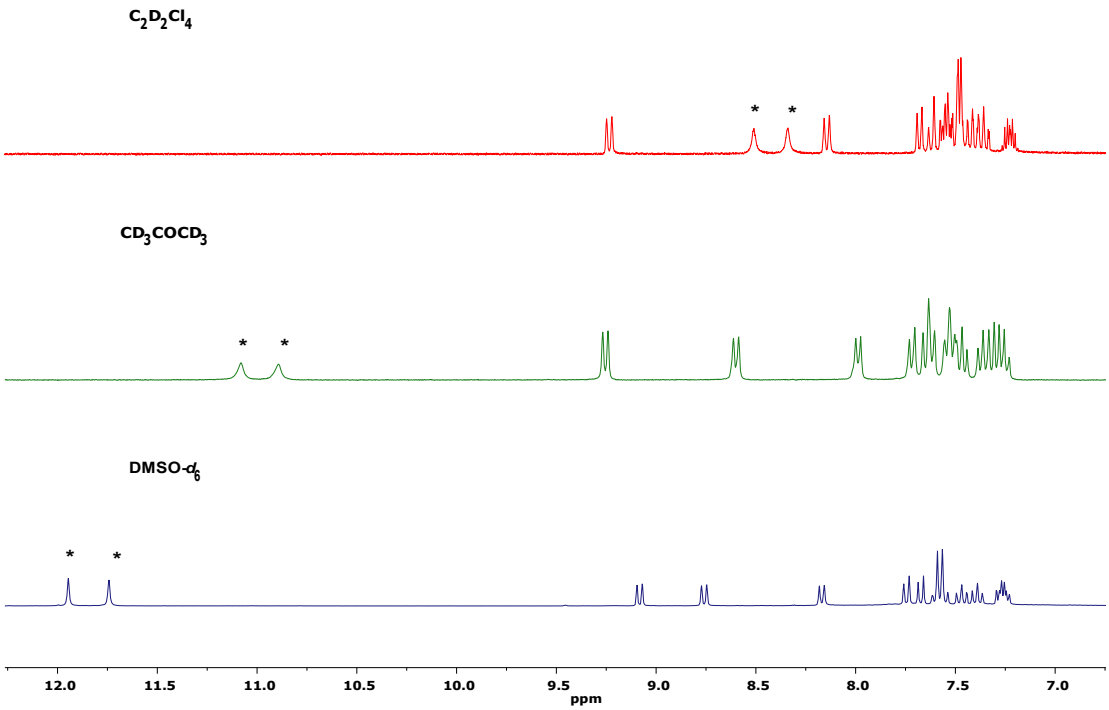


Figure S1. Variation of the NH ^{1}H-NMR signals (marked with asterisks) of compound **3** in different solvents.

