Supporting Information for

1,7-Dithienyl BODIPYs: Do Thienyls Outperform Phenyls?

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Experimental section

^{1}H NMR (300 MHz, 25 °C, TMS as an internal standard) and ^{13}C NMR (76 MHz, $CDCl_3$ as an internal standard) spectra were obtained on a Varian VXR-300 instrument.
The UV-Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer (Japan). The fluorescence spectra were measured on a Solar CM2203 fluorescence spectrophotometer (Belarus) with autocorrection by the instrument sensitivity. The relative fluorescent quantum yields (FQY; Φ_f) were determined relative to Rhodamine 6G (Φ_f = 0.95, EtOH) and indodicarbocyanine iodide (Φ_f = 0.25, EtOH) and corrected taking into account solvents' refractive indices.
The DFT and TD-DFT calculations were performed with the Gaussian 16 program suite using the hybrid B3LYP functional and the double-ζ basis set 6-31G(d,p).[1] The solvent effect was accounted for by the integral equation formalism polarizable continuum model (IEFPCM).[2] The ground-state geometry optimizations—the residual forces convergence criterion was set to 1×10^{-5} Hartree·Bohr^{-1} or Hartree·Rad^{-1}—were followed by frequency calculations to verify the true-minimum nature of the found stationary points. In the case of fast absorption processes (Franck–Condon principle), the nuclear relaxation was avoided by employing state-specific solvation calculations in terms of fast electronic cloud reorganizations and slow solvent and solute nuclear motions.[3] The NBO atomic charges were obtained using the algorithm, embedded in Gaussian 16.[4]

Synthesis of compounds **5** and **6**.

Ethyl 2-methyl-4-phenyl-1H-pyrrole-3-carboxylate (5).

1. 10 ml of saturated methanol solution of ammonia was added to Michael's product **3** (2.79 g, 0.01 mol). The reaction mixture was left overnight, then evaporated, and the resulting crude product was recrystallized from aqueous isopropanol (1:1) yielding **5** (0.69 g, 30%). Characterization data are identical to those reported in the literature.[5]
2. Acetoacetic ester (1.30 g, 1.26 ml, 0.01 mol) and 10 ml of methanol ammonia solution saturated at 0 °C were added to nitrostyrene **1** (1.49 g, 0.01 mol). The reaction mixture was left overnight and evaporated. The resulting crude product was recrystallized from aqueous isopropanol (1:1) yielding **5** (0.92 g, 40%).

Ethyl (Z)-3-amino-2-(2-nitro-1-phenylethyl)but-2-enoate (6). 10 ml of saturated methanol solution of ammonium acetate was added to the Michael product **3** (2.79 g, 0.01 mol). The reaction mixture was left overnight, then water (50 ml) was added, and the resulting solution was extracted with dichloromethane (3×30 ml), dried over Na_2SO_4 and evaporated to dryness. The crude product was recrystallized with isopropanol yielding **6** as white crystals (2.23 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.71 (br. s, 1 H, NH_2), 7.28 (t, $^{3}J_{HH}$ =7.50 Hz, 2 H, CH_{Ar}), 7.19 (m, 3 H CH_{Ar}), 5.14 (dd, $^{3}J_{HH}$ =12.00, 8.80 Hz, 1 H, CH), 5.06 (dd, $^{3}J_{HH}$ =12.00, 6.60 Hz, 1 H, CH_2NO_2), 4.70 (dd, $^{3}J_{HH}$ =8.80, 6.60 Hz, 1 H, CH_2NO_2), 4.04 (m, 2 H, CH_2), 2.15 (s, 3 H, CH_3), 1.09 (t, $^{3}J_{HH}$ =7.11 Hz, 3 H, CH_3) ppm.^{13}C NMR (76 MHz, $CDCl_3$) δ_C 169.4(s, CO), 159.9(s, C-NH_2), 141.1(s, C_{Ar}) , 128.3(s, C_{Ar}), 126.8(s, C_{Ar}) , 126.5(s, C_{Ar}), 92.3(s, CH_2NO_2), 78.8(s, C=C), 59.1(s, CH), 41.5 (s, CH_2), 21.8(s, CH_3), 14.2(s, CH_3) ppm. Anal. calc. for $C_{18}H_{14}N_2O_4$ C, 60.42; H, 6.52; N, 10.07; found C, 60.32; H, 6.61; N, 10.15 %

Synthesis of **7-12**.

Saturated solution of NH_3 in MeOH (15 mL) was added dropwise to a mixture of ethyl acetoacetate (1.3 g, 0.01 mol, 1.26 mL) and 0.01 mol of corresponding nitrostyrene at 0°C. The reaction mixture was stirred overnight at r.t. After the completion of reaction, solvent was removed under reduced pressure, resulting residue was extracted with cyclohexane (for **9**), hexane (for **10**)

or crystallized from aqueous isopropanol (1:1) solution (**11-12**) to give products **9-12** as colorless solids.

Ethyl 4-(4-(dimethylamino)phenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (7). White crystalline solid (0.140 g, 5%).

^{1}H NMR (300 MHz, DMSO-d_6) δ_H 11.17 (br. s, 1 H, NH), 7.15 (d, $^3J_{HH}$ = 8.15 Hz, 2 H, CH_{Ar}), 6.65 (d, $^3J_{HH}$ = 8.15 Hz, 2 H, CH_{Ar}), 6.56 (s, 1 H, CH_{Het}), 4.06 (q, $^3J_{HH}$ = 7.00 Hz, 2 H, CH_2), 2.87 (s, 6 H, $N(CH_3)_2$), 2.39 (s, 3 H CH_3), 1.14 (t, $^3J_{HH}$ = 7.00 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 168.1 (s, CO), 149.4 (s, C, CH_{Ar}), 135.9 (s, C, CH_{Ar}), 130.1 (s, C, CH_{Ar}), 127.4 (s, C, CH_{Ar}), 124.4 (s, C, CH_{Ar}), 114.9 (s, C, CH_{Ar}), 112.3 (s, C, CH_{Ar}), 109.9 (s, C, CH_{Ar}), 59.4 (s, CH_2), 41.0 (s, CH_3), 14.4 (s, CH_3), 14.3 (s, CH_3) ppm. Anal. calcd. for $C_{16}H_{20}N_2O_2$: C 70.56, H 7.40, N 10.29, found: C 70.47, H 7.45, N 10.18 %.

Ethyl 4-(4-hydroxyphenyl)-2-methyl-1*H*-pyrrole-3-carboxylate (8). White crystalline solid (0.615 g, 25%).

^{1}H NMR (300 MHz, DMSO-d_6) δ_H 11.20 (br. s, 1 H, NH), 9.18 (br. s, 1 H, OH), 7.10 (d, $^3J_{HH}$ =8.00 Hz, 2 H, CH_{Ar}), 6.67 (d, $^3J_{HH}$ =8.00 Hz, 2 H, CH_{Ar}), 6.57 (s, 1 H, CH_{Het}), 4.04 (q, $^3J_{HH}$ =7.00 Hz, 2 H, CH_2), 2.39 (s, 3 H, CH_3), 1.11 (t, $^3J_{HH}$ =7.00 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, DMSO-d_6): δ_C 165.1 (s, CO), 155.5 (s, C, CH_{Ar}), 135.5 (s, C, CH_{Ar}), 130.0 (s, C, CH_{Ar}), 126.9 (s, C, CH_{Ar}), 125.8 (s, C, CH_{Ar}), 115.2 (s, C, CH_{Ar}), 114.2 (s, C, CH_{Ar}), 108.6 (s, C, CH_{Ar}), 58.4 (s, CH_2), 14.2 (s, CH_3), 13.6 (s, CH_3) ppm. Anal. calcd. for $C_{14}H_{15}NO_3$: C 68.56, H 6.16, N 5.71, found: C 68.42, H 6.22, N 5.78 %.

Ethyl 2-methyl-4-(furan-2-yl)-1*H*-pyrrole-3-carboxylate (9). White crystalline solid (0.440 g, 20%).

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.34 (br. s, 1 H, NH), 7.35 (br. s, 1 H, CH_{Het}), 6.89 (br. s, 1 H, CH_{Het}), 6.78 (br. s, 1 H, CH_{Het}), 6.41 (br. s, 1 H, CH_{Het}), 4.29 (q, $^3J_{HH}$ = 7.10 Hz, 2 H, CH_2), 2.51 (s, 3 H, CH_3), 1.33 (t, $^3J_{HH}$ = 7.10 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 165.7 (s, CO), 149.5 (s, C_{Het}), 140.3 (s, C_{Het}), 136.5 (s, C_{Het}), 116.5 (s, C_{Het}), 115.7 (s, C_{Het}), 110.9 (s, C_{Het}), 108.7 (s, C_{Het}), 107.1 (s, C_{Het}), 59.6 (s, CH_2), 14.3 (s, CH_3), 14.1 (s, CH_3) ppm. Anal. calcd. for $C_{12}H_{13}NO_3$: C 65.74, H 5.98, N 6.39, found: C 65.61, H 5.91, N 6.45 %.

Ethyl 2-methyl-4-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (10). Ethyl 2-methyl-4-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (10). White crystalline solid (0.940 g, 40%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (br. s., 1 H, NH), 7.20 (d, $^3J_{HH}$ =5.01 Hz, 1 H, CH_{Het}), 7.16 (d, $^3J_{HH}$ =2.82 Hz, 1 H, CH_{Het}), 7.01 (m, 1 H, CH_{Het}), 6.69 (d, $^3J_{HH}$ =2.19 Hz, 1 H, CH_{Het}), 4.24 (q, $^3J_{HH}$ =7.10 Hz, 2 H, CH_2), 2.52 (s, 3 H, CH_3), 1.26 (t, $^3J_{HH}$ =7.1 Hz, 3 H, CH_3) ppm ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 165.9 (s, CO), 137.2 (s, C_{Het}), 136.7 (s, C_{Het}), 126.9 (s, C_{Het}), 126.1 (s, C_{Het}), 119.3 (s, C_{Het}) , 116.7 (s, C_{Het}), 111.11 (s, C_{Het}), 110.0 (s, C_{Het}), 59.8 (s, CH_2), 14.4 (s, CH_3) 14.2 (s, CH_3) ppm. Anal. calcd. for $C_{12}H_{13}NO_2S$: C 61.25, H 5.57, N 5.95, S 13.63 %, found: C 61.41, H 5.66, N 5.99, S 13.51 %.

Ethyl 5-formyl-4-(furan-2-yl)-2-methyl-1*H*-pyrrole-3-carboxylate (11). To pyrrole **9** (0.219 g, 0.001 mol) in anhydrous CH_2Cl_2 (mL) the Vilsmeier reagent ($POCl_3$ (0.169 g, 0.092 mL, 0.0011 mol) in DMF (2 mL)) was added dropwise at 0°C. The resulting mixture was stirred for 30 min, then washed with NaOH aqueous solution (1 g in 5 mL). The organic layer was dried over Na_2SO_4, and solvent was removed under reduced pressure to give **11** as white solid. Yield 0.225 g, 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 10.49 (br. s., 1 H, NH), 9.77 (s, 1 H, CHO), 7.54 (s, 1 H, CH_{Het}), 6.97 (br. s., 1 H, CH_{Het}), 6.52 (br. s., 1 H, CH_{Het}), 4.28 (q, J = 6.70 Hz, 2 H, CH_2), 2.61 (s, 3 H, CH_3), 1.31 (t, J = 6.70 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 181.2 (s, CO), 164.2 (s, CHO), 146.5 (s, C_{Het}), 142.9 (s, C_{Het}), 142.8 (s, C_{Het}), 128.5 (s, C_{Het}), 125.9 (s, C_{Het}), 112.6 (s, C_{Het}), 111.5 (s, C_{Het}), 60.0 (s, CH_2), 14.4 (s, CH_3), 14.3 (s, CH_3), ppm. Anal. calcd. for $C_{13}H_{13}NO_4$: C 63.15, H 5.03, N 5.67, found: C 63.22, H 5.12, N 5.74 %.

(*Z*)-4-(Ethoxycarbonyl)-2-((4-(ethoxycarbonyl)-5-methyl-3-(thiophen-2-yl)-1*H*-pyrrol-2-yl)methylene)-5-methyl-3-(thiophen-2-yl)-2*H*-pyrrol-1-ium chloride (13). To the solution of pyrrole **10** (2.35 g, 0.01 mol) in MTBE (20 mL), triethyl orthoformate (2.96 g, 0.02 mol, 3.32 mL) and 4M HCl/dioxane solution (2 mL) was added, the resulting mixture was stirred

for 0.5 h. After the reaction completion, a precipitate was collected by filtration and washed with MTBE (2×5 mL). Yield 4.1g, 95%. ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 14.87 (br. s, 2 H, NH), 7.49 (dd, $^{3}J_{HH}$ = 4.63, 1.70 Hz, 2 H, CH_{Het}), 7.30 (s, 1 H, CH_{Het}), 7.01 (m, 4 H, CH_{Het}), 4.23 (q, $^{3}J_{HH}$ = 7.10 Hz, 4 H, CH_2), 2.97 (s, 6 H, CH_3), 1.21 (t, $^{3}J_{HH}$ = 7.10 Hz, 6 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$) δ_C 162.5(s, CO), 159.3(s, CO), 144.5(s, C_{Het}), 131.6(s, C_{Het}), 131.3(s, C_{Het}), 131.0(s, C_{Het}), 129.7(s, C_{Het}), 128.6(s, C_{Het}), 127.1(s, C_{Het}), 119.6(s, C_{Het}), 61.0(s, CH_2), 15.2(s, CH_3), 14.1(s, CH_3). Anal. calc. for $C_{25}H_{25}ClN_2O_4S$ C, 58.07; H, 4.86; Cl, 6,86 N, 5.42; S, 12.40; found C, 58.12; H, 4.75; Cl, 6,90 N, 5.49; S, 12.50.

Diethyl 5,5-difluoro-3,7-dimethyl-1,9-di(thiophen-2-yl)-5*H*-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ylium-5-uide-2,8-dicarboxylate (BODIPY 14). To **13** (5.17 g, 0.01 mol) in anhydrous CH_2Cl_2 (50 mL) a solution of BF_3*Et_2O (7.05 g, 6.27 mL, 0.05 mol) and DIPEA (3.87 g, 4.90 mL, 0.03 mol) was added. The resulting mixture was stirred at r.t. for 2 h. After the completion of reaction, organic solution was washed with water (mL), dried over Na_2SO_4, solvent was evaporated *in vacuo*. A residue was crystallized from MeOH to give **14** as white solid. Yield 4.22 g, 80%. ^{1}H NMR (300 MHz, $CDCl_3$) 7.53-7.50 (m, 3 H, CH_{Het}), 7.26-7.21 (m, 2 H, CH_{Het}), 7.10-7.13 (m, 2 H, CH_{Het}), 4.25 (q, $^{3}J_{HH}$ = 7.20 Hz, 4 H, CH_2), 2.88 (s, 6 H, CH_3), 1.25 (t, $^{3}J_{HH}$ = 7.20 Hz, 6 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$) δ_C 163.5(s, CO), 160.7(s, C_{Het}) 139.5(s, C_{Het}), 134.1(s, C_{Het}), 131.9(s, C_{Het}), 130.8(s, C_{Het}), 129.3(s, C_{Het}), 127.6(s, C_{Het}), 120.7(s, C_{Het}), 60.8(s, CH_2), 15.1(s, CH_3), 14.2(s, CH_3) ppm. ^{19}F NMR (188 MHz, $CDCl_3$) δ_F -142.8–(-143.3) (m) ppm. Anal. calc. for $C_{25}H_{23}BF_2N_2O_4S_2$ C, 56.83; H, 4.39; N, 5.30; S, 12.13; found C, 56.91; H, 4.30; N, 5.23; S, 12.18.

Diethyl 5,5-difluoro-3,7-di((*E*)-styryl)-1,9-di(thiophen-2-yl)-5H-4λ^4,5λ^4-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinin-4-ylium-5-uide-2,8-dicarboxylate (BODIPY 15). To BODIPY **14** (200 mg, 0.18 mmol) in acetonitrile (10 mL), a mixture of benzaldehyde (150 mg, 1.6 mmol), piperidine (20 mg, 0.24 mmol) and acetic acid (20 mg, 0.33 mmol) was added. The resulting solution was refluxed for 2 h. After the reaction completion, the reaction mixture was cooled to r.t., and water (20 mL) was added. The resulting precipitate was collected by filtration and dried *in vacuo*. Yield 0.115 g, 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.16-7.77 (m, 21 H, CH_{Ar+Het}), 4.29 (q, $^{3}J_{HH}$ = 7.0 Hz, 4 H, CH_2), 1.22 (t, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 165.3 (s, CO), 153.0 (s, C_{Ar+Het}), 140.9 (s, C_{Ar+Het}), 136.4 (s, C_{Ar+Het}), 134.9 (s, C_{Ar+Het}), 131.9 (s, C_{Ar+Het}), 129.8 (s, C_{Ar+Het}), 129.0 (s, C_{Ar+Het}), 128.9 (s, C_{Ar+Het}), 128.1 (s, C_{Ar+Het}), 128.0 (s, C_{Ar+Het}), 125.8 (s, C_{Ar+Het}), 117.7 (s, C_{Ar+Het}), 61.7 (s, CH_2), 14.1 (s, CH_3), ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ_F -138.1–(-138.6) (m) ppm. Anal. calcd. for $C_{39}H_{31}BF_2N_2O_4S_2$: C 66.48, H 4.43, N 3.98, S 9.10; found: C 66.56, H 4.51, N 4.08. S 9.03 %.

Diethyl (E)-3-(2-(dimethylamino)vinyl)-5,5-difluoro-7-methyl-1,9-di(thiophen-2-yl)-5H-4λ^4,5λ^4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ylium-5-uide-2,8-dicarboxylate (BODIPY 16). The solution of BODIPY **14** (200 mg, 0.18 mmol), DMF-DMA (150 mg, 1.27 mmol) and acetic anhydride (20 mg, 0.2 mmol) in toluene (10 mL) was heated to reflux for 10 min. After completion of reaction, the reaction mixture was allowed to cool to r.t., and the precipitate was collected by filtration, washed with toluene (2x2 mL) and dried *in vacuo*. Yield 0.103 g, 98%.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.26 (d, $^{3}J_{HH}$ =12.80 Hz, 1 H, $(CH_3)_2$N-C), 7.45 (d, $^{3}J_{HH}$ =5.00 Hz, 1 H, C_{Het}), 7.36 (d, $^{3}J_{HH}$ = 5.00 Hz, 1 H, C_{Het}), 7.07 (m, 5 H, C_{Het}), 6.09 (d, $^{3}J_{HH}$ = 12.80 Hz, 1 H, $(CH_3)_2$N-C=C), 4.19 (m, 4 H, CH_2), 3.16 (s, 6 H, $(CH_3)_2$N), 2.83 (s, 3 H, CH_3), 1.20 (t, $^{3}J_{HH}$ = 7.03 Hz, 3 H, CH_3), 1.12 (t, $^{3}J_{HH}$ = 7.09 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 165.7 (s, CO), 164.8 (s, CO), 158.0 (s, C_{Het}), 154.3 (s, C_{Het}), 151.6 (s, C_{Het}), 137.6 (s, C_{Het}), 134.4 (s, C_{Het}), 132.0 (s, C_{Het}), 131.9 (s, C_{Het}), 129.4 (s, C_{Het}), 128.8 (s, C_{Het}), 128.3 (s, C_{Het}), 127.4 (s, C_{Het}), 126.9 (s, C_{Het}), 126.7 (s, C_{Het}), 118.1 (s, C_{Het}), 88.9 (s, CH), 61.2 (s, CH_2), 59.9 (s, CH_3), 14.2 (s, CH_3), 14.2 (s, CH_3), 13.9 (s, CH_3) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ_F -143.0–(-143.5) (m) ppm. Anal. calcd. for $C_{28}H_{28}BF_2N_3O_4S_2$: C 57.64, H 4.84, N 7.20, S 10.99; found: C 57.55, H 4.72, N 7.29. S 11.03 %.

Diethyl 3,7-bis((E)-2-(dimethylamino)vinyl)-5,5-difluoro-1,9-di(thiophen-2-yl)-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ylium-5-uide-2,8-dicarboxylate (BODIPY 17). The solution of BODIPY **14** (200 mg, 0.18 mmol), DMF-DMA (200 mg, 224 mL, 1.68 mmol) in DMF (200 mg, 211 mL) was heated to reflux for 15 min. After completion of reaction, the reaction mixture was allowed to cool to r.t., and water (2 mL) was added. The resulting precipitate was collected by filtration and dried *in vacuo*. Yield 0.113 g, 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, $^{3}J_{HH}$ =13.45 Hz, 2 H), 7.36 (dd, $^{3}J_{HH}$ =4.07, 2.19 Hz, 2 H), 7.04 (m, 4 H), 6.88 (s, 1 H), 6.03 (d, $^{3}J_{HH}$ =13.45 Hz, 2 H), 4.13 (q, $^{3}J_{HH}$ =7.30 Hz, 4 H), 3.04 (s, 12 H), 1.09 (t, $^{3}J_{HH}$ =7.30 Hz, 6 H) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 166.1 (s, CO), 153.8 (s, C_{Het}), 150.5 (s, C_{Het}), 134.5 (s, C_{Het}), 134.0 (s, C_{Het}), 128.4 (s, C_{Het}), 127.1 (s, C_{Het}), 116.1 (s, C_{Het}), 88.4 (s, CH), 60.5 (s, CH_2), 13.9 (s, CH_3) ppm.^{19}F NMR (188 MHz, $CDCl_3$): δ_F -141.9–(-142.5) (m) ppm. Anal. calcd. for $C_{31}H_{33}BF_2N_4O_4S_2$: C 58.31, H 5.21, N 8.77, S 10.04; found: C 58.45, H 5.29, N 8.70. S 10.19 %.

BODIPY 18 та 19. To compounds **19** or **20** (0,005 mol) in acetonitrile (5 mL), *n*-butylamine (1,46 g, 0,02 mol, 1,3 mL) was added, the resulting solution was left for 24 h. After completion of reaction, acetic acid (3 mL) was added, the precipitate was collected by filtration and washed with acetonitrile (2×2 mL).

Ethyl 2-butyl-6,6-difluoro-8-methyl-1-oxo-10,12-di(thiophen-2-yl)-2,6-dihydro-1*H*-5λ^4,6λ^4-pyrido[3',4':4,5]pyrrolo[2,1-*f*]pyrrolo[1,2-*c*][1,3,2]diazaborinin-5-ylium-6-uide-9-carboxylate (BODIPY 18). Yield 1.84 g, 65%.

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.87 (s, 1 H, CH_{Het}), 7.81 (d, $^{3}J_{HH}$ =3.76 Hz, 1 H, CH_{Het}), 7.57 (t, $^{3}J_{HH}$ =4.13 Hz, 2 H, CH_{Het}), 7.30 (m, 2 H, CH_{Het}), 7.19 (m, 2 H, CH_{Het}), 4.28 (q, $^{3}J_{HH}$ =7.1 Hz, 2 H, CH_2), 3.93 (t, $^{3}J_{HH}$ =7.30 Hz, 2 H, CH_2), 2.92 (s, 3 H, CH_3), 1.73 (quin, $^{3}J_{HH}$ =7.40 Hz, 2 H, CH_2), 1.39 (sxt, $^{3}J_{HH}$ =7.40 Hz, 2 H, CH_2), 1.27 (t, $^{3}J_{HH}$ =7.10 Hz, 3 H, CH_3), 0.95 (t, $^{3}J_{HH}$ =7.30 Hz, 3 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 163.4 (s, CO), 161.6 (s, CO), 159.3 (s, C_{Het}), 153.1 (s, C_{Het}), 140.3 (s, C_{Het}), 140.0 (s, C_{Het}), 138.00 (s, C_{Het}), 136.4 (s, C_{Het}), 136.0 (s, C_{Het}), 133.1 (s, C_{Het}), 131.9 (s, C_{Het}), 131.9 (s, C_{Het}), 131.1 (s, C_{Het}), 130.7 (s, C_{Het}), 129.7 (s, C_{Het}), 129.6 (s, C_{Het}), 128.3 (s, C_{Het}), 127.7 (s, C_{Het}), 97.0 (s, CH), 60.9 (s, CH_2), 49.0 (s, CH_2), 31.7 (s, CH_2), 20.1 (s, CH_2), 15.3 (s, CH_3), 14.1 (s, CH_3), 13.8 (s, CH_3) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ_F -143.4–(-143.9) (m) ppm. Anal. calcd. for $C_{28}H_{26}BF_2N_3O_3S_2$: C 59.47, H 4.63, N 7.43, S 11.34; found: C 59.55, H 4.69, N 7.50. S 11.21 %.

