ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Electronically Tunable Anion–π Interactions in Pyrylium Complexes: Experimental and Theoretical Studies

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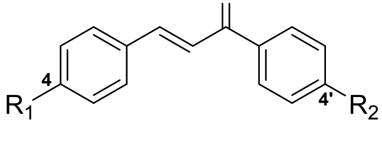
1. General Methods

All chemicals were purchased and used without further purification. Evaporations were conducted under reduced pressure. TLC was performed on aluminium sheets coated with Kieselgel 60 F_{254}; detection of compounds was accomplished with UV light (254 and 360 nm) and by charring with 10% H_2SO_4 or an anisaldehyde reagent. Silica gel 60 (230 mesh) was used for preparative column chromatography. Infrared (IR) spectra were recorded on a Jasco FT/IR-4100 spectrophotometer. UV-vis measurements were recorded on a Jasco V-630 spectrophotometer. Fluorescence measurements were carried out at 298.2 K in a spectrofluorimeter (Hitachi f-2500), interfaced to a PC for the reading and handling of the spectra. Acetone was used as solvent. Intensity measurements were performed at pyrylium complexes concentrations low enough to avoid inner filter effects (and other artifacts). In all cases, the sample absorbance measured at the excitation wavelength did not exceed 0.1. The selected excitation wavelength corresponded to the maximum of the UV-visible spectra for each complex and total luminescence intensity was recorded from 400-700 nm. It was checked that the results were independent of the excitation wavelength, provided that this one was in the range from 350 to 550 nm. ^{1}H (and ^{13}C) NMR spectra were recorded at 300 (75.5 for ^{13}C) and 500 (125.7 and 470 for ^{13}C and ^{19}F, respectively) MHz. Chemical shifts (δ) are expressed in ppm, referenced from TMS or by using the solvent peak as internal reference. Coupling constants (*J*) are expressed in Hz. Standard pulse sequences were used for 2D spectra. COSY, NOESY (mixing times: 400 and 500 ms), ^{1}H ^{13}C HSQC, and ^{1}H ^{13}C HMBC (optimized for a coupling constant of 8 Hz) experiments were used to assist NMR assignments. Mass spectra were recorded by using either CI, or EI techniques at 70 eV for EI and at 150 eV for CI. HRMS measurements were made with resolutions of 10000, by using a magnet sector analyzer.

2. Synthesis and spectral data of Chalcones



General Procedure

An equimolar mixture of *p*-substituted benzaldehyde and *p*-substituted acetophenone was dissolved in absolute EtOH. A solution of aqueous 2M NaOH (4 mol-eq) was added dropwise to the stirred mixture, and water was then added. The system was stirred at room temperature for a time between few minutes and hours, until precipitation of a solid occurred. The solid product was collected by filtration and washed with cold EtOH. The product was crystallized from EtOH to obtain a pure chalcone.

4-Phenylchalcone (2)

Application of the general procedure, starting from biphenyl-4-carboxaldehyde (200 mg, 1.1 mmol) and acetophenone (129 µL, 1.1 mmol) in EtOH (10 mL), after stirring the mixture for 30 min, and crystallization of the formed precipitate from EtOH, led to pure compound **2** (127.4 mg, 41 %) as a white solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (m, 2H), 7.86 (d, 1H, *J* = 15.7 Hz), 7.75-7.39 (m, 13H).

4'-Methyl-4-phenylchalcone (3)

Biphenyl-4-carboxaldehyde (200 mg, 1.1 mmol) and 4-methylacetophenone (155 µL, 1.1 mmol) in EtOH (10 mL) reacted following the general procedure, under stirring for 40 min, to afford compound **3** (249.3 mg, 76 %), pure enough to be used for further transformation; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, 2H, *J* = 8.2 Hz), 7.85 (d, 1H, *J* = 15.7 Hz), 7.74-7.62 (m, 7H), 7.57 (d, 1H, *J* = 15.7 Hz), 7.47 (t, 2H, *J* = 7.0 Hz), 7.38 (m, 1H), 7.32 (d, 2H, *J* = 8.1 Hz), 2.45 (s, 3H).

4-Fluorochalcone (4)

Application of the general procedure to 4-fluorobenzaldehyde (177 µL, 1.61 mmol) and acetophenone (188 µL, 1.61 mmol) in EtOH (5 mL), after stirring for 18 min, led to compound **4** (236.2 mg, 65 %), pure enough to be used for further transformation; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (dd, 2H, *J* = 1.5, *J* = 8.4 Hz), 7.78 (d, 1H, *J* = 15.7 Hz), 7.64 (dd, 2H, *J* = 5.4, *J* = 8.7 Hz), 7.59 (m, 1H), 7.52 (d, 2H, *J* = 7.6 Hz), 7.46 (d, 1H, *J* = 15.5 Hz), 7.12 (t, 2H, *J* = 8.6 Hz).

4,4'-Difluorochalcone (5)

Starting from 4-fluorobenzaldehyde (177 µL, 1.61 mmol) and 4-fluoroacetophenone (196 µL, 1.61 mmol) in EtOH (5 mL), application of the general procedure (stirring time: 2 min) afforded crystalline compound **5** (320.1 mg, 81 %), pure enough to be used for further transformation; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06 (dd, 2H, *J* = 5.4, *J* = 8.9 Hz), 7.78 (d, 1H, *J* = 15.7 Hz), 7.64 (dd, 2H, *J* = 5.4, *J* = 8.6 Hz), 7.43 (d, 1H, *J* = 15.7 Hz), 7.18 (t, 2H, *J* = 8.7 Hz), 7.12 (t, 2H, *J* = 8.6 Hz).

4'-Fluoro-4-nitrochalcone (6)

Application of the general procedure to 4-nitrobenzaldehyde (200 mg, 1.32 mmol) and 4-fluoroacetophenone (161 µL, 1.32 mmol) in EtOH (10 mL) (stirring time: 2 min) afforded crystalline compound **6** (200.7 mg, 56 %), pure enough to be used for further transformation; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, 2H, *J* = 8.9 Hz), 8.08 (dd, 2H, *J* = 5.4, *J* = 8.9 Hz), 7.83 (d, 1H, *J* = 15.4 Hz), 7.79 (d, 2H, *J* = 8.7 Hz), 7.61 (d, 1H, *J* = 15.7 Hz), 7.21 (t, 2H, *J* = 8.6 Hz).

4'-Methyl-4-nitrochalcone (7)

Starting compounds: 4-nitrobenzaldehyde (200 mg, 1.32 mmol) and 4-methylacetophenone (186 µL, 1.32 mmol) in EtOH (10 mL); stirring time: 2 min; crystallization from EtOH. Data of the obtained product **8** (255.5 g, 72 %), white solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, 2H, *J* = 8.8 Hz), 7.95 (d, 2H, *J* = 8.2 Hz), 7.81 (d, 1H, *J* = 15.6 Hz), 7.78 (d, 2H, *J* = 8.7 Hz), 7.64 (d, 1H, *J* = 15.8 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 2.45 (s, 3H).

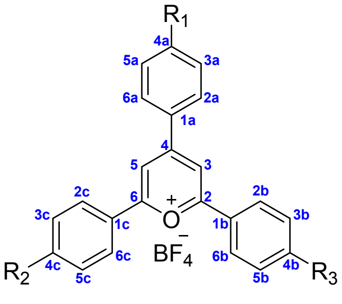
4-Methoxy-4'-methylchalcone (8)

Starting compounds: *p*-anisaldehyde (178 µL, 1.47 mmol) and 4-methylacetophenone (207 µL, 1.47 mmol) in EtOH (10 mL); stirring time: 2 h. Data of the obtained product **8** (238.6 mg, 64 %), pure enough to be used for further transformation; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, 2H, *J* = 8.2 Hz), 7.76 (d, 1H, *J* = 15.6 Hz), 7.60 (d, 2H, *J* = 8.8 Hz), 7.42 (d, 1H, *J* = 15.6 Hz), 7.30 (d, 2H, *J* = 8.0 Hz), 6.94 (d, 2H, *J* = 8.8 Hz), 3.86 (s, 3H), 2.44 (s, 3H).

4'-Fluoro-4-methoxychalcone (9)

Starting compounds: *p*-anisaldehyde (178 µL, 1.47 mmol) and 4-fluoroacetophenone (179 µL, 1.47 mmol) in EtOH (4 mL); stirring time: 30 min. Data of the obtained product **9** (196.8 mg, 52 %), pure enough to be used for further transformation; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (dd, 2H, *J* = 5.4, *J* = 9.0 Hz), 7.79 (d, 1H, *J* = 15.6 Hz), 7.60 (d, 2H, *J* = 8.6 Hz), 7.38 (d, 1H, *J* = 15.6 Hz), 7.17 (t, 2H, *J* = 8.7 Hz), 6.94 (d, 2H, *J* = 8.8 Hz), 3.86 (s, 3H).

3. Synthesis and spectral data of Pyrylium Salts.



2,4,6-Triphenylpyrylium Tetrafluoroborate (10)[34]

Route I. Starting compounds: benzaldehyde (1.02 mL, 10.1 mmol) and acetophenone (2.4 mL, 20.8 mmol). Refluxing time: 24 h. Crystallization from 1,2-dichloroethane led to compound **10** (1.01 g, 32 %) as a yellow solid.

Route II. Starting compounds: chalcone **1** (500 mg, 2.40 mmol) and acetophenone (840 µL, 7.20 mmol) in CH_2Cl_2 (2 mL). Refluxing time: 20 h. Crystallization from 1,2-dichloroethane afforded compound **10** (254 mg, 34 %) as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.17 (s, 2H, H-3 and H-5), 8.60 (d, 6H, J = 7.5 Hz, H-2a, 6a, 2b, 6b, 2c and 6c), 7.88 (t, 3H, J = 7.5 Hz, H-4a, 4b and 4c), 7.81 (t, 6H, J = 8.0 Hz, H-3a, 5a, 3b, 5b, 3c and 5c); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −148.3269 (br s, $^{10}BF_4^-$), −148.3812 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$).

2,6-Di-(4-methylphenyl)-4-phenylpyrylium tetrafluoroborate (11)[35]

Starting compounds: benzaldehyde (476 µL, 4.71 mmol) and 4-methylacetophenone (943 µL, 7.07 mmol). Refluxing time: 9 h. Crystallization from acetone led to pure compound **11** (189.1 mg, 12 %) as a yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.05 (s, 2H, H-3 and H-5), 8.56 (d, 2H, J = 8.2 Hz, H-2a and 6a), 8.48 (d, 4H, J = 8.3 Hz, H-2b, 6b, 2c and 6c), 7.86 (t, 1H, J = 7.4 Hz, H-4a), 7.77 (t, 2H, J = 8.0 Hz, H-3a and 5a), 7.61 (d, 4H, J = 8.1 Hz, H-3b, 5b, 3c and 5c), 2.51 (s, 6H, CH_3); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −148.3251 (br s, $^{10}BF_4^-$), −148.3793 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$).

4-Biphenyl-2,6-diphenylpyrylium tetrafluoroborate (12)[36]

Starting compounds: chalcone **2** (127 mg, 0.45 mmol) and acetophenone (156.3 µL, 1.34 mmol) in CH_2Cl_2 (4 mL). Refluxing time: 21 h. Treatment with ice-water (5 mL) and EtOH (4 mL) afforded pure compound **12** (95 mg, 70 %) as an orange solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.21 (s, 2H, H-3 and H-5), 8.75 (d, 2H, J = 8.6 Hz, H-2a and 6a), 8.61 (d, 4H, J = 8.2, H-2b, 6b, 2c and 6c), 8.12 (d, 2H, J = 8.6 Hz, H-3a and 5a), 7.94 (d, 2H, J = 8.1 Hz, H-2d and 6d), 7.88 (t, 2H, J = 7.4 Hz, H-3d and 5d), 7.81 (t, 4H, J = 7.9 Hz, H-3b, 5b, 3c and 5c), 7.58 (t, 2H, J = 7.2 Hz, H-4b and 4c), 7.52 (t, 1H, J = 7.3 Hz, H-4d); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −148.3182 (br s, $^{10}BF_4^-$), −148.3725 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$).

4-Biphenyl-2,6-di-(4-methylphenyl)pyrylium tetrafluoroborate (13)

Starting compounds: chalcone **3** (100 mg, 0.34 mmol) and 4-methylacetophenone (134 µL, 1.0 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 37 h. Crystallization from 1,2-dichloroethane afforded pure compound **13** (45.2 mg, 32 %) as an orange solid; m.p. (decomp.) 291-292 ºC. IR 1597, 1481, 1458, 1002, 840, 817, 765, 727, 687 cm^{-1}. UV-visible: λ_{max} (acetone) 418 nm; (DMSO) 422, 344, and 326 nm. ^{1}H NMR (500 MHz, DMSO-d_6): δ =9.09 (s, 2H, H-3 and H-5), 8.70 (d, 2H, J = 8.6 Hz, H-2a and 6a), 8.49 (d, 4H, J = 8.3 Hz, H-2b, 6b, 2c and 6c), 8.09 (d, 2H, J = 8.5 Hz, H-3a and 5a), 7.92 (d, 2H, J = 8.6 Hz, H-2d and 6d), 7.61 (d, 4H, J = 8.3 Hz, H-3b, 5b, 3c and 5c), 7.58 (t, 2H, J = 7.8 Hz, H-3d and 5d), 7.51 (t, 1H, J = 7.3 Hz, H-4d), 2.52 (s, 6H, CH_3); ^{13}C NMR

(125 MHz, DMSO-d_6): δ =169.1 (C-2 and C-6), 166.6 (C-4), 146.3, 146.1, 138.1, 131.4, 130.7 (*C*-2a and 6a), 130.5 (*C*-3b, 5b, 3c and 5c), 129.2 (*C*-3d and 5d), 129.1 (*C*-4d), 128.7 (*C*-2b, 6b, 2c and 6c), 127.8 (*C*-3a and 5a), 127.3 (*C*-2d and 6d), 126.6, 113.9 (*C*-3 and *C*-5), 21.5 (*C*H$_3$); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −148.3178 (^{10}BF_4^-), −148.3720 ($J_{\mathrm{F,B11}}$ = 1.1 Hz,^{11}BF_4^-). CIHRMS: *m/z* 414.1983, calcd for $C_{31}H_{26}O^+$ + H: 414.1984.

2-(4-Fluorophenyl)-4,6-diphenylpyrylium tetrafluoroborate (14)

Starting compounds: chalcone **1** (200 mg, 0.96 mmol) and 4-fluoroacetophenone (350 µL, 2.88 mmol) in CH_2Cl_2 (2 mL). Refluxing time: 23 h. Crystallization from 1,2 dichloroethane led to pure compound **14** (91.9 mg, 29 %) as a yellow solid; IR: 1621, 1589, 1491, 1466, 1241, 1164, 1031, 840, 770 and 676 cm^{-1}; UV-visible: $\lambda_{\max}$ (acetone) 409 and 356 nm; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.16 (s, 2H, H-3 and H-5), 8.70 (dd, 2H, *J* = 5.2, *J* = 9.0 Hz, H-2b and 6b), 8.60 (4H, *J* = 7.7 Hz, H-2a, 6a, 2c and 6c), 7.88 (t, 2H, *J* = 7.4 Hz, H-4a and 4c), 7.80 (dt, 4H, 2H, *J* = 3.0, *J* = 8.0 Hz, H-3a, 5a, 3c and 5c), 7.67 (t, 2H, *J* = 8.8 Hz, H-3b and 5b); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.0 (*C*-6), 169.2 (*C*-2), 166.1 (d, *J* = 255.9 Hz, *C*-4b), 165.1 (*C*-4), 135.2 (*C*-4c), 135.0 (*C*-4a), 132.5 (*C*-1a or *C*-1c), 132.0 (d, *J* = 9.9 Hz, *C*-2b and 6b), 130.0 (*C*-2a and 6a), 129.9 (*C*-3a, 5a, 3c and 5c), 129.1 (*C*-1c or *C*-1a), 128.9 (*C*-2c and 6c), 125.9 (d, *J* = 2.4 Hz, *C*-1b), 117.3 (d, *J* = 22.3 Hz, *C*-3b and 5b), 115.2 (*C*-3 or *C*-5), 115.1 (*C*-5 or *C*-3); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.28 (m, C-*F*), −148.3250 (br s, ^{10}BF$_4^-$), −148.3804 ($J_{\mathrm{F,B11}}$ = 1.1 Hz, ^{11}BF_4^-). CIHRMS: *m/z* 328.1255, calcd for $C_{23}H_{17}OF^+$ + H: 328.1263.

4-(4-Fluorophenyl)-2,6-diphenylpyrylium tetrafluoroborate (15)[37]

Starting compounds: 4-fluorobenzaldehyde (432 µL, 4.03 mmol) and acetophenone (940 µL, 8.06 mmol). Refluxing time: 24 h. Crystallization from acetone afforded pure compound **15** (705.5 mg, 53 %) as a yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.16 (s, 2H, H-3 and H-5), 8.73 (dd, 2H, *J* = 5.4, *J* = 9.0 Hz, H-2a and 6a), 8.59 (d, 4H, *J* = 7.5, H-2b, 6b, 2c and 6c), 7.88 (t, 2H, *J* = 7.5 Hz, H-4b and 4c), 7.80 (t, 4H, *J* = 8.0 Hz, H-3b, 5b, 3c and 5c), 7.68 (t, 2H, *J* = 8.8 Hz, H-3a and 5a); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.41 (m, C-*F*), −148.3230 (br s, ^{10}BF_4^-), −148.3771 ($J_{\mathrm{F,B11}}$ = 1.1 Hz, ^{11}BF_4^-).

4,6-Di-(4-fluorophenyl)-2-phenylpyrylium tetrafluoroborate (16)

Starting compounds: chalcone **4** (100 mg, 0.44 mmol) and 4-fluoroacetophenone (161 µL, 1.33 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 22 h. Crystallization from 1,2 dichloroethane led to pure compound **16** (32.6 mg, 21 %) as a yellow solid; IR: 1629, 1594, 1493, 1231, 1164, 1055, 840, 777 and 684 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.14 (br d, *J* = 1.7, 1H, H-3 or H-5), 9.12 (s,1H, H-5 or H-3), 8.74-8.66 (m, 4H, H-2a, 6a, 2c and 6c), 8.58 (d, 2H, *J* = 7.6, H-2b and 6b), 7.88(t, 1H, *J* = 7.1, H-4b), 7.80 (t, 2H, *J* = 7.9, H-3b and 5b), 7.69-7.64 (m, 4H, H-3a, 5a, 3c and 5c); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.0 (*C*-6), 169.1 (*C*-2), 165.1 (*C*-4) 135.0 (*C*-4c), 166.5 (d, *J* = 255.6

Hz, *C*-4a or *C*-4b), 166.1 (d, *J* = 255.6 Hz, *C*-4b or *C*-4a), 133.3 (d, *J* = 9.6 Hz, *C*-2a and 6a), 132.0 (d, *J* = 9.8 Hz, *C*-2b and 6b), 129.8 (*C*-3c and 5c), 129.1 (*C*-1c), 129.0 (d, *J* = 2.2 Hz, *C*-1a), 128.8 (*C*-2c and 6c), 125.8 (d, *J* = 2.3 Hz, *C*-1b), 117.2 (d, *J* = 22.5 Hz, *C*-3b and 5b), 117.1 (d, *J* = 22.0 Hz, *C*-3b and 5b), 114.9 (*C*-5), 114.8 (*C*-3); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.25 (m, C-*F*), −102.33 (m, C-*F*), −148.3192 (br s, ^{10}BF_4^-), −148.3736 ($J_{F,B11}$ = 1.1 Hz, ^{11}BF_4^-). CIHRMS: *m/z* 346.1163, calcd for $C_{23}H_{16}OF_2^+$ + H: 346.1169.