5. Concentration variation of ^{1}H NMR signals of compound 6.

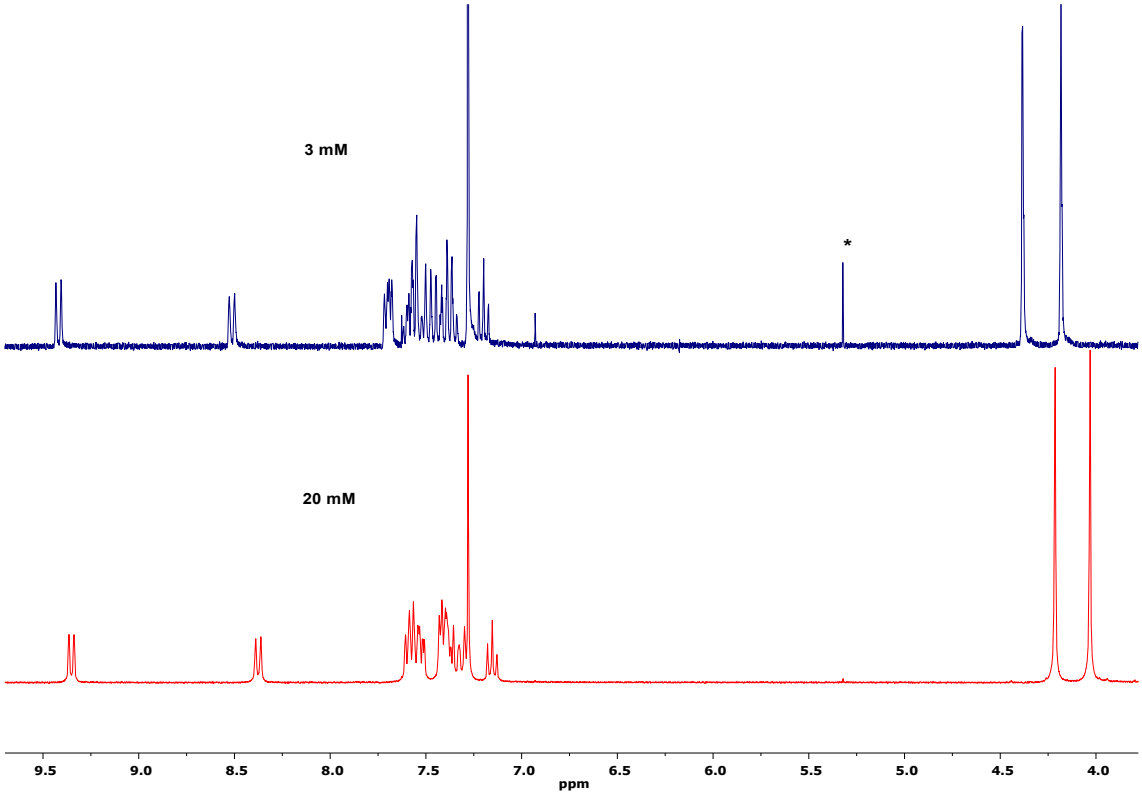


Figure S2. Variation of the aromatic and methylenic ^{1}H-NMR signals of compound **6** upon increasing the concentration.

6. Absorption spectra of compounds 6-8.

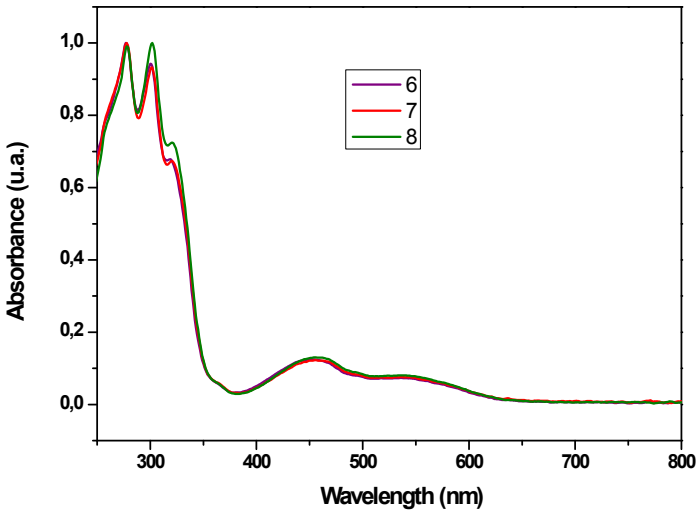


Figure S3. Experimental UV-vis spectra of **6, 7** and **8** in CH_2Cl_2 solutions, c = 1 x 10^{-5} M