2,10-Dibutyl-6,6-difluoro-12,14-di(thiophen-2-yl)-6,10-dihydro-1*H*-5λ^4,6λ^4-pyrido[3',4':4,5]pyrrolo[1,2-*c*]pyrido[3',4':4,5]pyrrolo[2,1-*f*][1,3,2]diazaborinin-5-ylium-6-uide-1,11(2*H*)-dione (BODIPY 19). Yield 1.95 g, 65%,

^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.19 (s, 1 H, CH_{Het}), 7.90 (d, $^{3}J_{HH}$ = 3.13 Hz, 2 H, CH_{Het}), 7.64 (d, $^{3}J_{HH}$ = 5.01 Hz, 2 H, CH_{Het}), 7.33 (d, $^{3}J_{HH}$ = 7.51 Hz, 2 H, CH_{Het}), 7.24 (m, 2 H, CH_{Het}), 6.76 (d, $^{3}J_{HH}$ = 6.88 Hz, 2 H, CH_{Het}), 3.93 (q, $^{3}J_{HH}$ = 7.20 Hz, 4 H, CH_2), 1.73 (m, 4 H, CH_2), 1.39 (m, 4 H, CH_2), 0.95 (t, $^{3}J_{HH}$ =7.20 Hz, 6 H, CH_3) ppm. ^{13}C NMR (76 MHz, $CDCl_3$): δ_C 159.2 (s, C), 153.5 (s, C) 140.5 (s, C), 138.9 (s, C), 138.3 (s, C), 133.6 (s, C), 132.0 (s, C), 131.3 (s, C), 129.5 (s, C), 128.43 (s, C), 117.9 (s, C), 97.1 (s, CH), 49.0 (s, CH_2), 31.7 (s, CH_2), 20.0 (s, CH_2), 13.8 (s, CH_3) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ_F -144.5–(-145.0) (m) ppm. Anal. calcd. for $C_{31}H_{29}BF_2N_4O_2S_2$: C 61.80, H 4.85, N 9.30, S 10.64; found: C 61.65, H 4.91, N 9.42. S 10.72 %.

X-ray analysis

X-Ray diffraction studies were performed on an automatic "Bruker APEX II" diffractometer (graphite monochromated MoKα radiation, CCD-detector, φ- and ω-scanning). The structures were solved by direct method using OLEX2 [6] package with SHELXT [7] and SHELXL modules [8]. Positions of the hydrogen atoms were calculated geometrically and refined by "riding" model with U_{iso} = nU_{eq} of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). The crystallographic data and experimental parameters are listed in Table S1. Final atomic coordinates, geometrical parameters and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, 11 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The deposition numbers are given in Table S1.

Table S1. The crystallographic data and experimental parameters for compounds **6, 14, 14a**.

Parameter	**6**	**14**	**14a**
Formula	$C_{14}H_{18}N_2O_4$	$C_{25}H_{23}BF_2N_2O_4S_2$	$C_{29}H_{27}BF_2N_2O_4$
Mr	278.30	528.38	516.33
Unit cell a, Å	7.5005(6)	19.774(5)	11.3899(7)
b, Å	9.6788(8)	8.0609(19)	7.8490(5)
c, Å	20.8739(18)	30.271(7)	28.9675(17)
α, deg	90.0	90.0	90.0
β, deg	92.351(5)	91.235(16)	100.595(4)
γ, deg	90.0	90.0	90.0
V, Å^3	1514.1(2)	4824.1(19)	2545.5(3)
F(000)	592	2192	1080
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Z	4	8	4
T, K	173(2)	173(2)	173(2)
μ, mm^{-1}	0.090	0.273	0.099
D_{calc}, g/cm^3	1.221	1.455	1.347
$2\Theta_{max}$, grad	50.0	50.0	50.0
Measured reflections	20225	49567	34675
Independent reflections	2666	8498	4488
R_{int}	0.0426	0.0817	0.0690
Reflections with F>4σ(F)	2072	3061	3070
Parameters	185	622	347
R_1	0.0536	0.1162	0.0559
wR_2	0.1466	0.2882	0.1454
S	1.061	1.010	1.030
CCDC number	2401284	2401283	2401285

Hydrolytic and Photo-stability measurements

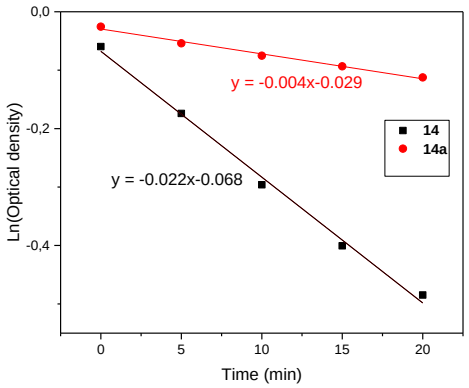


Fig. S1. Kinetic curves of hydrolytic stability measurements of **14** and **14a**.

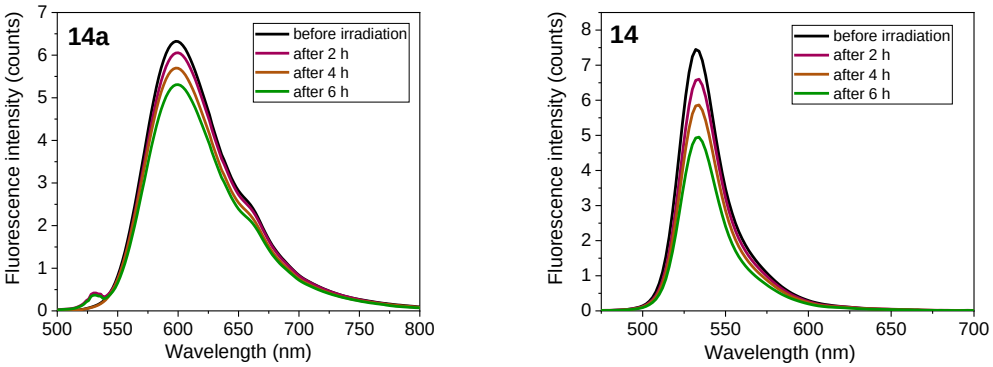
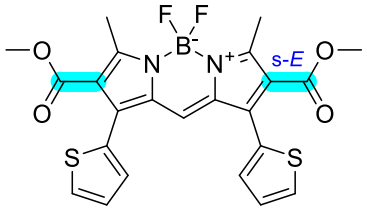


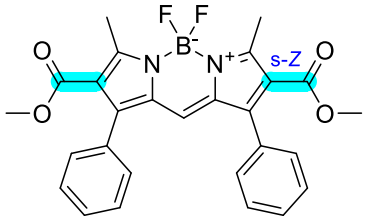
Fig. S2. Fluorescence intensity before (black) and after two hours of irradiation by UV light (λ_{ex} = 300 nm).

Computation Details

The molecular structures of the 'pruned' studied molecules **14′** and **14a′** are shown below. The possible conformations of the methoxycarbonyl groups are highlighted; the thienyl substituents in **14′** are shown with the distal ('out') orientation of the sulfur atoms.

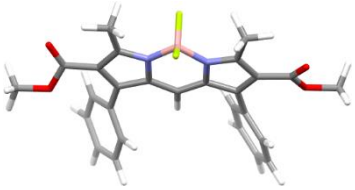
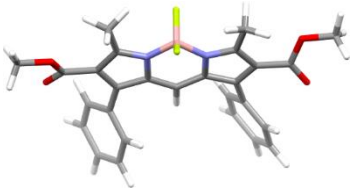
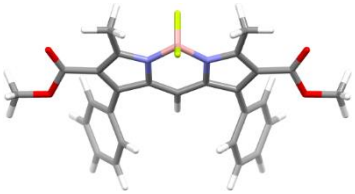
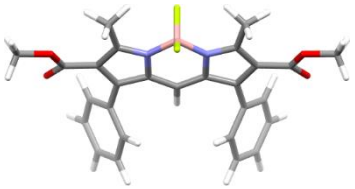
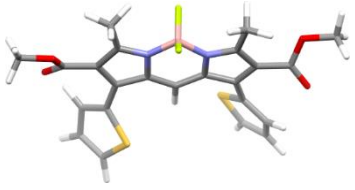


14′



14a′

Table S2 The optimized structures, absolute and relative energies of the studied conformers of **14′** and **14a′**, obtained using the B3LYP/6-31G(d,p) level of theory. The lowest relative energies of the conformers, chosen for further computations in the solvent fields, are highlighted with green.

Dye **(conformer)**	**Structure**	***E*, Hartree**	**Δ*E*, Hartree**	**Δ*E*, kJ/mol**
14a′ ***C*2_s-*Z***		-1677.929247	0.000000	0.00
14a′ ***C*2_s-*E***		-1677.927368	0.001879	4.93
14a′ ***C*s_s-*Z***		-1677.928962	0.000285	0.75
14a′ ***C*s_s-*E***		-1677.926918	0.002329	6.11
14′ ***C*2_s-*Z*_in**		-2319.431285	0.001740	4.57
14′ ***C*2_s-*E*_in**		-2319.432981	0.000043	0.11

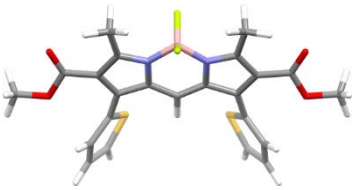
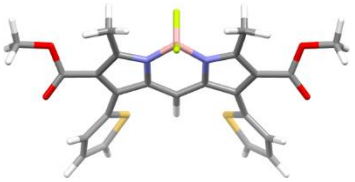
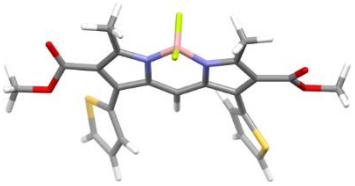
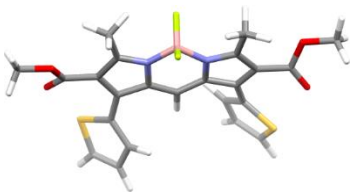
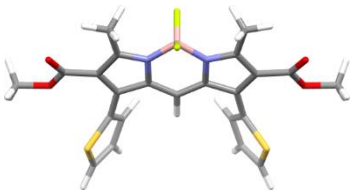
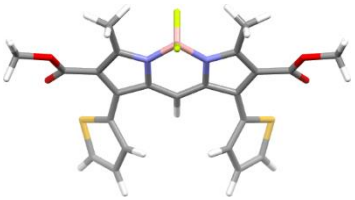
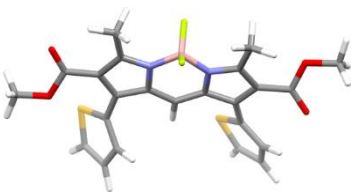
14′ **C_S_s-*Z*_in**		-2319.430535	0.002489	6.53
14′ **C_S_s-*E*_in**		-2319.432342	0.000682	1.79
14′ **C_2_s-*Z*_out**		-2319.432991	0.000033	0.09
14′ **C_2_s-*E*_out**		-2319.432240	0.000784	2.06
14′ **C_S_s-*Z*_out**		-2319.432479	0.000545	1.43
14′ **C_S_s-*E*_out**		-2319.431217	0.001807	4.74
14′ **unsymm1**		-2319.432783	0.000241	0.63
14′ **unsymm2**		-2319.433024	0.000000	0.00

Table S3 The optimized structures, absolute and relative energies of the studied conformers of **14′** and **14a′**, obtained using the PCM_{CH2Cl2}/B3LYP/6-31G(d,p) level of theory. The lowest relative energies of the conformers are highlighted with green. Their data are mostly used in the discussion.

Dye **(conformer)**	**Structure**	***E*, Hartree**	**Δ*E*, Hartree**	**Δ*E*, kJ/mol**

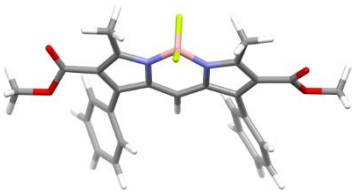
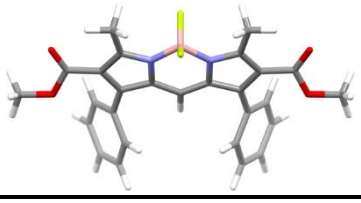
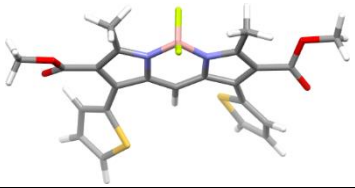
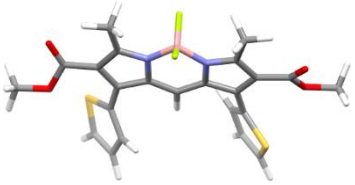
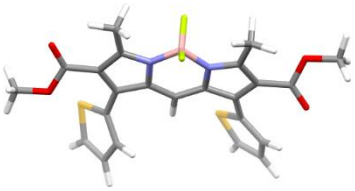
14a′ ***C*$_2$_s-*Z***		-1677.942485	0	0
14a′ ***C*s_s-*Z***		-1677.942312	0.000173	0.45
14′ ***C*$_2$_s-*E*_in**		-2319.444817	0.0016301	4.28
14′ ***C*$_2$_s-*Z*_out**		-2319.446447	0	0
14′ **unsymm2**		-2319.445629	0.0008181	2.15

Table S4 The molecular dipole moments (Debye) of the most stable conformers (see Table Q2) of **14′** and **14a′**, calculated at the PCM$_{CH2Cl2}$/(TD)-B3LYP/6-31G(d,p) level of theory.

Dye	**S_0**	**S_1^{FC}**	**S_1**	**S_0^{FC}**
14a′	9.2	12.0	12.7	9.9
14′	9.5	14.3	13.5	10.9

Ground state optimized coordinates of four conformers of molecule 14a′
(B3LYP/6-31G(d,p), see Table Q1 for details)

14a′ C2_s-Z

C	-0.129476	2.544234	0.136620
C	0.129476	-2.544234	0.136620
C	-0.243986	3.376027	-0.995531
C	0.243986	-3.376027	-0.995531
C	-0.212398	2.533153	-2.150817
C	0.212398	-2.533153	-2.150817
N	-0.087941	1.254829	-1.759320
N	0.087941	-1.254829	-1.759320
B	0.000000	0.000000	-2.704924
C	-0.044724	1.214909	-0.366498
C	0.044724	-1.214909	-0.366498
C	0.000000	0.000000	0.309951
F	-1.144402	-0.075784	-3.483661
F	1.144402	0.075784	-3.483661
C	-0.140569	2.869763	1.575468
C	0.140569	-2.869763	1.575468
C	0.878824	2.394172	2.417585
C	-0.878824	-2.394172	2.417585
C	0.851471	2.656774	3.787674
C	-0.851471	-2.656774	3.787674
C	-0.197551	3.391540	4.339027
C	0.197551	-3.391540	4.339027
C	-1.217948	3.867852	3.511366
C	1.217948	-3.867852	3.511366
C	-1.189249	3.613343	2.143351
C	1.189249	-3.613343	2.143351
C	-0.277379	2.900259	-3.595814
C	0.277379	-2.900259	-3.595814
C	-0.302769	4.847890	-1.072875
C	0.302769	-4.847890	-1.072875
O	-0.602130	5.487192	-2.066562
O	0.602130	-5.487192	-2.066562
O	0.035534	5.439853	0.095186
O	-0.035534	-5.439853	0.095186
C	0.000000	6.875068	0.088230
C	0.000000	-6.875068	0.088230
H	0.000000	0.000000	1.393162
H	1.708548	1.840749	1.988820
H	-1.708548	-1.840749	1.988820
H	1.653442	2.289301	4.420996
H	-1.653442	-2.289301	4.420996
H	-0.221070	3.594123	5.405660
H	0.221070	-3.594123	5.405660
H	-2.040597	4.436813	3.934629
H	2.040597	-4.436813	3.934629
H	-1.987174	3.978665	1.505679
H	1.987174	-3.978665	1.505679
H	-0.225138	3.978785	-3.720570
H	0.225138	-3.978785	-3.720570
H	0.530170	2.401349	-4.138178
H	-0.530170	-2.401349	-4.138178
H	-1.217001	2.534553	-4.023910
H	1.217001	-2.534553	-4.023910
H	0.261992	7.176949	1.101963
H	-0.261992	-7.176949	1.101963
H	0.720531	7.274686	-0.629644
H	-0.720531	-7.274686	-0.629644
H	-0.996132	7.237618	-0.177085
H	0.996132	-7.237618	-0.177085

14a′ C2_s-E

C	0.147128	2.543544	0.313207
C	-0.147128	-2.543544	0.313207
C	0.120114	3.384568	-0.819547
C	-0.120114	-3.384568	-0.819547
C	0.054335	2.545495	-1.975404
C	-0.054335	-2.545495	-1.975404
N	0.029789	1.259989	-1.585626
N	-0.029789	-1.259989	-1.585626
B	0.000000	0.000000	-2.528040
C	0.085253	1.213626	-0.193392
C	-0.085253	-1.213626	-0.193392
C	0.000000	0.000000	0.481289
F	-1.145857	0.014612	-3.309750
F	1.145857	-0.014612	-3.309750
C	0.253672	2.859976	1.749722
C	-0.253672	-2.859976	1.749722
C	1.225734	2.211196	2.534437
C	-1.225734	-2.211196	2.534437
C	1.315905	2.454067	3.904363
C	-1.315905	-2.454067	3.904363
C	0.431566	3.342751	4.515644
C	-0.431566	-3.342751	4.515644
C	-0.535963	3.993832	3.746855
C	0.535963	-3.993832	3.746855
C	-0.623302	3.761956	2.376874
C	0.623302	-3.761956	2.376874
C	0.014001	2.915039	-3.422596
C	-0.014001	-2.915039	-3.422596
C	0.225640	4.854642	-0.803480
C	-0.225640	-4.854642	-0.803480
O	0.000000	5.571861	0.152921
O	0.000000	-5.571861	0.152921
O	0.632303	5.352617	-2.000422
O	-0.632303	-5.352617	-2.000422
C	0.752730	6.783221	-2.053968
C	-0.752730	-6.783221	-2.053968
H	0.000000	0.000000	1.564191
H	1.931516	1.537496	2.058606
H	-1.931516	-1.537496	2.058606
H	2.080314	1.952257	4.490130
H	-2.080314	-1.952257	4.490130
H	0.499164	3.532498	5.582861
H	-0.499164	-3.532498	5.582861
H	-1.225183	4.689716	4.215888
H	1.225183	-4.689716	4.215888
H	-1.364395	4.280754	1.783103
H	1.364395	-4.280754	1.783103
H	-0.447427	3.891554	-3.558669
H	0.447427	-3.891554	-3.558669
H	1.031329	2.972564	-3.825966
H	-1.031329	-2.972564	-3.825966
H	-0.532214	2.157443	-3.984608
H	0.532214	-2.157443	-3.984608
H	1.061578	7.012245	-3.073718
H	-1.061578	-7.012245	-3.073718
H	-0.202268	7.261768	-1.823822
H	0.202268	-7.261768	-1.823822
H	1.501163	7.132585	-1.338817
H	-1.501163	-7.132585	-1.338817

14a′ CS_s-Z

C	-0.136139	0.001333	2.547543
C	-0.136139	0.001333	-2.547543
C	0.997231	-0.047839	3.383756
C	0.997231	-0.047839	-3.383756
C	2.152459	-0.027500	2.540313
C	2.152459	-0.027500	-2.540313
N	1.759477	0.032217	1.257887
N	1.759477	0.032217	-1.257887
B	2.704561	0.056987	0.000000
C	0.365921	0.041359	1.215890
C	0.365921	0.041359	-1.215890
C	-0.310343	0.022207	0.000000
F	3.455855	1.223641	0.000000
F	3.509965	-1.069525	0.000000
C	-1.574711	-0.026767	2.874384
C	-1.574711	-0.026767	-2.874384
C	-2.436062	0.960956	2.368257
C	-2.436062	0.960956	-2.368257
C	-3.805035	0.916742	2.634182
C	-3.805035	0.916742	-2.634182
C	-4.335953	-0.118796	3.402324
C	-4.335953	-0.118796	-3.402324
C	-3.488891	-1.108097	3.908922
C	-3.488891	-1.108097	-3.908922
C	-2.121866	-1.061774	3.651599
C	-2.121866	-1.061774	-3.651599
C	3.598051	-0.050529	2.910056
C	3.598051	-0.050529	-2.910056
C	1.073804	-0.040094	4.856728
C	1.073804	-0.040094	-4.856728
O	2.075484	-0.279174	5.508808
O	2.075484	-0.279174	-5.508808
O	-0.105692	0.285435	5.432990
O	-0.105692	0.285435	-5.432990
C	-0.100270	0.311841	6.868401
C	-0.100270	0.311841	-6.868401
H	-1.392979	-0.017013	0.000000
H	-2.022614	1.780378	1.788305
H	-2.022614	1.780378	-1.788305
H	-4.453937	1.695104	2.243665
H	-4.453937	1.695104	-2.243665
H	-5.401758	-0.155993	3.607067
H	-5.401758	-0.155993	-3.607067
H	-3.896173	-1.920418	4.503729
H	-3.896173	-1.920418	-4.503729
H	-1.468825	-1.835573	4.040889
H	-1.468825	-1.835573	-4.040889
H	4.130703	0.730930	2.361782
H	4.130703	0.730930	-2.361782
H	3.721290	0.070382	3.983278
H	3.721290	0.070382	-3.983278
H	4.038262	-1.006088	2.604958
H	4.038262	-1.006088	-2.604958
H	-1.122477	0.553745	7.158247
H	-1.122477	0.553745	-7.158247
H	0.196218	-0.658768	7.273500
H	0.196218	-0.658768	-7.273500
H	0.593329	1.071584	7.237085
H	0.593329	1.071584	-7.237085

14a′ CS_s-E

C	-0.309770	-0.062395	2.547103
C	-0.309770	-0.062395	-2.547103
C	0.822925	-0.105478	3.386513
C	0.822925	-0.105478	-3.386513
C	1.980388	-0.082972	2.547109
C	1.980388	-0.082972	-2.547109
N	1.591453	-0.037535	1.261639
N	1.591453	-0.037535	-1.261639
B	2.532002	0.010700	0.000000
C	0.197683	-0.021308	1.217020
C	0.197683	-0.021308	-1.217020
C	-0.476040	-0.039545	0.000000
F	3.258502	1.187118	0.000000
F	3.366515	-1.102827	0.000000
C	-1.748443	-0.019574	2.869980
C	-1.748443	-0.019574	-2.869980
C	-2.561011	0.976795	2.297897
C	-2.561011	0.976795	-2.297897
C	-3.932178	1.010753	2.548030
C	-3.932178	1.010753	-2.548030
C	-4.516641	0.044629	3.366776
C	-4.516641	0.044629	-3.366776
C	-3.719801	-0.948129	3.941568
C	-3.719801	-0.948129	-3.941568
C	-2.348570	-0.979363	3.703015
C	-2.348570	-0.979363	-3.703015
C	3.426654	-0.101243	2.921944
C	3.426654	-0.101243	-2.921944
C	0.801968	-0.092992	4.860177
C	0.801968	-0.092992	-4.860177
O	-0.151943	-0.380672	5.558149
O	-0.151943	-0.380672	-5.558149
O	1.990248	0.302791	5.386937
O	1.990248	0.302791	-5.386937
C	2.038118	0.333516	6.822439
C	2.038118	0.333516	-6.822439
H	-1.558266	-0.079623	0.000000
H	-2.105607	1.744604	1.680060
H	-2.105607	1.744604	-1.680060
H	-4.540359	1.795201	2.107397
H	-4.540359	1.795201	-2.107397
H	-5.584810	0.067855	3.561534
H	-5.584810	0.067855	-3.561534
H	-4.167879	-1.701298	4.582770
H	-4.167879	-1.701298	-4.582770
H	-1.733329	-1.741572	4.163092
H	-1.733329	-1.741572	-4.163092
H	3.786887	0.921103	3.083946
H	3.786887	0.921103	-3.083946
H	3.576221	-0.648288	3.851496
H	3.576221	-0.648288	-3.851496
H	4.014683	-0.549868	2.122078
H	4.014683	-0.549868	-2.122078
H	3.051749	0.644796	7.074227
H	3.051749	0.644796	-7.074227
H	1.309128	1.045868	7.215894
H	1.309128	1.045868	-7.215894
H	1.823449	-0.653664	7.238807
H	1.823449	-0.653664	-7.238807

Ground state optimized coordinates of ten conformers of molecule 14′
(B3LYP/6-31G(d,p), see Table Q1 for details)

14′ C2_s-Z_in

C	-0.120319	4.859563	-1.072649
C	0.120319	-4.859563	-1.072649
O	0.300969	5.465845	0.059419
O	-0.300969	-5.465845	0.059419
C	0.329292	6.900732	0.010503
C	-0.329292	-6.900732	0.010503
C	0.000000	2.910510	1.579306
C	0.000000	-2.910510	1.579306
S	1.168662	2.200477	2.684560
S	-1.168662	-2.200477	2.684560
C	0.515927	3.073972	4.027184
C	-0.515927	-3.073972	4.027184
C	-0.535517	3.866193	3.649831
C	0.535517	-3.866193	3.649831
C	-0.823554	3.777934	2.260529
C	0.823554	-3.777934	2.260529
N	-0.040509	1.256955	-1.723854
N	0.040509	-1.256955	-1.723854
C	-0.191669	2.897492	-3.567214
C	0.191669	-2.897492	-3.567214
C	-0.125455	2.537791	-2.120281
C	0.125455	-2.537791	-2.120281
O	-0.445759	5.486697	-2.065979
O	0.445759	-5.486697	-2.065979
C	-0.112151	3.386932	-0.972195
C	0.112151	-3.386932	-0.972195
C	-0.015968	2.554181	0.165953
C	0.015968	-2.554181	0.165953
C	0.011154	1.216685	-0.333166
C	-0.011154	-1.216685	-0.333166
C	0.000000	0.000000	0.342733
F	-1.146379	-0.031421	-3.447345
F	1.146379	0.031421	-3.447345
B	0.000000	0.000000	-2.668777
H	0.654597	7.218382	1.000846
H	-0.654597	-7.218382	1.000846
H	-0.661327	7.301491	-0.217831
H	0.661327	-7.301491	-0.217831
H	1.030830	7.246374	-0.752713
H	-1.030830	-7.246374	-0.752713
H	0.949375	2.956266	5.010545
H	-0.949375	-2.956266	5.010545
H	-1.087953	4.492108	4.341071
H	1.087953	-4.492108	4.341071
H	-1.619231	4.326191	1.772340
H	1.619231	-4.326191	1.772340
H	-1.164516	2.600424	-3.973861
H	1.164516	-2.600424	-3.973861
H	0.566846	2.337147	-4.119509
H	-0.566846	-2.337147	-4.119509
H	-0.066013	3.968378	-3.703891
H	0.066013	-3.968378	-3.703891
H	0.000000	0.000000	1.425072