2,6-Di-(4-fluorophenyl)-4-phenylpyrylium tetrafluoroborate (17) [35]

Starting compounds: benzaldehyde (303 µL, 3.0 mmol) and 4-fluoroacetophenone (728 µL, 6.0 mmol). Refluxing time: 16 h. Treatment with Et_2O (4 mL) and crystallization from 1,2-dichloroethane afforded pure compound **17** (393 mg, 38 %) as a yellow solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.14 (s, 2H, H-3 and H-5), 8.69 (dd, 4H, *J* = 5.2, *J* = 9.0 Hz, H-2b, 6b, 2c and 6c), 8.59 (d, 2H, *J* = 7.4, H-2a and 6a), 7.88 (t, 1H, *J* = 7.5, H-4a), 7.79 (t, 2H, *J* = 8.1, H-3a and 5a), 7.66 (t, 4H, *J* = 8.8, H-3b, 5b, 3c and 5c); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.27 (m, C-*F*), −148.3192 (br s, ^{10}BF_4^-), −148.3730 ($J_{F,B11}$ = 1.1 Hz, ^{11}BF_4^-).

2,4,6-Tri-(4-fluorophenyl)pyrylium tetrafluoroborate (18)[38]

Starting compounds: chalcone **5** (100 mg, 0.41 mmol) and 4-fluoroacetophenone (149 µL, 1.23 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 24 h. The mixture was diluted with CH_2Cl_2 (10 mL), thus obtaining a precipitate of compound **18** (28.3 mg, 19 %) as a yellow solid, pure enough for characterization; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.12 (s, 2H, H-3 and H-5), 8.71 (dd, 2H, *J* = 5.4, *J* = 9.0 Hz, H-2a and 6a), 8.68 (dd, 4H, *J* = 5.3, *J* = 9.0 Hz, H-2b, 6b, 2c and 6c), 7.67 (m, 6H, H-3a, 5a, 3b, 5b, 3c and 5c); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.24 (m, C-*F*), −148.3112 (br s, ^{10}BF_4^-), −148.3656 ($J_{F,B11}$ = 1.1 Hz, ^{11}BF_4^-).

4-(4-Nitrophenyl)-2,6-diphenylpyrylium tetrafluoroborate (19)[39]

Starting compounds: 4-nitrobenzaldehyde (500 mg, 3.31 mmol) and acetophenone (579 µL, 4.97 mmol) in toluene (2 mL). Refluxing time: 19 h. Crystallization from 1,2-dichloroethane afforded pure compound **19** (84 mg, 9 %) as a yellowish solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ =9.28 (s, 2H, H-3 and H-5), 8.78 (d, 2H, *J* = 8.7 Hz, H-2a and 6a), 8.63 (d, 4H, *J* = 7.4 Hz, H-2b, 6b, 2c and 6c), 8.57 (d, 2H, *J* = 8.9 Hz, H-3a and 5a), 7.91 (t, 2H, *J* = 7.4 Hz, H-4b and 4c), 7.83 (t, 4H, *J* = 8.0 Hz, H-3b, 5b, 3c and 5c); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −148.3193 (br s, ^{10}BF_4^-), −148.3731 ($J_{F,B11}$ = 1.1 Hz, ^{11}BF_4^-).

6-(4-Fluorophenyl)-4-(4-nitrophenyl)-2-(phenyl)pyrylium tetrafluoroborate (20)

Starting compounds: chalcone **6** (69 mg, 0.27 mmol) and 4-fluoroacetophenone (131.1 µL, 0.54 mmol) in CH_2Cl_2 (2 mL). Refluxing time: 22 h. Crystallization from 1,2-dichloroethane afforded pure compound **20** (2 mg, 2 %) as an orange solid; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.27 (s, 1H, H-3 or H-5), 9.13 (s, 1H, H-5 or H-3), 8.78 (d, 2H, J = 8.9 Hz, H-2a and 6a), 8.73 (dd, 2H, J = 5.6 and J = 9.1 Hz, H-2c and 6c), 8.61 (d, 2H, J = 7.5 Hz, H-3a and 5a), 8.57 (d, 2H, J = 8.7 Hz, H-3b and 5b), 7.82 (t, 2H, J = 7.7 Hz, H-3c and 5c), 7.68 (d, 2H, J = 8.4 Hz, H-2b and 6b), 7.56 (t, 1H, J = 7.9 Hz, H-4b).

2-(4-Fluorophenyl)-6-(4-methylphenyl)-4-(4-nitrophenyl)pyrylium tetrafluoroborate (21)

Starting compounds: chalcone **7** (100 mg, 0.37 mmol) and 4-fluoroacetophenone (46 µL, 0.37 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 22 h. Crystallization from 1,2-dichloroethane led to pure compound **21** (79.7 mg, 56 %) as an orange solid; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.21 (s, 1H, H-3 or H-5), 9.19 (s, 1H, H-5 or H-3), 8.76 (d, 2H, J = 8.9 Hz, H-2a and 6a), 8.70 (dd, 2H, J = 5.2 and J = 9.0 Hz, H-2b and 6b), 8.56 (d, 2H, J = 9.0 Hz, H-3a and 5a), 8.53 (d, 2H, J = 8.6 Hz, H-3c and 5c), 7.71 (m, 2H, H-2c and 6c), 7.65 (t, 2H, J = 8.7 Hz, H-3b and 5b), 2.53 (s, 3H, CH_3).

2,6-Di-(4-methylphenyl)-4-(4-nitrophenyl)pyrylium tetrafluoroborate (22)

Route I. Starting compounds: 4-nitrobenzaldehyde (500 mg, 3.31 mmol) and 4-methylacetophenone (884 µL, 6.62 mmol) in toluene (2 mL). Refluxing time: 22 h. Crystallization from acetone afforded pure compound **22** (130.3 mg, 10 %) as an intense orange solid.

Route II. Starting compounds: chalcone **7** (270.4 mg, 1.01 mmol) and 4-methylacetophenone (404.6 µL, 3.03 mmol) in CH_2Cl_2 (4 mL). Refluxing time: 25 h. Crystallization from 1,2 dichloroethane led to pure compound **22** (52.9 mg, 14 %) as an intense orange solid; m.p. (decomp.) 314-317 ºC. IR: 3108, 1615, 1524, 1492, 1455, 1348, 1273, 1190, 1051, 825 cm^{-1}. UV-visible (CH_2Cl_2): 460, 366 and 312 nm. ^{1}H NMR (500 MHz, acetone-d_6): δ = 9.21 (s, 2H, H-3 and H-5), 8.74 (d, 2H, J = 8.7 Hz, H-2a and 6a), 8.57 (d, 4H, J = 8.2 Hz, H-2b, 6b, 2c and 6c), 8.56 (d, 2H, J = 8.7 Hz, H-3a and 5a), 7.67 (d, 4H, J = 8.2 Hz, H-3b, 5b, 3c and 5c), 2.56 (s, 6H, CH_3); ^{13}C NMR (125 MHz, acetone-d_6): δ= 172.7 (*C*-2 and *C*-6), 164.7 (*C*-4), 152.0, 140.1, 131.8 (*C*-2a and *C*-6a), 131.8 (*C*-3b, 5b, 3c and *C*-5c), 130.0 (*C*-2b, 6b, 2c and *C*-6c), 127.5 (*C*-3a and *C*-5a), 125.4, 117.0 (*C*-3 and *C*-5), 22.0 (CH_3); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −148.3072 ($^{10}BF_4^-$), −148.3613 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$). CIHRMS: *m/z* 383.1526, calcd for $C_{25}H_{21}NO_3^+$ + H: 383.1521.

2,6-Di-(4-fluorophenyl)-4-(4-nitrophenyl)pyrylium tetrafluoroborate (23)

Route I. Starting compounds: 4-nitrobenzaldehyde (500 mg, 3.31 mmol) and 4-fluoroacetophenone (804 µL, 6.62 mmol) in toluene (3 mL). Refluxing time: 20 h. Crystallization from acetone afforded pure compound **23** (67.9 mg, 5 %) as a yellow solid.

Route II. Starting compounds: chalcone **6** (100 mg, 0.37 mmol) and 4-fluoroacetophenone (269.5 µL, 1.11 mmol) in CH_2Cl_2 (3 mL). Refluxing time: 24 h. Crystallization from 1,2-dichloroethane led to pure compound **23** (4.2 mg, 3 %) as a yellow solid; m.p. 289-292 ºC. IR: 3119, 3080, 1623, 1599, 1494, 1457, 1344, 1239, 1216, 1166, 1057, 1001, 847 and 757 cm^{-1}. UV-visible (CH_2Cl_2): 437, 356 and 297 nm. ^{1}H NMR (500 MHz, acetone-d_6): δ = 9.30 (s, 2H, H-3 and H-5), 8.79 (dd, 4H, *J* = 5.2, *J* = 9.1 Hz, H-2b, 6b, 2c and 6c), 8.77 (d, 2H, *J* = 9.1 Hz, H-2a and 6a), 8.55 (d, 2H, *J* = 9.1 Hz, H-3a and 5a), 7.61 (t, 2H, *J* = 8.8 Hz, H-3b, 5b, 3c and 5c); ^{13}C NMR (125 MHz, acetone-d_6): δ= 172.0 (*C*-2 and *C*-6), 169.1, 167.1, 165.4 (*C*-4), 152.1, 139.8, 133.3 (d, *J* = 10.1 Hz*,* *C*-2b, 6b, 2c and 6c), 132.1 (*C*-2a and 6a), 126.7 (d, *J* = 3.0 Hz, *C*-1b and 1c), 125.5 (*C*-3a and 5a), 118.5, 118.1 (d, *J* = 75.6 Hz*,* *C*-3b, 5b, 3c and 6c), 117.7 (*C*-3 and *C*-5). ^{19}F NMR (470 MHz, DMSO-d_6): δ = −101.49 (m, C-*F*), −148.3084 ($^{10}BF_4^-$), −148.3628 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$). CIHRMS: *m/z* 390.0947, calcd for $C_{23}H_{14}NO_3F_2^+$: 390.0942.

4-Biphenyl-2-(4-fluorophenyl)-6-(4-methylphenyl)pyrylium tetrafluoroborate (24)

Starting compounds: chalcone **3** (100 mg, 0.34 mmol) and 4-fluoroacetophenone (124 µL, 1.02 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 22 h. Crystallization from 1,2 dichloroethane afforded pure compound **24** (22.3 mg, 16 %) as a dull ruby-red solid; m.p. (decomp.) 291-293 ºC. IR: 2361, 2327, 1622, 1599, 1490, 1463, 1244, 1226, 1164, 1067, 1005, 840, 768 and 728 cm^{-1}. UV-visible (CH_2Cl_2): 435, 292 and 252 nm. ^{1}H NMR (500 MHz, acetone-d_6): δ = 9.19 (s, 1H, H-3 or H-5), 9.18 (s, 1H, H-5 or H-3), 8.75 (dd, 2H, *J* = 5.1, *J* = 9.0 Hz, H-2c and 6c), 8.68 (d, 2H, *J* = 8.6 Hz, H-2a and 6a), 8.56 (d, 2H, *J* = 8.4 Hz, H-2b and 6b), 8.10 (d, 2H, *J* = 8.7 Hz, H-3a and 5a), 7.86 (d, 2H, *J* = 7.0 Hz, H-2d and 6d), 7.65 (d, 2H, *J* = 8.0 Hz, H-3b and 5b), 7.62-7.55 (m, 4H, H-3b, 5b, 3d and 5d), 7.51 (m, 1H, H-4d), 2.56 (s, 3H, C*H*$_3$).^{13}C NMR (125 MHz, acetone-d_6): δ= 172.2 (*C*-2 or *C*-6), 170.4 (*C*-6 or *C*-2), 166.3 (*C*-4), 157.4, 148.6, 148.1, 139.6, 138.1, 136.1, 132.8 (d, *J* = 10.0 Hz, C-2c and 6c), 131.7 (*C*-2a and 6a), 131.5 (*C*-3d and 5d), 130.2 (*C*-3d and 5d), 130.1 (*C*-4d), 129.9 (*C*-2b and 6b), 129.2 (*C*-3a and 5a), 128.2 (*C*-2d and 6d), 127.6, 118.2 (d, *J* = 22.8 Hz, C-3c and 5c), 115.5 (*C*-3 or *C*-5), 115.4 (*C*-5 or *C*-3), 21.9 (*C*H$_3$). CIHRMS: *m/z* 418.1733, calcd for $C_{30}H_{23}OF^+$ + H: 418.1733.

4-Biphenyl-2,6-di-(4-fluorophenyl)pyrylium tetrafluoroborate (25)

Starting compounds: biphenyl-4-carboxaldehyde (500 mg, 2.74 mmol) and 4-fluoroacetophenone (667 µL, 5.49 mmol) in toluene (2 mL). Refluxing time: 40 min. After washing with CH_2Cl_2 (5 mL) the obtained precipitate it was pure enough to be characterized as compound **25** (196.7 mg, 74 %), an orange solid; m.p. (decomp.) 307-312 ºC. IR: 3051, 1621, 1599, 1491, 1462, 1160, 1065, 1021, 838 and 728 cm^{-1}. UV-visible (MeOH): 414 nm. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.19 (s, 2H, H-3 and H-5), 8.73 (d, 2H, *J* = 8.7 Hz, H-2a and 6a), 8.70 (dd, 4H, *J* = 5.3, *J* = 9.0 Hz, H-2b, 6b, 2c and 6c), 8.12 (d, 2H, *J* = 8.6 Hz, H-3a and 5a), 7.94 (d, 2H, *J* = 7.2 Hz, H-2d and 6d), 7.67 (t, 4H, *J* = 8.8, H-3b, 5b, 3c and 5c), 7.58 (t, 2H, *J* = 7.2 Hz, H-3d and 5d), 7.51 (t, 1H, *J* = 7.4 Hz, H-4d); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 168.8 (*C*-2 and *C*-6), 167.1 (*C*-4), 105.4 (d, *J* = 105.4 Hz, *C*-4b and 4c), 146.7, 138.0, 132.0 (d, *J* = 9.8 Hz, *C*-2b, 6b, 2c and 4c), 131.2, 130.9 (*C*-2a and 6a), 129.2 (*C*-3d, 4d and 5d), 127.8 (*C*-3a and

5a), 127.3 (*C*-2d and 6d), 125.9 (d, *J* = 2.4 Hz, *C*-1b and 1c), 117.2 (d, *J* = 22.4 Hz, *C*-3b, 5b, 3c and 5c), 114.5 (*C*-3 and *C*-5); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.38 (m, C-*F*), −148.3183 (br s, $^{10}BF_4^-$), −148.3729 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$), CIHRMS: *m/z* 422.1482, calcd for $C_{29}H_{20}OF_2^+$ + H: 422.1482.

4-(4-Methoxyphenyl)-2,6-di-(4-methylphenyl)pyrylium tetrafluoroborate (26)[40]

Starting compounds: chalcone **8** (100 mg, 0.40 mmol) and 4-methylacetophenone (144.3 μL, 1.19 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 22 h. Crystallization from 1,2-dichloroethane afforded pure compound **26** (11.4 mg, 8 %) as a yellow-brown solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.93 (s, 2H, H-3 and H-5), 8.66 (d, 2H, *J* = 8.9 Hz, H-2a and 6a), 8.43 (d, 4H, *J* = 8.2, H-2b, 6b, 2c and 6c), 7.58 (d, 4H, *J* = 8.1, H-3b, 5b, 3c and 5c), 7.30 (d, 2H, *J* = 9.0 Hz, H-3a and 5a), 3.99 (s, 3H, OC*H*$_3$), 2.50 (overlap C*H*$_3$); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −102.27 (m, C-*F*), −148.3157 (br s, $^{10}BF_4^-$), −148.3700 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$).

2,6-Di-(4-fluorophenyl)-4-(4-methoxyphenyl)pyrylium tetrafluoroborate (27)

Route I. Starting compounds: *p*-anisaldehyde (445.2 μL, 3.67 mmol) and 4-fluoroacetophenone (891 μL, 7.34 mmol). Refluxing time: 6 h. Crystallization from 1,2-dichloroethane afforded pure compound **27** (260 mg, 19 %) as an intense orange solid;

Route II. Starting compounds: chalcone **9** (100 mg, 0.39 mmol) and 4-fluoroacetophenone (142 μL, 1.17 mmol) in CH_2Cl_2 (1 mL). Refluxing time: 22 h. Crystallization from 1,2-dichloroethane led to pure compound **27** (30.5 mg, 21 %) as an intense orange solid; m.p. 280-283 ºC. IR: 3127, 1705, 1631, 1579, 1486, 1236, 1189, 1164, 1049, 1030 and 836 cm^{-1}. UV-visible (CH_2Cl_2): 435, 283 and 243 nm; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.02 (s, 2H, H-3 and H-5), 8.70 (d, 2H, *J* = 9.1 Hz, H-2a and 6a), 8.64 (dd, 4H, *J* = 5.3, *J* = 8.9 Hz, H-2b, 6b, 2c and 6c), 7.64 (t, 2H, *J* = 8.9 Hz, H-3b, 5b, 3c and 5c), 7.33 (d, 2H, *J* = 9. 1 Hz, H-3a and 5a), 4.00 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 167.9 (*C*-2 and *C*-6), 166.0 (*C*-4), 165.9 (d, *J* = 255.3 Hz, *C*-4b and 4c), 163.6 (*C*-4a), 133.1 (*C*-2a and *C*-6a), 131.7 (d, *J* = 9.7 Hz, *C*-2b, 6b, 2c and 6c), 126.0 (d, *J* = 2.3 Hz, *C*-1b and 1c), 124.3, 117.1 (d, *J* = 22.4 Hz, *C*-3b, 5b, 3c and 5c), 115.6 (*C*-3a and *C*-5a), 113.0 (*C*-3 and *C*-5), 56.3 (O*C*H$_3$); ^{19}F NMR (470 MHz, DMSO-d_6): δ = −103.00 (m, C-*F*), −148.32 ($^{10}BF_4^-$), −148.37 ($J_{F,B11}$ = 1.1 Hz, $^{11}BF_4^-$). CIHRMS: *m/z* 376.1267, calcd for $C_{24}H_{18}O_2F_2^+$ + H: 376.1275.

4-[4-(Benzoyloxy[*O*-benzoyl])phenyl]-2,6-(4-methylphenyl)pyrylium tetrafluoroborate (28)

Starting compounds: 4-(benzoyloxy)benzaldehyde (206.1 mg, 0.91 mmol) and 4-methylacetophenone (244 μL, 1.82 mmol) in toluene (2 mL). Refluxing time: 5 h. Treatment with Et_2O (4 mL) at 0 ºC and crystallization from acetone led to pure compound **28** (18.1 mg, 4 %) as an orange solid; IR: 1737, 1620, 1594, 1490, 1217, 1169, 1050, 820 and 707 cm^{-1}. UV-visible (MeOH): 429, 368, 287, 231 and 203 nm. ^{1}H NMR (500 MHz, acetone-d_6): δ = 9.13 (s, 2H, H-3 and H-5), 8.67 (d, 2H, *J* = 8.9 Hz, H-

2a and 6a), 8.55 (d, 4H, J = 8.4 Hz, H-2b, 6b, 2c and 6c), 8.24 (dd, 2H, J = 1.3, J = 8.3 Hz, H-2d and 6d), 7.79 (tt, 1H, J = 1.3, J = 7.5 Hz, H-4d), 7.76 (d, 2H, J = 8.9 Hz, H-3a and 5a), 7.67-7.64 (m, 6H, H-3b, 5b, 3c, 5c, 3d and 5d), 2.56 (s, 6H, CH_3); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.09 (s, 2H, H-3 and H-5), 8.72 (d, 2H, J = 8.6 Hz, H-2a and 6a), 8.49 (d, 4H, J = 8.1 Hz, H-2b, 6b, 2c and 6c), 8.21 (d, 2H, J = 7.5 Hz, H-2d and 6d), 7.81 (t, 1H, J = 7.1 Hz, H-4d), 7.77 (d, 2H, J = 8.6 Hz, H-3a and 5a), 7.67 (t, 2H, J = 7.7 Hz, H-3d and 5d), 7.61 (d, 4H, J = 8.1 Hz, H-3b, 5b, 3c and 5c), 2.51 (overlap CH_3); ^{13}C NMR (125 MHz, acetone-d_6): δ = 171.9 (*C*-2 and *C*-6), 165.8 (O*C*OPh), 165.1 (*C*-4), 157.6, 148.0, 135.2 (*C*-4d), 132.4 (*C*-2a and 6a), 131.7 (*C*-3b, 5b, 3c and *C*-5c), 131.0 (*C*-2d and 6d), 130.0, 129.9 (*C*-3d and 5d), 129.8 (*C*-2b, 6b, 2c and *C*-6c), 127.7, 124.6 (*C*-3a and 5a), 115.5 (*C*-3 and *C*-5), 21.9 (CH_3); CIHRMS: *m/z* 458.1878, calcd for $C_{32}H_{26}O_3^+$ + H: 458.1882.