7. Cyclic voltammograms of compounds 6-8.

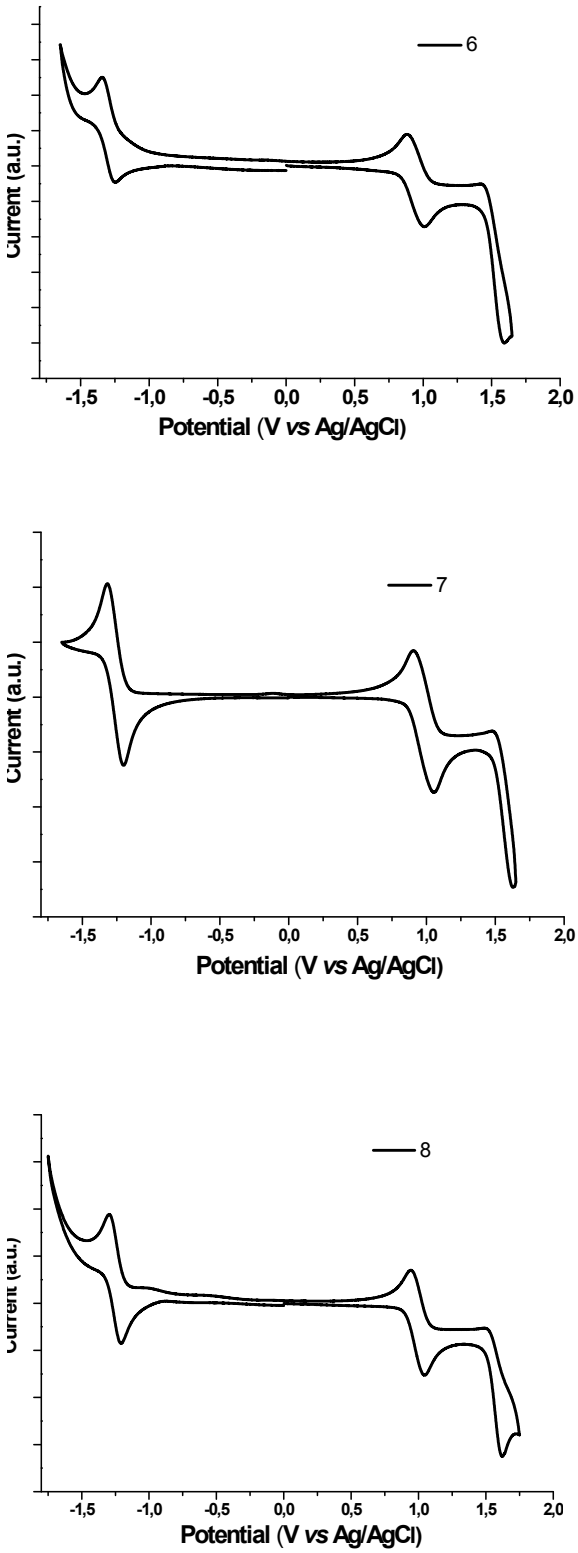


Figure S4. CV of **6, 7** and **8** at c = 1 x 10^{-3} M recordered at a scan rate 100 mV/s in CH_2Cl_2/0.1 M $TBAPF_6$ measured versus Ag/AgCl (3 M NaCl).

8. DFT Calculations.

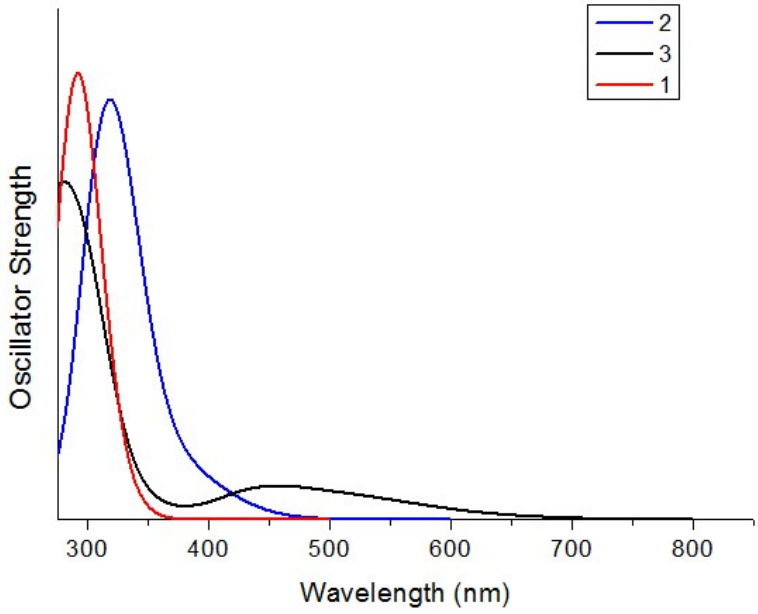


Figure S5. Simulated absorption spectra of triindole **1**, truxenone **2** and diazatruxenone **3** as determined with TD-DFT at the B3LYP/6-31G** level.