14′ C2_s-E_in

C	0.346524	4.850411	-0.813925
C	-0.346524	-4.850411	-0.813925
O	0.908754	5.300631	-1.964811
O	-0.908754	-5.300631	-1.964811
C	1.032247	6.728861	-2.064880
C	-1.032247	-6.728861	-2.064880
C	0.423265	2.897901	1.748599
C	-0.423265	-2.897901	1.748599
S	1.466604	1.931632	2.794722
S	-1.466604	-1.931632	2.794722
C	1.131185	2.940298	4.156677
C	-1.131185	-2.940298	4.156677
C	0.276542	3.960194	3.832202
C	-0.276542	-3.960194	3.832202
C	-0.118094	3.943712	2.467565
C	0.118094	-3.943712	2.467565
N	0.070057	1.256716	-1.543266
N	-0.070057	-1.256716	-1.543266
C	0.080717	2.902301	-3.389342
C	-0.080717	-2.902301	-3.389342
C	0.128182	2.539716	-1.940466
C	-0.128182	-2.539716	-1.940466
O	0.000000	5.606719	0.074922
O	0.000000	-5.606719	0.074922
C	0.230275	3.381815	-0.795738
C	-0.230275	-3.381815	-0.795738
C	0.253147	2.545323	0.347593
C	-0.253147	-2.545323	0.347593
C	0.137779	1.210478	-0.153358
C	-0.137779	-1.210478	-0.153358
C	0.000000	0.000000	0.520133
F	-1.144891	0.048872	-3.267204
F	1.144891	-0.048872	-3.267204
B	0.000000	0.000000	-2.484610
H	1.465662	6.915942	-3.047091
H	-1.465662	-6.915942	-3.047091
H	1.685661	7.113047	-1.278081
H	-1.685661	-7.113047	-1.278081
H	0.055282	7.210163	-1.976102
H	-0.055282	-7.210163	-1.976102
H	1.591248	2.727577	5.111763
H	-1.591248	-2.727577	5.111763
H	-0.058540	4.705570	4.544053
H	0.058540	-4.705570	4.544053
H	-0.769138	4.674243	2.010772
H	0.769138	-4.674243	2.010772
H	-0.547206	2.191914	-3.927909
H	0.547206	-2.191914	-3.927909
H	1.086939	2.857546	-3.820802
H	-1.086939	-2.857546	-3.820802
H	-0.292842	3.915482	-3.524632
H	0.292842	-3.915482	-3.524632
H	0.000000	0.000000	1.601689

14′ CS_s-Z_in

C	1.089020	-0.047775	4.860261
C	1.089020	-0.047775	-4.860261
O	-0.072313	-0.340418	5.488100
O	-0.072313	-0.340418	-5.488100
C	-0.028161	-0.257743	6.921497
C	-0.028161	-0.257743	-6.921497
C	-1.579432	-0.160466	2.890767
C	-1.579432	-0.160466	-2.890767
S	-2.707148	1.000552	2.200263
S	-2.707148	1.000552	-2.200263
C	-4.048212	0.265062	3.006865
C	-4.048212	0.265062	-3.006865
C	-3.655590	-0.808370	3.761011
C	-3.655590	-0.808370	-3.761011
C	-2.254778	-1.044965	3.700623
C	-2.254778	-1.044965	-3.700623
N	1.730594	0.021879	1.259607
N	1.730594	0.021879	-1.259607
C	3.573545	0.066313	2.909734
C	3.573545	0.066313	-2.909734
C	2.128734	-0.003101	2.541771
C	2.128734	-0.003101	-2.541771
O	2.107572	0.222339	5.473274
O	2.107572	0.222339	-5.473274
C	0.981252	-0.086406	3.390181
C	0.981252	-0.086406	-3.390181
C	-0.159342	-0.107558	2.553901
C	-0.159342	-0.107558	-2.553901
C	0.340083	-0.039808	1.217678
C	0.340083	-0.039808	-1.217678
C	-0.332568	-0.092790	0.000000
F	3.370878	1.284855	0.000000
B	2.671875	0.093015	0.000000
F	3.525637	-1.003973	0.000000
H	-1.037250	-0.495859	7.257261
H	-1.037250	-0.495859	-7.257261
H	0.255899	0.747345	7.241881
H	0.255899	0.747345	-7.241881
H	0.691993	-0.972226	7.327462
H	0.691993	-0.972226	-7.327462
H	-5.042420	0.671685	2.884078
H	-5.042420	0.671685	-2.884078
H	-4.343380	-1.411379	4.342522
H	-4.343380	-1.411379	-4.342522
H	-1.751013	-1.842053	4.230363
H	-1.751013	-1.842053	-4.230363
H	4.162550	-0.520745	2.203236
H	4.162550	-0.520745	-2.203236
H	3.727396	-0.273481	3.930757
H	3.727396	-0.273481	-3.930757
H	3.920674	1.104071	2.843361
H	3.920674	1.104071	-2.843361
H	-1.410627	-0.187919	0.000000

14′ CS_s-E_in

C	-0.836341	0.197842	4.862262
C	-0.836341	0.197842	-4.862262
O	-1.917646	-0.448915	5.367976
O	-1.917646	-0.448915	-5.367976
C	-2.016456	-0.441917	6.801740
C	-2.016456	-0.441917	-6.801740
C	1.736746	0.180435	2.934991
C	1.736746	0.180435	-2.934991
S	2.891155	-0.865217	2.107804
S	2.891155	-0.865217	-2.107804
C	4.198976	-0.282830	3.075806
C	4.198976	-0.282830	-3.075806
C	3.778643	0.653199	3.982716
C	3.778643	0.653199	-3.982716
C	2.383078	0.910293	3.911181
C	2.383078	0.910293	-3.911181
N	-1.555393	0.043287	1.258668
N	-1.555393	0.043287	-1.258668
C	-3.408389	0.033786	2.897751
C	-3.408389	0.033786	-2.897751
C	-1.958037	0.078994	2.540977
C	-1.958037	0.078994	-2.540977
O	-0.001251	0.719036	5.578276
O	-0.001251	0.719036	-5.578276
C	-0.817055	0.169944	3.388815
C	-0.817055	0.169944	-3.388815
C	0.330735	0.175602	2.559303
C	0.330735	0.175602	-2.559303
C	-0.164304	0.100282	1.219211
C	-0.164304	0.100282	-1.219211
C	0.506573	0.154303	0.000000
F	-3.205875	-1.206727	0.000000
B	-2.493365	-0.021140	0.000000
F	-3.344312	1.081425	0.000000
H	-2.942273	-0.968280	7.032746
H	-2.942273	-0.968280	-7.032746
H	-2.048602	0.581371	7.183638
H	-2.048602	0.581371	-7.183638
H	-1.161629	-0.956198	7.247108
H	-1.161629	-0.956198	-7.247108
H	5.196570	-0.671765	2.925415
H	5.196570	-0.671765	-2.925415
H	4.443136	1.142384	4.685359
H	4.443136	1.142384	-4.685359
H	1.854713	1.597773	4.554976
H	1.854713	1.597773	-4.554976
H	-3.987897	0.587586	2.158280
H	-3.987897	0.587586	-2.158280
H	-3.577907	0.439065	3.892979
H	-3.577907	0.439065	-3.892979
H	-3.763260	-1.002972	2.891597
H	-3.763260	-1.002972	-2.891597
H	1.583150	0.261113	0.000000

14′ C2_s-Z_out

C	-0.347645	4.846425	-1.049205
C	0.347645	-4.846425	-1.049205
O	0.053584	5.445034	0.094118
O	-0.053584	-5.445034	0.094118
C	0.000000	6.880265	0.087481
C	0.000000	-6.880265	0.087481
C	-0.104017	2.845187	1.595839
C	0.104017	-2.845187	1.595839
S	-1.335836	3.801558	2.395133
S	1.335836	-3.801558	2.395133
C	-0.612632	3.539144	3.945598
C	0.612632	-3.539144	3.945598
C	0.514043	2.767405	3.857836
C	-0.514043	-2.767405	3.857836
C	0.798430	2.364908	2.522410
C	-0.798430	-2.364908	2.522410
N	-0.110485	1.253070	-1.724520
N	0.110485	-1.253070	-1.724520
C	-0.342667	2.893591	-3.560722
C	0.342667	-2.893591	-3.560722
C	-0.256877	2.530408	-2.115935
C	0.256877	-2.530408	-2.115935
O	-0.700873	5.476924	-2.030251
O	0.700873	-5.476924	-2.030251
C	-0.279100	3.375213	-0.964545
C	0.279100	-3.375213	-0.964545
C	-0.135125	2.545473	0.168712
C	0.135125	-2.545473	0.168712
C	-0.051399	1.213372	-0.334572
C	0.051399	-1.213372	-0.334572
C	0.000000	0.000000	0.343198
F	-1.142789	-0.096999	-3.448851
F	1.142789	0.096999	-3.448851
B	0.000000	0.000000	-2.671097
H	0.315752	7.187346	1.083997
H	-0.315752	-7.187346	1.083997
H	-1.014529	7.228611	-0.119981
H	1.014529	-7.228611	-0.119981
H	0.673386	7.285817	-0.671503
H	-0.673386	-7.285817	-0.671503
H	-1.058297	3.976099	4.828591
H	1.058297	-3.976099	4.828591
H	1.124356	2.498830	4.712070
H	-1.124356	-2.498830	4.712070
H	1.659736	1.770860	2.240004
H	-1.659736	-1.770860	2.240004
H	-1.270285	2.493092	-3.983301
H	1.270285	-2.493092	-3.983301
H	0.479703	2.423100	-4.106606
H	-0.479703	-2.423100	-4.106606
H	-0.328809	3.973014	-3.687275
H	0.328809	-3.973014	-3.687275
H	0.000000	0.000000	1.425980

14′ C2_s-E_out

C	0.287426	4.847788	-0.789754
C	-0.287426	-4.847788	-0.789754
O	0.720762	5.360085	-1.968446
O	-0.720762	-5.360085	-1.968446
C	0.786707	6.795139	-2.021001
C	-0.786707	-6.795139	-2.021001
C	0.498955	2.821800	1.747390
C	-0.498955	-2.821800	1.747390
S	-0.250401	4.132371	2.643465
S	0.250401	-4.132371	2.643465
C	0.443309	3.584151	4.125562
C	-0.443309	-3.584151	4.125562
C	1.244576	2.485191	3.951690
C	-1.244576	-2.485191	3.951690
C	1.271243	2.049729	2.602820
C	-1.271243	-2.049729	2.602820
N	0.058129	1.258043	-1.555342
N	-0.058129	-1.258043	-1.555342
C	0.030841	2.913855	-3.393413
C	-0.030841	-2.913855	-3.393413
C	0.099343	2.543838	-1.947463
C	-0.099343	-2.543838	-1.947463
O	0.000000	5.553972	0.160037
O	0.000000	-5.553972	0.160037
C	0.215198	3.380361	-0.800035
C	-0.215198	-3.380361	-0.800035
C	0.275800	2.540127	0.337954
C	-0.275800	-2.540127	0.337954
C	0.147229	1.208026	-0.166855
C	-0.147229	-1.208026	-0.166855
C	0.000000	0.000000	0.507420
F	-1.145372	0.037612	-3.279754
F	1.145372	-0.037612	-3.279754
B	0.000000	0.000000	-2.497744
H	1.122809	7.034681	-3.029545
H	-1.122809	-7.034681	-3.029545
H	1.495095	7.173420	-1.280358
H	-1.495095	-7.173420	-1.280358
H	-0.194093	7.235458	-1.826158
H	0.194093	-7.235458	-1.826158
H	0.252457	4.129880	5.039876
H	-0.252457	-4.129880	5.039876
H	1.803662	2.012820	4.750761
H	-1.803662	-2.012820	4.750761
H	1.873008	1.220481	2.251403
H	-1.873008	-1.220481	2.251403
H	-0.570687	2.183595	-3.935061
H	0.570687	-2.183595	-3.935061
H	1.036456	2.914356	-3.829104
H	-1.036456	-2.914356	-3.829104
H	-0.382838	3.912758	-3.518458
H	0.382838	-3.912758	-3.518458
H	0.000000	0.000000	1.588769

14′ CS_s-Z_out

C	1.048661	-0.009488	4.858149
C	1.048661	-0.009488	-4.858149
O	-0.098648	0.410460	5.435954
O	-0.098648	0.410460	-5.435954
C	-0.091851	0.428696	6.872076
C	-0.091851	0.428696	-6.872076
C	-1.595287	0.128818	2.850044
C	-1.595287	0.128818	-2.850044
S	-2.394753	-1.070775	3.845511
S	-2.394753	-1.070775	-3.845511
C	-3.943598	-0.350182	3.567968
C	-3.943598	-0.350182	-3.567968
C	-3.855085	0.752307	2.762208
C	-3.855085	0.752307	-2.762208
C	-2.520048	1.019442	2.346415
C	-2.520048	1.019442	-2.346415
N	1.724859	0.046608	1.257915
N	1.724859	0.046608	-1.257915
C	3.559966	-0.117829	2.908636
C	3.559966	-0.117829	-2.908636
C	2.116120	-0.037559	2.540742
C	2.116120	-0.037559	-2.540742
O	2.032931	-0.321246	5.505286
O	2.032931	-0.321246	-5.505286
C	0.964471	-0.015908	3.385449
C	0.964471	-0.015908	-3.385449
C	-0.168277	0.082944	2.549251
C	-0.168277	0.082944	-2.549251
C	0.334637	0.103910	1.214862
C	0.334637	0.103910	-1.214862
C	-0.343213	0.104603	0.000000
F	3.452977	1.192074	0.000000
B	2.671064	0.046373	0.000000
F	3.444355	-1.101606	0.000000
H	-1.091412	0.749856	7.163257
H	-1.091412	0.749856	-7.163257
H	0.660600	1.128642	7.243428
H	0.660600	1.128642	-7.243428
H	0.125169	-0.565154	7.270572
H	0.125169	-0.565154	-7.270572
H	-4.826633	-0.780448	4.019933
H	-4.826633	-0.780448	-4.019933
H	-4.708754	1.356684	2.478724
H	-4.708754	1.356684	-2.478724
H	-2.235820	1.861423	1.726020
H	-2.235820	1.861423	-1.726020
H	3.961106	-1.090776	2.604894
H	3.961106	-1.090776	-2.604894
H	3.689595	-0.001667	3.981656
H	3.689595	-0.001667	-3.981656
H	4.122710	0.641388	2.359247
H	4.122710	0.641388	-2.359247
H	-1.426119	0.089493	0.000000

14′ CS_s-E_out

C	0.794141	-0.145521	4.853915
C	0.794141	-0.145521	-4.853915
O	1.946085	0.303483	5.411719
O	1.946085	0.303483	-5.411719
C	1.997775	0.226827	6.846342
C	1.997775	0.226827	-6.846342
C	-1.753779	0.143955	2.861171
C	-1.753779	0.143955	-2.861171
S	-2.607679	-0.816108	4.056000
S	-2.607679	-0.816108	-4.056000
C	-4.122986	-0.124995	3.604707
C	-4.122986	-0.124995	-3.604707
C	-3.991255	0.824590	2.624485
C	-3.991255	0.824590	-2.624485
C	-2.646754	0.971944	2.199005
C	-2.646754	0.971944	-2.199005
N	1.560279	0.038638	1.260378
N	1.560279	0.038638	-1.260378
C	3.401867	-0.089008	2.911092
C	3.401867	-0.089008	-2.911092
C	1.954238	-0.041498	2.544278
C	1.954238	-0.041498	-2.544278
O	-0.135668	-0.557829	5.523477
O	-0.135668	-0.557829	-5.523477
C	0.805299	-0.067982	3.386178
C	0.805299	-0.067982	-3.386178
C	-0.336191	0.021698	2.554959
C	-0.336191	0.021698	-2.554959
C	0.168597	0.068299	1.217943
C	0.168597	0.068299	-1.217943
C	-0.504646	0.045399	0.000000
F	3.254178	1.228713	0.000000
B	2.500787	0.069253	0.000000
F	3.310755	-1.063229	0.000000
H	2.985181	0.595942	7.122532
H	2.985181	0.595942	-7.122532
H	1.862194	-0.803300	7.184342
H	1.862194	-0.803300	-7.184342
H	1.217298	0.848265	7.291472
H	1.217298	0.848265	-7.291472
H	-5.025068	-0.431349	4.117021
H	-5.025068	-0.431349	-4.117021
H	-4.818149	1.404094	2.231167
H	-4.818149	1.404094	-2.231167
H	-2.325637	1.694491	1.458575
H	-2.325637	1.694491	-1.458575
H	3.963953	-0.612911	2.138036
H	3.963953	-0.612911	-2.138036
H	3.541698	-0.573413	3.875386
H	3.541698	-0.573413	-3.875386
H	3.802162	0.928424	2.988989
H	3.802162	0.928424	-2.988989
H	-1.583996	-0.024130	0.000000

14′ unsymm1

C	4.959305	-0.486763	0.253240
C	-4.715660	-1.372638	-0.075611
O	5.571243	-1.554907	-0.318175
O	-5.377888	-0.258838	-0.459774
C	7.007610	-1.532772	-0.270244
C	-6.806506	-0.387088	-0.528871
C	2.818969	1.910587	0.069755
C	-2.940665	1.436111	-0.003595
S	1.909552	2.941742	-1.036897
S	-4.042783	2.075432	1.199417
C	2.748719	4.354795	-0.501669
C	-3.876996	3.682314	0.578108
C	3.674274	4.057042	0.462407
C	-3.029121	3.727898	-0.494969
C	3.722518	2.672958	0.780544
C	-2.489429	2.451421	-0.820494
N	1.434604	-1.517552	0.038165
N	-1.071672	-1.736224	-0.046291
C	3.224733	-3.220757	0.152733
C	-2.562575	-3.711289	-0.031062
C	2.744060	-1.806260	0.125053
C	-2.318415	-2.239211	-0.024505
O	5.587696	0.433058	0.744181
O	-5.284382	-2.423341	0.164768
C	3.490893	-0.593281	0.187416
C	-3.256952	-1.164102	-0.013380
C	2.568437	0.478169	0.121152
C	-2.518192	0.039681	-0.024172
C	1.277071	-0.132625	0.035559
C	-1.146362	-0.347472	-0.029178
C	0.005352	0.431732	0.036027
F	0.374439	-3.300099	-1.209869
F	0.284040	-3.385656	1.079641
B	0.260456	-2.566208	-0.040748
H	7.329157	-2.463666	-0.736630
H	-7.173462	0.599230	-0.811011
H	7.360485	-1.476254	0.762326
H	-7.215358	-0.688274	0.438510
H	7.395930	-0.673376	-0.821777
H	-7.089359	-1.131346	-1.277308
H	2.517113	5.317400	-0.936184
H	-4.418897	4.496613	1.039005
H	4.308066	4.801744	0.929563
H	-2.799772	4.636791	-1.038716
H	4.400150	2.234314	1.497919
H	-1.815440	2.273336	-1.650239
H	3.321000	-3.603692	-0.869476
H	-2.271700	-4.134932	0.936362
H	2.502448	-3.846383	0.677821
H	-1.932729	-4.186438	-0.787507
H	4.201699	-3.290786	0.626758
H	-3.614139	-3.924638	-0.205937
H	-0.102385	1.506382	0.105416

14′ unsymm2

C	-4.965261	-0.478113	0.212881
C	4.711613	-1.382698	-0.036066
O	-5.564861	-1.548054	-0.368048
O	5.383453	-0.315480	0.450402
C	-7.001912	-1.524624	-0.353541
C	6.813240	-0.447336	0.471688
C	-2.812944	1.915988	0.068946
C	2.940399	1.418466	0.231623
S	-1.858620	2.942103	-1.005115
S	4.029495	2.181322	-0.909736
C	-2.711848	4.358210	-0.503233
C	3.867580	3.715248	-0.124586
C	-3.673932	4.066105	0.426747
C	3.030798	3.648276	0.956078
C	-3.739264	2.683184	0.745368
C	2.496181	2.343891	1.153457
N	-1.438714	-1.515998	0.087240
N	1.065527	-1.739073	-0.019989
C	-3.233960	-3.214995	0.152738
C	2.546723	-3.706474	-0.251794
C	-2.750518	-1.801210	0.140252
C	2.310055	-2.238930	-0.119176
O	-5.604392	0.443767	0.685988
O	5.275067	-2.399489	-0.401805
C	-3.495882	-0.586338	0.181353
C	3.251879	-1.169870	-0.040590
C	-2.569583	0.483220	0.130616
C	2.517491	0.027399	0.115503
C	-1.277665	-0.131743	0.083051
C	1.144719	-0.356504	0.104923
C	-0.005055	0.428064	0.123205
F	-0.287512	-3.390106	1.116472
F	-0.390544	-3.297233	-1.172323
B	-0.267554	-2.567218	-0.002821
H	-7.313328	-2.456976	-0.823871
H	7.187143	0.504209	0.848317
H	-7.376566	-0.666981	-0.917107
H	7.198962	-0.643216	-0.531569
H	-7.378649	-1.464045	0.670342
H	7.113375	-1.266296	1.129946
H	-2.460795	5.318979	-0.931040
H	4.404425	4.573771	-0.503987
H	-4.321955	4.814160	0.868404
H	2.805900	4.495521	1.593199
H	-4.444251	2.248174	1.438175
H	1.833205	2.078824	1.968760
H	-2.521422	-3.844743	0.686279
H	2.080655	-4.069006	-1.173600
H	-3.314783	-3.592498	-0.872720
H	2.057043	-4.232900	0.573018
H	-4.218525	-3.285628	0.610858
H	3.611511	-3.923247	-0.270423
H	0.105388	1.503500	0.171687

Ground state optimized coordinates of two conformers of molecule 14a′
(PCM$_{CH2Cl2}$/B3LYP/6-31G(d,p), see Table Q2 for details)

14a′ C2_s-Z

C	-0.191867	2.539355	0.144172
C	0.191867	-2.539355	0.144172
C	-0.330647	3.366712	-0.988890
C	0.330647	-3.366712	-0.988890
C	-0.276333	2.528577	-2.142848
C	0.276333	-2.528577	-2.142848
N	-0.115912	1.251728	-1.752958
N	0.115912	-1.251728	-1.752958
B	0.000000	0.000000	-2.689917
C	-0.073196	1.213117	-0.358291
C	0.073196	-1.213117	-0.358291
C	0.000000	0.000000	0.318417
F	-1.141015	-0.098056	-3.481231
F	1.141015	0.098056	-3.481231
C	-0.217214	2.875420	1.579441
C	0.217214	-2.875420	1.579441
C	0.798728	2.415153	2.435255
C	-0.798728	-2.415153	2.435255
C	0.758367	2.696460	3.801646
C	-0.758367	-2.696460	3.801646
C	-0.299076	3.434412	4.334426
C	0.299076	-3.434412	4.334426
C	-1.315636	3.895357	3.492393
C	1.315636	-3.895357	3.492393
C	-1.274775	3.622594	2.127620
C	1.274775	-3.622594	2.127620
C	-0.351760	2.906142	-3.584662
C	0.351760	-2.906142	-3.584662
C	-0.440297	4.835350	-1.067483
C	0.440297	-4.835350	-1.067483
O	-0.861624	5.449264	-2.036134
O	0.861624	-5.449264	-2.036134
O	0.000000	5.447459	0.049058
O	0.000000	-5.447459	0.049058
C	-0.094752	6.884177	0.054434
C	0.094752	-6.884177	0.054434
H	0.000000	0.000000	1.401315
H	1.635424	1.860240	2.022591
H	-1.635424	-1.860240	2.022591
H	1.556580	2.341419	4.446343
H	-1.556580	-2.341419	4.446343
H	-0.332052	3.651237	5.397810
H	0.332052	-3.651237	5.397810
H	-2.144095	4.465914	3.901288
H	2.144095	-4.465914	3.901288
H	-2.071932	3.973370	1.480570
H	2.071932	-3.973370	1.480570
H	-0.169171	3.970982	-3.710899
H	0.169171	-3.970982	-3.710899
H	0.365459	2.320621	-4.163042
H	-0.365459	-2.320621	-4.163042
H	-1.350526	2.684163	-3.977520
H	1.350526	-2.684163	-3.977520
H	0.261931	7.194876	1.035303
H	-0.261931	-7.194876	1.035303
H	0.530515	7.311863	-0.732417
H	-0.530515	-7.311863	-0.732417
H	-1.128495	7.202679	-0.096019
H	1.128495	-7.202679	-0.096019