4. **Table S1**. Hammett substituent constants[44] for the pyrylium salts used in this work

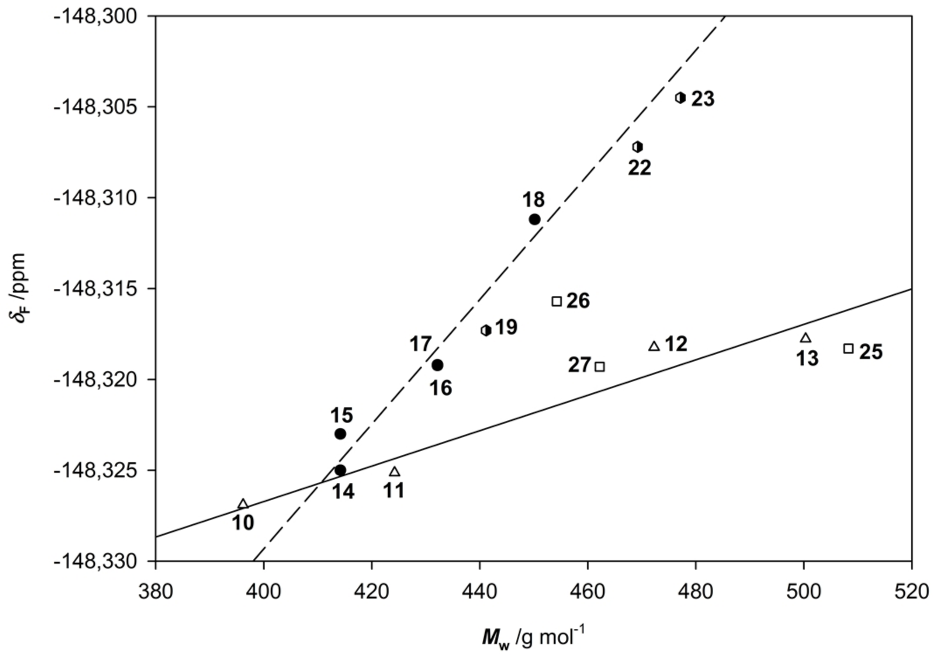
Compound	**σ_p (A)**	**σ_p (B)**	**σ_p (C)**	**$\Sigma\sigma$**
10	0	0	0	0
11	0	-0.17	-0.17	-0.34
12	-0.01	0	0	-0.01
13	-0.01	-0.17	-0.17	-0.35
14	0	0.06	0	0.06
15	0.06	0	0	0.06
16	0.06	0.06	0	0.12
17	0	0.06	0.06	0.12
18	0.06	0.06	0.06	0.18
19	0.78	0	0	0.78
22	0.78	-0.17	-0.17	0.44
23	0.78	0.06	0.06	0.90
25	-0.01	0.06	0.06	0.11
26	-0.27	-0.17	-0.17	-0.61
27	-0.27	0.06	0.06	-0.15

5. **Table S2**. UV-vis absorption and fluorescence data of some pyrylium tetrafluoroborate.

Compound	**λ abs.** (nm) (CH_2Cl_2)	**λ abs.** (nm) (Acetone)	**λ ems.** (nm) (Acetone)	$t_{1/2}$ (min)
10	420, 360 and 290	408, 357	465	-
13	-	417	533	-
14	322, 254[a] 409, 357[b]	409, 356	468	-
15	-	406, 359	464	214.2
22	460, 366 and 312	439	518	166.3
23	437, 356 and 297	424	498	-
26	-	421	490	272.2
27	435, 283 and 243	417	518	-
28	429, 368, 287, 231 and 203[a]	430, 368	492	-

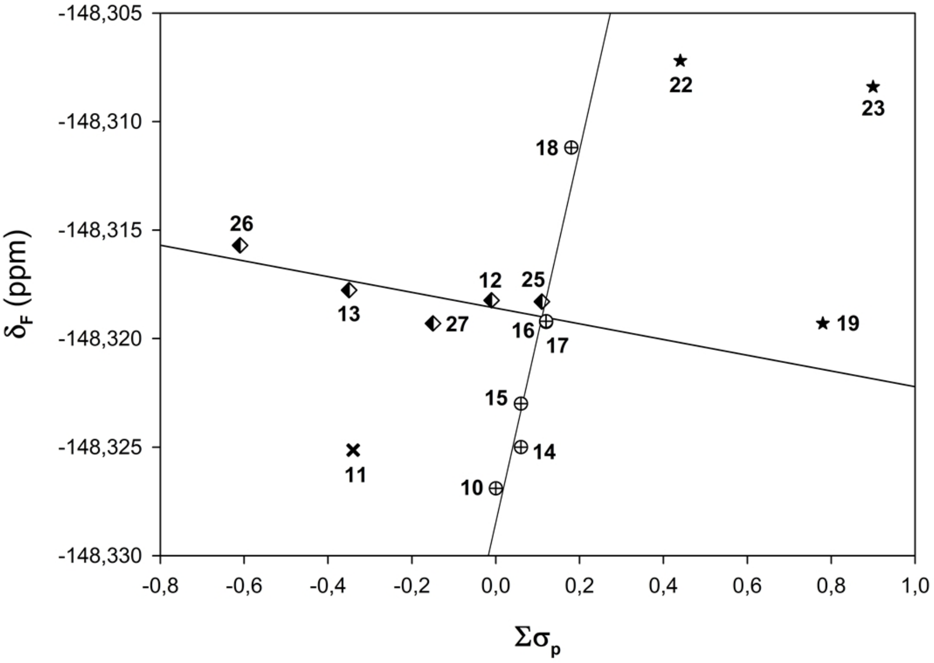
[a]UV-vis absorption spectrum was achieved in MeOH; [b]UV-vis absorption spectrum in MeOH in acidic medium.

6. **Figure S1**. Tetrafluoroborate anion chemical shift in ^{19}F NMR for different pyrylium salts[a] in DMSO-d_6 at a constant concentration of 20 mM for coupling with ^{10}B *vs* molecular weight of the pyrylium cation.

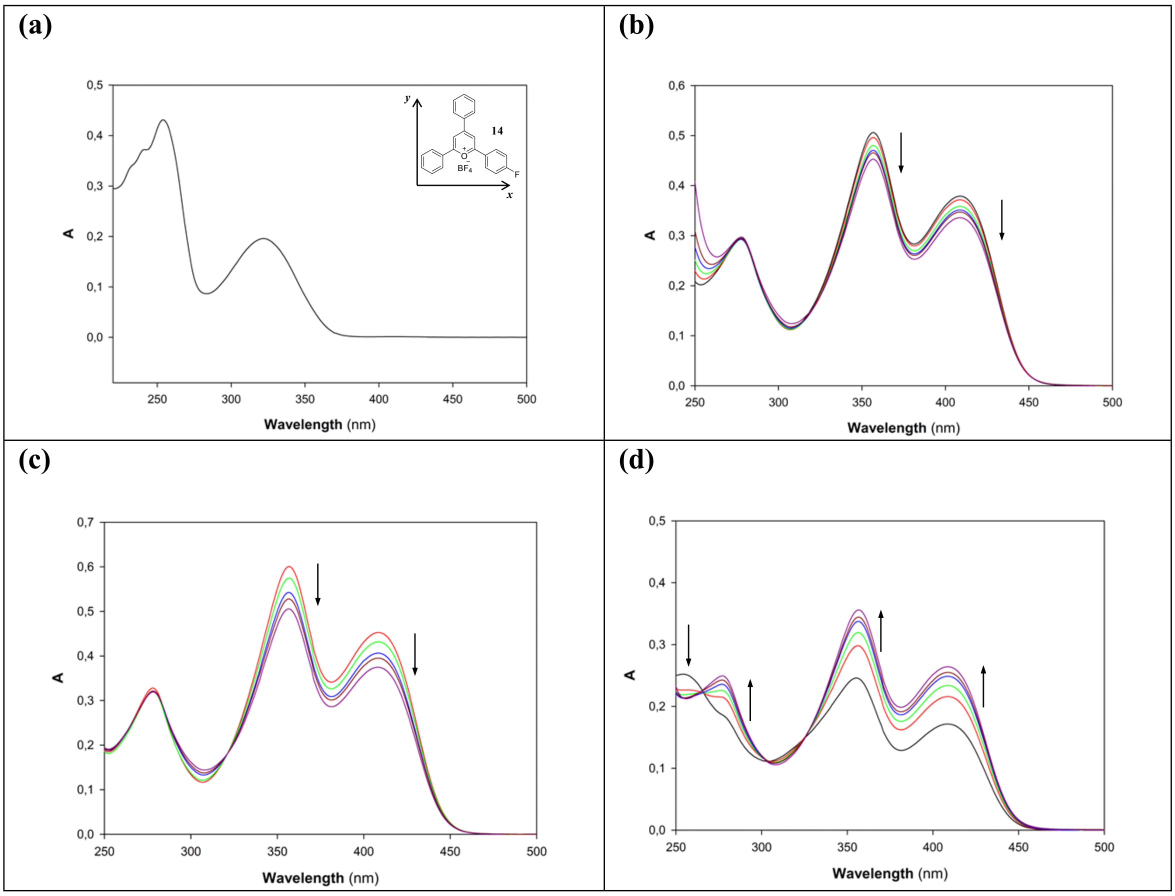


[a] In this graphic, triangles correspond to compound of series (a); circles to series (b); hexagons for series (c); squares to series (d).

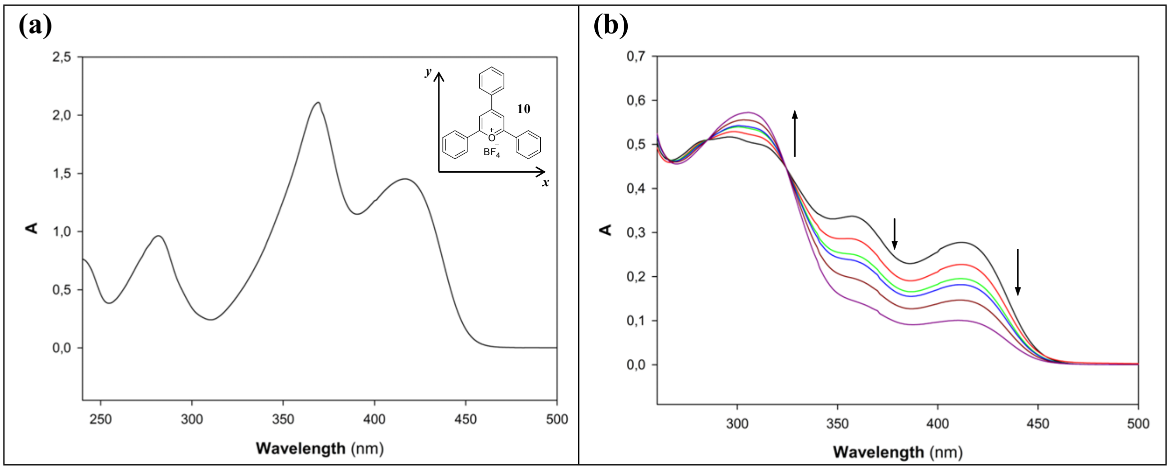
7. **Figure S2**. Tetrafluoroborate anion chemical shift in ^{19}F NMR for different pyrylium salts in DMSO-d_6 at a constant concentration of 20 mM for coupling with ^{10}B *vs* Hammett constants for the substituents ($\Sigma\sigma_p$).



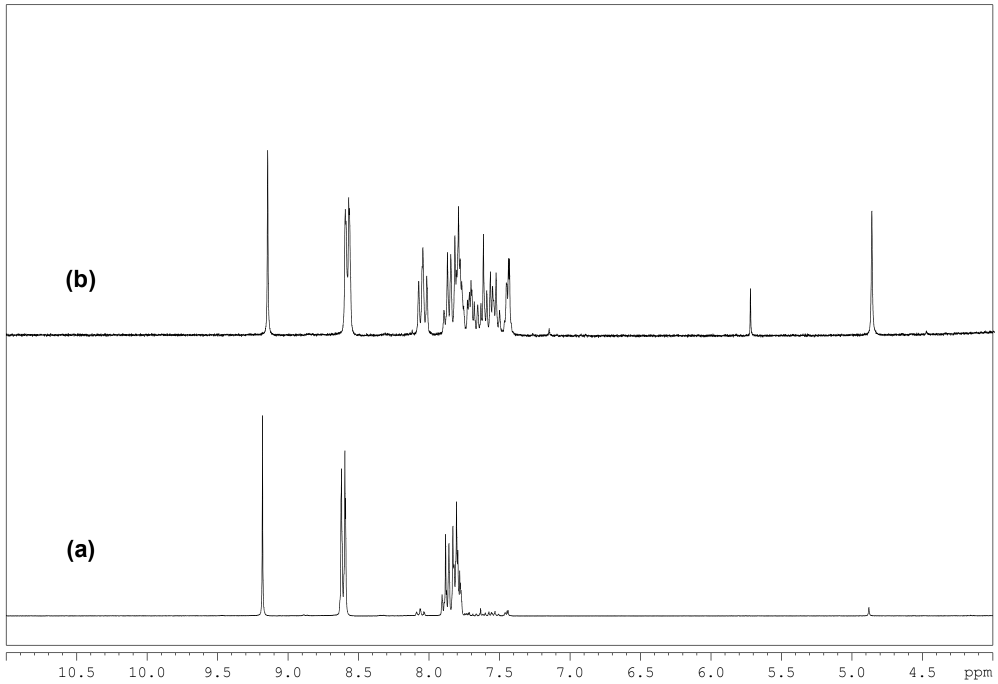
8. **Figure S3.** UV-vis absorption spectra and titration of pyrylium tetrafluoroborate **14** in methanol: (a) UV-vis absorption spectrum of **14** in methanol; (b) UV-vis spectra (0.2 – 4.0 equiv of TFAA); (c) UV-vis spectra (0.2 – 4.0 equiv of HClO$_4$); (d) UV-vis spectra (0.2 – 4.0 equiv of AcOH).



9. **Figure S4**. UV-vis absorption spectra of pyrylium tetrafluoroborate **10**: (a) in CH$_2$Cl$_2$; (b) variation in the UV-vis Absorption spectrum in DMSO with the time.



10. Figure S5. ^{1}H NMR spectra of compound **10** in DMSO-d_6 (a) and after a 10 cycles of UV radiation (b).



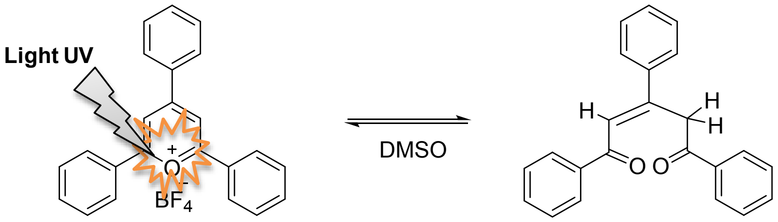
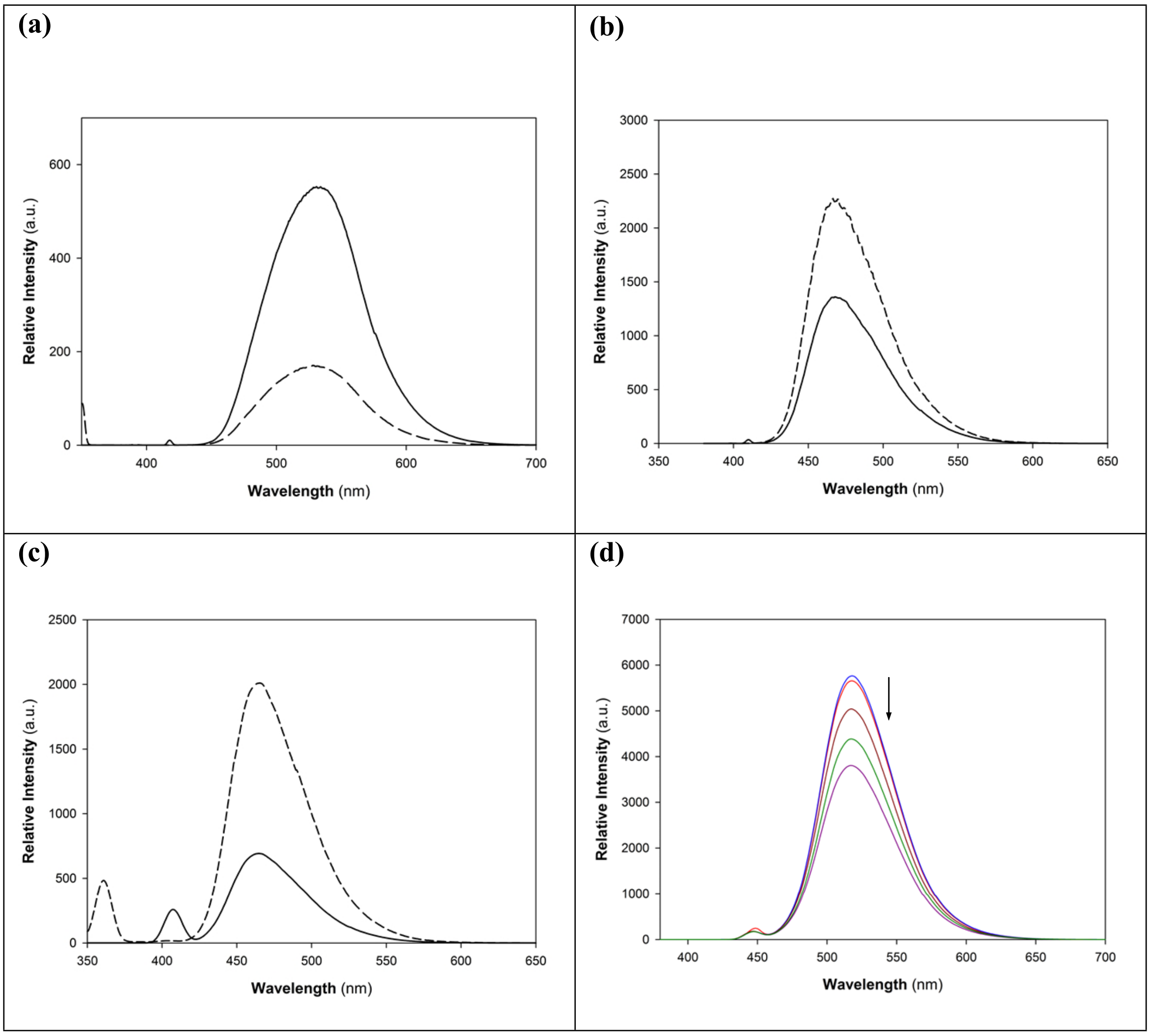


Fig. S5a **Fig. S5b**

11. Figure S6. Fluorescence spectra of pyrylium tetrafluoroborates: (a) Compound **13**, (b) **14** and (c) **15** in acetone; (d) Variation in the emission wavelength of compound **22** in acetone with the time.