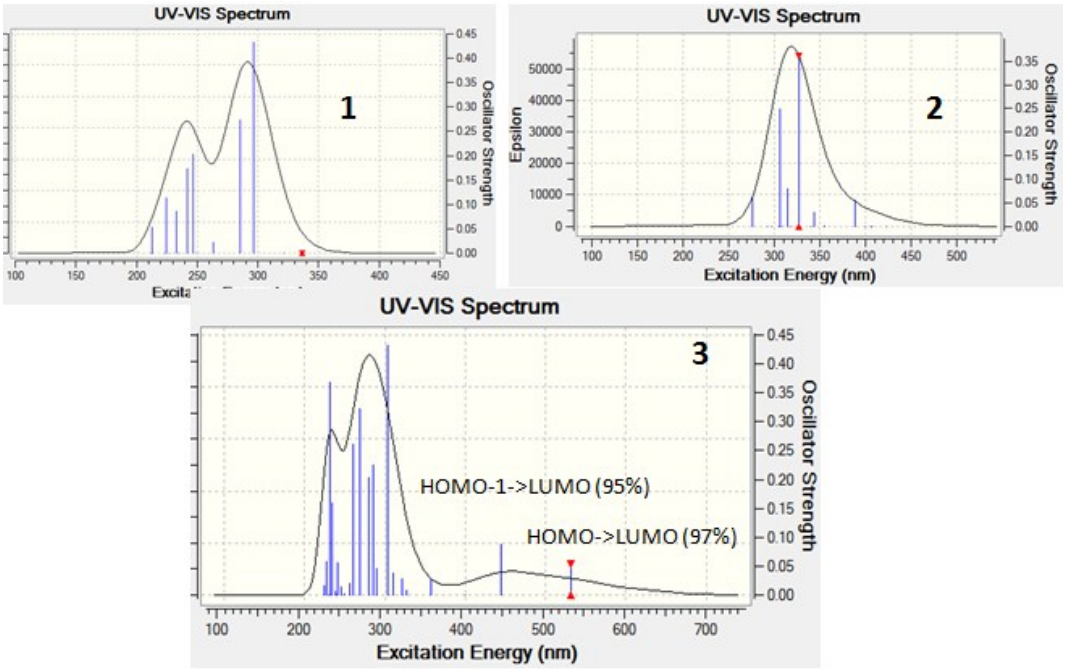


Figure S6. Simulated absorption spectra together with the excitations (wavelength vs. oscillator strength) shown as vertical bars for triindole **1**, truxenone **2** and diazatruxenone **3** as determined with TD-DFT at the B3LYP/6-31G** level.

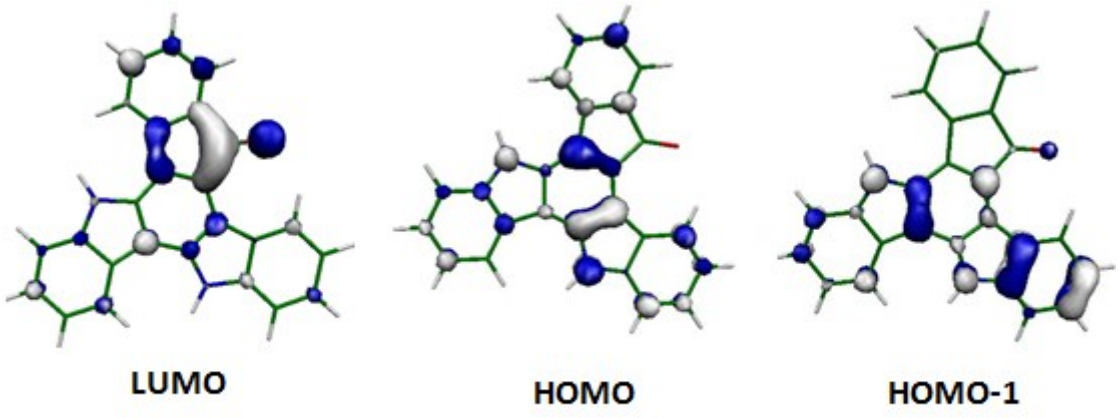


Figure S7. Frontier molecular orbital energies (B3LYP/6-31G**) of diazatruxenone **3** involved in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions.