14a′ CS_s-Z

C	-0.143464	0.002329	2.546630
C	-0.143464	0.002329	-2.546630
C	0.991120	-0.050237	3.381768
C	0.991120	-0.050237	-3.381768
C	2.144833	-0.025992	2.541637
C	2.144833	-0.025992	-2.541637
N	1.753168	0.039445	1.257035
N	1.753168	0.039445	-1.257035
B	2.689739	0.065399	0.000000
C	0.357865	0.045698	1.215503
C	0.357865	0.045698	-1.215503
C	-0.318617	0.025421	0.000000
F	3.450980	1.233668	0.000000
F	3.509799	-1.056291	0.000000
C	-1.578508	-0.033718	2.883772
C	-1.578508	-0.033718	-2.883772
C	-2.454691	0.935536	2.365578
C	-2.454691	0.935536	-2.365578
C	-3.820152	0.883569	2.649341
C	-3.820152	0.883569	-2.649341
C	-4.331511	-0.140102	3.447587
C	-4.331511	-0.140102	-3.447587
C	-3.468974	-1.110547	3.966303
C	-3.468974	-1.110547	-3.966303
C	-2.105049	-1.057269	3.691253
C	-2.105049	-1.057269	-3.691253
C	3.587671	-0.047834	2.922153
C	3.587671	-0.047834	-2.922153
C	1.069152	-0.057728	4.854548
C	1.069152	-0.057728	-4.854548
O	2.049081	-0.404486	5.496569
O	2.049081	-0.404486	-5.496569
O	-0.063067	0.385638	5.434899
O	-0.063067	0.385638	-5.434899
C	-0.069155	0.387750	6.874727
C	-0.069155	0.387750	-6.874727
H	-1.400786	-0.017582	0.000000
H	-2.058402	1.746564	1.762722
H	-2.058402	1.746564	-1.762722
H	-4.481052	1.646357	2.249028
H	-4.481052	1.646357	-2.249028
H	-5.394160	-0.182505	3.666330
H	-5.394160	-0.182505	-3.666330
H	-3.861134	-1.912834	4.584041
H	-3.861134	-1.912834	-4.584041
H	-1.441814	-1.818926	4.087682
H	-1.441814	-1.818926	-4.087682
H	4.150920	0.646452	2.295443
H	4.150920	0.646452	-2.295443
H	3.708887	0.199249	3.974384
H	3.708887	0.199249	-3.974384
H	4.002078	-1.048874	2.757320
H	4.002078	-1.048874	-2.757320
H	-1.061722	0.732969	7.160209
H	-1.061722	0.732969	-7.160209
H	0.113360	-0.616848	7.262265
H	0.113360	-0.616848	-7.262265
H	0.696313	1.065178	7.259623
H	0.696313	1.065178	-7.259623

Excited state (S_1) optimized coordinates of two conformers of molecule 14a′
(PCM$_{CH2Cl2}$/B3LYP/6-31G(d,p), see Table Q2 for details)

14a′ C2_s-Z

C	-0.263950	2.570863	0.175473
C	0.263950	-2.570863	0.175473
C	-0.431143	3.376706	-0.985878
C	0.431143	-3.376706	-0.985878
C	-0.343494	2.531164	-2.111061
C	0.343494	-2.531164	-2.111061
N	-0.139843	1.244011	-1.689450
N	0.139843	-1.244011	-1.689450
B	0.000000	0.000000	-2.620881
C	-0.094476	1.220245	-0.311081
C	0.094476	-1.220245	-0.311081
C	0.000000	0.000000	0.384539
F	-1.138470	-0.123296	-3.418819
F	1.138470	0.123296	-3.418819
C	-0.357056	2.928658	1.580983
C	0.357056	-2.928658	1.580983
C	0.503895	2.342512	2.542305
C	-0.503895	-2.342512	2.542305
C	0.399769	2.668304	3.889286
C	-0.399769	-2.668304	3.889286
C	-0.573675	3.576114	4.322075
C	0.573675	-3.576114	4.322075
C	-1.437137	4.164297	3.388283
C	1.437137	-4.164297	3.388283
C	-1.329174	3.853509	2.040301
C	1.329174	-3.853509	2.040301
C	-0.399963	2.862858	-3.560721
C	0.399963	-2.862858	-3.560721
C	-0.527672	4.842390	-1.103144
C	0.527672	-4.842390	-1.103144
O	-1.000952	5.441092	-2.058366
O	1.000952	-5.441092	-2.058366
O	0.000000	5.481325	-0.037019
O	0.000000	-5.481325	-0.037019
C	-0.071104	6.918553	-0.070639
C	0.071104	-6.918553	-0.070639
H	0.000000	0.000000	1.462836
H	1.285579	1.665694	2.214751
H	-1.285579	-1.665694	2.214751
H	1.082483	2.220391	4.604762
H	-1.082483	-2.220391	4.604762
H	-0.660273	3.822414	5.375782
H	0.660273	-3.822414	5.375782
H	-2.201193	4.860812	3.719698
H	2.201193	-4.860812	3.719698
H	-2.018138	4.294614	1.329323
H	2.018138	-4.294614	1.329323
H	-0.432675	3.939627	-3.707348
H	0.432675	-3.939627	-3.707348
H	0.459067	2.425963	-4.079137
H	-0.459067	-2.425963	-4.079137
H	-1.294357	2.415403	-4.010457
H	1.294357	-2.415403	-4.010457
H	0.349339	7.252748	0.876827
H	-0.349339	-7.252748	0.876827
H	0.512311	7.311477	-0.906344
H	-0.512311	-7.311477	-0.906344
H	-1.106482	7.252057	-0.169175
H	1.106482	-7.252057	-0.169175

14a′ CS_s-Z

C	-0.174058	0.017029	2.582813
C	-0.174058	0.017029	-2.582813
C	0.986633	-0.079237	3.402455
C	0.986633	-0.079237	-3.402455
C	2.112425	-0.071204	2.553740
C	2.112425	-0.071204	-2.553740
N	1.692080	0.010882	1.252419
N	1.692080	0.010882	-1.252419
B	2.623578	0.017274	0.000000
C	0.314211	0.059933	1.223452
C	0.314211	0.059933	-1.223452
C	-0.381011	0.049644	0.000000
F	3.415502	1.168175	0.000000
F	3.426390	-1.122455	0.000000
C	-1.579928	-0.045283	2.943684
C	-1.579928	-0.045283	-2.943684
C	-2.542116	0.754666	2.276907
C	-2.542116	0.754666	-2.276907
C	-3.889419	0.679619	2.609408
C	-3.889419	0.679619	-2.609408
C	-4.322169	-0.205546	3.603229
C	-4.322169	-0.205546	-3.603229
C	-3.388020	-1.009124	4.270893
C	-3.388020	-1.009124	-4.270893
C	-2.039871	-0.928284	3.953941
C	-2.039871	-0.928284	-3.953941
C	3.562130	-0.096181	2.889886
C	3.562130	-0.096181	-2.889886
C	1.101821	-0.035442	4.870841
C	1.101821	-0.035442	-4.870841
O	2.059288	-0.441959	5.513342
O	2.059288	-0.441959	-5.513342
O	0.030674	0.542959	5.455504
O	0.030674	0.542959	-5.455504
C	0.063064	0.611537	6.892845
C	0.063064	0.611537	-6.892845
H	-1.458234	-0.006905	0.000000
H	-2.213708	1.470563	1.531263
H	-2.213708	1.470563	-1.531263
H	-4.605436	1.316054	2.098652
H	-4.605436	1.316054	-2.098652
H	-5.376189	-0.270760	3.854673
H	-5.376189	-0.270760	-3.854673
H	-3.719822	-1.705955	5.034472
H	-3.719822	-1.705955	-5.034472
H	-1.328392	-1.571897	4.457997
H	-1.328392	-1.571897	-4.457997
H	4.080180	0.720605	2.377892
H	4.080180	0.720605	-2.377892
H	3.708400	-0.031471	3.965224
H	3.708400	-0.031471	-3.965224
H	4.012595	-1.026676	2.524490
H	4.012595	-1.026676	-2.524490
H	-0.886098	1.059321	7.183992
H	-0.886098	1.059321	-7.183992
H	0.164223	-0.386284	7.325468
H	0.164223	-0.386284	-7.325468
H	0.896454	1.233009	7.228126
H	0.896454	1.233009	-7.228126

Ground state optimized coordinates of three conformers of molecule 14′
(PCM$_{CH2Cl2}$/B3LYP/6-31G(d,p), see Table Q2 for details)

14′ C2_s-E_in

C	-0.346753	4.850640	0.815495
C	0.346753	-4.850640	0.815495
O	-0.915814	5.292701	1.959824
O	0.915814	-5.292701	1.959824
C	-1.044690	6.722671	2.080659
C	1.044690	-6.722671	2.080659
C	-0.396817	2.896257	-1.749629
C	0.396817	-2.896257	-1.749629
S	-1.459775	1.955596	-2.799067
S	1.459775	-1.955596	-2.799067
C	-1.085121	2.947709	-4.164048
C	1.085121	-2.947709	-4.164048
C	-0.200892	3.942387	-3.838745
C	0.200892	-3.942387	-3.838745
C	0.182621	3.920387	-2.470325
C	-0.182621	-3.920387	-2.470325
N	-0.066918	1.256992	1.546218
N	0.066918	-1.256992	1.546218
C	-0.076997	2.914943	3.388291
C	0.076997	-2.914943	3.388291
C	-0.123178	2.542503	1.942001
C	0.123178	-2.542503	1.942001
O	0.000000	5.606868	-0.076386
O	0.000000	-5.606868	-0.076386
C	-0.221253	3.381981	0.796026
C	0.221253	-3.381981	0.796026
C	-0.240534	2.544492	-0.346522
C	0.240534	-2.544492	-0.346522
C	-0.131591	1.210473	0.154906
C	0.131591	-1.210473	0.154906
C	0.000000	0.000000	-0.518883
F	1.144325	0.046990	3.272410
F	-1.144325	-0.046990	3.272410
B	0.000000	0.000000	2.480363
H	-1.484165	6.892799	3.062391
H	1.484165	-6.892799	3.062391
H	-1.696796	7.114042	1.297067
H	1.696796	-7.114042	1.297067
H	-0.067448	7.204855	2.008803
H	0.067448	-7.204855	2.008803
H	-1.545926	2.742906	-5.120561
H	1.545926	-2.742906	-5.120561
H	0.163273	4.671594	-4.552934
H	-0.163273	-4.671594	-4.552934
H	0.858653	4.629474	-2.015845
H	-0.858653	-4.629474	-2.015845
H	0.517780	2.188714	3.942193
H	-0.517780	-2.188714	3.942193
H	-1.088132	2.922064	3.810495
H	1.088132	-2.922064	3.810495
H	0.338862	3.912539	3.517997
H	-0.338862	-3.912539	3.517997
H	0.000000	0.000000	-1.600350

14′ C2_s-Z_out

C	0.000000	4.857266	-1.041000
C	0.000000	-4.857266	-1.041000
O	0.555461	5.421295	0.048801
O	-0.555461	-5.421295	0.048801
C	0.605594	6.860846	0.052777
C	-0.605594	-6.860846	0.052777
C	0.092324	2.855601	1.601136
C	-0.092324	-2.855601	1.601136
S	-1.055221	3.936584	2.370034
S	1.055221	-3.936584	2.370034
C	-0.375324	3.634228	3.933801
C	0.375324	-3.634228	3.933801
C	0.675167	2.758787	3.871417
C	-0.675167	-2.758787	3.871417
C	0.936370	2.308541	2.546138
C	-0.936370	-2.308541	2.546138
N	-0.017230	1.256837	-1.716512
N	0.017230	-1.256837	-1.716512
C	-0.133765	2.921242	-3.549231
C	0.133765	-2.921242	-3.549231
C	-0.073573	2.543753	-2.106708
C	0.073573	-2.543753	-2.106708
O	-0.400089	5.509332	-1.993000
O	0.400089	-5.509332	-1.993000
C	-0.035044	3.384884	-0.956811
C	0.035044	-3.384884	-0.956811
C	0.049951	2.547414	0.177653
C	-0.049951	-2.547414	0.177653
C	0.037535	1.213306	-0.324741
C	-0.037535	-1.213306	-0.324741
C	0.000000	0.000000	0.353562
F	-1.145419	-0.009239	-3.444645
F	1.145419	0.009239	-3.444645
B	0.000000	0.000000	-2.654569
H	1.048230	7.133113	1.009609
H	-1.048230	-7.133113	1.009609
H	-0.398368	7.280791	-0.038295
H	0.398368	-7.280791	-0.038295
H	1.223424	7.223259	-0.771612
H	-1.223424	-7.223259	-0.771612
H	-0.790529	4.124820	4.803418
H	0.790529	-4.124820	4.803418
H	1.247170	2.448129	4.737652
H	-1.247170	-2.448129	4.737652
H	1.742229	1.631961	2.286751
H	-1.742229	-1.631961	2.286751
H	-1.130373	2.703617	-3.948955
H	1.130373	-2.703617	-3.948955
H	0.581405	2.325039	-4.120424
H	-0.581405	-2.325039	-4.120424
H	0.062824	3.983021	-3.676610
H	-0.062824	-3.983021	-3.676610
H	0.000000	0.000000	1.436097

14′ unsymm2

C	-4.971460	-0.477091	0.201337
C	4.704436	-1.373717	-0.052624
O	-5.558855	-1.545778	-0.382255
O	5.373763	-0.365737	0.539749
C	-6.999838	-1.544231	-0.381571
C	6.808790	-0.487857	0.549896
C	-2.815636	1.918680	0.079700
C	2.942144	1.423794	0.214651
S	-1.886816	2.945074	-1.015680
S	4.061199	2.153586	-0.921906
C	-2.721407	4.363044	-0.486297
C	3.911883	3.701427	-0.159545
C	-3.657333	4.071709	0.470991
C	3.056825	3.662013	0.908603
C	-3.718454	2.687212	0.785927
C	2.498292	2.368886	1.117077
N	-1.443609	-1.514598	0.097214
N	1.060302	-1.734032	-0.008896
C	-3.251277	-3.208774	0.165621
C	2.555317	-3.697013	-0.250413
C	-2.757659	-1.798673	0.149636
C	2.307287	-2.231500	-0.115186
O	-5.613696	0.450123	0.665277
O	5.262779	-2.356708	-0.515115
C	-3.500806	-0.583369	0.186479
C	3.244849	-1.161947	-0.044976
C	-2.573884	0.485427	0.136757
C	2.510290	0.035770	0.113165
C	-1.282625	-0.128764	0.090658
C	1.138864	-0.349348	0.109865
C	-0.011924	0.433768	0.127822
F	-0.292269	-3.390492	1.125727
F	-0.388579	-3.296810	-1.161132
B	-0.271166	-2.556084	0.007841
H	-7.291478	-2.484557	-0.846933
H	7.174034	0.419171	1.028973
H	-7.379988	-0.698539	-0.958490
H	7.195200	-0.565551	-0.468536
H	-7.384362	-1.485157	0.638855
H	7.112785	-1.369640	1.118032
H	-2.477915	5.323471	-0.919337
H	4.467647	4.545240	-0.544763
H	-4.287384	4.821613	0.934735
H	2.835199	4.521970	1.529445
H	-4.400421	2.255223	1.503312
H	1.819580	2.128211	1.926947
H	-2.524110	-3.854500	0.657495
H	2.281653	-4.029823	-1.257794
H	-3.394037	-3.571423	-0.858469
H	1.928231	-4.247971	0.454131
H	-4.211878	-3.276509	0.673313
H	3.606044	-3.924623	-0.087588
H	0.095704	1.509496	0.172576

Excited state (S_1) optimized coordinates of three conformers of molecule 14′
(PCM$_{CH2Cl2}$/B3LYP/6-31G(d,p), see Table Q2 for details)

14′ C2_s-E_in

C	-0.434490	4.861902	0.883030
C	0.434490	-4.861902	0.883030
O	-1.129113	5.247774	1.977712
O	1.129113	-5.247774	1.977712
C	-1.265446	6.670572	2.160951
C	1.265446	-6.670572	2.160951
C	-0.404166	2.944793	-1.746820
C	0.404166	-2.944793	-1.746820
S	-1.203873	1.873614	-2.921969
S	1.203873	-1.873614	-2.921969
C	-0.988869	3.015554	-4.196892
C	0.988869	-3.015554	-4.196892
C	-0.346918	4.156095	-3.764345
C	0.346918	-4.156095	-3.764345
C	-0.021313	4.123176	-2.393635
C	0.021313	-4.123176	-2.393635
N	-0.098211	1.249819	1.494535
N	0.098211	-1.249819	1.494535
C	-0.181302	2.863894	3.383591
C	0.181302	-2.863894	3.383591
C	-0.199719	2.548442	1.924883
C	0.199719	-2.548442	1.924883
O	0.000000	5.670967	0.077646
O	0.000000	-5.670967	0.077646
C	-0.288650	3.396741	0.810441
C	0.288650	-3.396741	0.810441
C	-0.266167	2.572332	-0.366376
C	0.266167	-2.572332	-0.366376
C	-0.140196	1.217307	0.119476
C	0.140196	-1.217307	0.119476
C	0.000000	0.000000	-0.572044
F	1.143091	0.074580	3.221176
F	-1.143091	-0.074580	3.221176
B	0.000000	0.000000	2.422063
H	-1.814320	6.791585	3.093741
H	1.814320	-6.791585	3.093741
H	-1.821747	7.110037	1.330387
H	1.821747	-7.110037	1.330387
H	-0.284927	7.146775	2.228153
H	0.284927	-7.146775	2.228153
H	-1.344518	2.784453	-5.191972
H	1.344518	-2.784453	-5.191972
H	-0.110070	4.985965	-4.419744
H	0.110070	-4.985965	-4.419744
H	0.483168	4.916243	-1.862353
H	-0.483168	-4.916243	-1.862353
H	0.576100	2.255877	3.882839
H	-0.576100	-2.255877	3.882839
H	-1.146668	2.614470	3.839671
H	1.146668	-2.614470	3.839671
H	0.013334	3.919538	3.555332
H	-0.013334	-3.919538	3.555332
H	0.000000	0.000000	-1.649180

14′ C2_s-Z_out

C	-0.538379	4.840163	-1.074461
C	0.538379	-4.840163	-1.074461
O	0.000000	5.481097	-0.014342
O	0.000000	-5.481097	-0.014342
C	-0.077911	6.918272	-0.045888
C	0.077911	-6.918272	-0.045888
C	-0.349691	2.890859	1.611895
C	0.349691	-2.890859	1.611895
S	-1.492195	4.078873	2.256355
S	1.492195	-4.078873	2.256355
C	-1.012797	3.742865	3.878491
C	1.012797	-3.742865	3.878491
C	-0.022988	2.783712	3.940338
C	0.022988	-2.783712	3.940338
C	0.345785	2.297858	2.669277
C	-0.345785	-2.297858	2.669277
N	-0.144251	1.244412	-1.646883
N	0.144251	-1.244412	-1.646883
C	-0.414914	2.858545	-3.523145
C	0.414914	-2.858545	-3.523145
C	-0.352273	2.530459	-2.070815
C	0.352273	-2.530459	-2.070815
O	-1.020307	5.436715	-2.026013
O	1.020307	-5.436715	-2.026013
C	-0.437772	3.376347	-0.952357
C	0.437772	-3.376347	-0.952357
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C	0.267550	-2.566331	0.214952
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C	0.099656	-1.218514	-0.269491
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F	1.138237	0.127022	-3.375249
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H	-0.355362	-7.254059	0.895114
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H	1.116206	-7.246613	-0.128385
H	0.491325	7.312721	-0.890457
H	-0.491325	-7.312721	-0.890457
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H	1.475096	-4.275157	4.698845
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H	-0.425863	-2.452425	4.869137
H	1.135726	1.574486	2.510703
H	-1.135726	-1.574486	2.510703
H	-1.315746	2.419181	-3.966463
H	1.315746	-2.419181	-3.966463
H	0.438862	2.416127	-4.044317
H	-0.438862	-2.416127	-4.044317
H	-0.439694	3.935276	-3.671951
H	0.439694	-3.935276	-3.671951
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14′ unsymm2