12. Cartesian coordinates for some pyrylium complexes.

Compound 10:

Atom	Z	*x*	*y*	*z*
C	6.0	-1.1889626107	-0.8718606371	-0.2907587768
C	6.0	-0.0107115967	-1.1667080920	0.3665901543
O	8.0	0.7767646612	-0.1576479243	0.7744946232
C	6.0	0.5748177346	1.1151906576	0.3996348288
C	6.0	-0.6037605685	1.4493177293	-0.2409454956
C	6.0	-1.5360004782	0.4587434269	-0.5943478126
C	6.0	-2.8245737024	0.7992207926	-1.2450987998
C	6.0	0.4639138721	-2.4931133825	0.7544395100
C	6.0	1.6300341873	2.0403071447	0.8053858476
C	6.0	-3.2078818225	2.1399711159	-1.4471179499
C	6.0	-4.4127877060	2.4615661968	-2.0653154398
C	6.0	-5.2759453689	1.4507955753	-2.4919496134
C	6.0	-4.9195282551	0.1156258372	-2.2943463648
C	6.0	-3.7123919072	-0.2046248182	-1.6793343882
C	6.0	2.5721695097	1.6756085897	1.7806130106
C	6.0	3.5829876915	2.5606708395	2.1416813518
C	6.0	3.6729003085	3.8137549156	1.5308672539
C	6.0	2.7506193202	4.1755460399	0.5453594995
C	6.0	1.7371105563	3.2963614211	0.1815977417
C	6.0	1.5120088752	-2.6351280212	1.6793980685
C	6.0	1.9513448752	-3.9027014555	2.0472779213
C	6.0	1.3742402334	-5.0413918610	1.4805545056
C	6.0	0.3536392579	-4.9064488543	0.5350409446
C	6.0	-0.1041418763	-3.6436127801	0.1779745721
H	1.0	-1.8412957812	-1.6929231407	-0.5437282562
H	1.0	-0.7722131473	2.4901223178	-0.4694675494
H	1.0	-2.5681233797	2.9527828820	-1.1236563024
H	1.0	-4.6783499773	3.5049819607	-2.2096578593
H	1.0	-6.2160194157	1.7013564275	-2.9754366555
H	1.0	-5.5830223113	-0.6812742271	-2.6173671029
H	1.0	-3.4629353049	-1.2525659933	-1.5591427663
H	1.0	2.5197105549	0.6968618551	2.2401711527
H	1.0	4.3009368292	2.2727469744	2.9033994089
H	1.0	4.4695190780	4.4981170529	1.8089188237
H	1.0	2.8441594547	5.1298092258	0.0337644108
H	1.0	1.0702095256	3.5631239484	-0.6316620536
H	1.0	1.9870116584	-1.7550593501	2.0921083609
H	1.0	2.7572972869	-4.0017133706	2.7684064224
H	1.0	1.7313052705	-6.0291014758	1.7583696000
H	1.0	-0.0731328869	-5.7868590575	0.0625178036
H	1.0	-0.8588918783	-3.5552593643	-0.5959812704
B	5.0	2.6582882378	-0.5903309964	-1.5516693198
F	9.0	3.6444380801	-0.6921484709	-2.5141252744
F	9.0	1.9615249828	0.6508061939	-1.6813031144
F	9.0	1.6992051687	-1.6283995053	-1.6903263674
F	9.0	3.2086127649	-0.6572163426	-0.2511272835

Compound 13:

Atom	*Z*	*x*	*y*	*z*
C	6.0	-0.7553539930	0.5396826666	-0.7452050349
C	6.0	-1.9643831687	0.1686746000	-0.2094894753
O	8.0	-2.0116787162	-0.4162672324	0.9973498297
C	6.0	-0.8929910388	-0.7800943397	1.6507961306
C	6.0	0.3325258978	-0.4220943178	1.1563186988
C	6.0	0.4365063826	0.2753704722	-0.0599175235
C	6.0	1.7296044073	0.7017529927	-0.5866345486
C	6.0	-3.2645007715	0.3999268455	-0.8088346673
C	6.0	-1.1360796046	-1.4947746530	2.8920806394
C	6.0	2.9255452966	0.4185788262	0.0932985034
C	6.0	4.1459091475	0.8486780703	-0.3933063280
C	6.0	4.2457667558	1.5770635953	-1.5935504689
C	6.0	3.0426681937	1.8694575661	-2.2630723881
C	6.0	1.8215581517	1.4403257330	-1.7782800111
C	6.0	-2.3398539425	-2.1867874937	3.0899856584
C	6.0	-2.5742439173	-2.8342233745	4.2968730720

C	6.0	-1.6176182806	-2.8292961296	5.3212461817
C	6.0	-0.4052135903	-2.1573469936	5.1019080895
C	6.0	-0.1661551800	-1.4940345267	3.9090219437
C	6.0	-4.3545319795	-0.4169174624	-0.4747055725
C	6.0	-5.6043208469	-0.1535908555	-1.0212726904
C	6.0	-5.7939516901	0.9045934167	-1.9210944756
C	6.0	-4.6876511416	1.6932762363	-2.2741768938
C	6.0	-3.4390623837	1.4501017486	-1.7249684588
C	6.0	-1.8826034002	-3.5022696947	6.6424200324
C	6.0	5.5542488298	2.0233082847	-2.1220388123
C	6.0	5.6431042841	2.7663585074	-3.3130350390
C	6.0	6.8695451947	3.2055572080	-3.7997560539
C	6.0	8.0473220770	2.9045039857	-3.1141720078
C	6.0	7.9772585078	2.1923361959	-1.9156466584
C	6.0	6.7505774240	1.7439894949	-1.4373565610
C	6.0	-7.1503087039	1.2054945104	-2.5034733373
B	5.0	-1.1587172789	-2.8552931244	-1.2126486029
F	9.0	-1.1605586370	-4.0903306761	-1.8281914031
F	9.0	-2.1169555373	-2.8285907513	-0.1475375640
F	9.0	0.1122732621	-2.5668674773	-0.6650753096
F	9.0	-1.5057371594	-1.8322149953	-2.1277313044
H	1.0	-0.7596276403	0.9546401413	-1.7393065033
H	1.0	1.2079466234	-0.7597793129	1.6874279330
H	1.0	2.9159623097	-0.1477657723	1.0167023260
H	1.0	5.0315198831	0.5925693189	0.1746952127
H	1.0	3.0467202537	2.4323876610	-3.1879566418
H	1.0	0.9314611361	1.6947311000	-2.3407056218
H	1.0	-3.0571025682	-2.2439599333	2.2801574959
H	1.0	-3.5116863746	-3.3657052683	4.4400075301
H	1.0	0.3537849423	-2.1458510353	5.8801952324
H	1.0	0.7658851932	-0.9526322273	3.7755277450
H	1.0	-4.1916087701	-1.2727921364	0.1690342461
H	1.0	-6.4465673850	-0.7855241442	-0.7532311431
H	1.0	-4.8127033455	2.5100841032	-2.9805004352
H	1.0	-2.6022247752	2.0916919679	-1.9839706684
H	1.0	-2.7338915465	-4.1861244219	6.5799219988
H	1.0	-1.0090541799	-4.0713035685	6.9803823184
H	1.0	-2.1043452410	-2.7565305660	7.4173199397
H	1.0	4.7504516085	2.9975743568	-3.8830681079
H	1.0	6.9022816185	3.7583170665	-4.7343576293
H	1.0	9.0054293177	3.2442706757	-3.4947276425
H	1.0	8.8814923120	1.9563260151	-1.3618618006
H	1.0	6.7294768798	1.2103770360	-0.4939175372
H	1.0	-7.5306215181	2.1661639285	-2.1313242422
H	1.0	-7.1000759274	1.2791716081	-3.5960713142
H	1.0	-7.8788806566	0.4318905488	-2.2454912795

Compound 14:

Atom	Z	*x*	*y*	*z*
C	6.0	-1.2537223740	0.9500953971	0.2364024654
C	6.0	-1.2583000745	-0.4183642254	0.3665131134
O	8.0	-0.0977412416	-1.0804081066	0.4938316812
C	6.0	1.0970793221	-0.4784541560	0.3851784156
C	6.0	1.1397042774	0.9000358585	0.2883284175
C	6.0	-0.0380619436	1.6598191606	0.2026335997
C	6.0	-0.0086223455	3.1335169706	0.0874800687
C	6.0	-2.4328453794	-1.2845905309	0.4184726807
C	6.0	2.2356524149	-1.3875565301	0.4701355883
C	6.0	1.1979281115	3.8273642265	-0.1292162449
C	6.0	1.2243326067	5.2157010910	-0.2168794836
C	6.0	0.0433013871	5.9501271325	-0.0969740280
C	6.0	-1.1661265088	5.2813657845	0.0956541626
C	6.0	-1.1905737865	3.8934732334	0.1865750531
C	6.0	2.0415306824	-2.7531322519	0.7449285084
C	6.0	3.1303932118	-3.6133406508	0.8321478103
C	6.0	4.4258127690	-3.1283549044	0.6396543368
C	6.0	4.6277795013	-1.7784419464	0.3424359470
C	6.0	3.5428556182	-0.9148506901	0.2542483265
C	6.0	-2.3320160784	-2.6304849210	0.0186392261
C	6.0	-3.4341764169	-3.4717594078	0.1226563590
C	6.0	-4.6299816707	-2.9578059581	0.6195106561
C	6.0	-4.7678090542	-1.6231117549	0.9942452190
C	6.0	-3.6609640240	-0.7902854949	0.8917956634

F	9.0	-5.6986664737	-3.7670238904	0.7131133192
H	1.0	-2.2025440725	1.4439820490	0.0792019264
H	1.0	2.1095332334	1.3698204534	0.2528037943
H	1.0	2.1309446894	3.2859323093	-0.2508898920
H	1.0	2.1712854864	5.7233670225	-0.3755753801
H	1.0	0.0633855790	7.0344157562	-0.1680374995
H	1.0	-2.0952140644	5.8386729820	0.1760155519
H	1.0	-2.1442260839	3.4084878350	0.3665870120
H	1.0	1.0360260851	-3.1373744671	0.8706506757
H	1.0	2.9677750372	-4.6658154097	1.0457732940
H	1.0	5.2770933473	-3.7995880615	0.7230505724
H	1.0	5.6311911587	-1.3984488245	0.1761914239
H	1.0	3.7126615315	0.1149831673	-0.0391425601
H	1.0	-1.4059762003	-2.9779258466	-0.4300188956
H	1.0	-3.3857320432	-4.5107058308	-0.1885010304
H	1.0	-5.7235168143	-1.2601621438	1.3565310624
H	1.0	-3.7440617721	0.2404803631	1.2279649253
B	5.0	0.5704095810	-0.9907317715	-2.6823281422
F	9.0	1.7937999812	-0.3795282712	-2.3134212831
F	9.0	-0.4840876943	-0.1235228723	-2.2856203161
F	9.0	0.5233316702	-1.2342902899	-4.0385403752
F	9.0	0.4273928340	-2.1961245842	-1.9375667250

Compound 27:

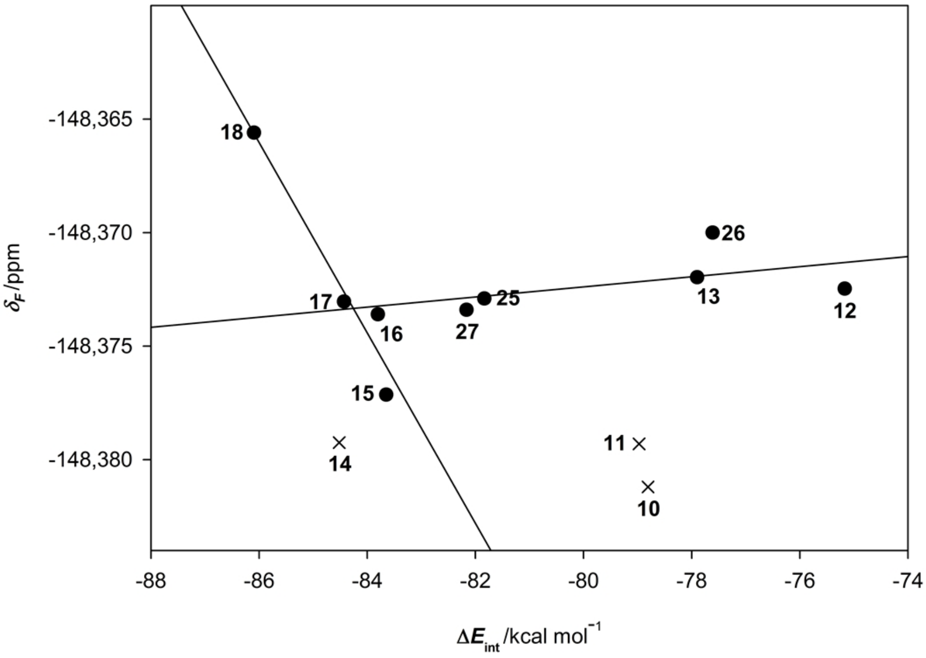
Atom	*Z*	*x*	*y*	*z*
C	6.0	-1.1597878159	0.2236609431	0.3129293239
C	6.0	-1.1591058749	-1.1349399234	0.4657997757
O	8.0	0.0073338533	-1.8006260464	0.5902650139
C	6.0	1.1939330301	-1.1798697907	0.4029290445
C	6.0	1.2326795705	0.1874127250	0.2439921991
C	6.0	0.0530274898	0.9495134663	0.2357313455
C	6.0	0.0657494331	2.4134761647	0.1428732824
C	6.0	-2.3325644327	-2.0042775359	0.5603538276
C	6.0	2.3341884199	-2.0899404493	0.3808793167
C	6.0	1.2639520777	3.1362515670	-0.0643116848
C	6.0	1.2768955258	4.5171946690	-0.1234831873
C	6.0	0.0825063964	5.2450006921	0.0227136984
C	6.0	-1.1207602912	4.5547732048	0.2329515126
C	6.0	-1.1140352007	3.1663477937	0.2944017052
C	6.0	2.1687960830	-3.4299900831	-0.0156015491
C	6.0	3.2423001634	-4.3091977668	0.0081860471
C	6.0	4.4971123275	-3.8272545946	0.3724833511
C	6.0	4.7030362656	-2.4992506402	0.7361473490
C	6.0	3.6174338730	-1.6329503345	0.7325833689
C	6.0	-2.2457184272	-3.3547246932	0.1765675153
C	6.0	-3.3507852921	-4.1929160135	0.2733763279
C	6.0	-4.5493871672	-3.6665630015	0.7488366708
C	6.0	-4.6753272949	-2.3318592085	1.1244957299
C	6.0	-3.5614146464	-1.5057874456	1.0304630385
F	9.0	-5.6181263370	-4.4745329100	0.8534998953
F	9.0	5.5433436120	-4.6714495012	0.3773336911
O	8.0	0.1908599297	6.5908329738	-0.0378560003
C	6.0	-0.9937349857	7.3820305797	0.0009102184
B	5.0	0.7228739118	-0.9742528899	-2.7860022647
F	9.0	2.0419330360	-0.7332634827	-2.3439119164
F	9.0	-0.0859226524	0.1533458946	-2.5326034808
F	9.0	0.7027503625	-1.3159546976	-4.1273234037
F	9.0	0.1981252905	-2.0677424809	-2.0105743931
H	1.0	-2.1139784375	0.7094437240	0.1607866901
H	1.0	2.1966421886	0.6342564271	0.0572032295
H	1.0	2.2009659364	2.6148640241	-0.2207444658
H	1.0	2.1984669498	5.0653489657	-0.2872461190
H	1.0	-2.0564761247	5.0849452858	0.3622907948
H	1.0	-2.0616482224	2.6717318123	0.4729693407
H	1.0	1.2001941811	-3.7610510082	-0.3654943707
H	1.0	3.1379774265	-5.3401614843	-0.3161355725
H	1.0	5.6967659017	-2.1673708258	1.0165846031
H	1.0	3.7621992287	-0.6044657616	1.0510902332
H	1.0	-1.3161353563	-3.7260910795	-0.2422904857
H	1.0	-3.3026274019	-5.2335768387	-0.0261800010
H	1.0	-5.6292764523	-1.9663990834	1.4901029542
H	1.0	-3.6438855766	-0.4715901286	1.3502442889
H	1.0	-0.6693241652	8.4160934228	-0.1137421427

H	1.0	-1.6691354556	7.1126884840	-0.8224051442
H	1.0	-1.5161348535	7.2639788802	0.9580447985

Compound 28:

Atom	*Z*	*x*	*y*	*z*
C	6.0	0.5136189770	-0.4187239633	0.7084335434
C	6.0	0.4260520387	-1.7599754765	1.0051793469
O	8.0	-0.1827582733	-2.5895830174	0.1402101901
C	6.0	-0.5222560340	-2.1971957506	-1.1029180663
C	6.0	-0.4596424368	-0.8672064093	-1.4340997447
C	6.0	0.0326162851	0.0823526824	-0.5145426443
C	6.0	0.0564853180	1.5183215808	-0.8225571317
C	6.0	0.9172351722	-2.4212522229	2.2075369919
C	6.0	-0.9581618626	-3.2906674178	-1.9642604761
C	6.0	-0.3606778228	2.0190262334	-2.0745962343
C	6.0	-0.3951278599	3.3787218896	-2.3405956089
C	6.0	0.0035764865	4.2881055160	-1.3533653157
C	6.0	0.4479958729	3.8230402775	-0.1106915611
C	6.0	0.4643660080	2.4599519703	0.1415135202
C	6.0	-1.8167180956	-3.0601423705	-3.0538315210
C	6.0	-2.2357189724	-4.1161100233	-3.8513625629
C	6.0	-1.8287783879	-5.4334236342	-3.5838321357
C	6.0	-0.9518982770	-5.6498183864	-2.5123751560
C	6.0	-0.5098973185	-4.5983944754	-1.7172620612
C	6.0	1.1836628214	-3.8007296375	2.1865191850
C	6.0	1.6440523211	-4.4428586510	3.3295144805
C	6.0	1.8628847910	-3.7390181388	4.5214778348
C	6.0	1.6203357268	-2.3559237676	4.5275174523
C	6.0	1.1475813594	-1.7049420237	3.3954977512
C	6.0	2.3320825140	-4.4440292075	5.7700686431
C	6.0	-2.3287149913	-6.5756432722	-4.4331917096
O	8.0	-0.0785841955	5.6166578084	-1.6666770225
C	6.0	0.2467387437	6.5717410791	-0.6854313314
C	6.0	-2.8219458362	7.5366782639	2.1273770249
C	6.0	-3.1067004668	6.6404201121	1.0935228110
C	6.0	-2.1238534981	6.3131223261	0.1620996125
C	6.0	-0.8469625316	6.8869372230	0.2645658796
C	6.0	-0.5648005715	7.7873074838	1.3051577694
C	6.0	-1.5509138777	8.1109641132	2.2313113678
O	8.0	1.3342041381	7.0854989899	-0.6975822584
H	1.0	1.0625848541	0.2062191407	1.3947426496
H	1.0	-0.7190679310	-0.5886492274	-2.4436902130
H	1.0	-0.6617281549	1.3430323910	-2.8662910828
H	1.0	-0.7198846070	3.7539837296	-3.3055528605
H	1.0	0.7817172603	4.5165021645	0.6527944362
H	1.0	0.7976080136	2.1372921071	1.1203169098
H	1.0	-2.1793047568	-2.0573661967	-3.2617554638
H	1.0	-2.9043218033	-3.9210978296	-4.6863817305
H	1.0	-0.5967900512	-6.6567923567	-2.3062052856
H	1.0	0.2158453851	-4.7691272284	-0.9320318508
H	1.0	1.0758103855	-4.3474524522	1.2587038972
H	1.0	1.8492782569	-5.5097112020	3.2924834475
H	1.0	1.7996315415	-1.7847891626	5.4352207609
H	1.0	0.9530328438	-0.6375030644	3.4391137065
H	1.0	2.7108518320	-5.4460695969	5.5468259914
H	1.0	3.1275120238	-3.8822238559	6.2718897698
H	1.0	1.5094819331	-4.5540869776	6.4905262558
H	1.0	-2.0067222574	-6.4674587336	-5.4765845176
H	1.0	-1.9612924710	-7.5390177847	-4.0671482442
H	1.0	-3.4254462836	-6.6102163275	-4.4373542246
B	5.0	3.0126270713	-1.8619883346	-1.0552775388
H	1.0	-3.5893866430	7.7837306812	2.8564256664
H	1.0	-4.0928884961	6.1907940305	1.0186783054
H	1.0	-2.3444082578	5.6234679887	-0.6452866025
H	1.0	0.4280583402	8.2214259480	1.3632559268
H	1.0	-1.3301587686	8.8065824025	3.0359723704
F	9.0	4.2500449442	-2.2249191896	-1.5460467094
F	9.0	2.3330419786	-1.0131552017	-1.9578854435
F	9.0	2.2025114422	-3.0284809832	-0.8488882275
F	9.0	3.1317591112	-1.1985855821	0.1882470389

13. **Figure S7.** Tetrafluoroborate anion chemical shift in ^{19}F NMR for different pyrylium salts vs. theoretical Binding Energies calculated at M06-2X/6-31G (d) level of theory.