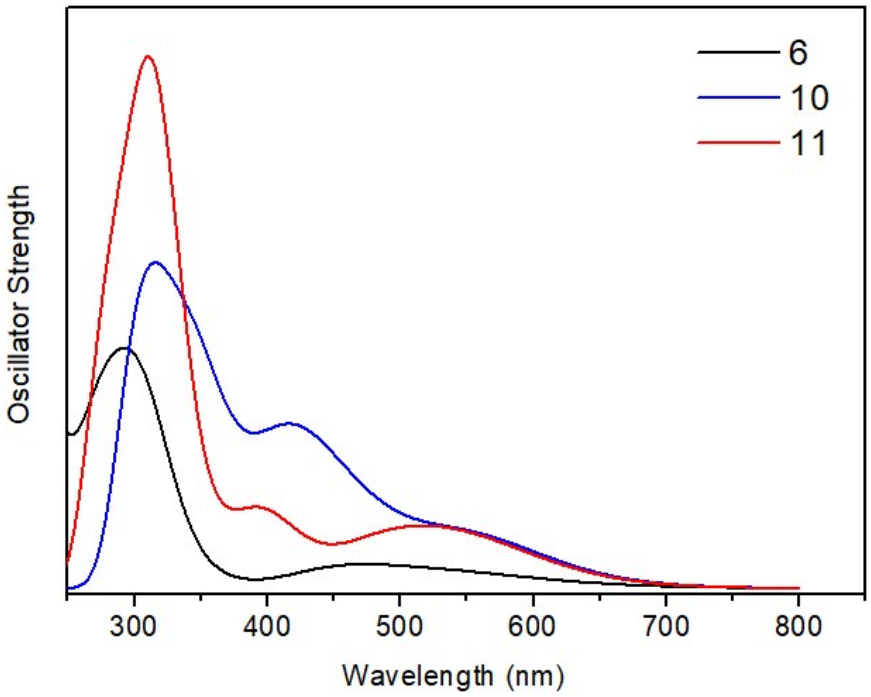


Figure S8. Simulated absorption spectra of peripherally unsubstituted diazatruxenone **6** and peripherally substituted diazatruxenones **10** and **11**.