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C	4.703322	-1.400522	-0.036881
O	-5.543030	-1.562729	-0.578030
O	5.383453	-0.420554	0.596949
C	-6.982516	-1.628832	-0.591613
C	6.814413	-0.574059	0.633170
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C	2.976889	1.435621	0.127547
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C	4.063887	3.645918	-0.358051
C	-3.916924	4.013798	0.420553
C	3.039779	3.747914	0.561208
C	-3.969804	2.626072	0.660480
C	2.422731	2.509259	0.829772
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C	2.310856	-2.197636	-0.089431
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H	-7.226544	-2.512642	-1.179248
H	7.190352	0.317970	1.132082
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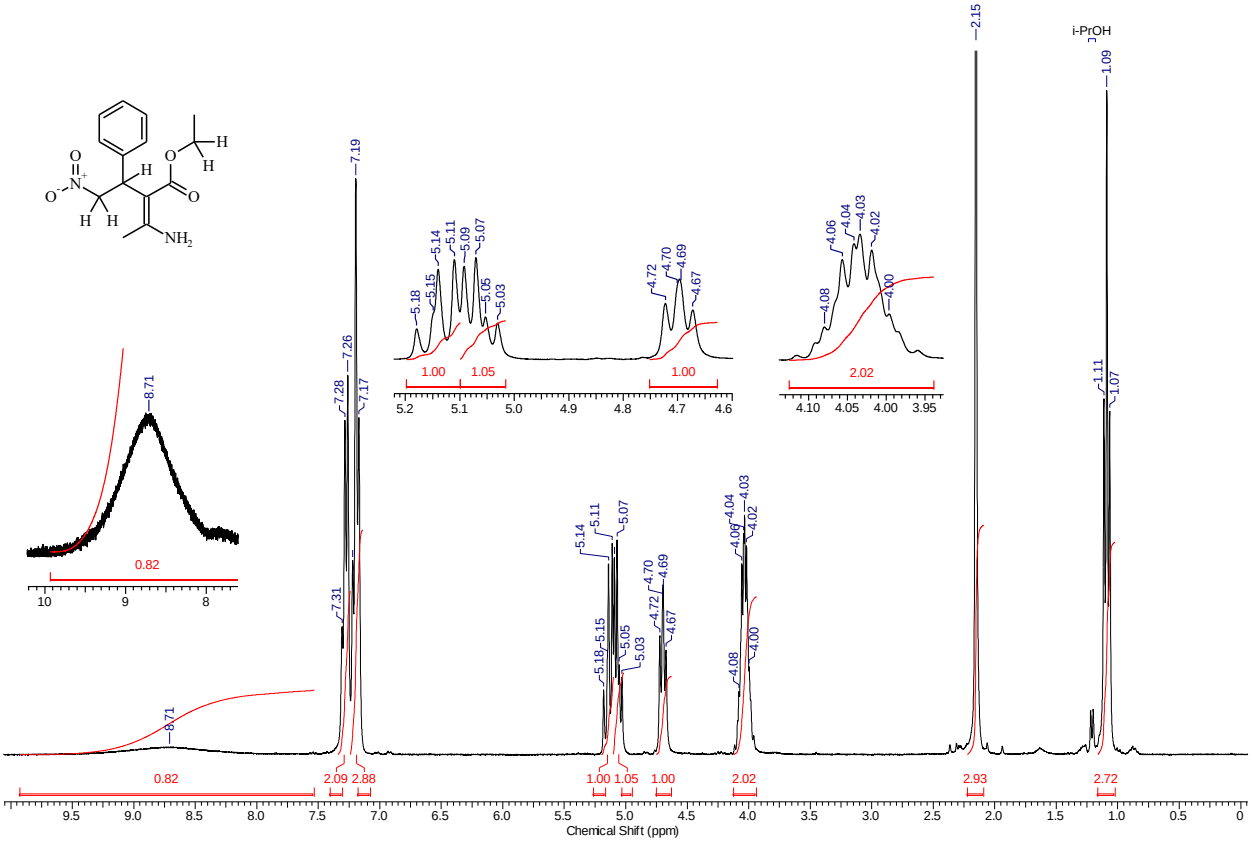
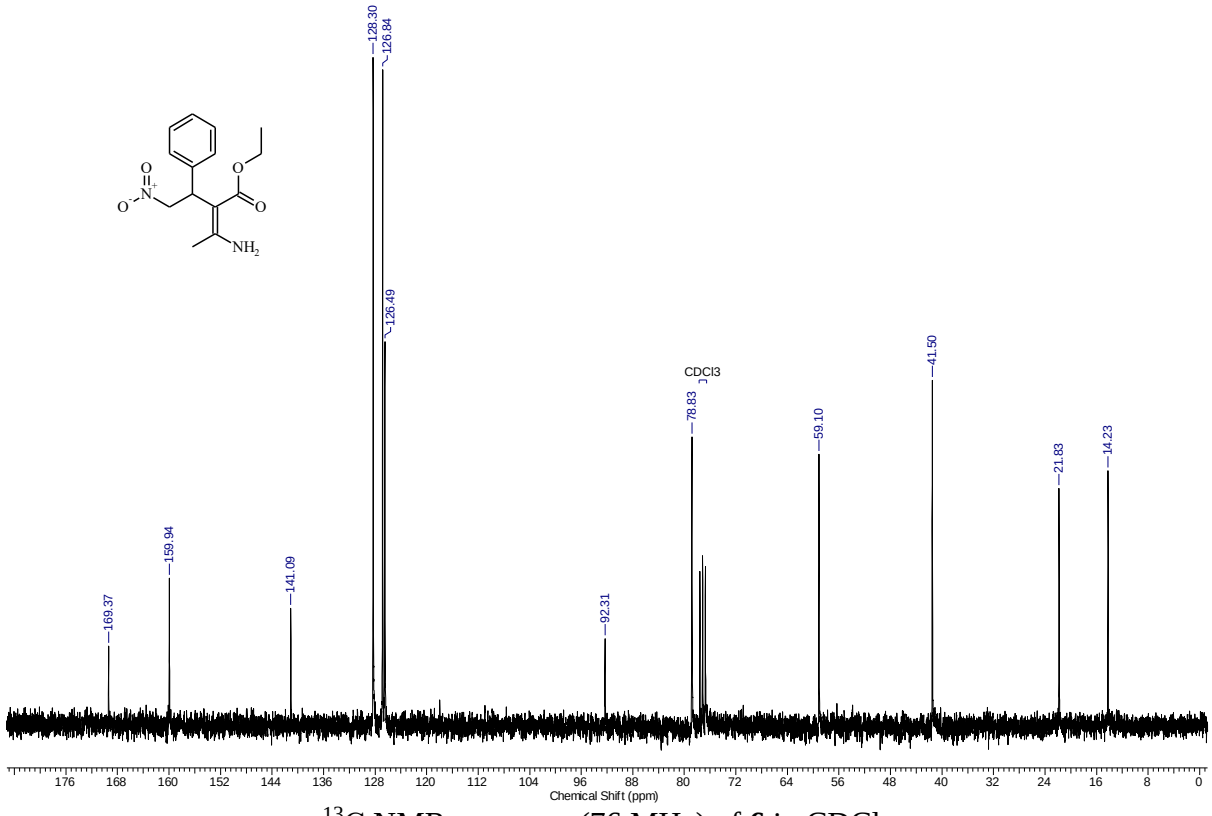
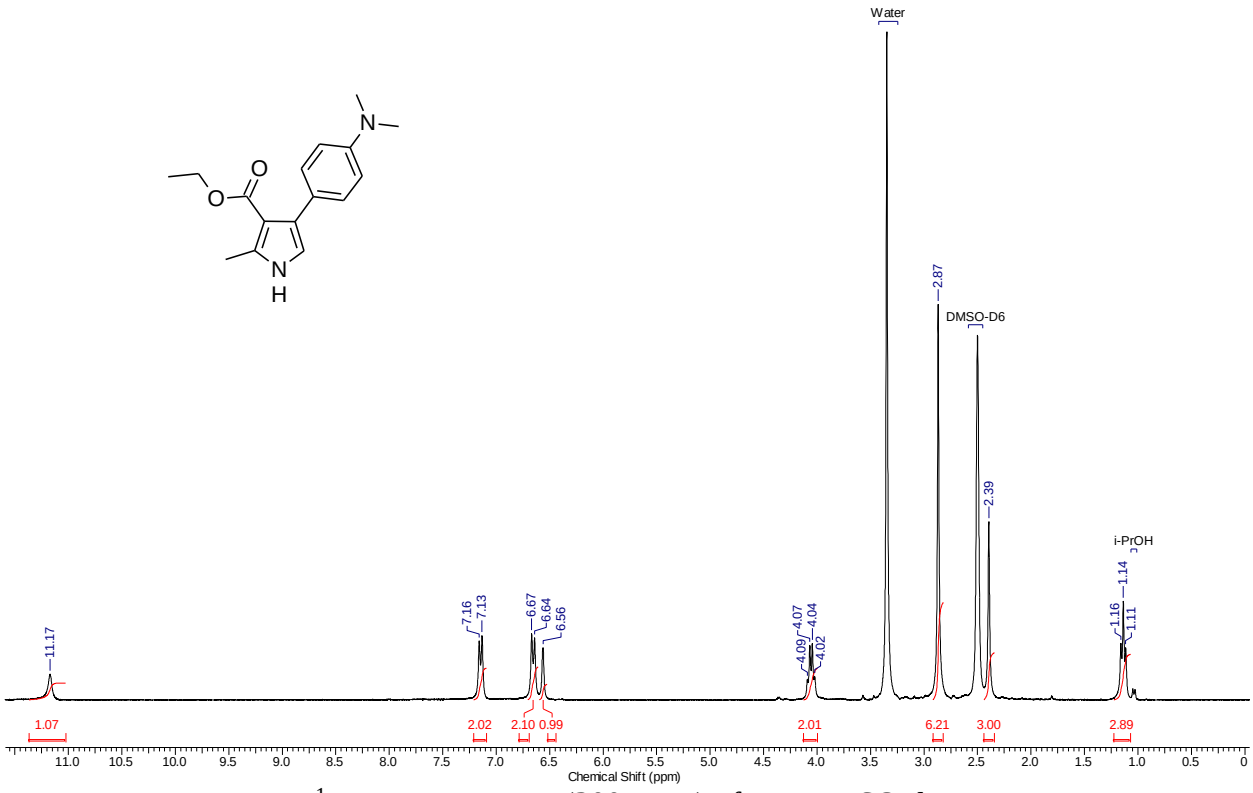
NMR spectra



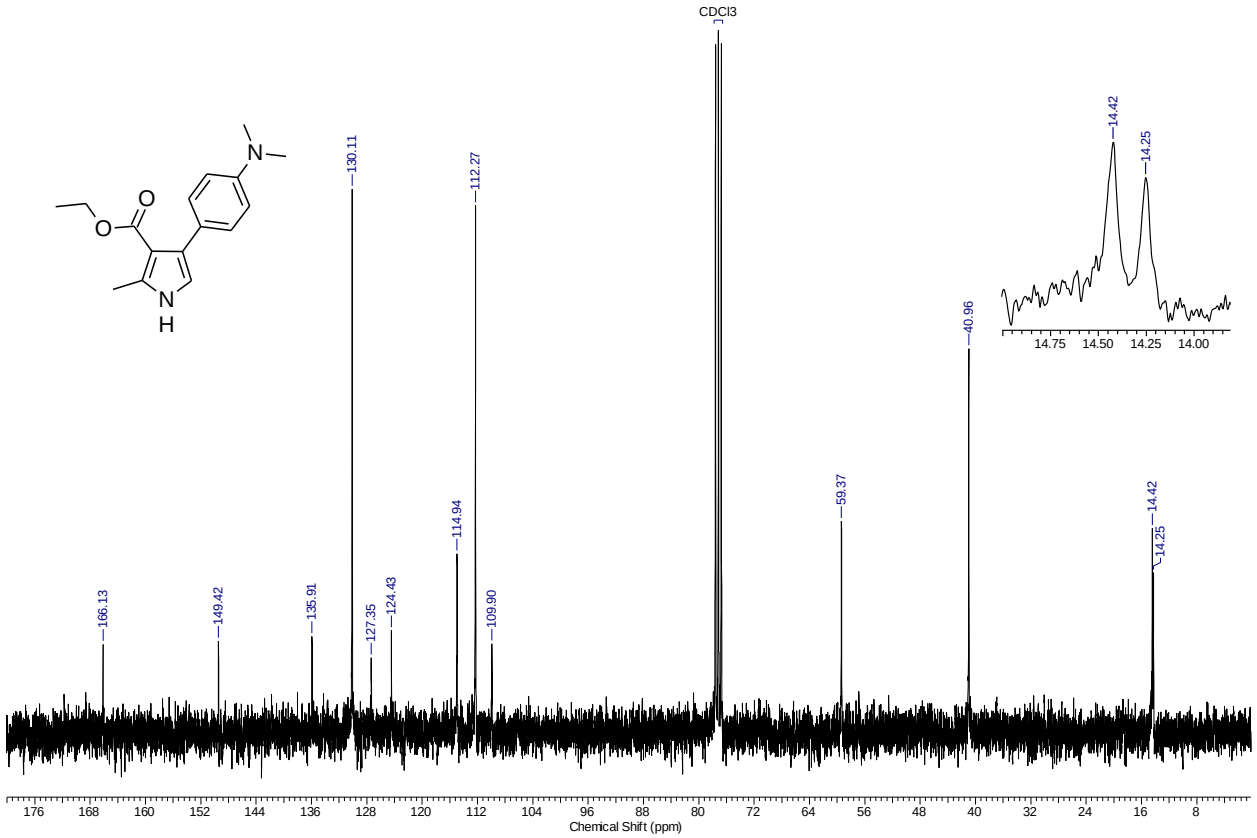
^{1}H NMR spectrum (300 MHz) of **6** in $CDCl_3$



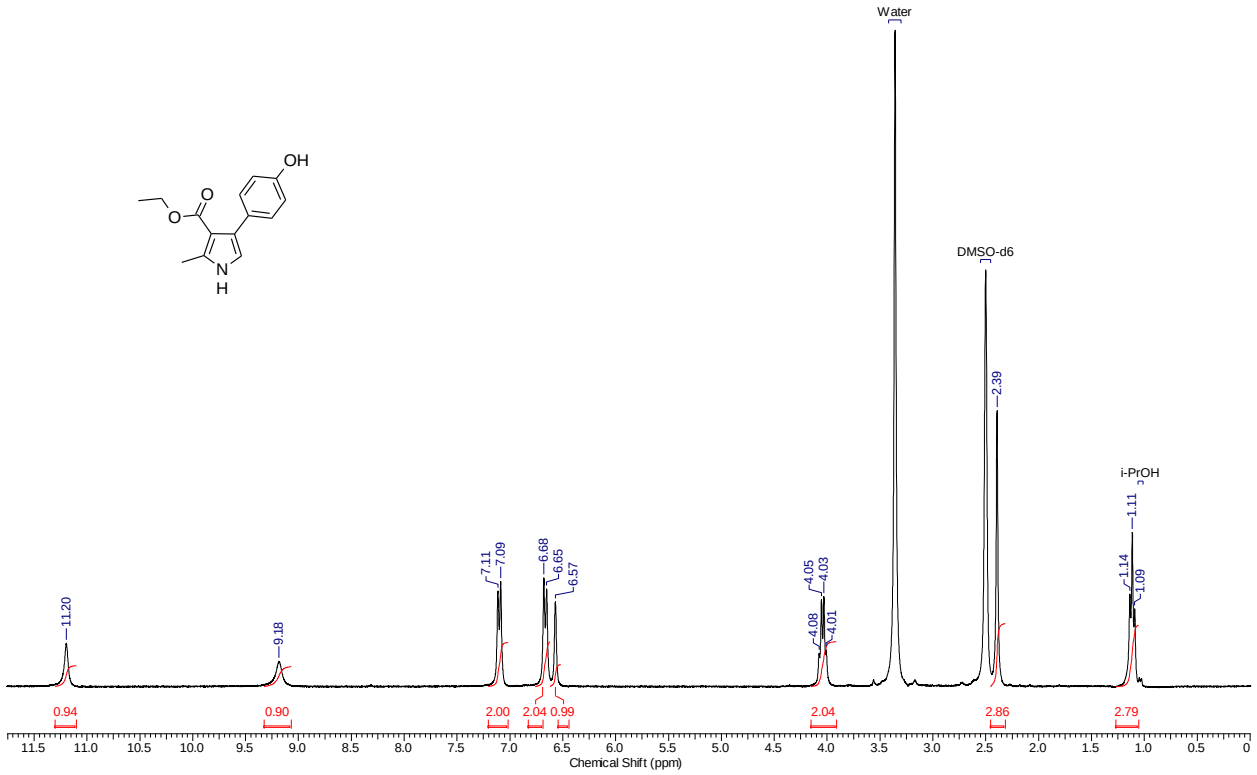
^{13}C NMR spectrum (76 MHz) of **6** in $CDCl_3$



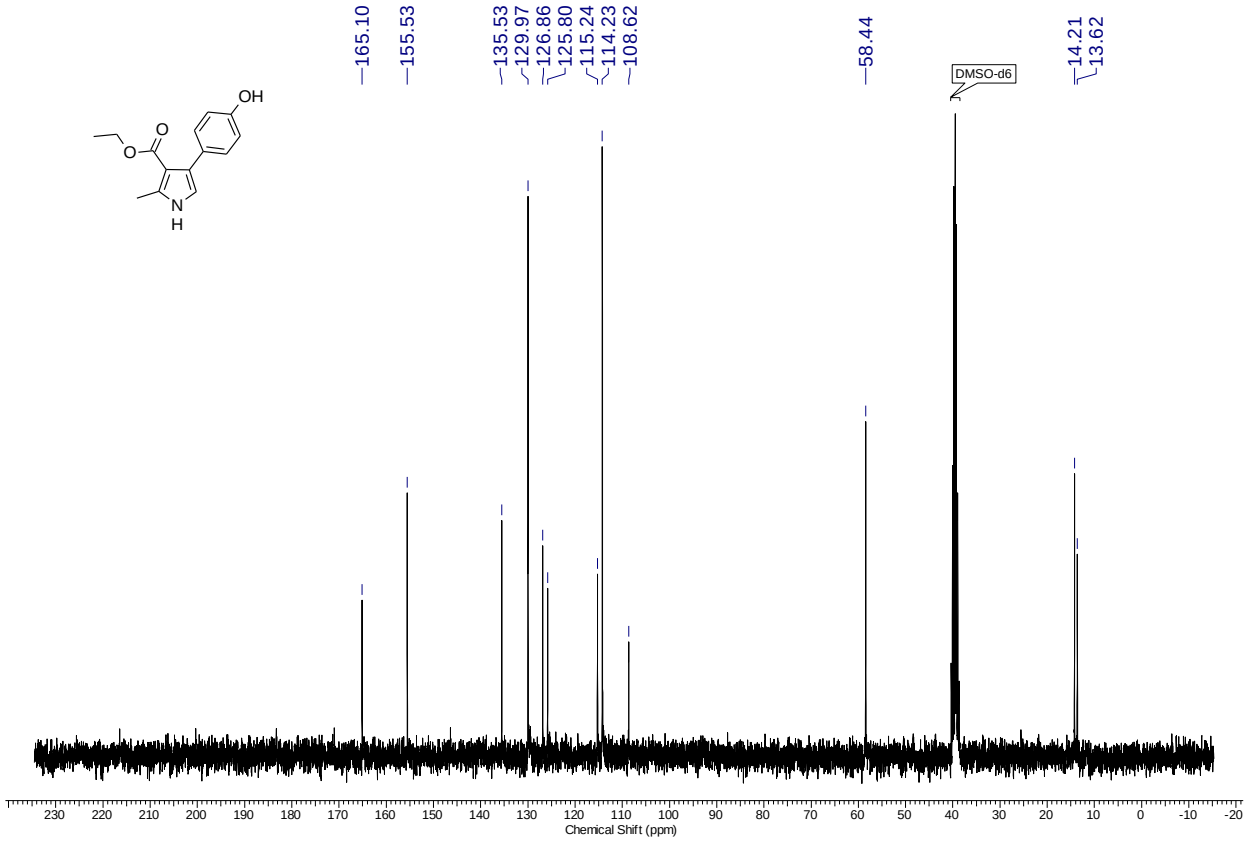
^{1}H NMR spectrum (300 MHz) of **7** in DMSO-d_6



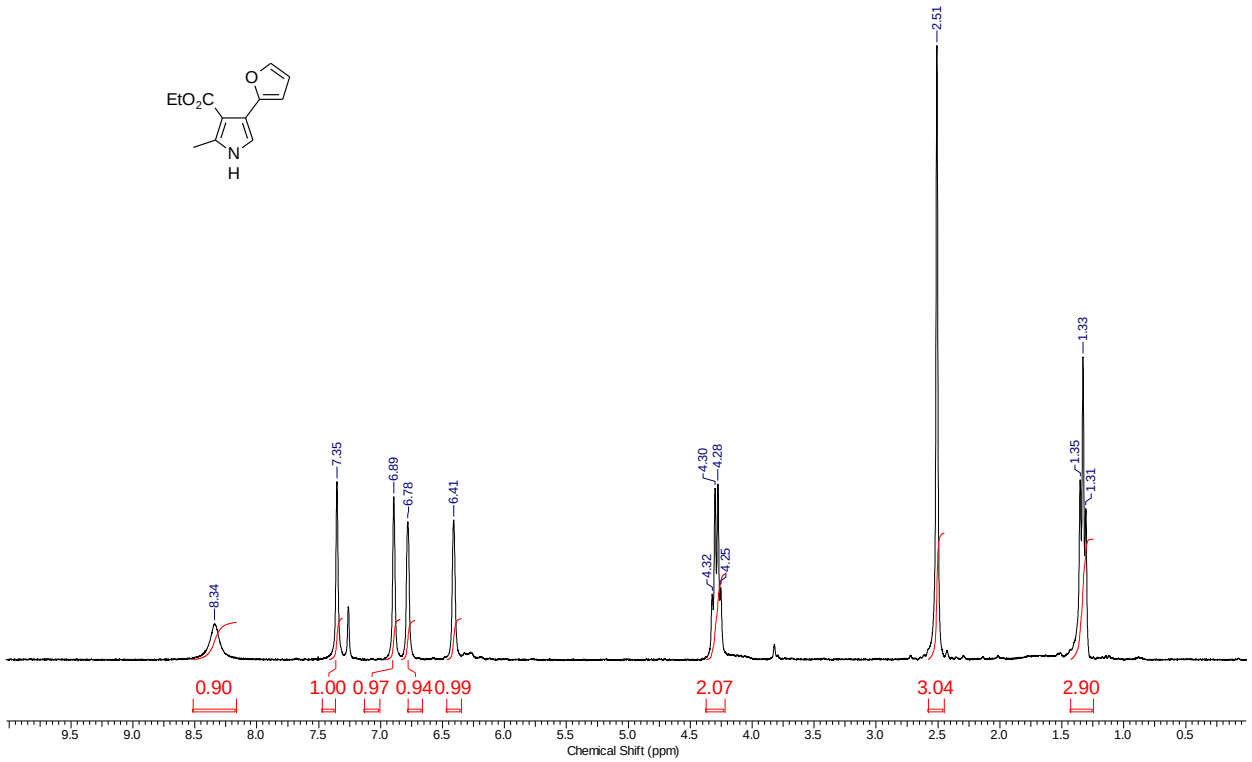
^{13}C NMR spectrum (76 MHz) of **7** in DMSO-d_6



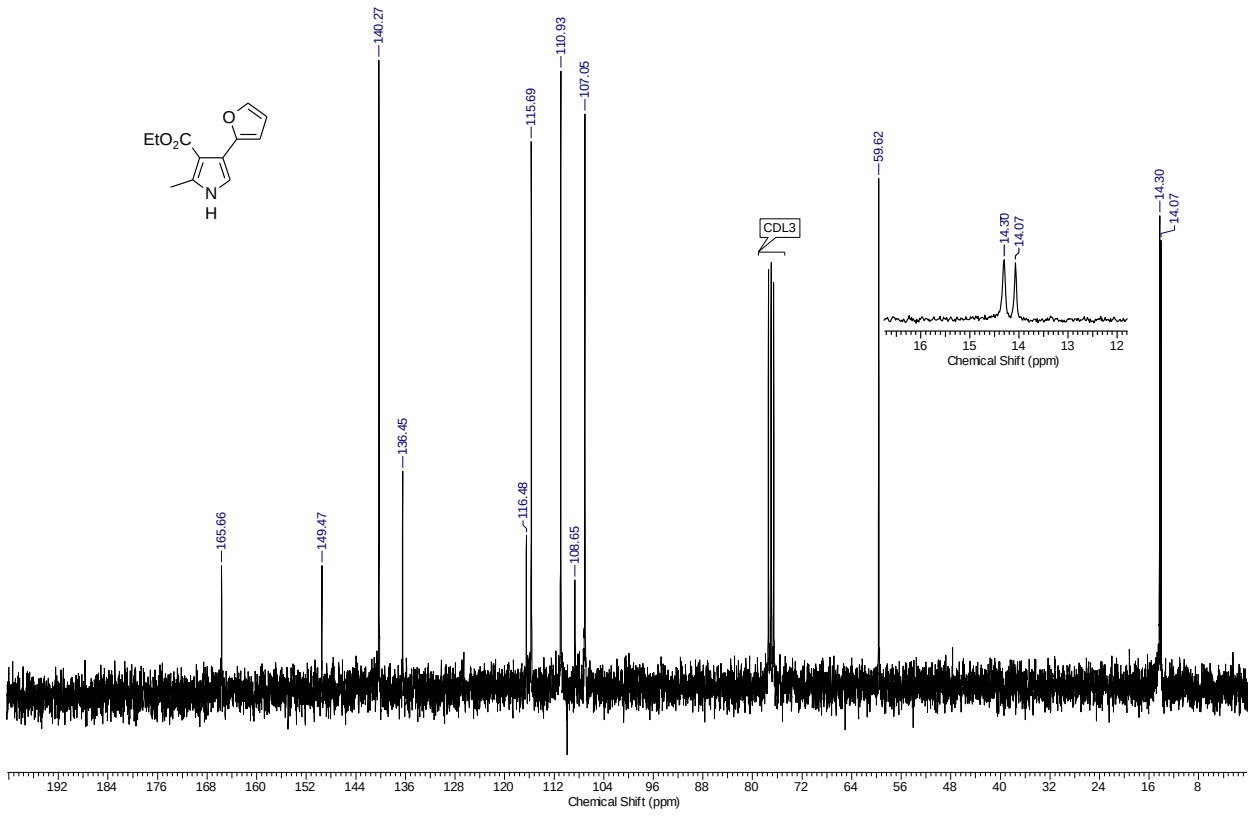
^{1}H NMR spectrum (300 MHz) of **8** in DMSO-d_6



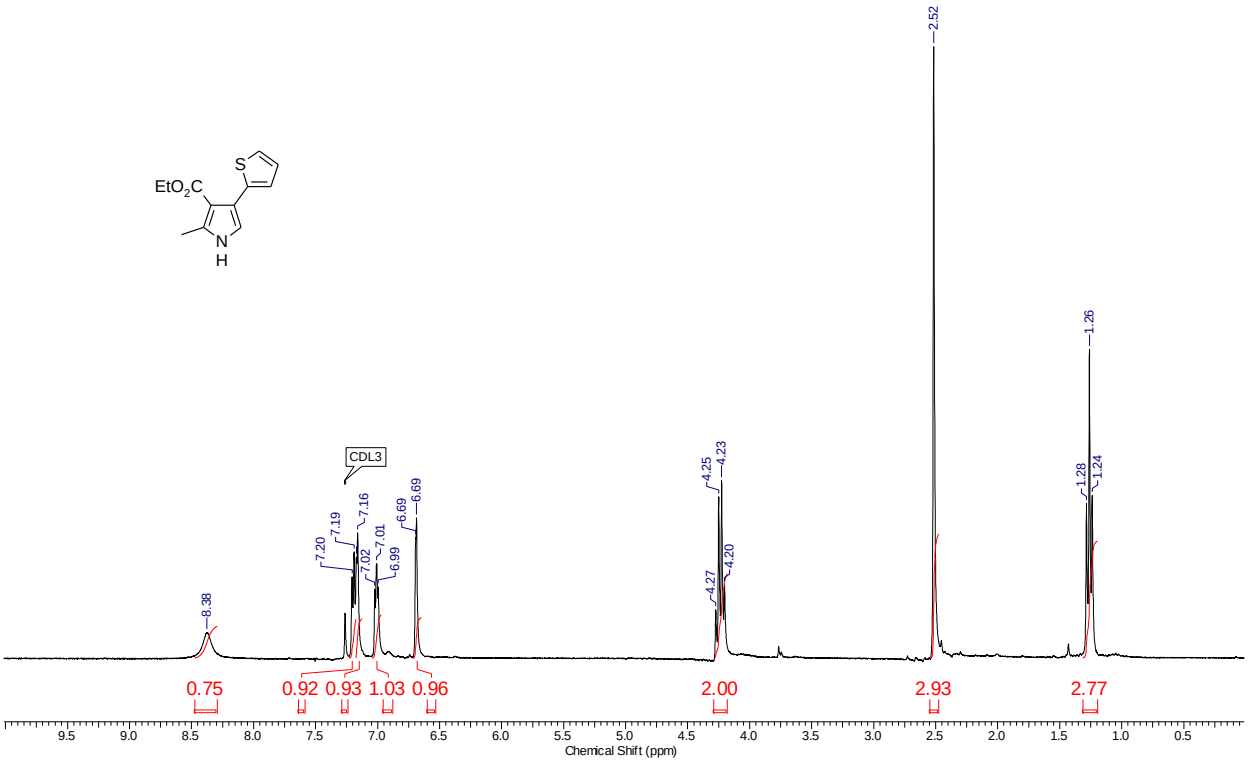
^{13}C NMR spectrum (76 MHz) of **8** in $CDCl_3$