14. ^{1}H and ^{13}C NMR spectra of new pyrylium compounds:

Fig. S8. Compound **13**: ^{1}H NMR spectrum (DMSO-d_6 500 MHz)

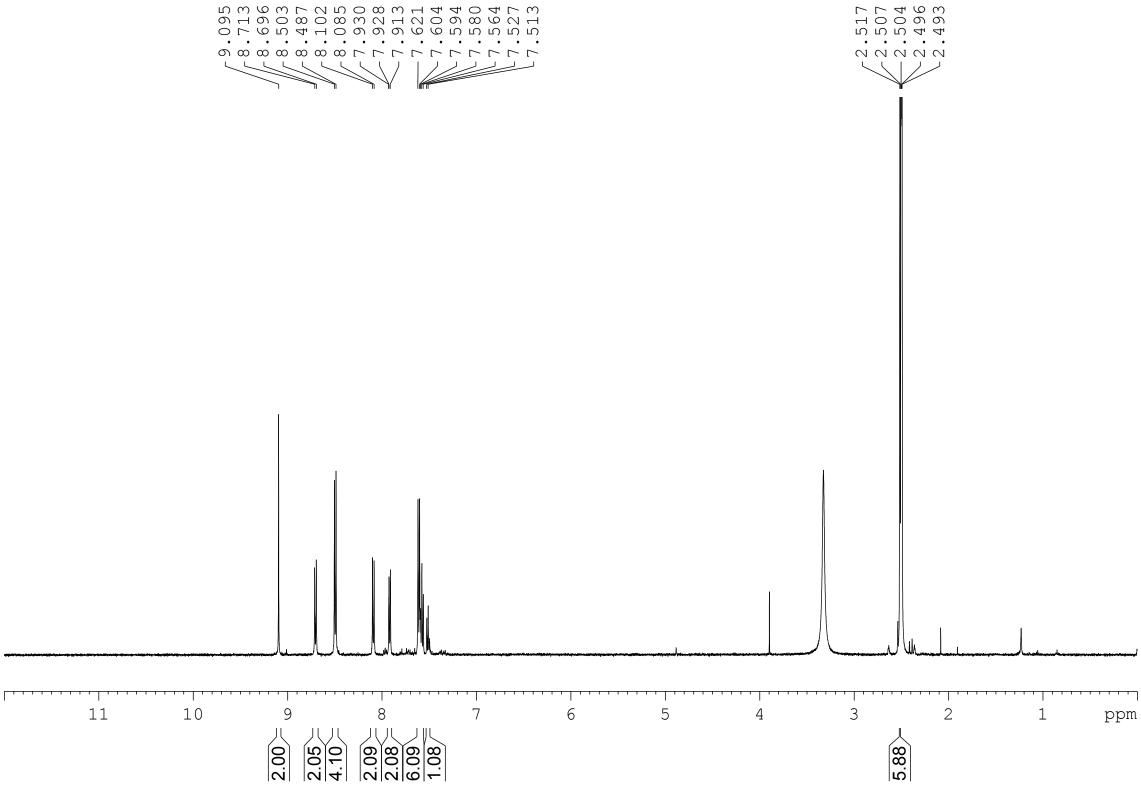


Fig. S9. Compound **13**: ^{13}C NMR spectrum (DMSO-d_6 125 MHz)

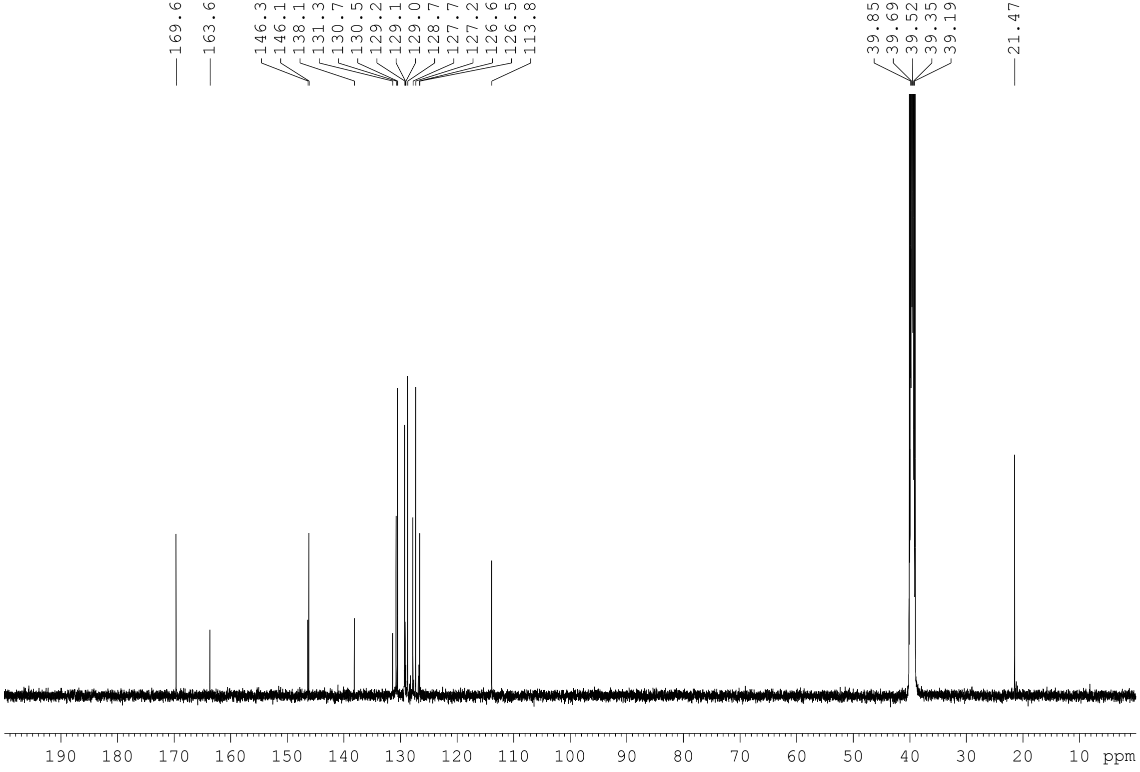


Fig. S10. Compound **14**: ^{1}H NMR spectrum (DMSO-d_6 500 MHz)

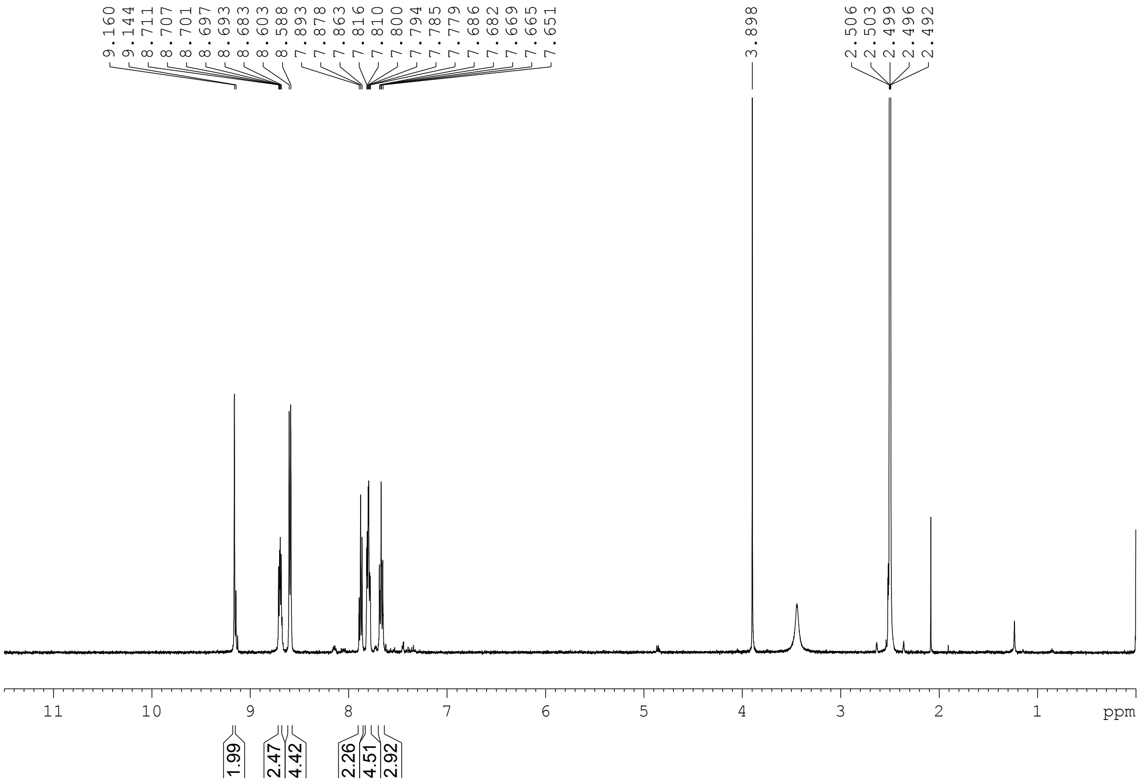


Fig. S11. Compound **14**: ^{1}H NMR spectrum (acetone-d_6 300 MHz)

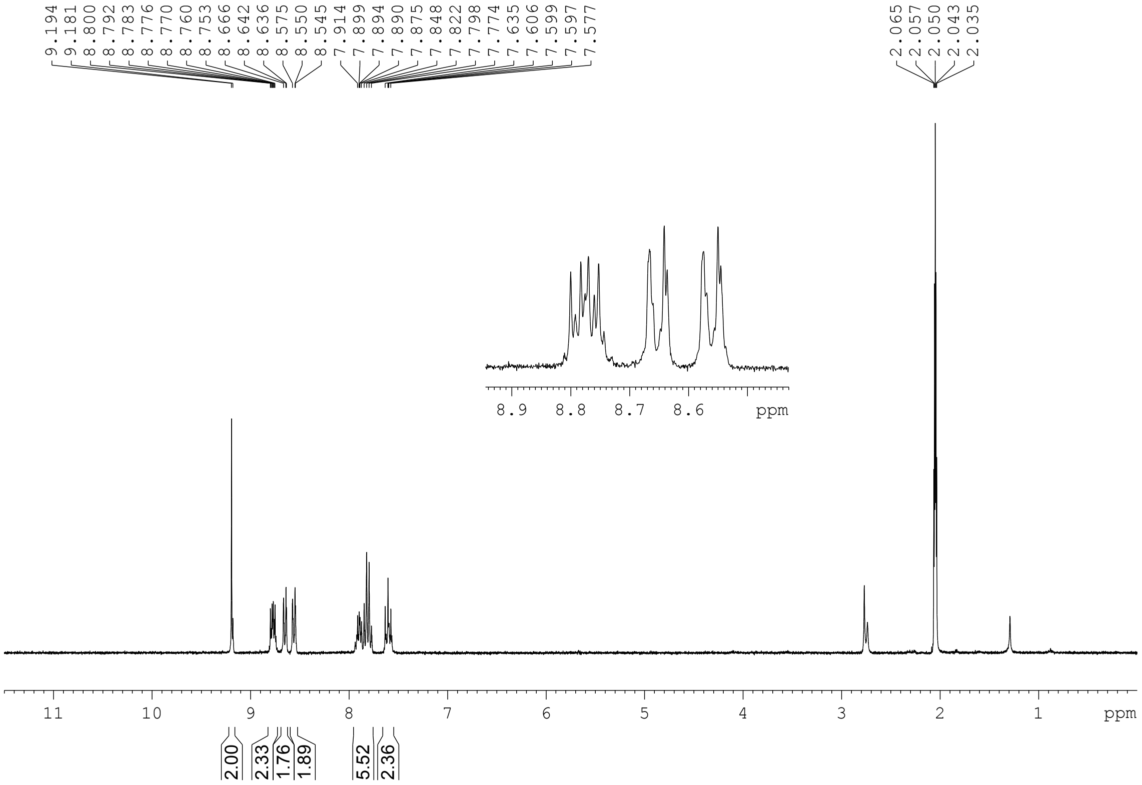


Fig. S12. Compound **14**: ^{13}C NMR spectrum (DMSO-d_6 125 MHz)

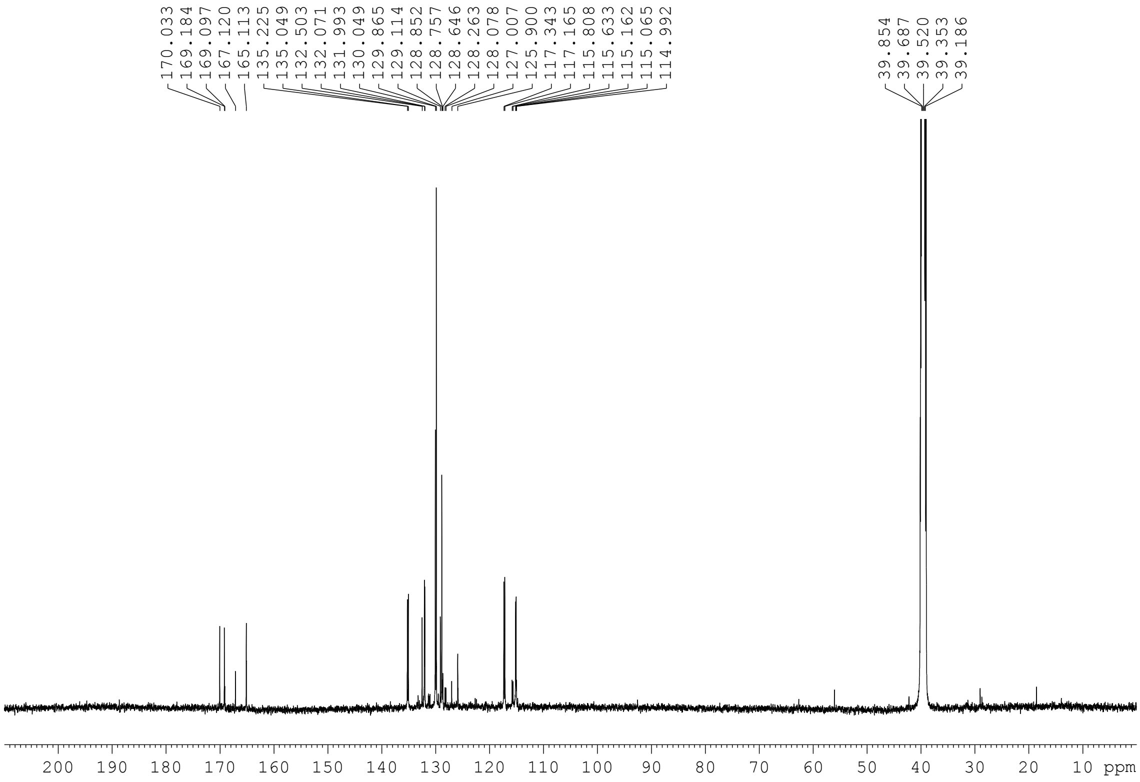


Fig. S13. Compound **16**: ^{1}H NMR spectrum (DMSO-d_6 500 MHz)

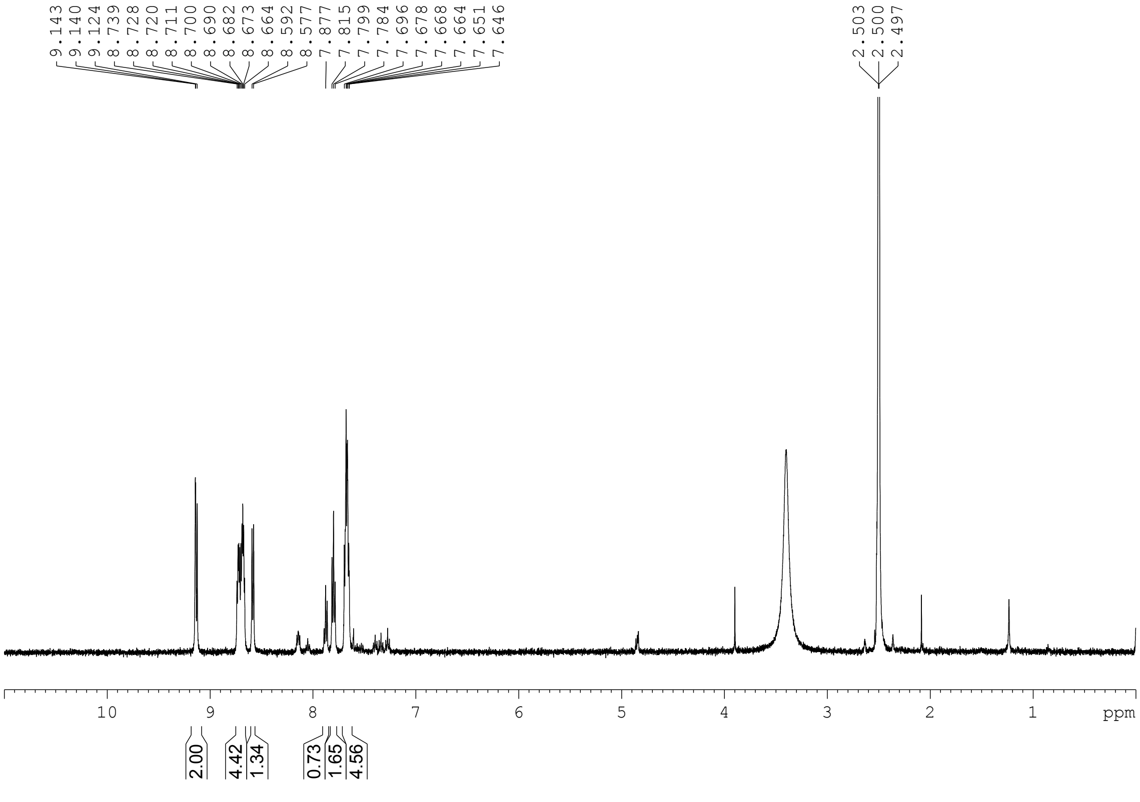


Fig. S14. Compound **16**: ^{13}C NMR spectrum (DMSO-d_6 125 MHz)

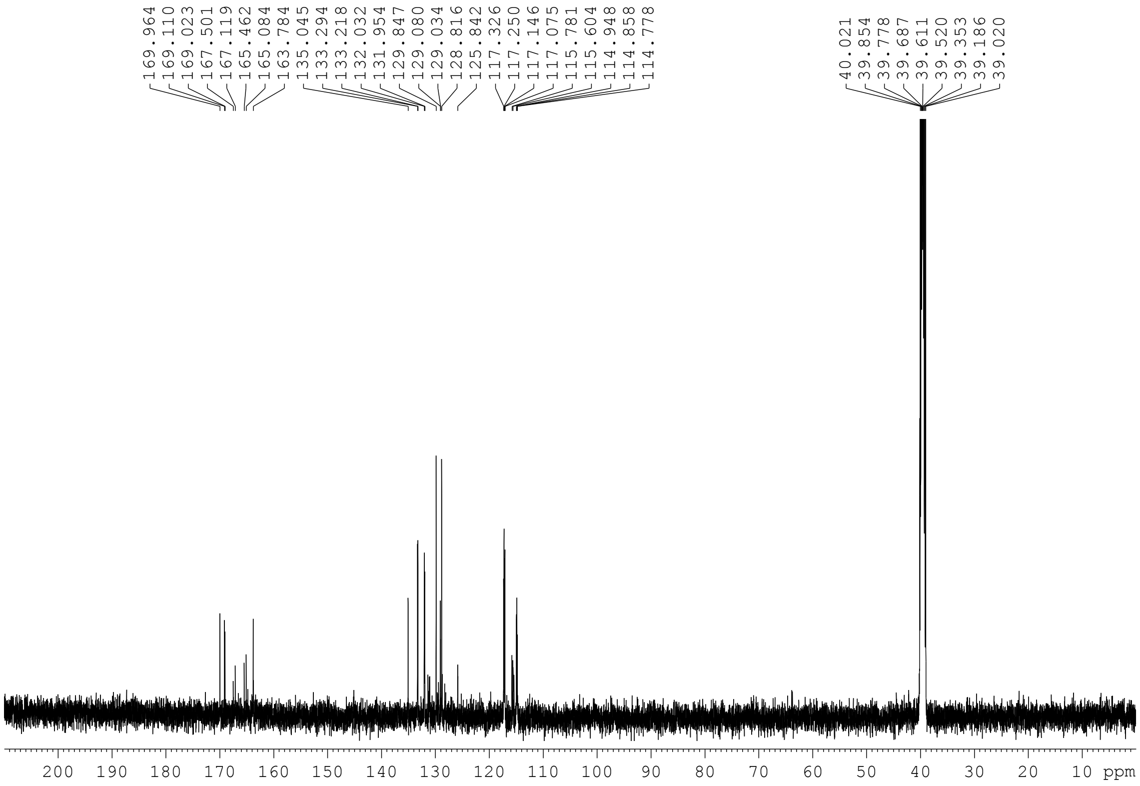


Fig. S15. Compound **19*/19a**: ^{1}H NMR spectrum (DMSO-d_6 300 MHz)