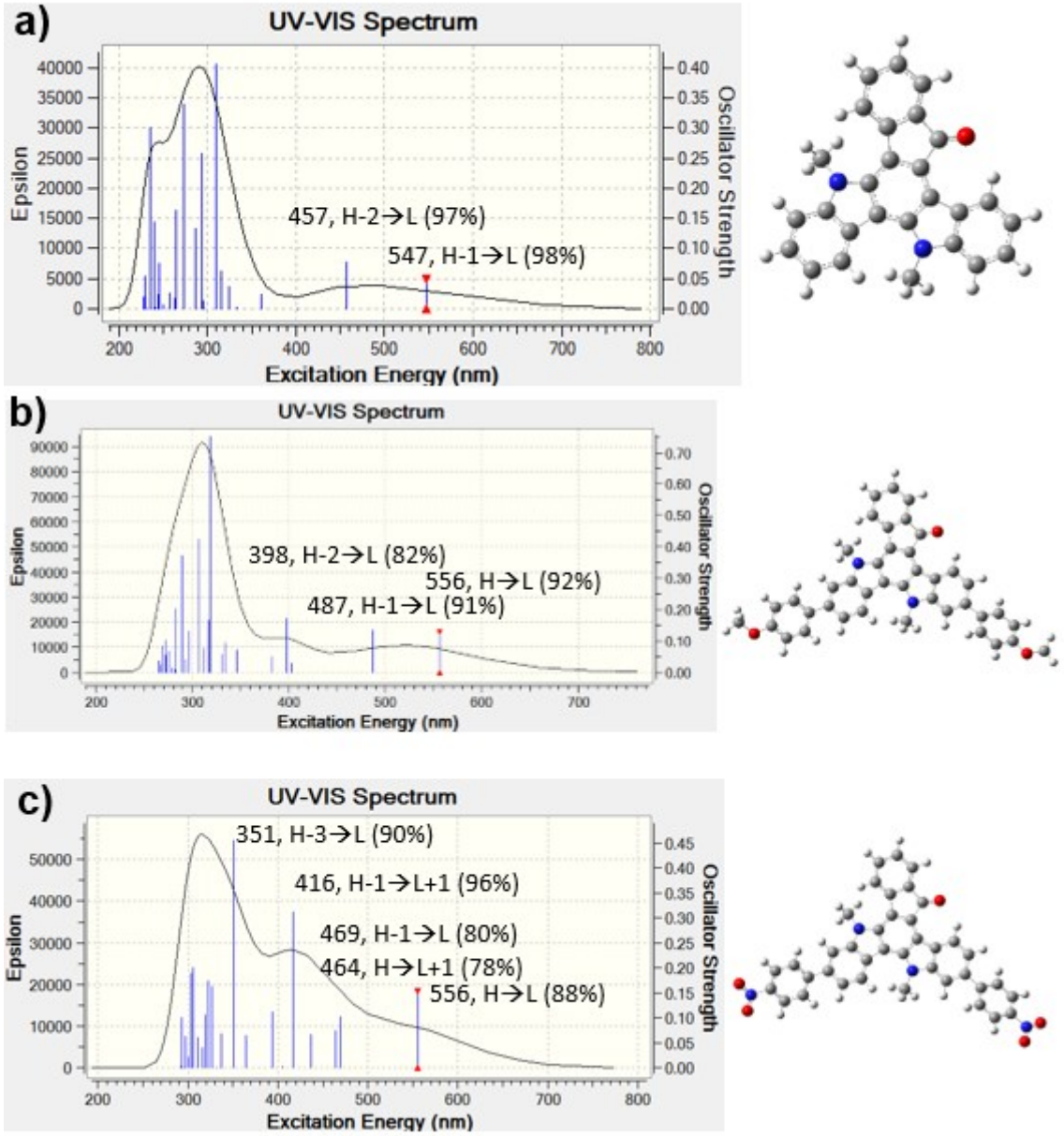


Figure S9. Simulated absorption spectra together with the excitations (wavelength vs. oscillator strength) shown as vertical bars for peripherally unsubstituted diazatruxenone **6** (a) and peripherally substituted diazatruxenones **10** (b) and **11** (c) as determined with TD-DFT at the B3LYP/6-31G** level.