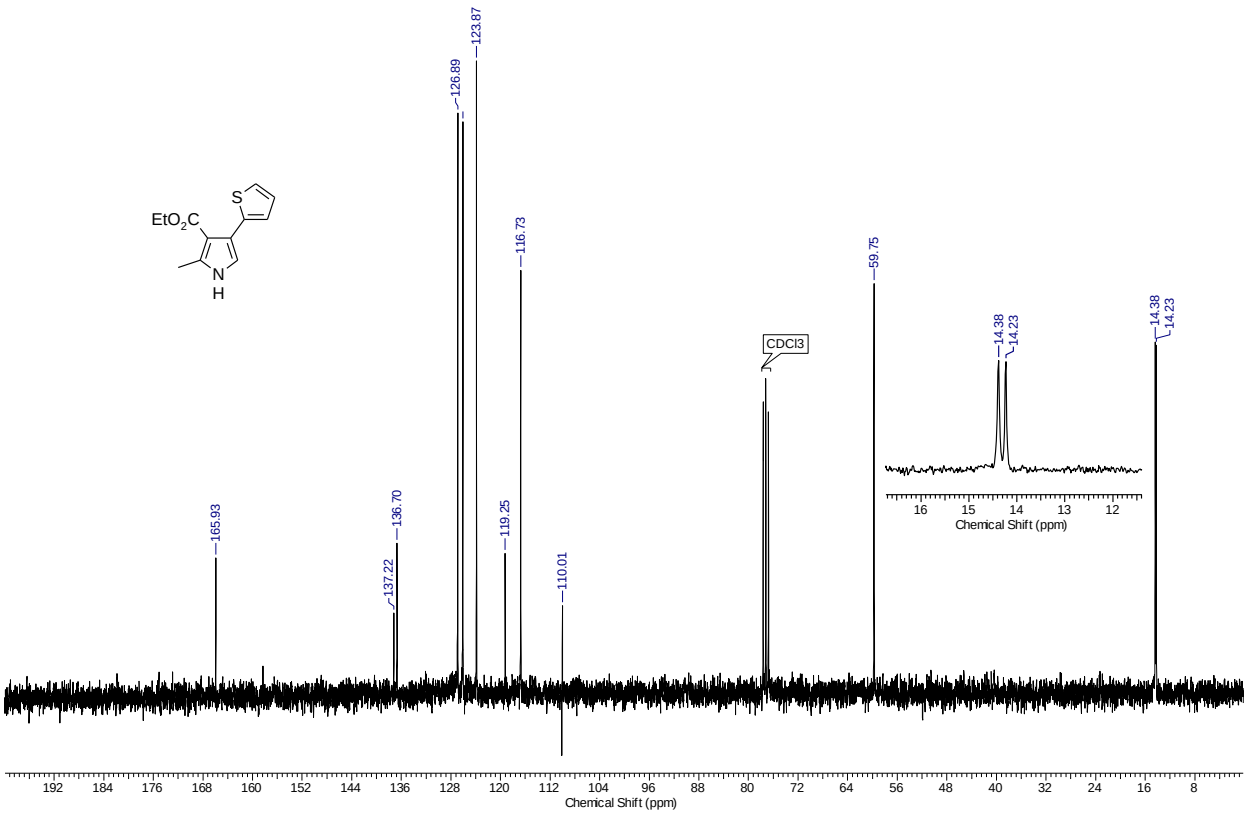
^{1}H NMR spectrum (300 MHz) of **9** in $CDCl_3$



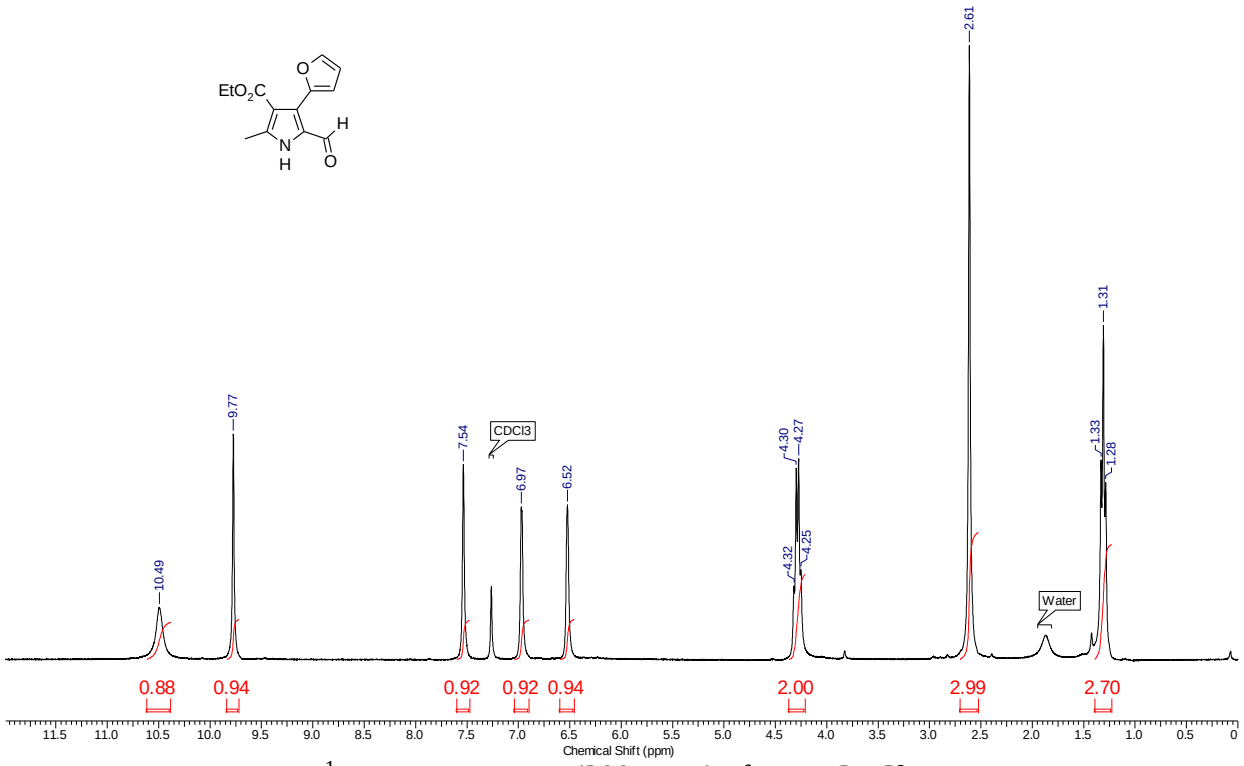
^{13}C NMR spectrum (76 MHz) of **9** in $CDCl_3$



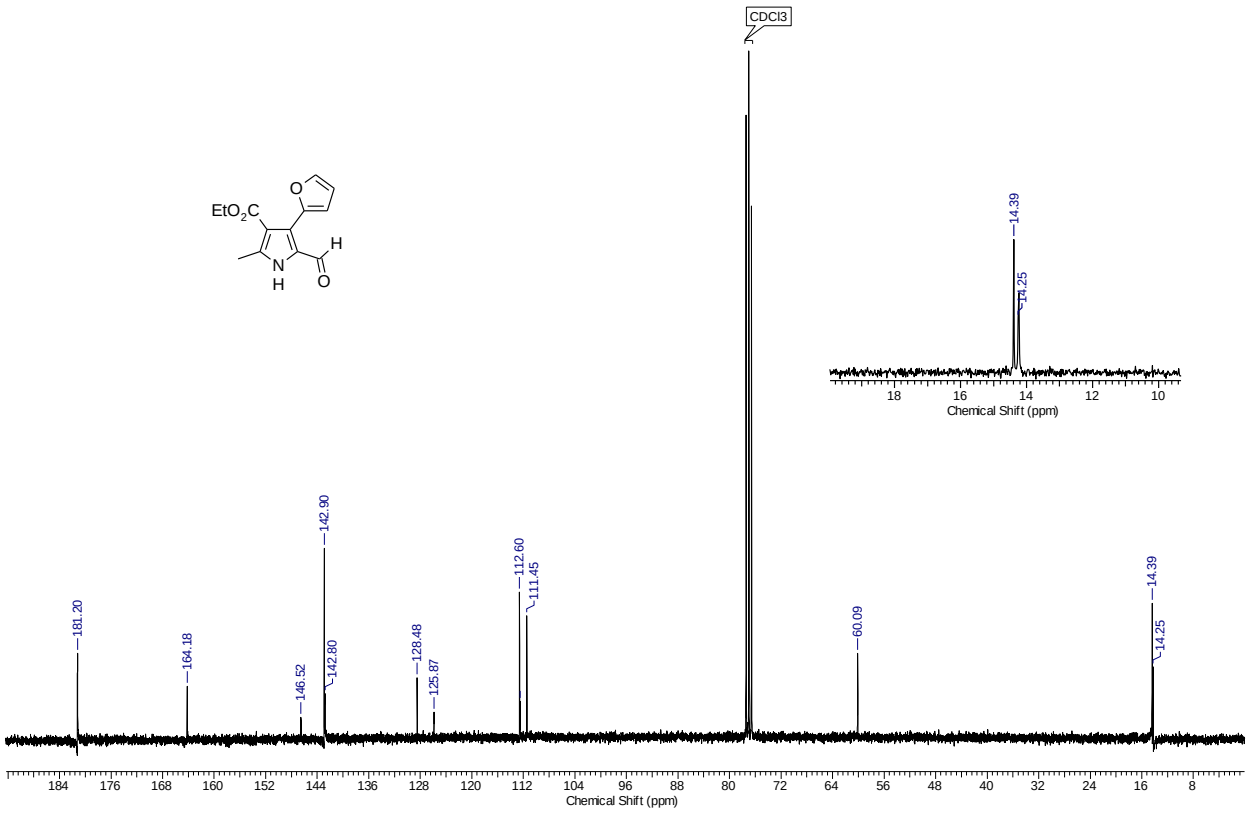
^{1}H NMR spectrum (300 MHz) of **10** in $CDCl_3$



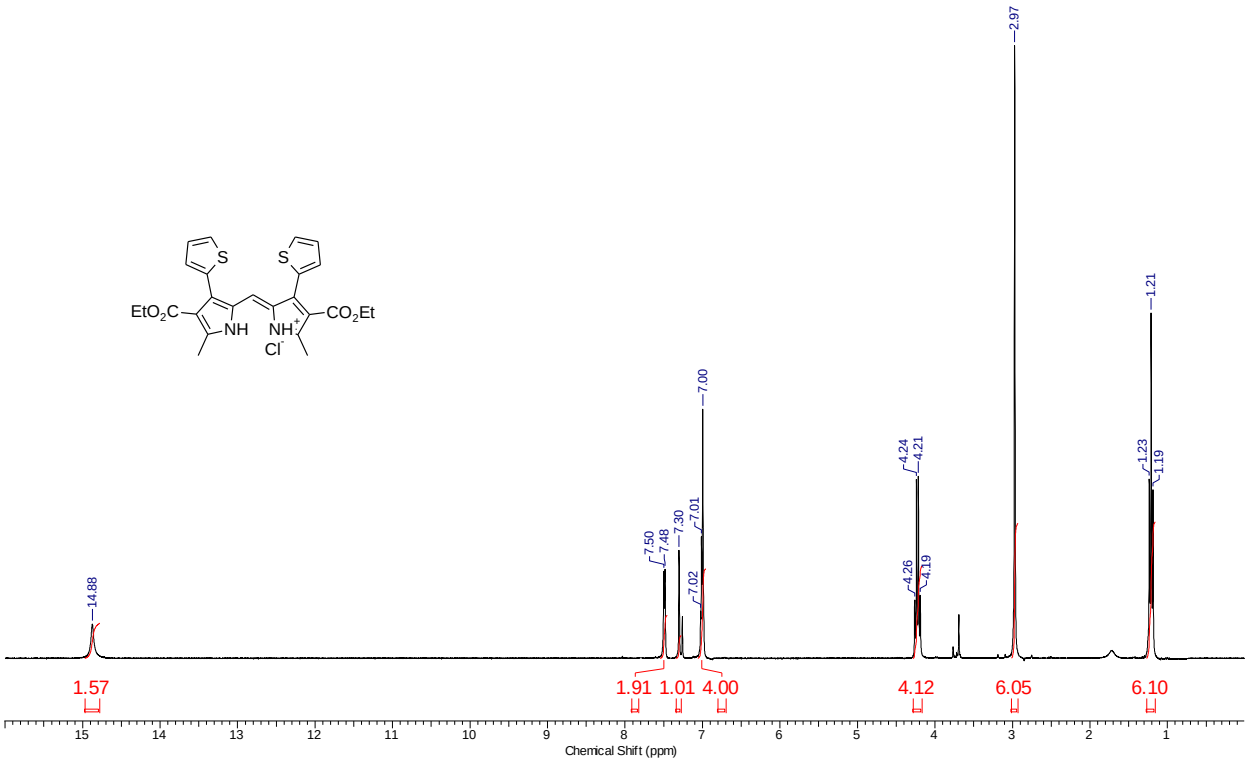
^{13}C NMR spectrum (76 MHz) of **10** in $CDCl_3$



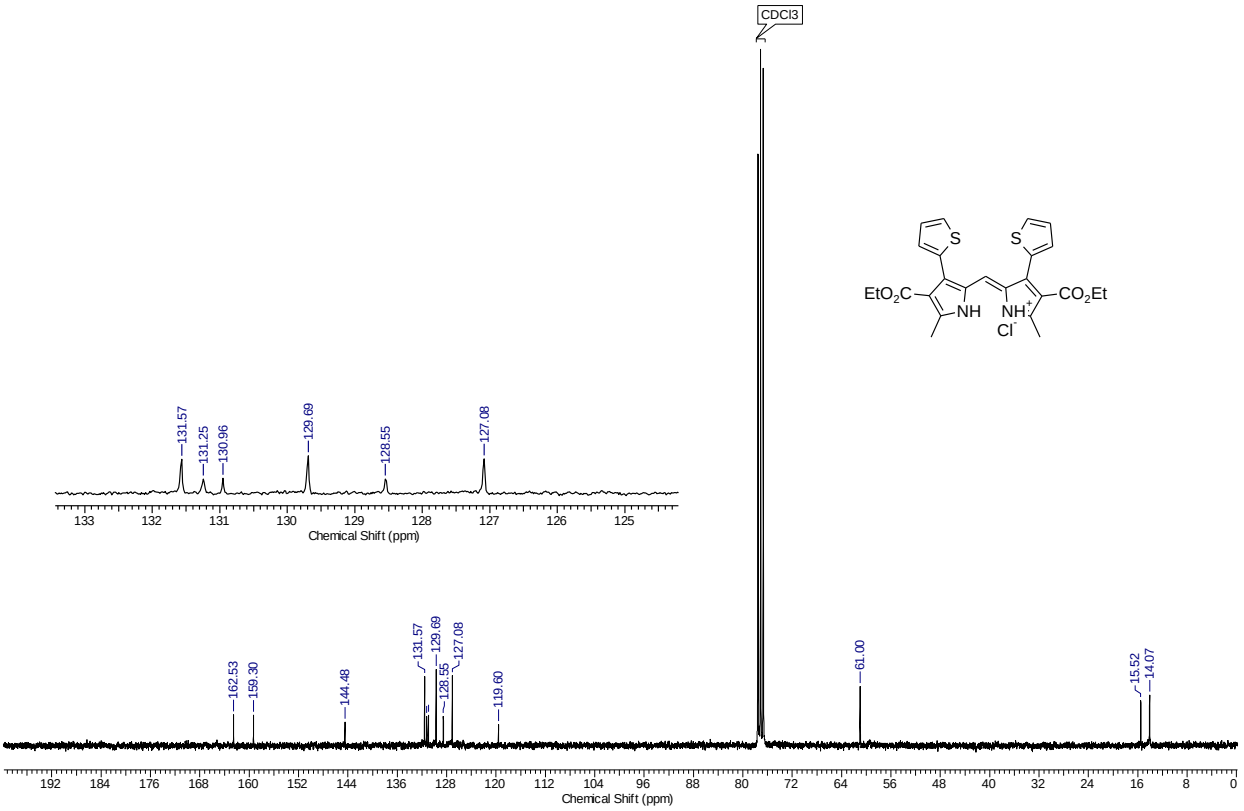
^{1}H NMR spectrum (300 MHz) of **11** in $CDCl_3$



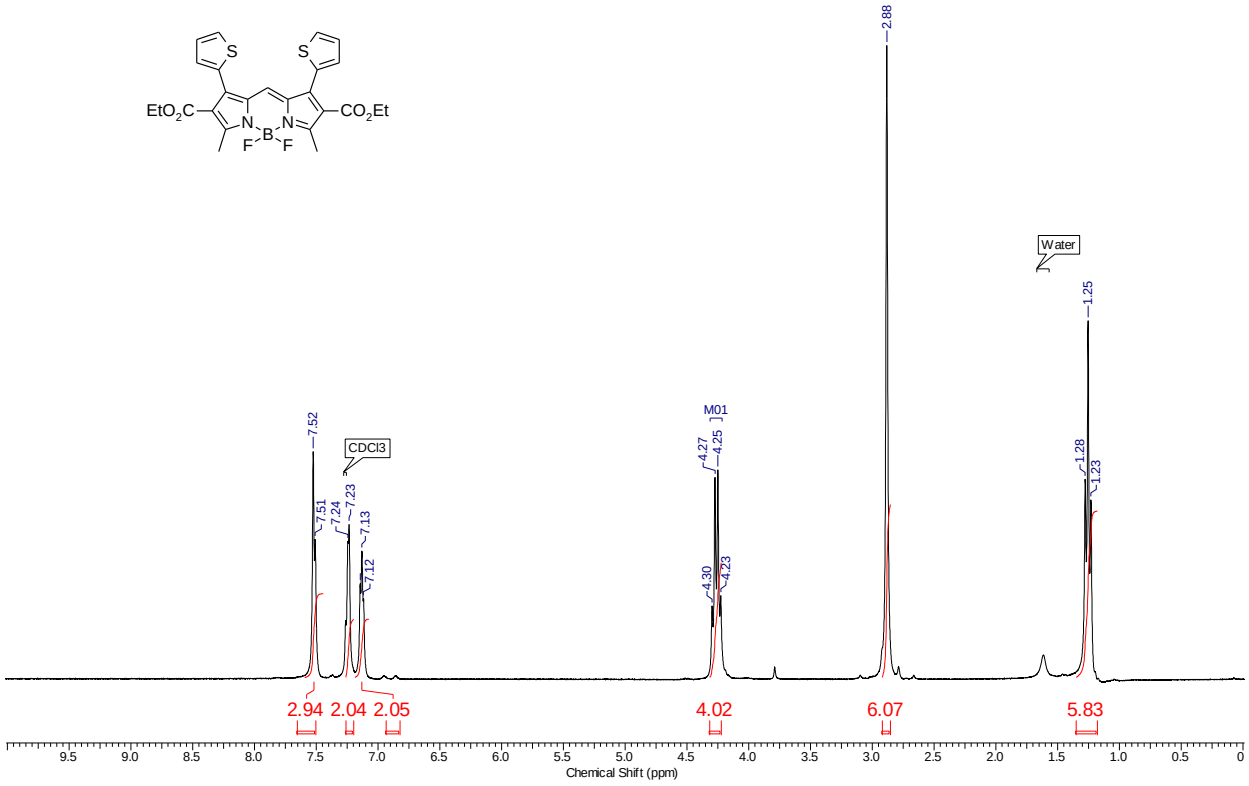
^{13}C NMR spectrum (76 MHz) of **11** in $CDCl_3$



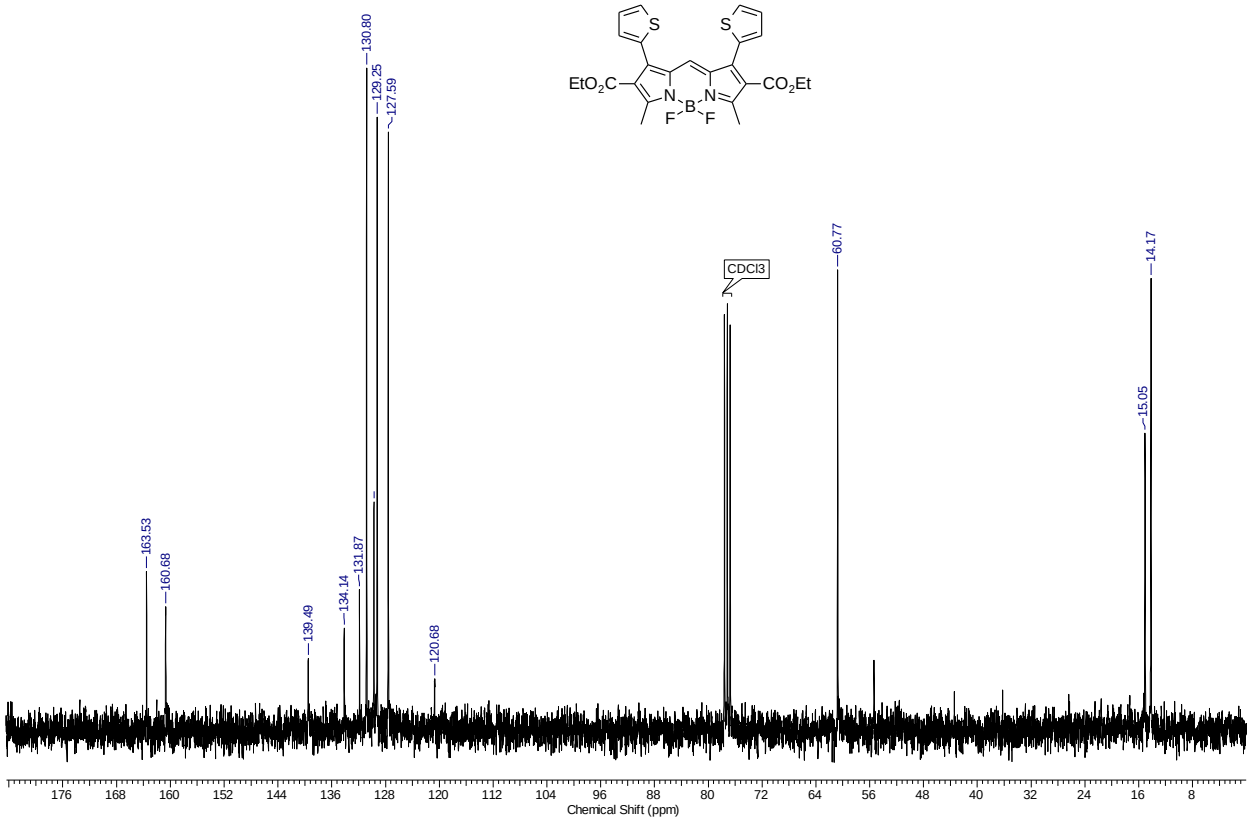
^{1}H NMR spectrum (300 MHz) of **13** in $CDCl_3$



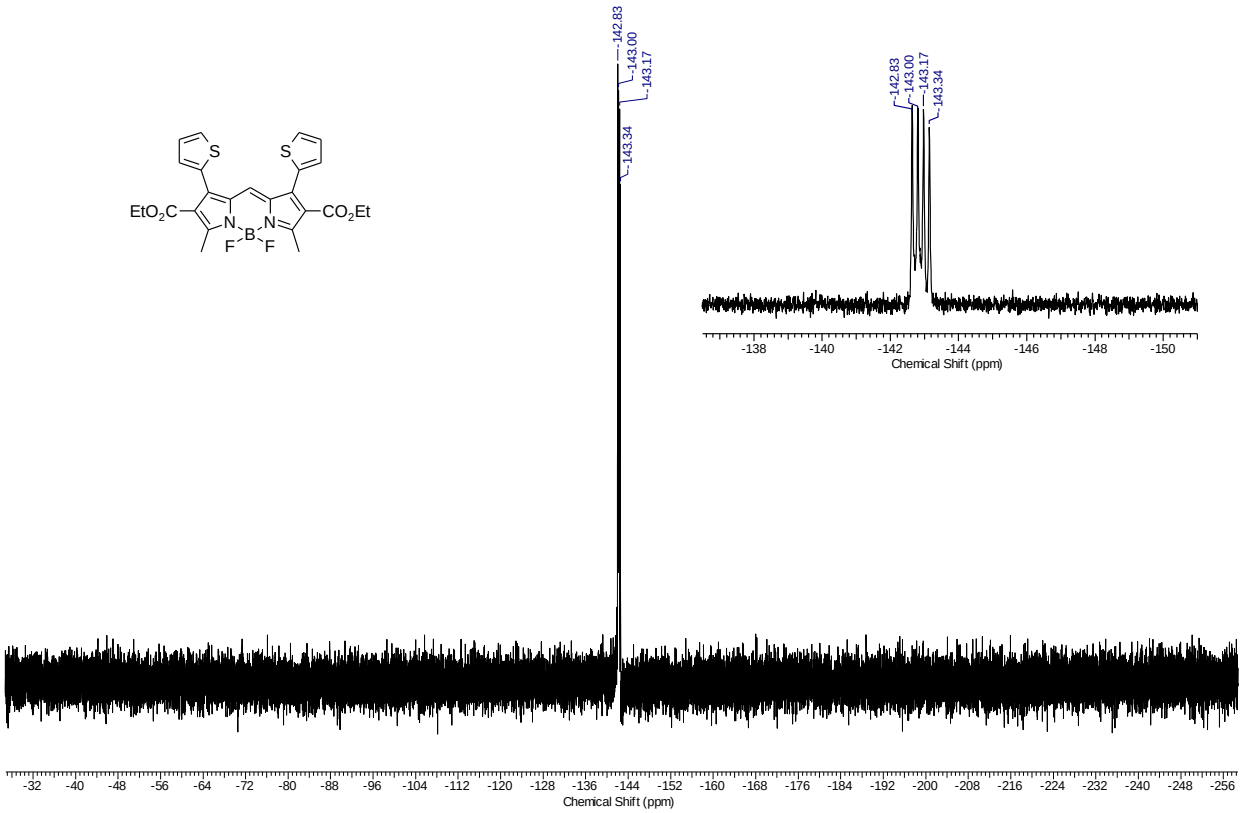
^{13}C NMR spectrum (76 MHz) of **13** in $CDCl_3$