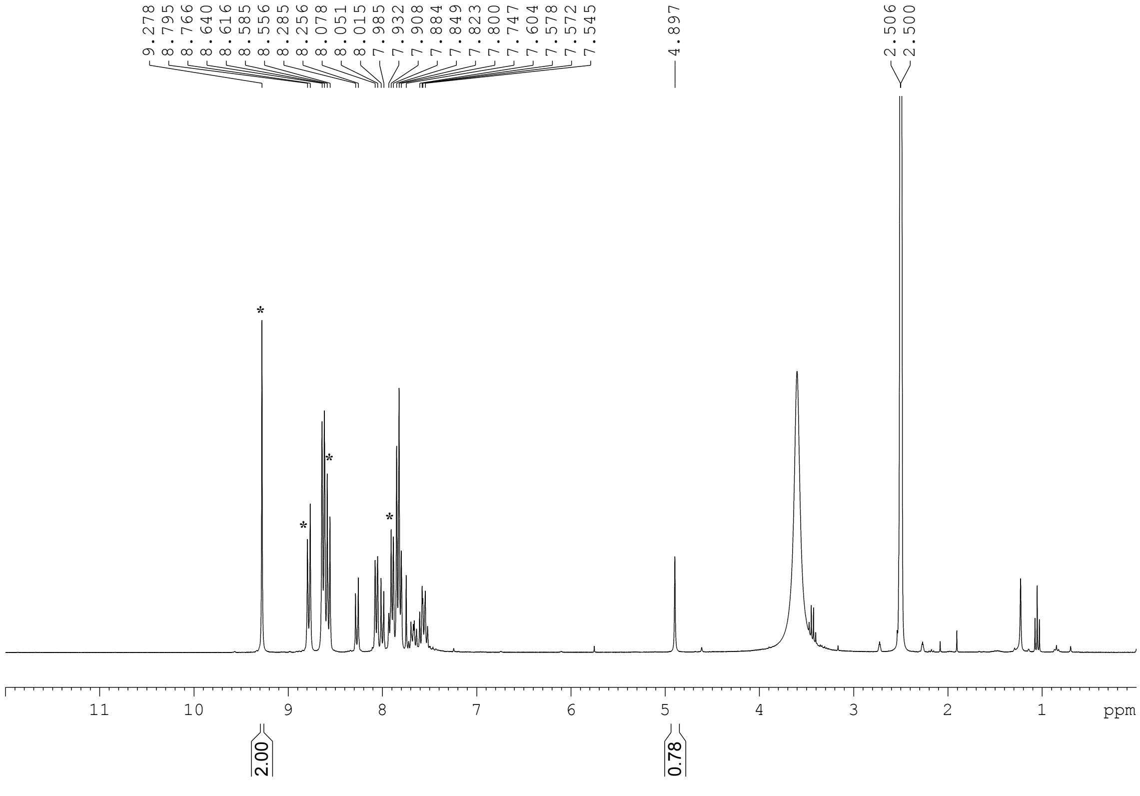


Fig. S16. Compound **20**/**20a**: ^{1}H NMR spectrum (DMSO-d_6 300 MHz)

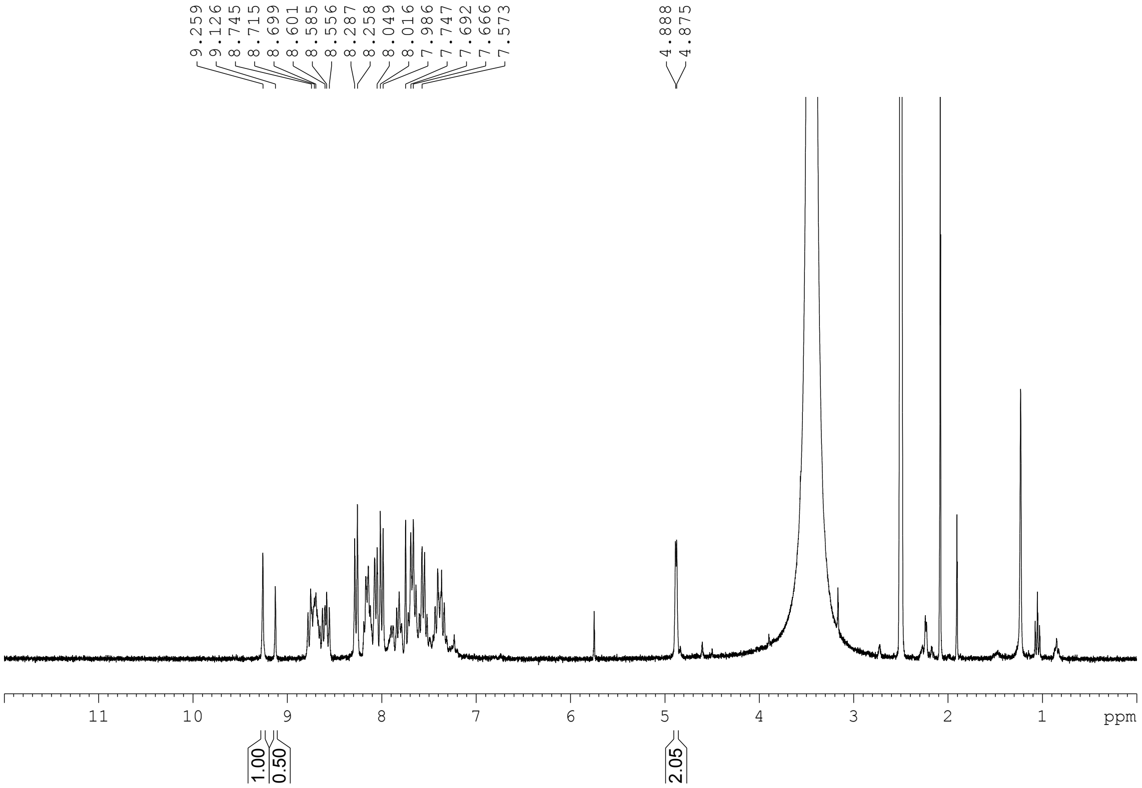


Fig. S17. Compound **21**/**21a**: ^{1}H NMR spectrum (DMSO-d_6 300 MHz)

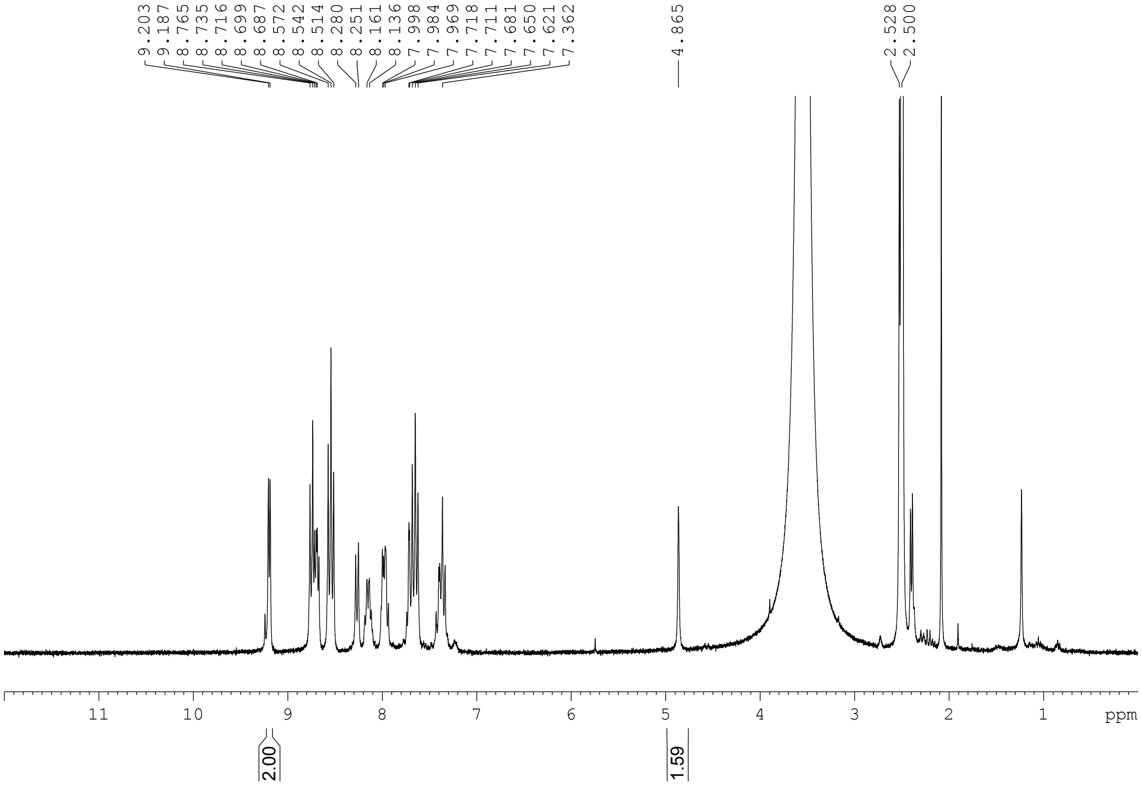


Fig. S18. Compound **22**: ^{1}H NMR spectrum (acetone-d_6 500 MHz)

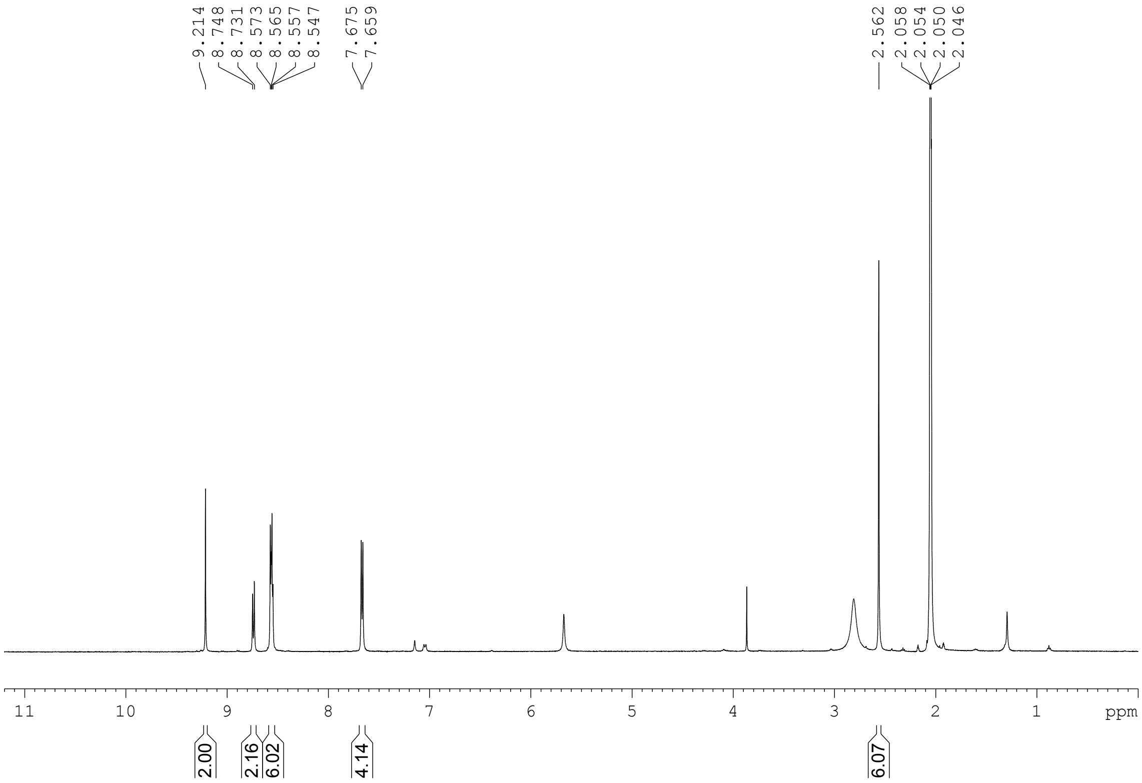


Fig. S19. Compound **22**: ^{13}C NMR spectrum (acetone-d_6 125 MHz)

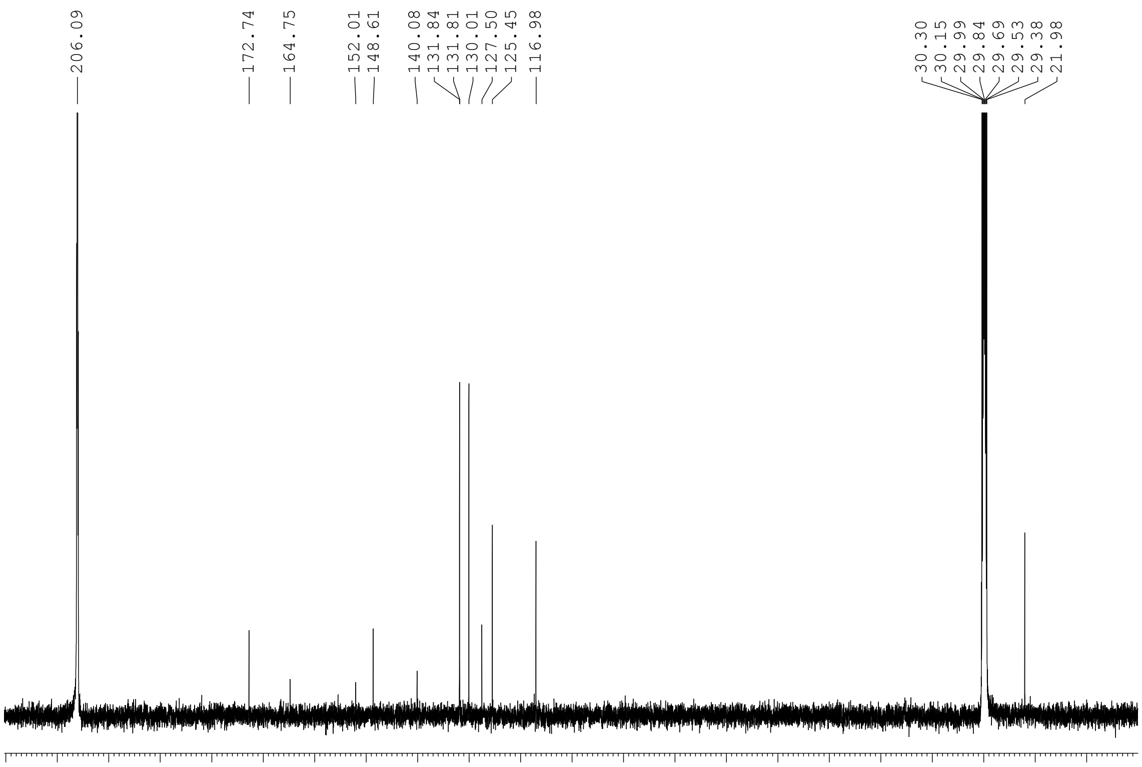


Fig. S20. Compound **22/22a**: ^{1}H NMR spectrum (DMSO-d_6 500 MHz)

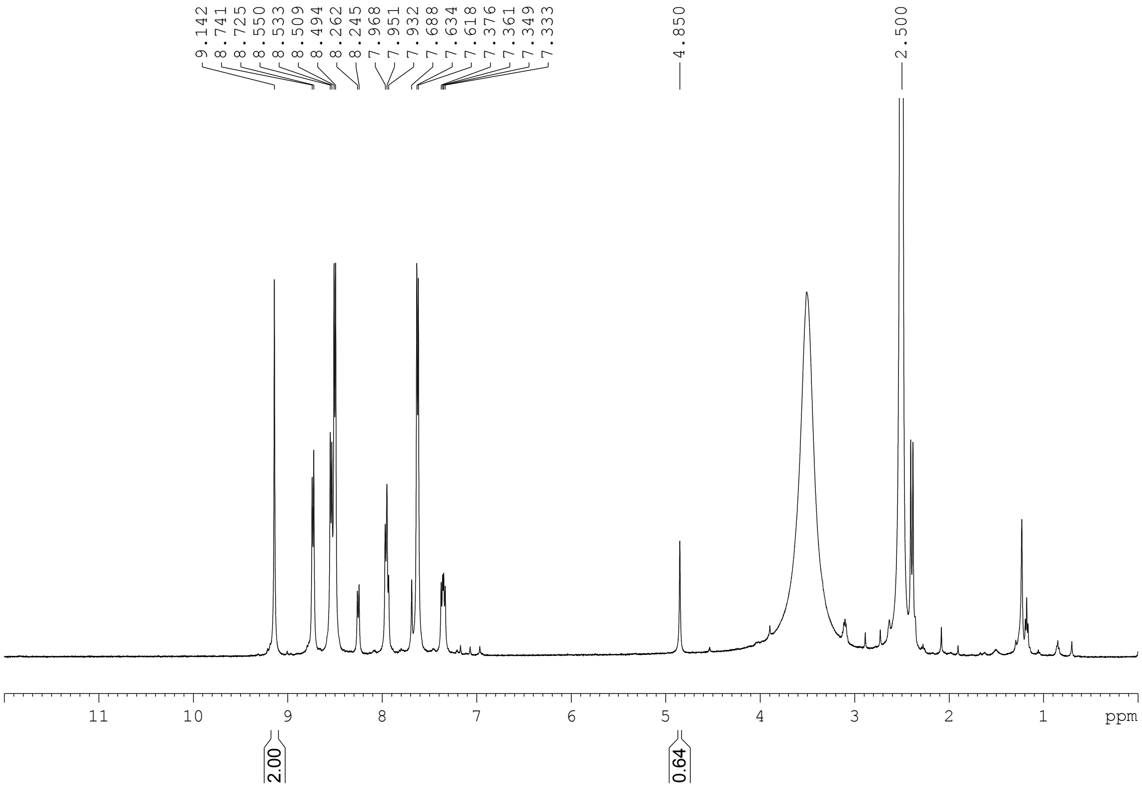


Fig. S21. Compound **23**: ^{1}H NMR spectrum (acetone-d_6 500 MHz)