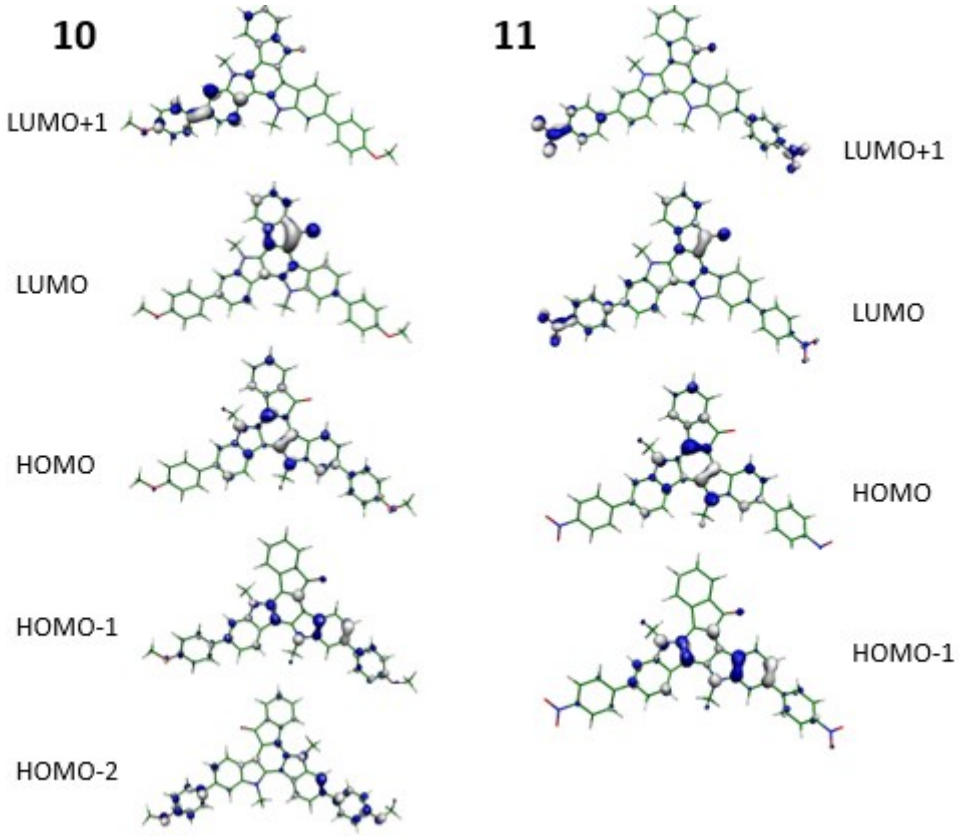


Figure S10. Frontier molecular orbital energies (B3LYP/6-31G**) of peripherally substituted diazatruxenones **10** and **11** involved in the most intense electronic transitions.

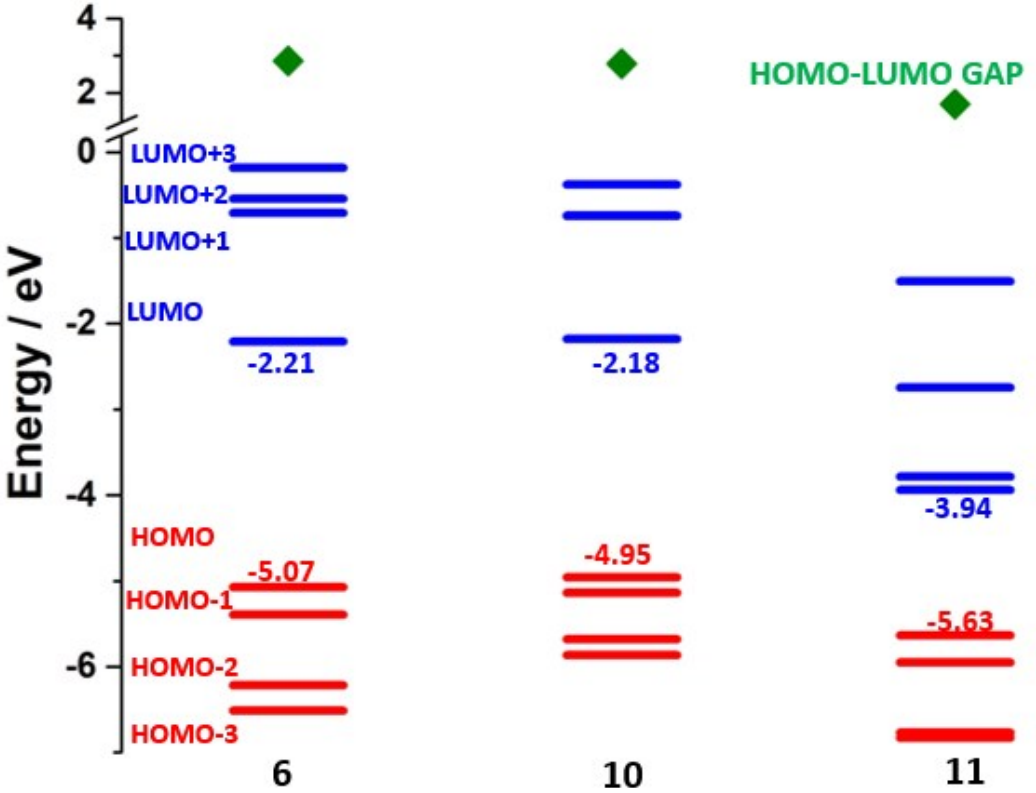


Figure S11. DFT-calculated molecular orbital energies (B3LYP/6-31G**) and HOMO-LUMO gaps for peripherally unsubstituted diazatruxenone **6** and peripherally substituted diazatruxenones **10** and **11**.