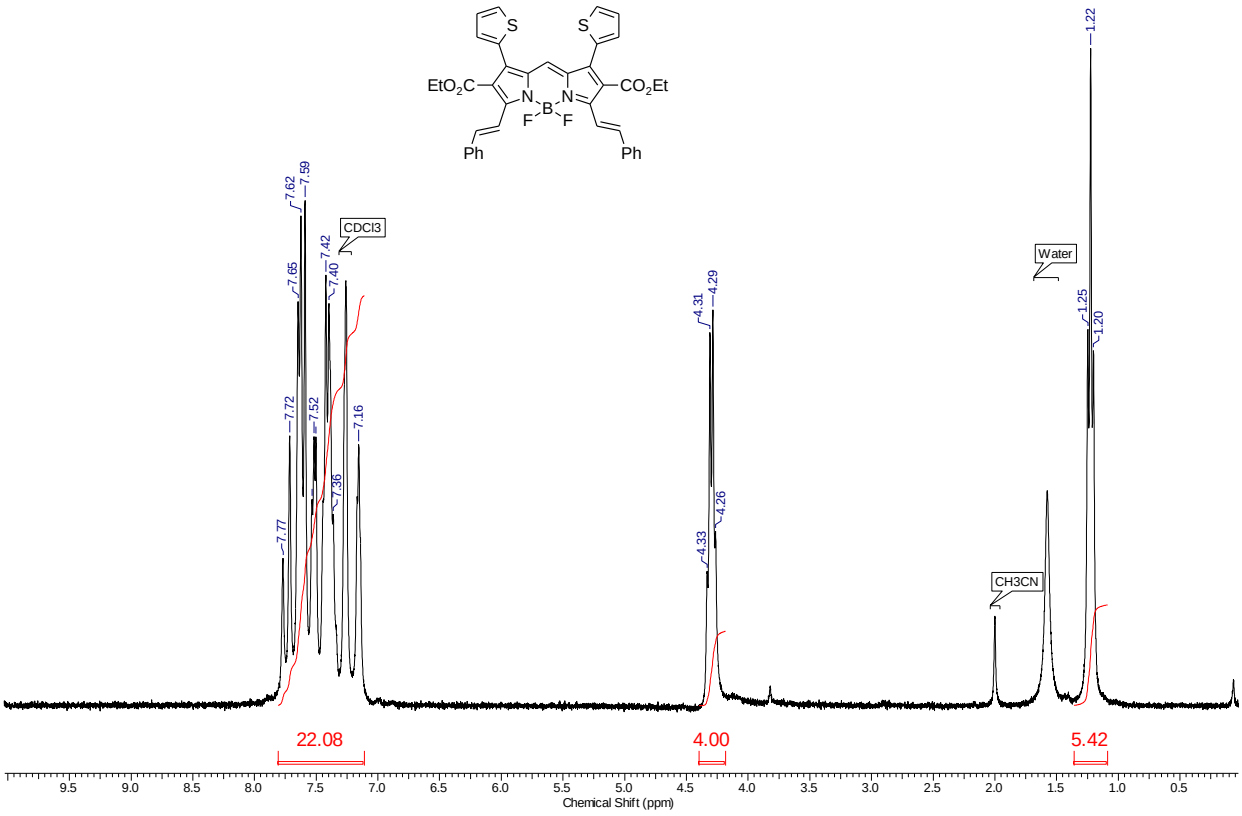
^{1}H NMR spectrum (300 MHz) of **14** in $CDCl_3$



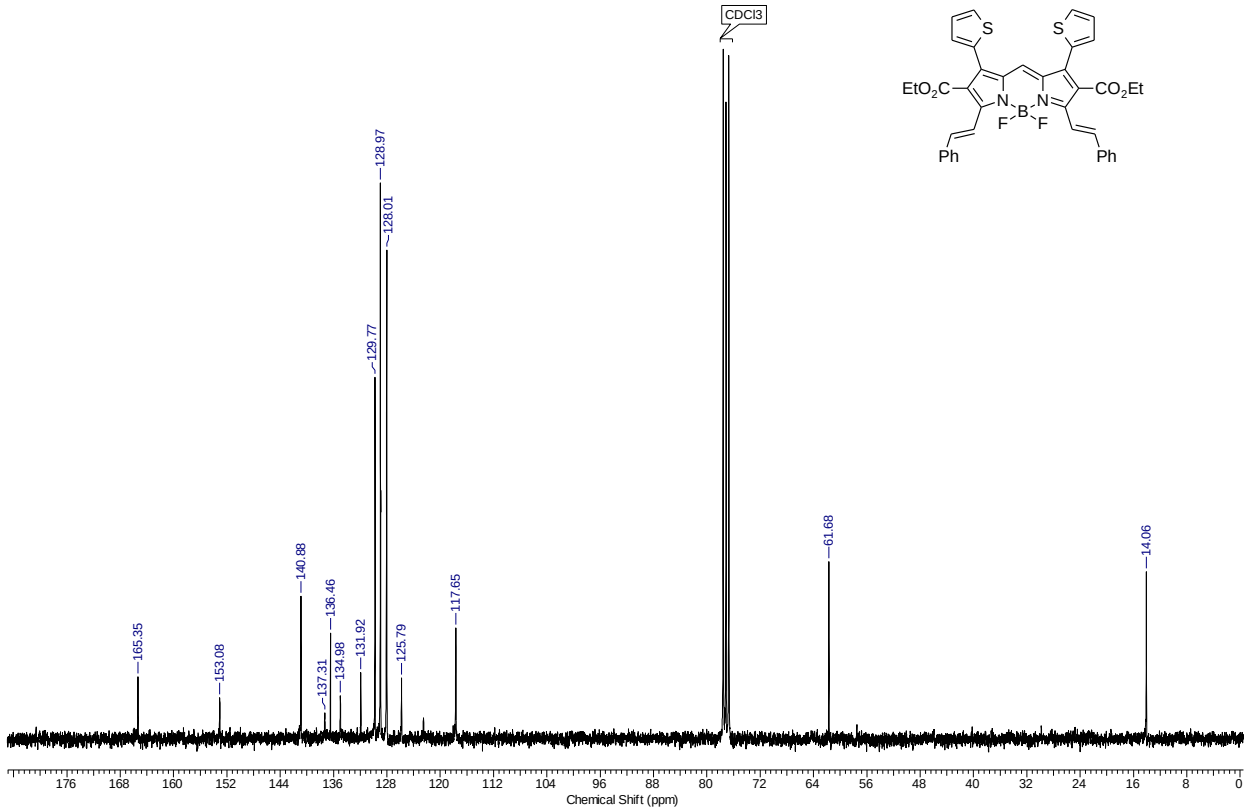
^{13}C NMR spectrum (76 MHz) of **14** in $CDCl_3$



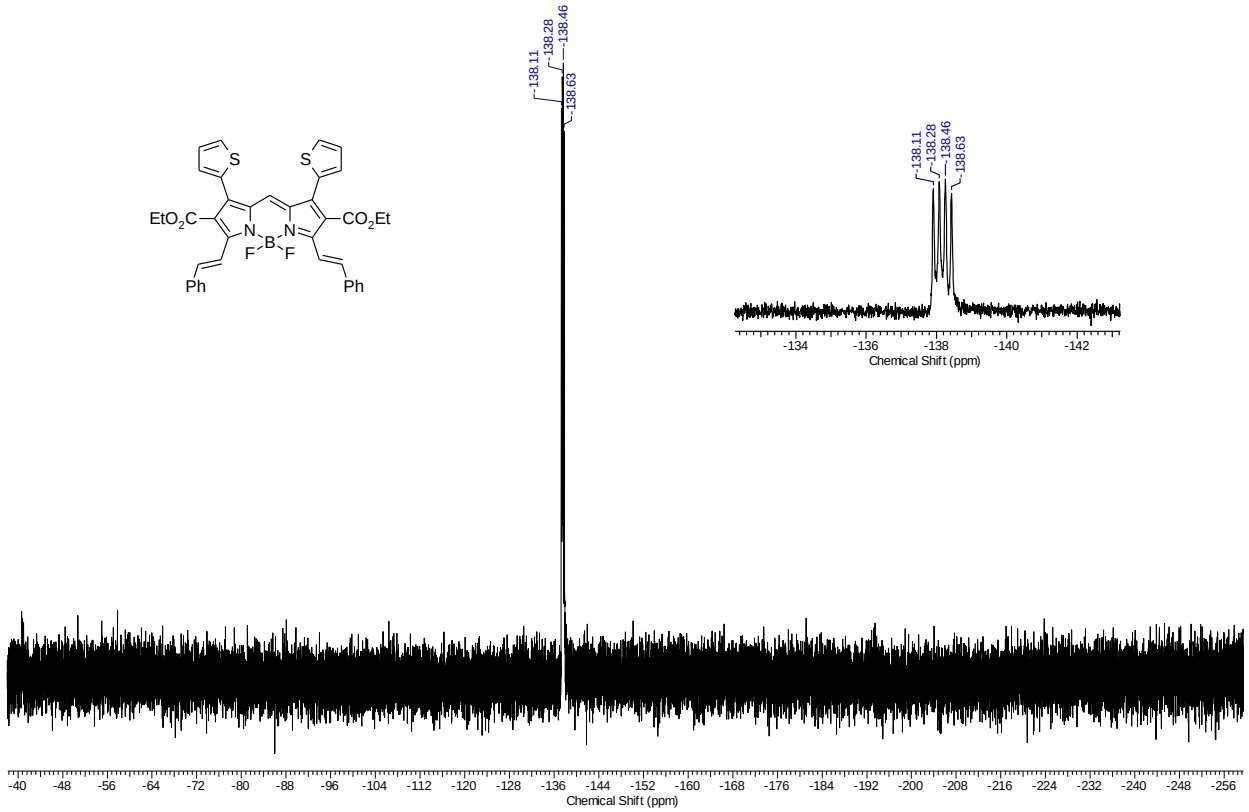
^{19}F NMR spectrum (188 MHz) of **14** in $CDCl_3$



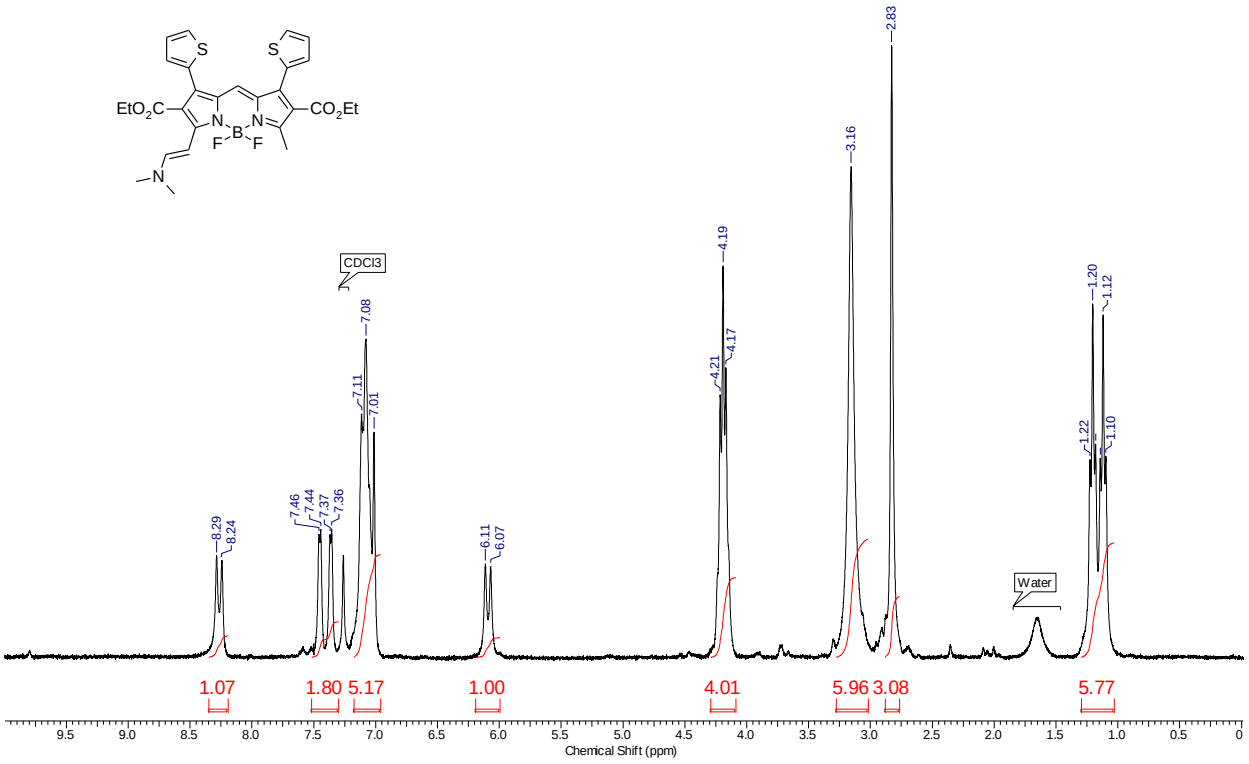
^{1}H NMR spectrum (300 MHz) of **15** in $CDCl_3$



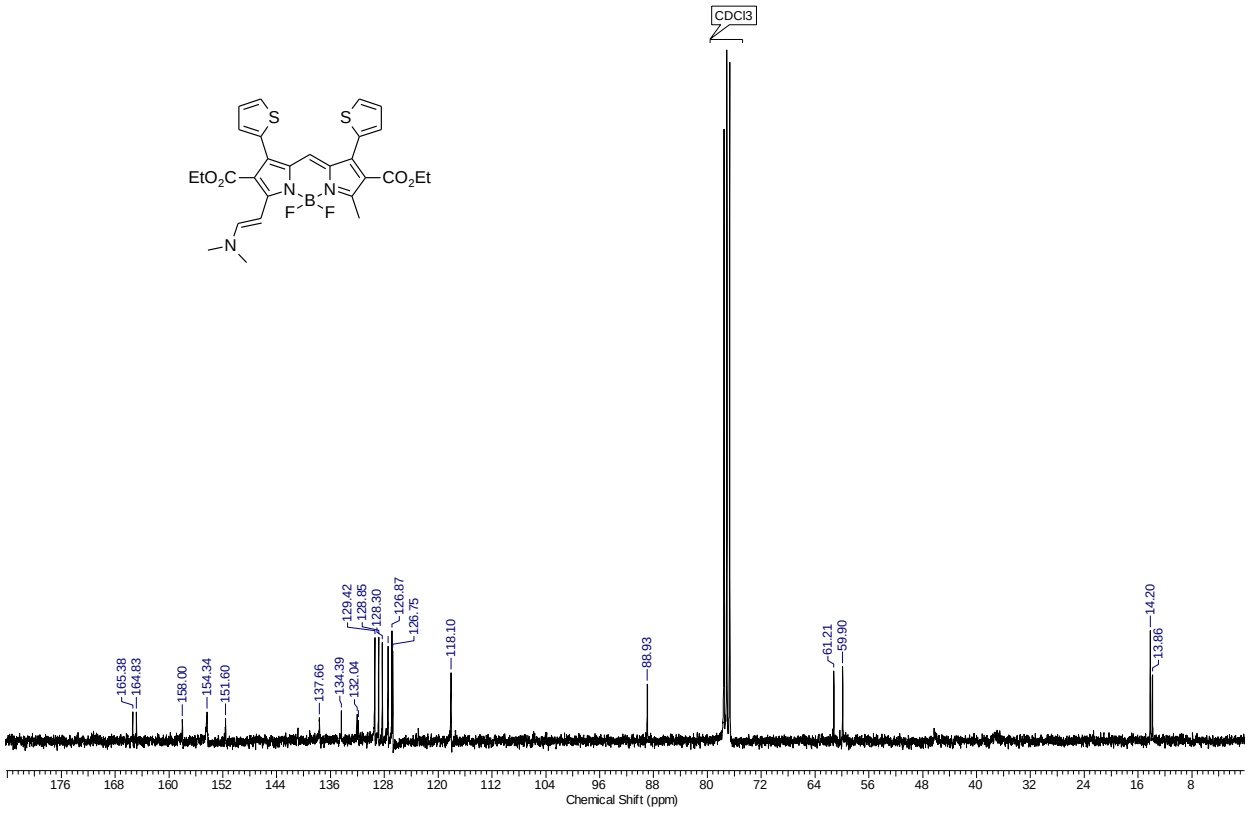
^{13}C NMR spectrum (76 MHz) of **15** in $CDCl_3$



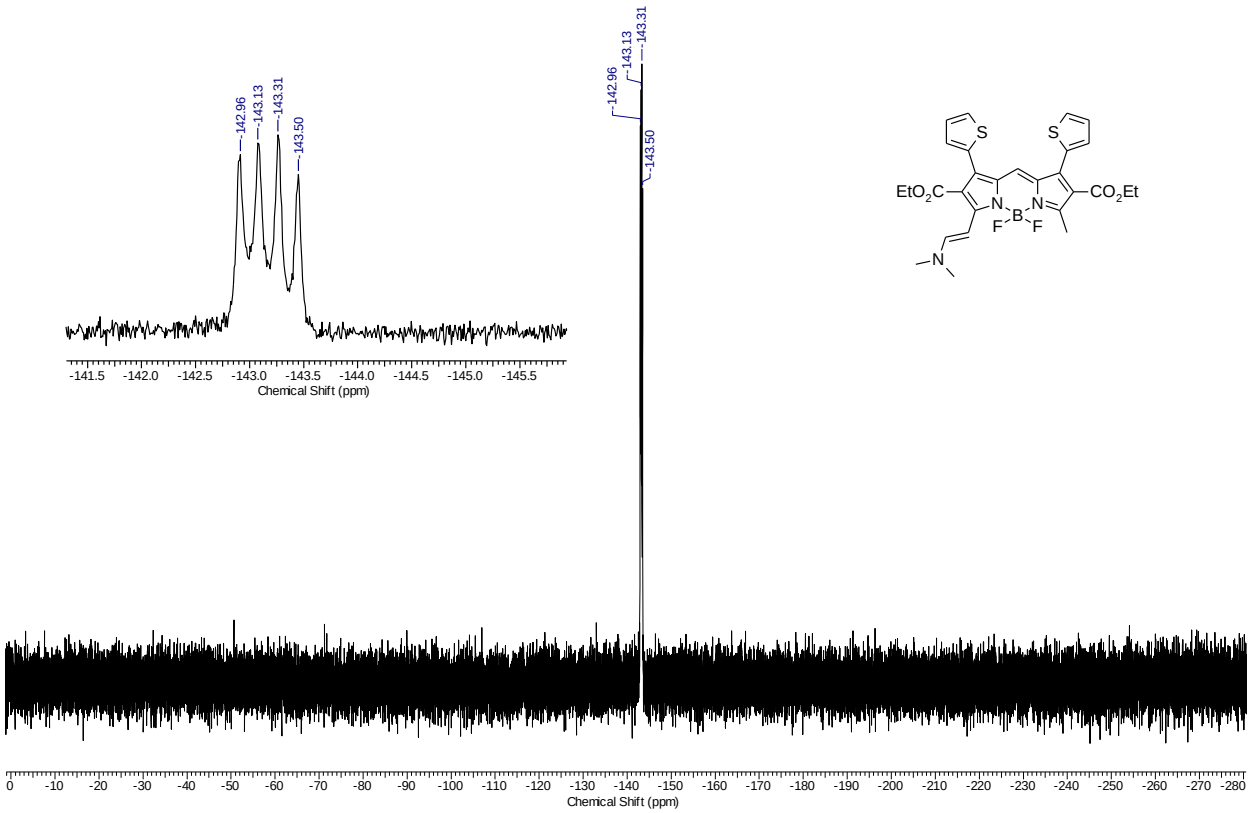
^{19}F NMR spectrum (188 MHz) of **15** in $CDCl_3$



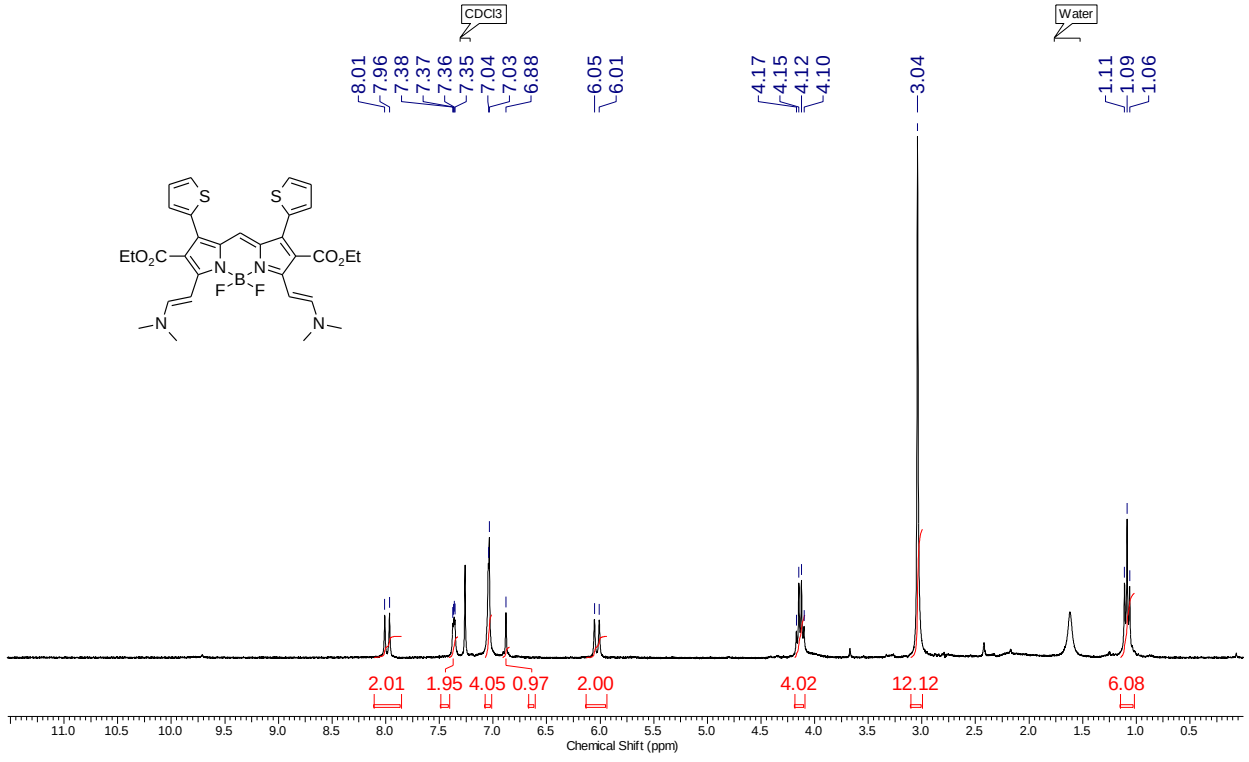
^{1}H NMR spectrum (300 MHz) of **16** in $CDCl_3$