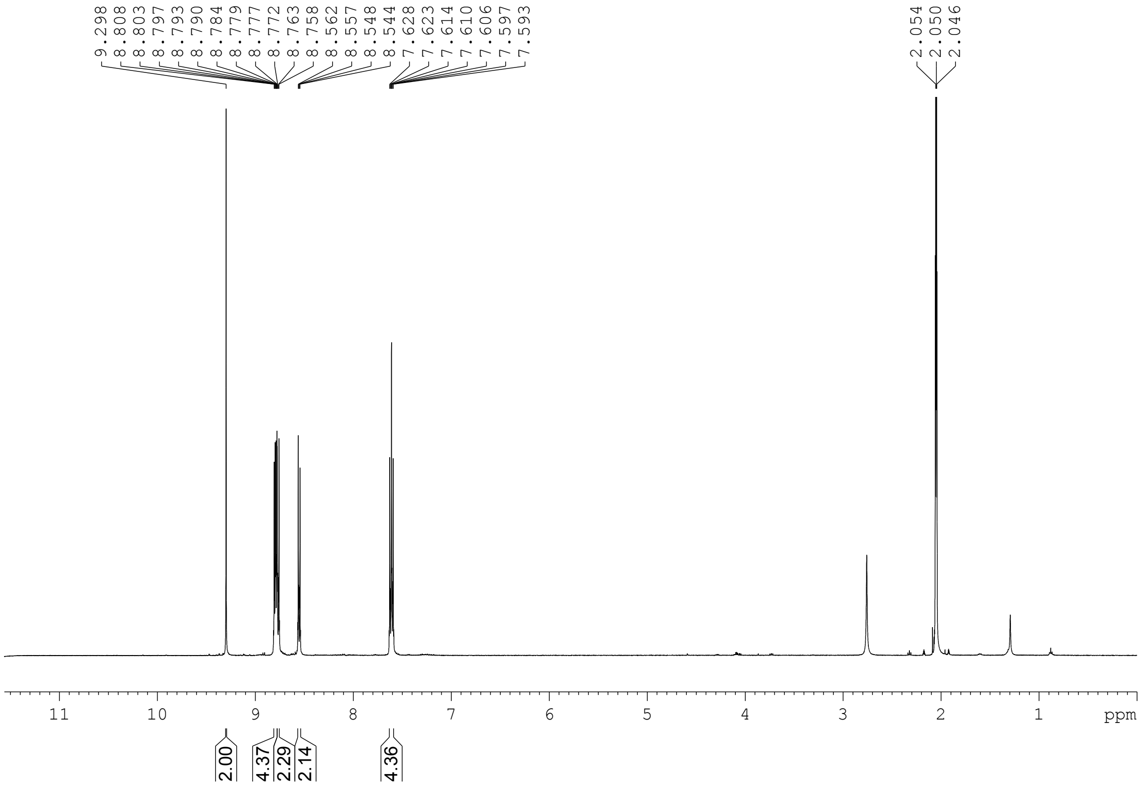


Fig. S22. Compound **23**: ^{13}C NMR spectrum (acetone-d_6 125 MHz)

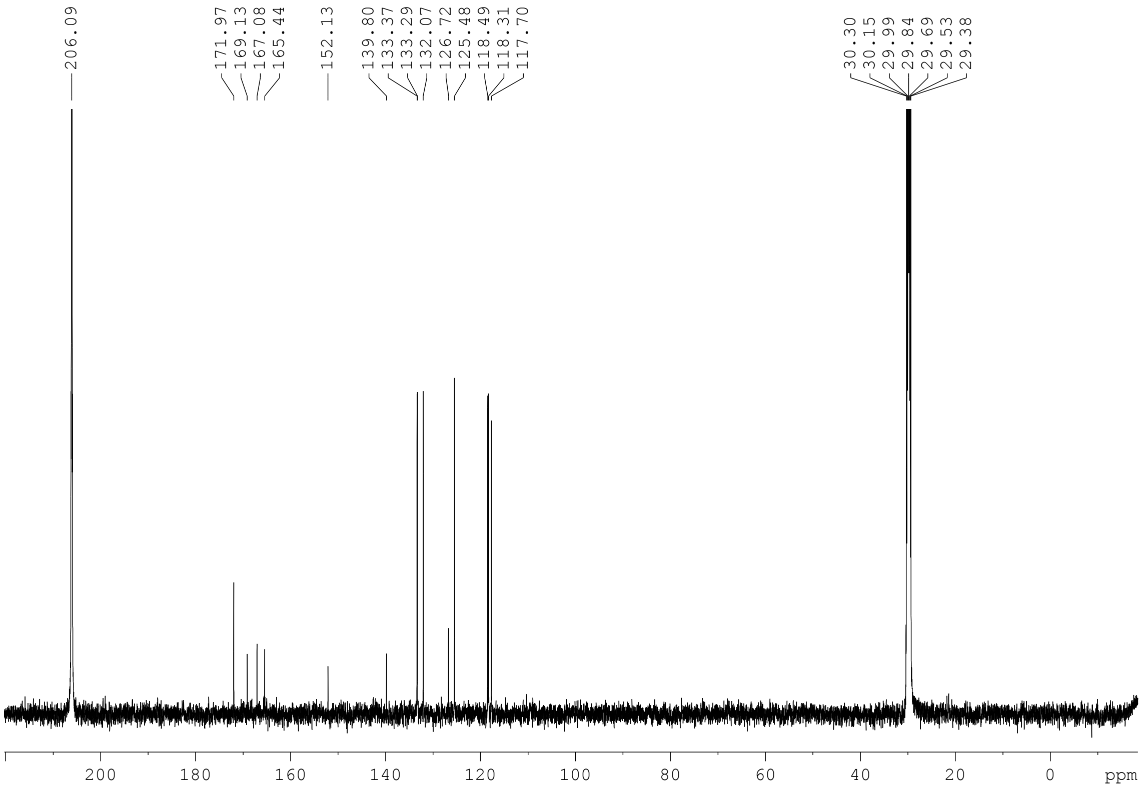


Fig. S23. Compound **23***/**23a**: ^{1}H NMR spectrum (DMSO-d_6 300 MHz)

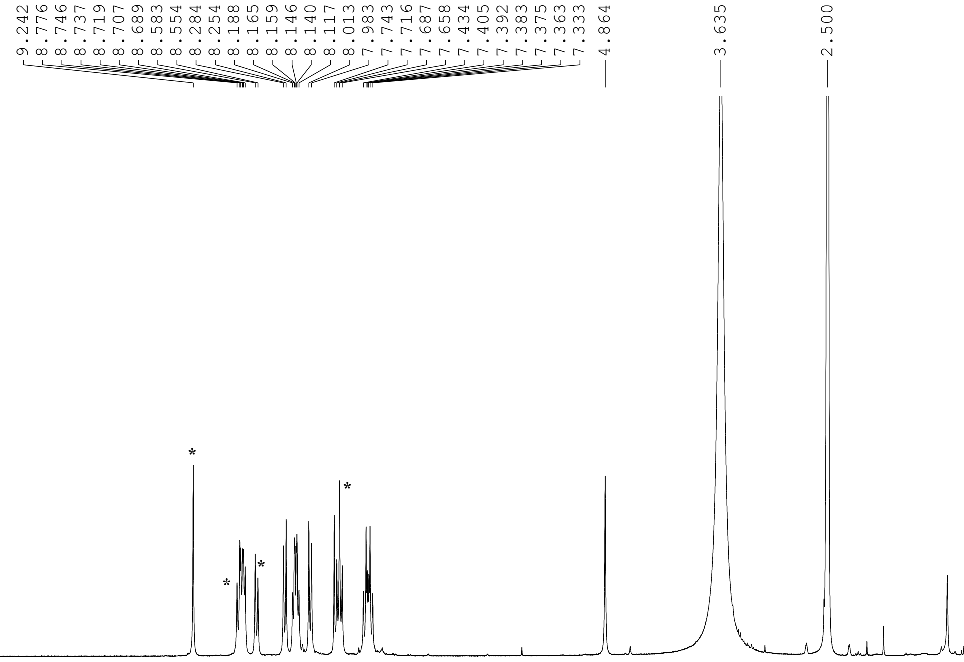


Fig. S24. Compound **24**: ^{1}H NMR spectrum (acetone-d_6 500 MHz)

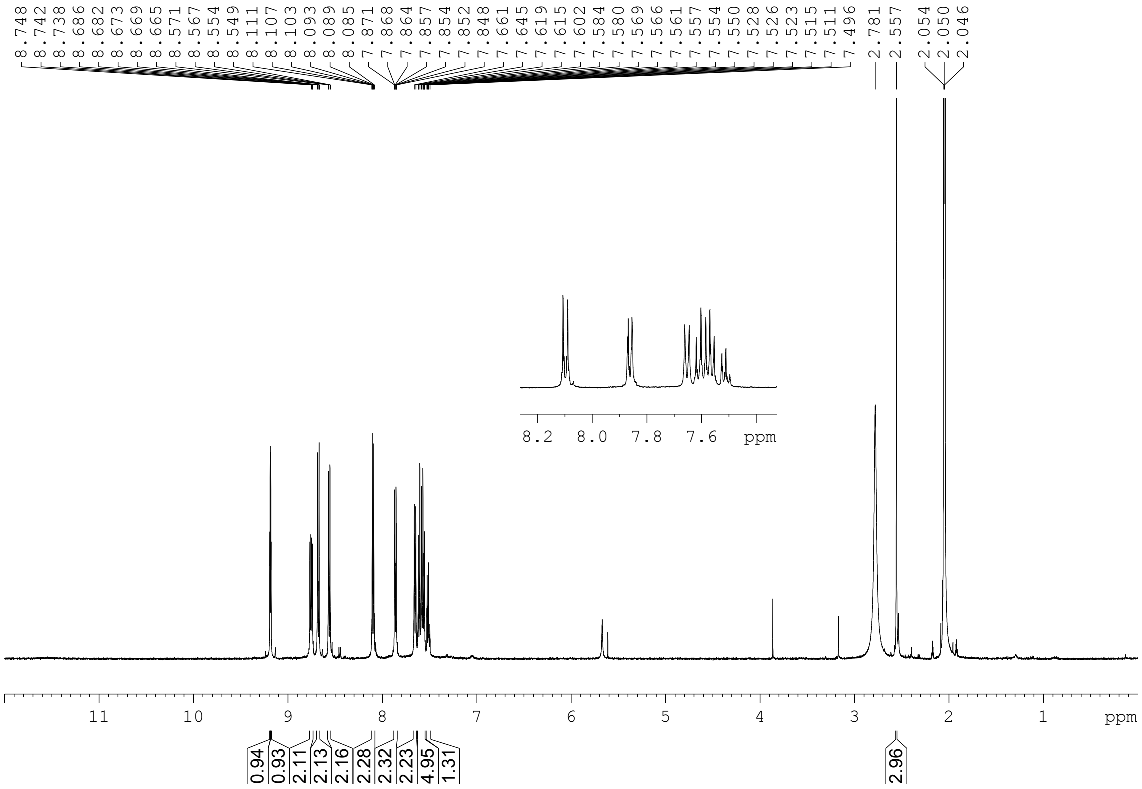


Fig. S25. Compound **24**: ^{13}C NMR spectrum (acetone-d_6 125 MHz)

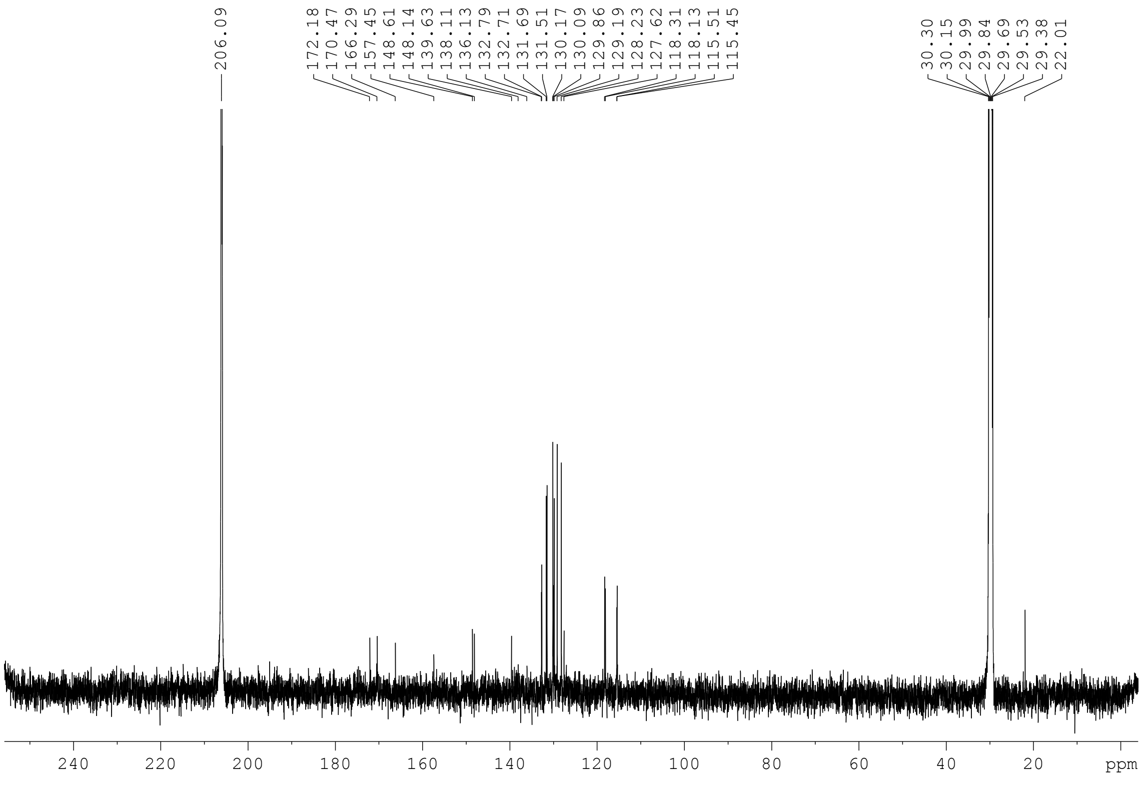


Fig. S26. Compound **25**: ^{1}H NMR spectrum (DMSO-d_6 500 MHz)

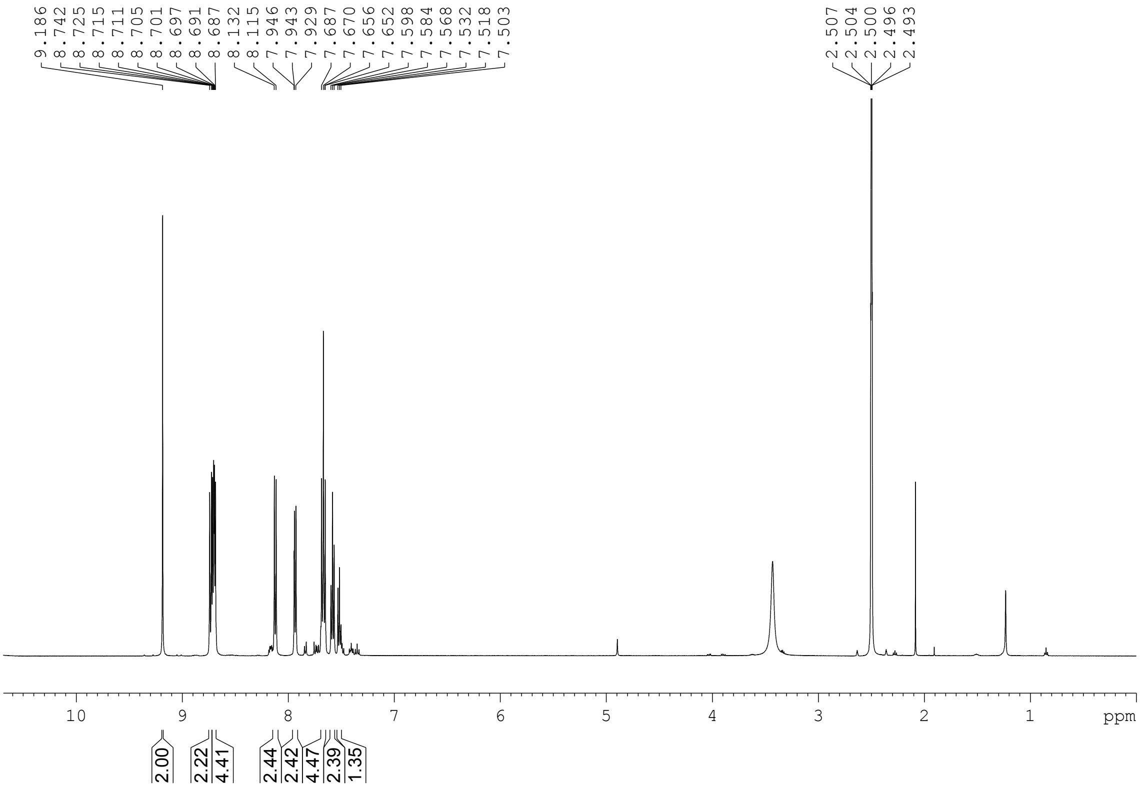


Fig. S27. Compound **25**: ^{13}C NMR spectrum (DMSO-d_6 125 MHz)

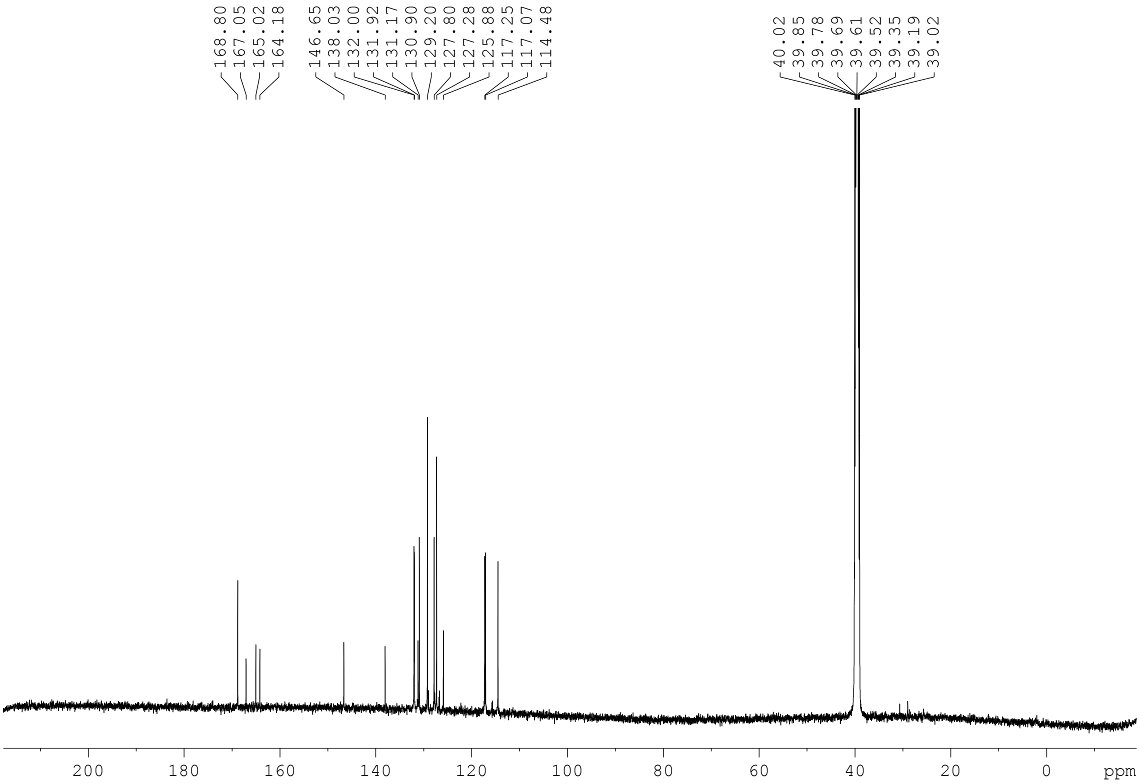


Fig. S28. Compound **27**: ^{1}H NMR spectrum (DMSO-d_6 500 MHz)