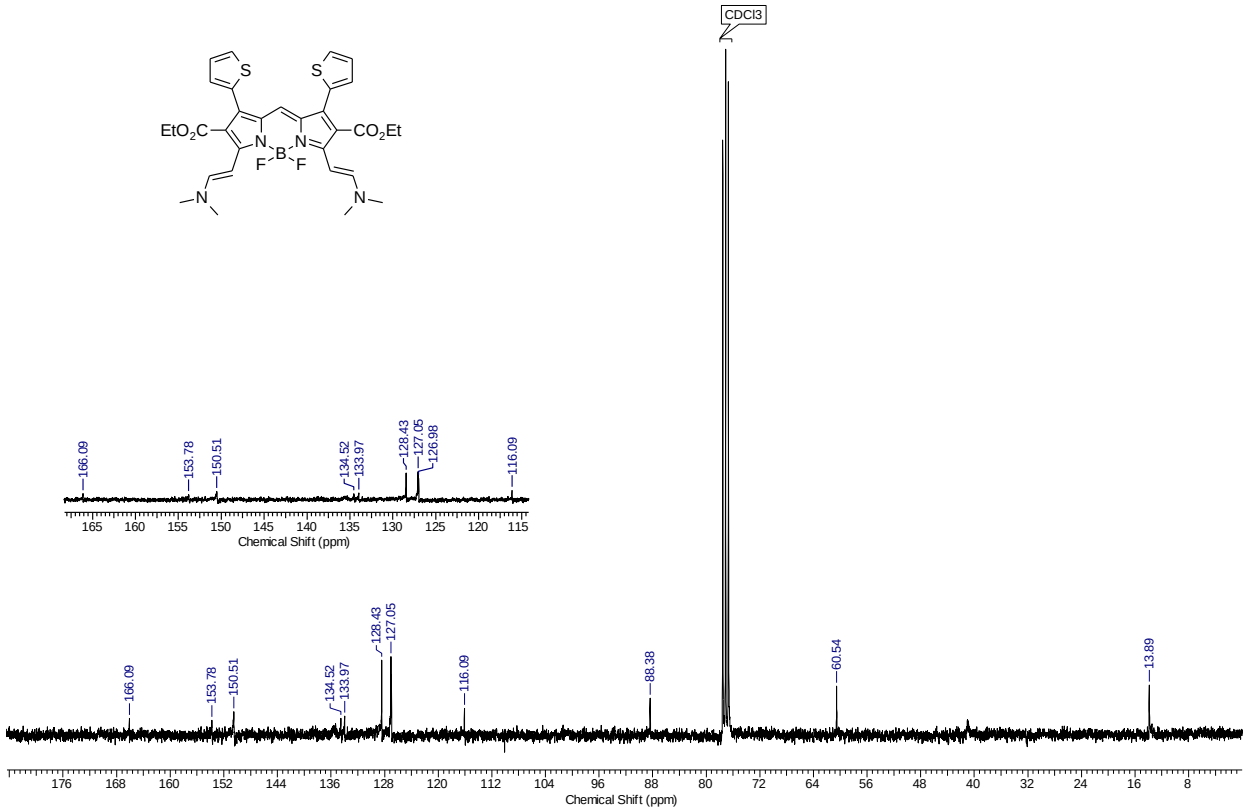
^{13}C NMR spectrum (76 MHz) of **16** in $CDCl_3$



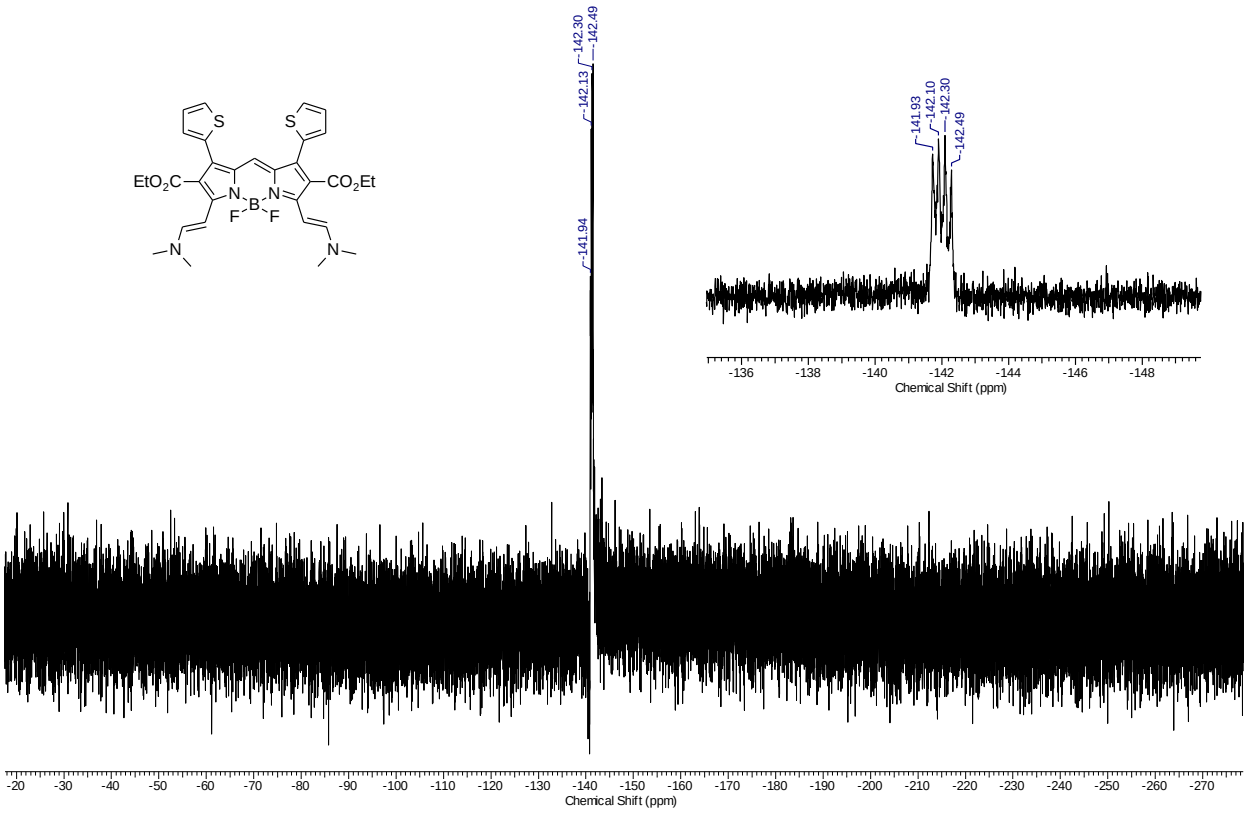
^{19}F NMR spectrum (188 MHz) of **16** in $CDCl_3$



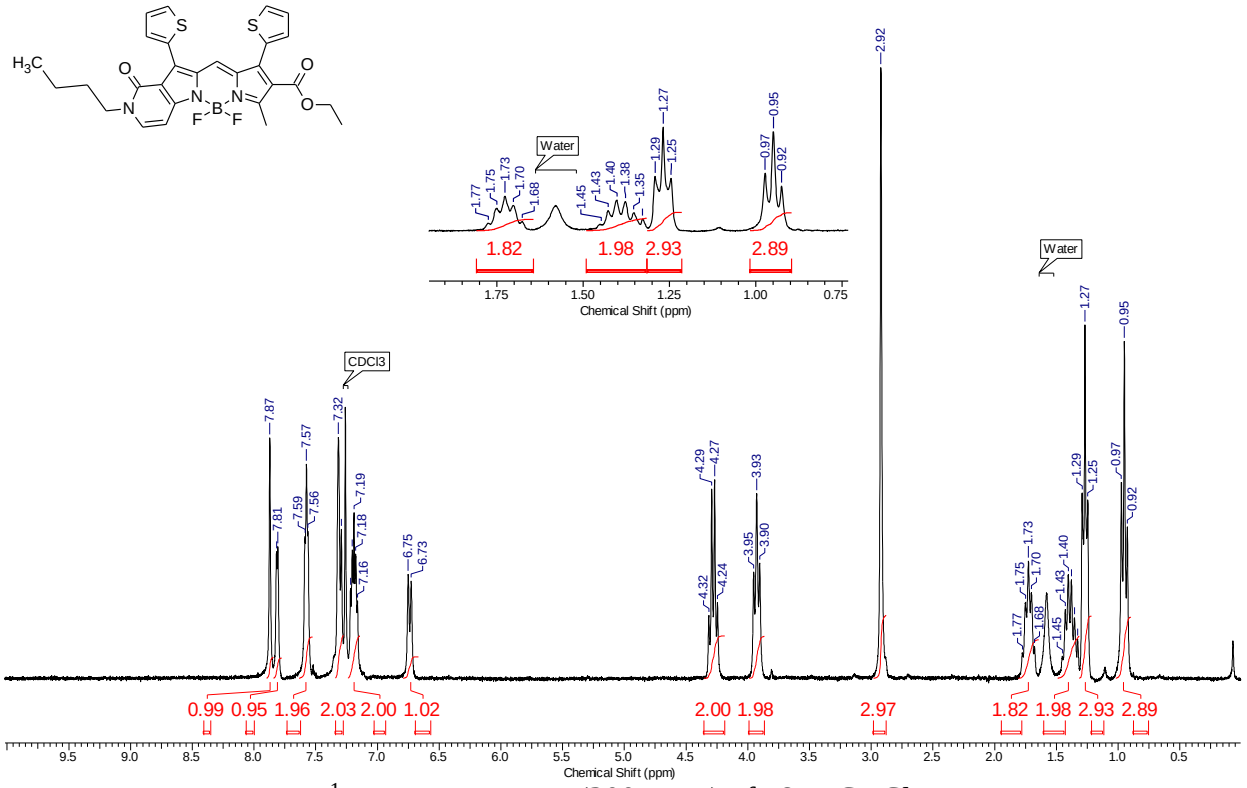
^{1}H NMR spectrum (300 MHz) of **17** in $CDCl_3$



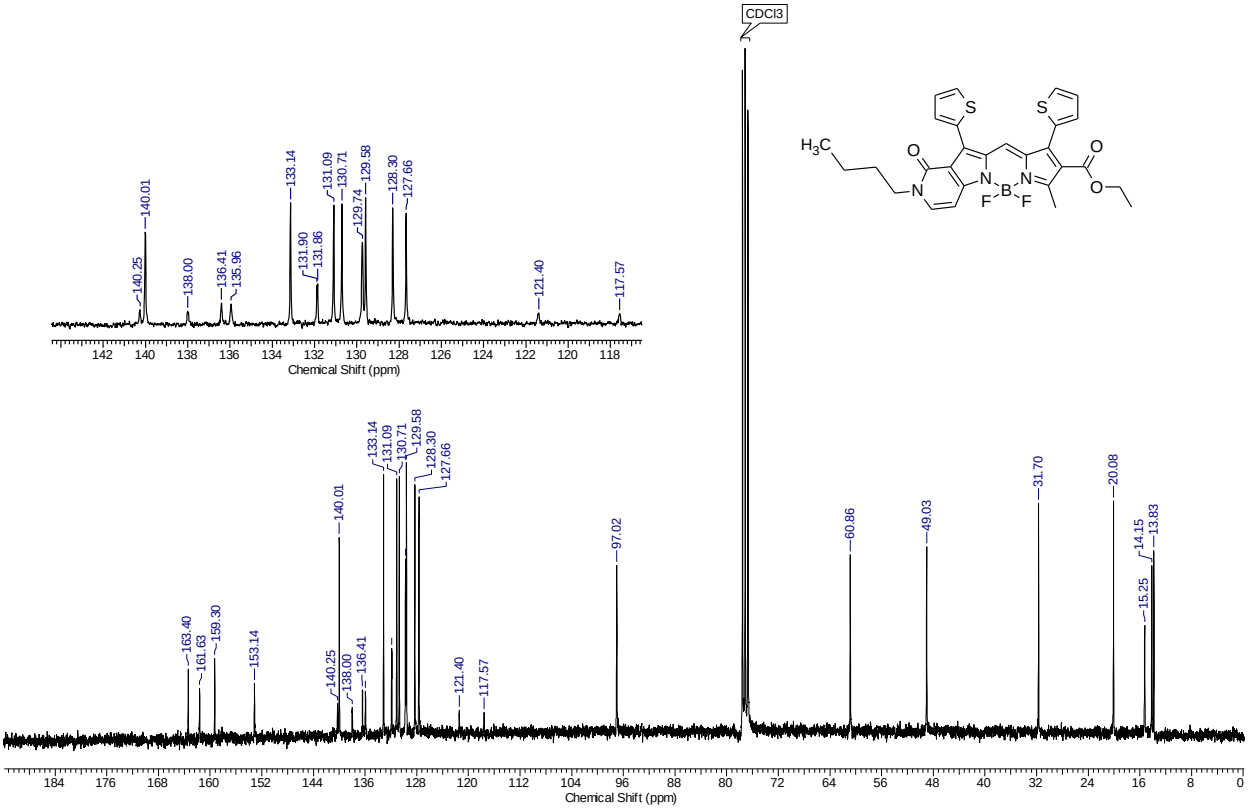
^{13}C NMR spectrum (76 MHz) of **17** in $CDCl_3$



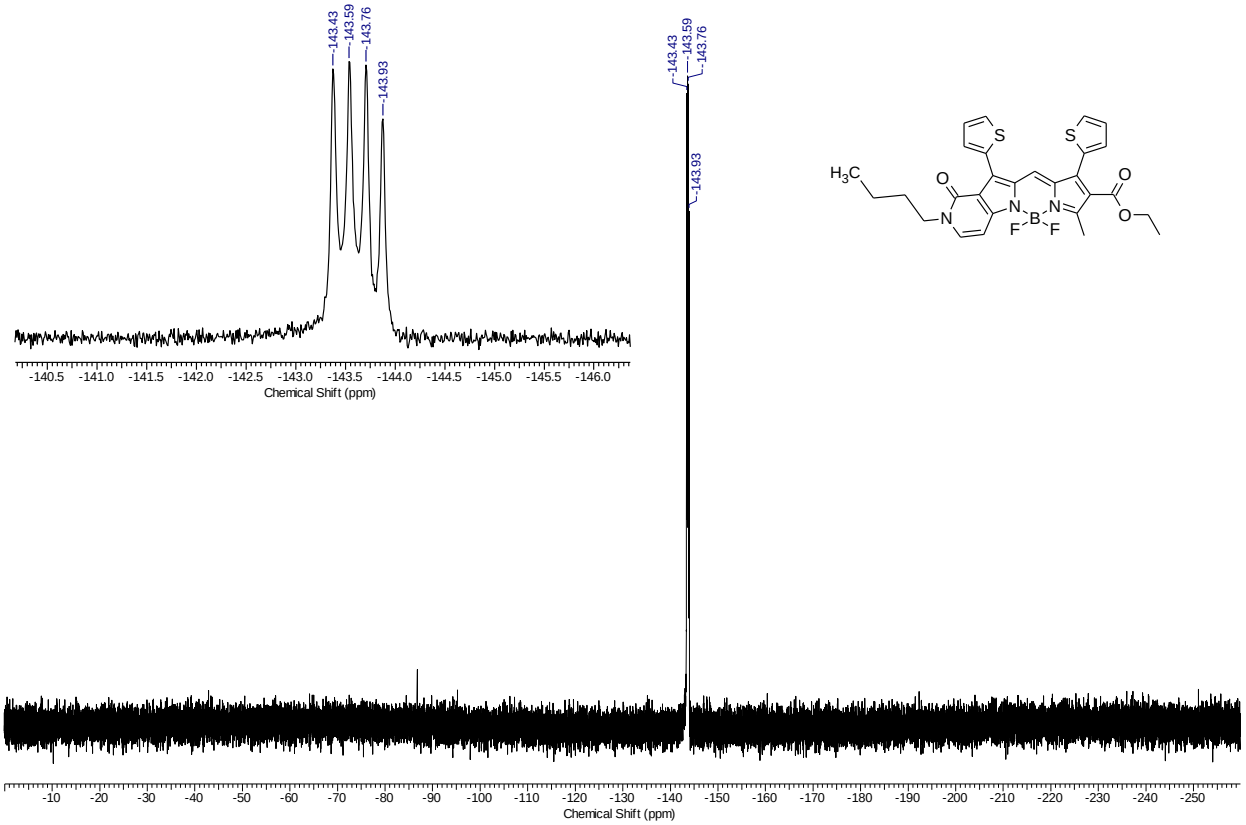
^{19}F NMR spectrum (188 MHz) of **17** in $CDCl_3$



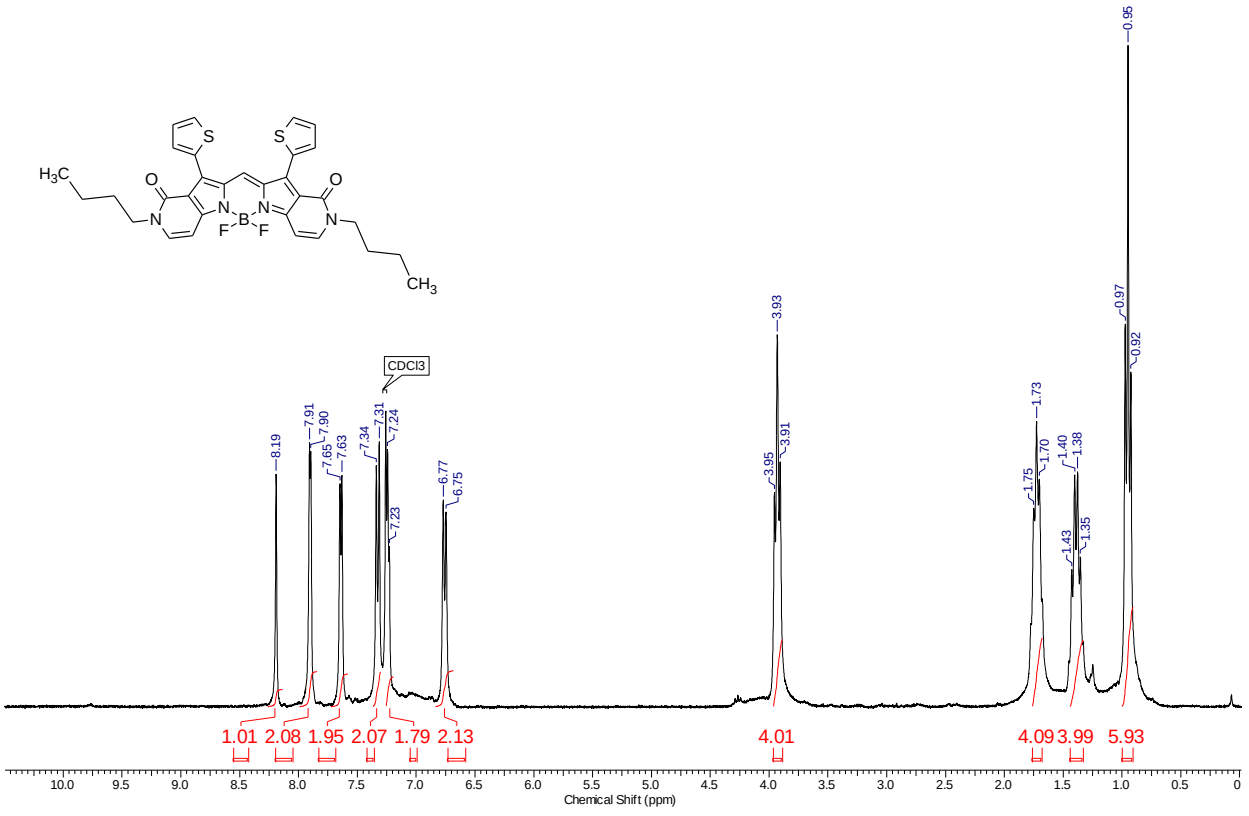
^{1}H NMR spectrum (300 MHz) of **18** in $CDCl_3$



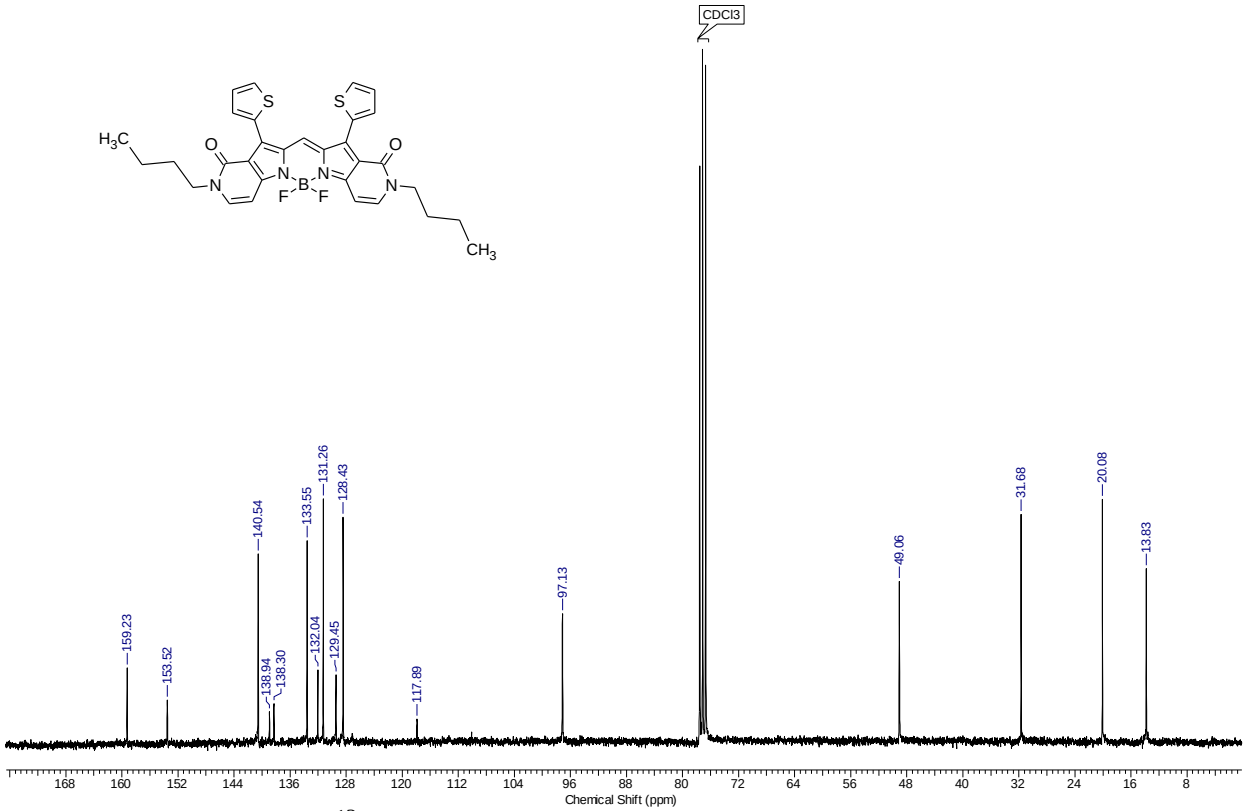
^{13}C NMR spectrum (76 MHz) of **18** in $CDCl_3$



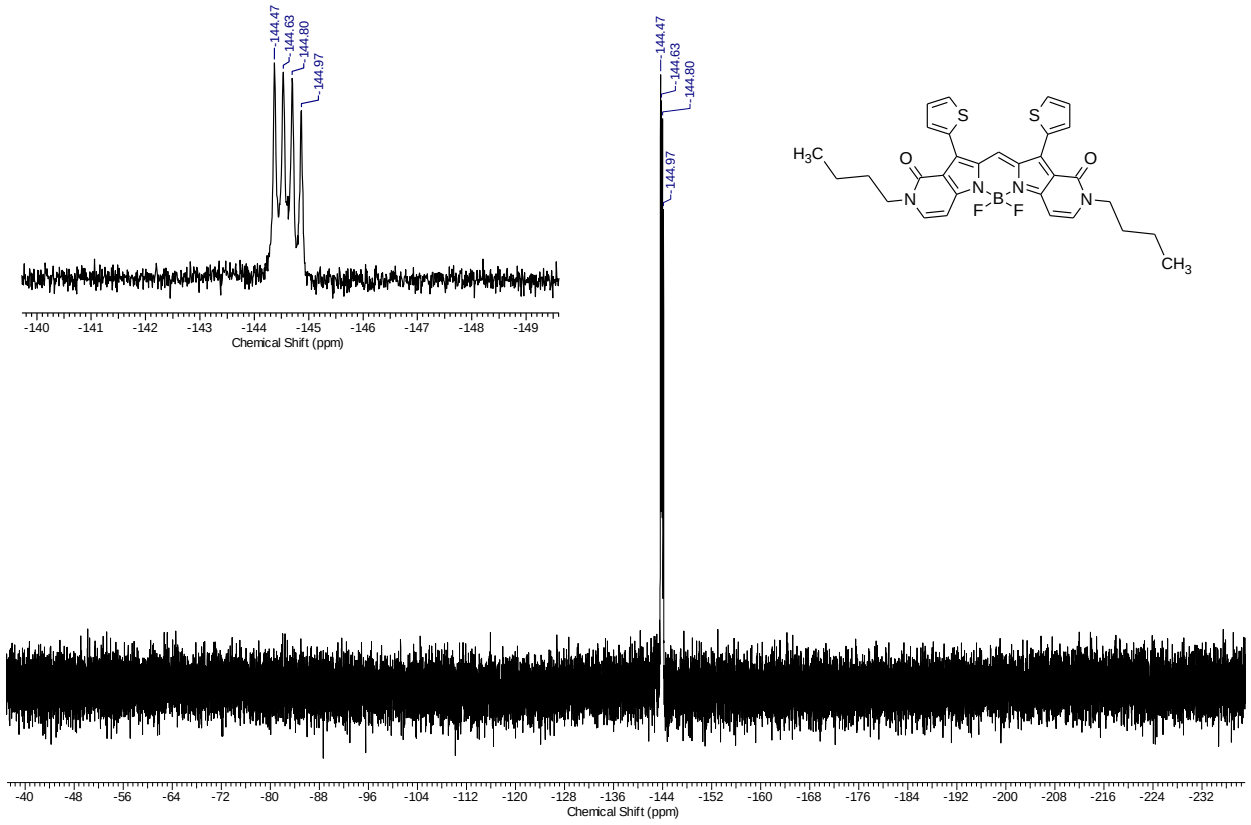
^{19}F NMR spectrum (188 MHz) of **18** in $CDCl_3$



^{1}H NMR spectrum (300 MHz) of **19** in $CDCl_3$



^{13}C NMR spectrum (76 MHz) of **19** in $CDCl_3$



^{19}F NMR spectrum (188 MHz) of **19** in $CDCl_3$

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