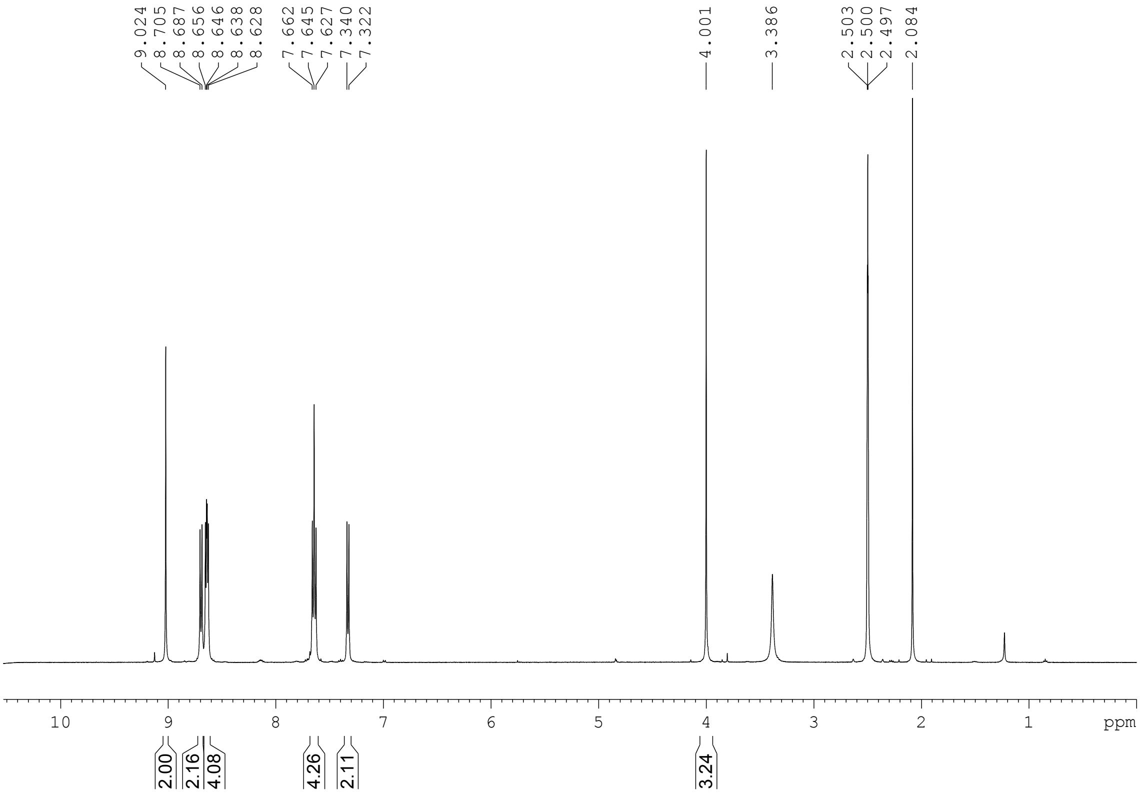


Fig. S29. Compound **27**: ^{13}C NMR spectrum (DMSO-d_6 125 MHz)

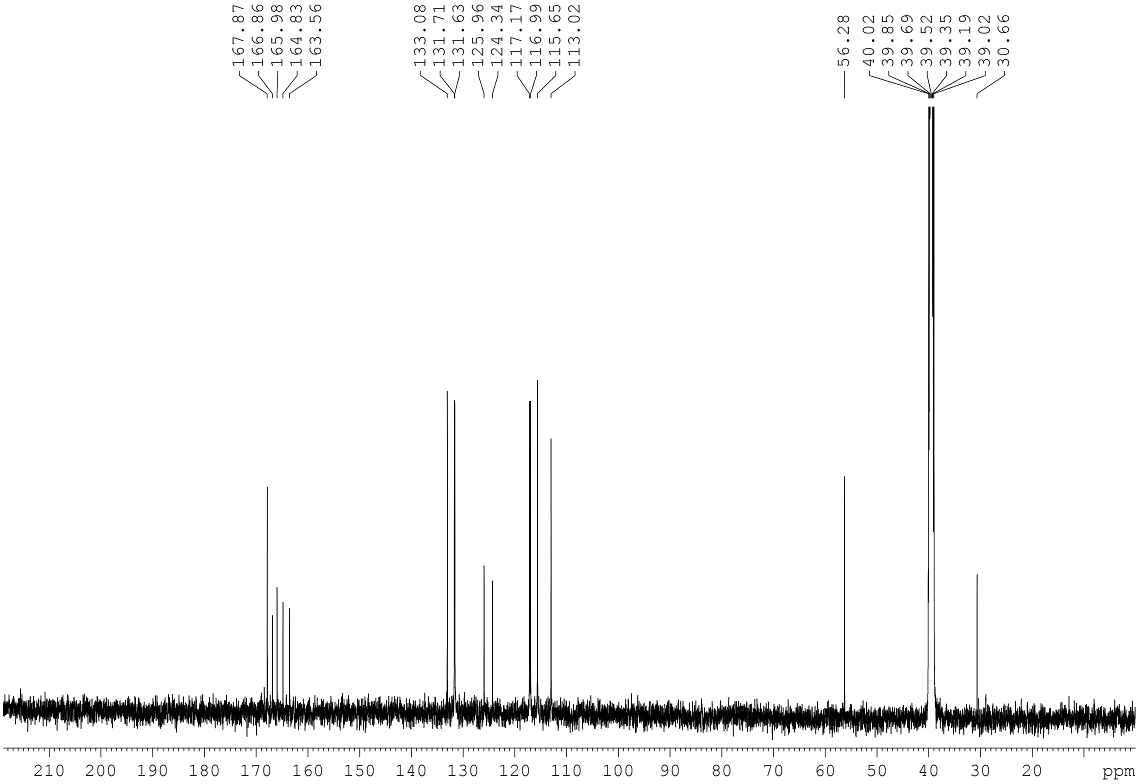


Fig. S30. Compound **28**: ^{1}H NMR spectrum (acetone-d_6 500 MHz)

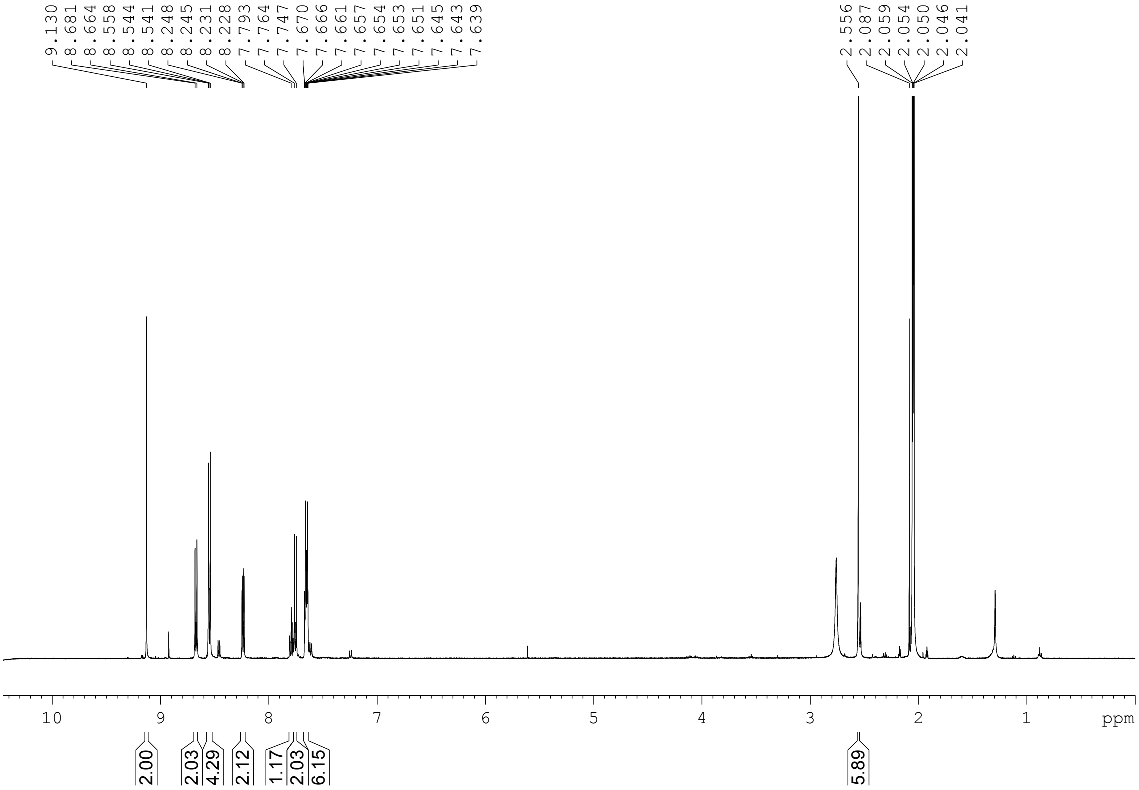
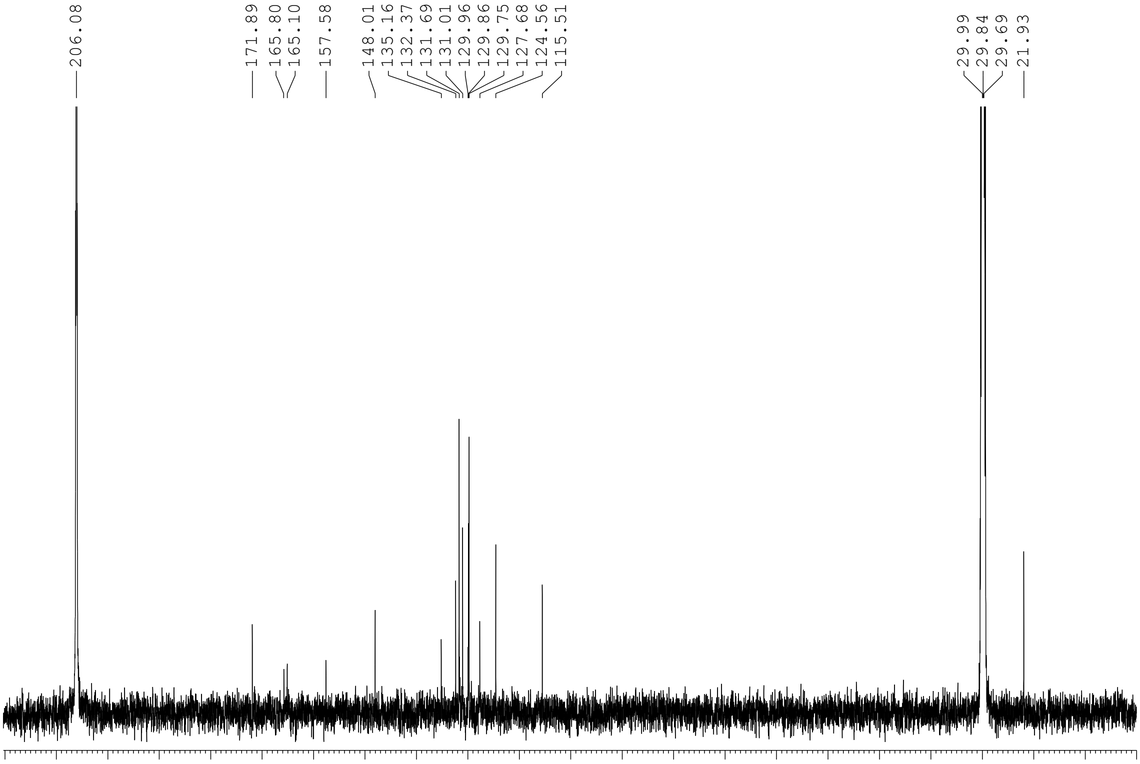


Fig. S31. Compound **28**: ^{13}C NMR spectrum (acetone-d_6 125 MHz)



15. ^{19}F NMR spectra of pyrylium salts:

Fig. S32. Compound **10**: ^{19}F NMR spectrum (470 MHz)

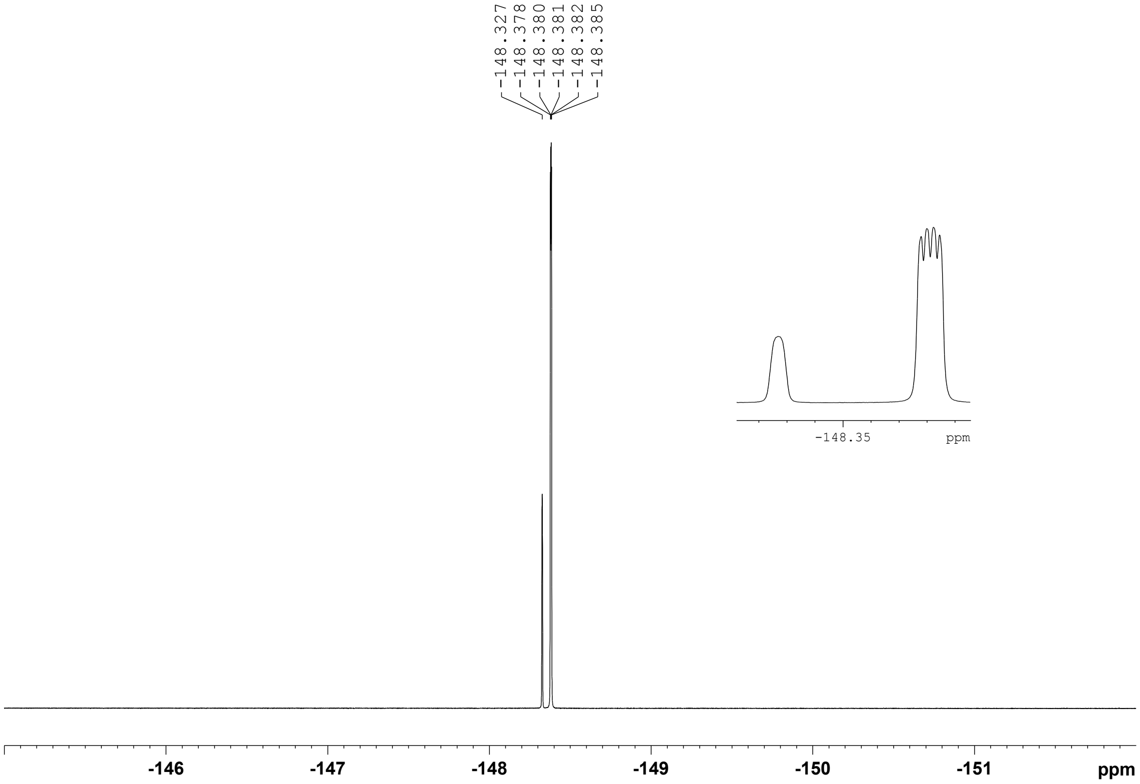


Fig. S33. Compound **11**: ^{19}F NMR spectrum (470 MHz)

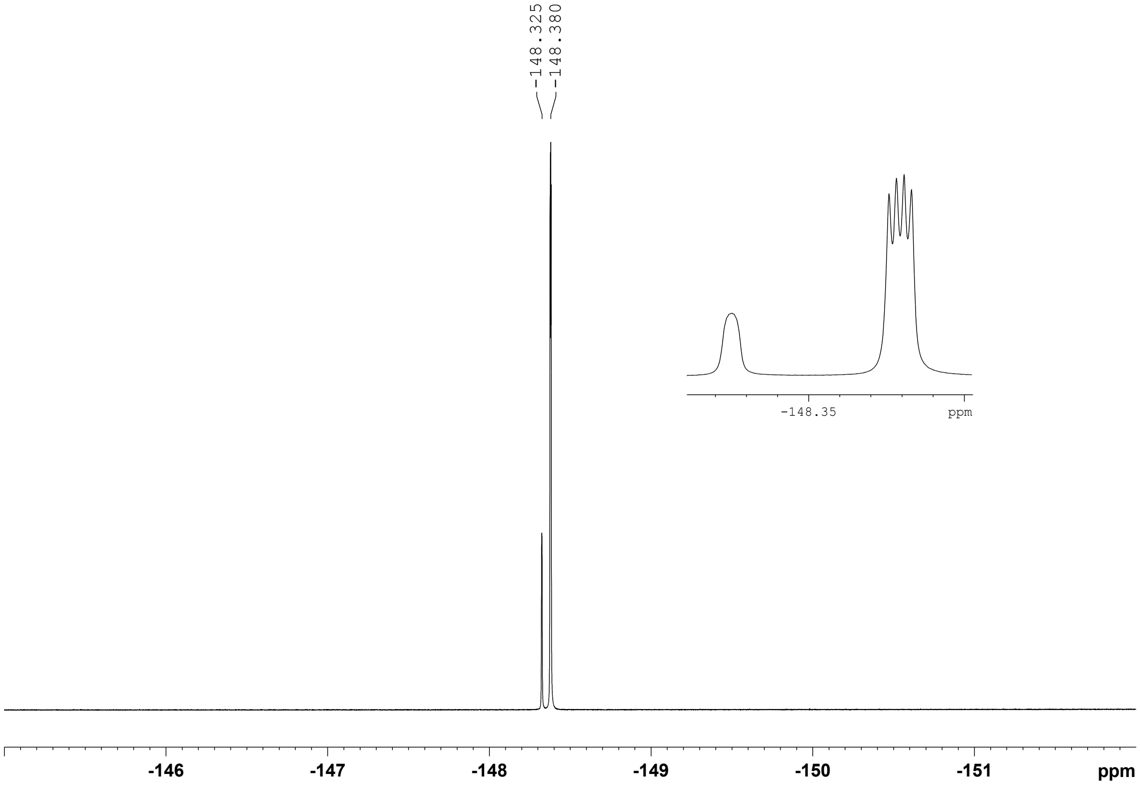


Fig. S34. Compound **12**: ^{19}F NMR spectrum (470 MHz)

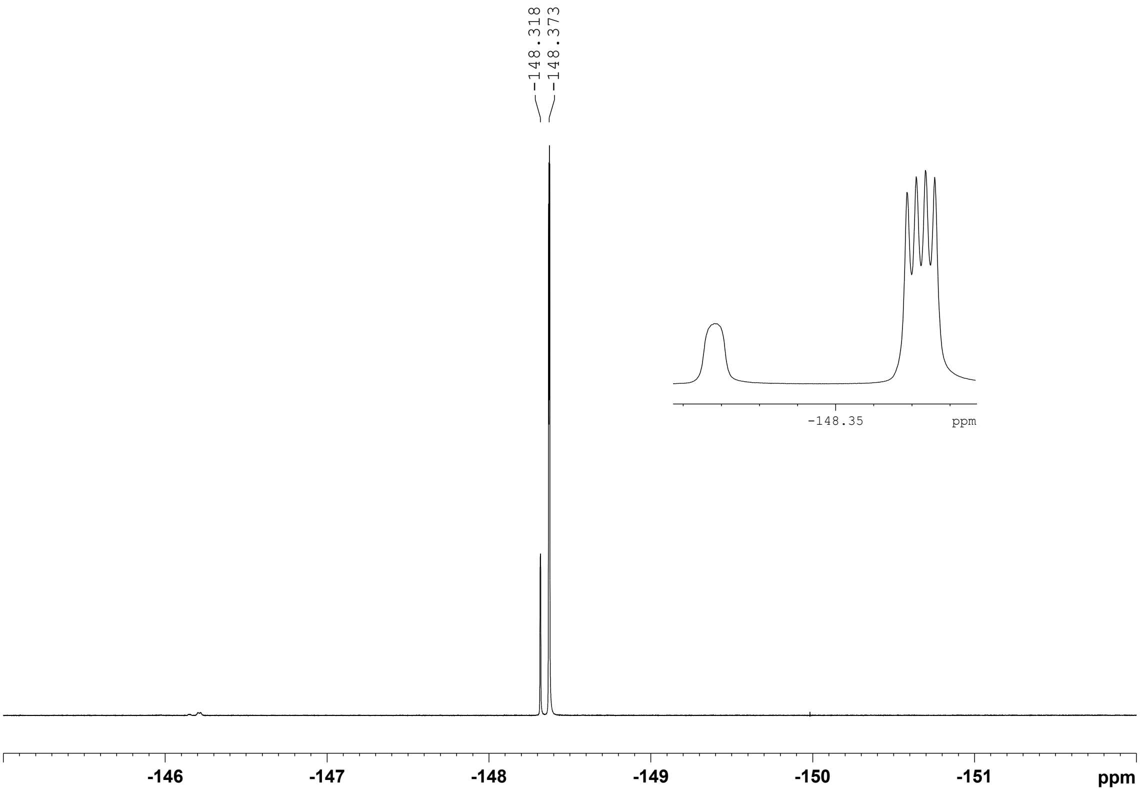


Fig. S35. Compound **13**: ^{19}F NMR spectrum (470 MHz)

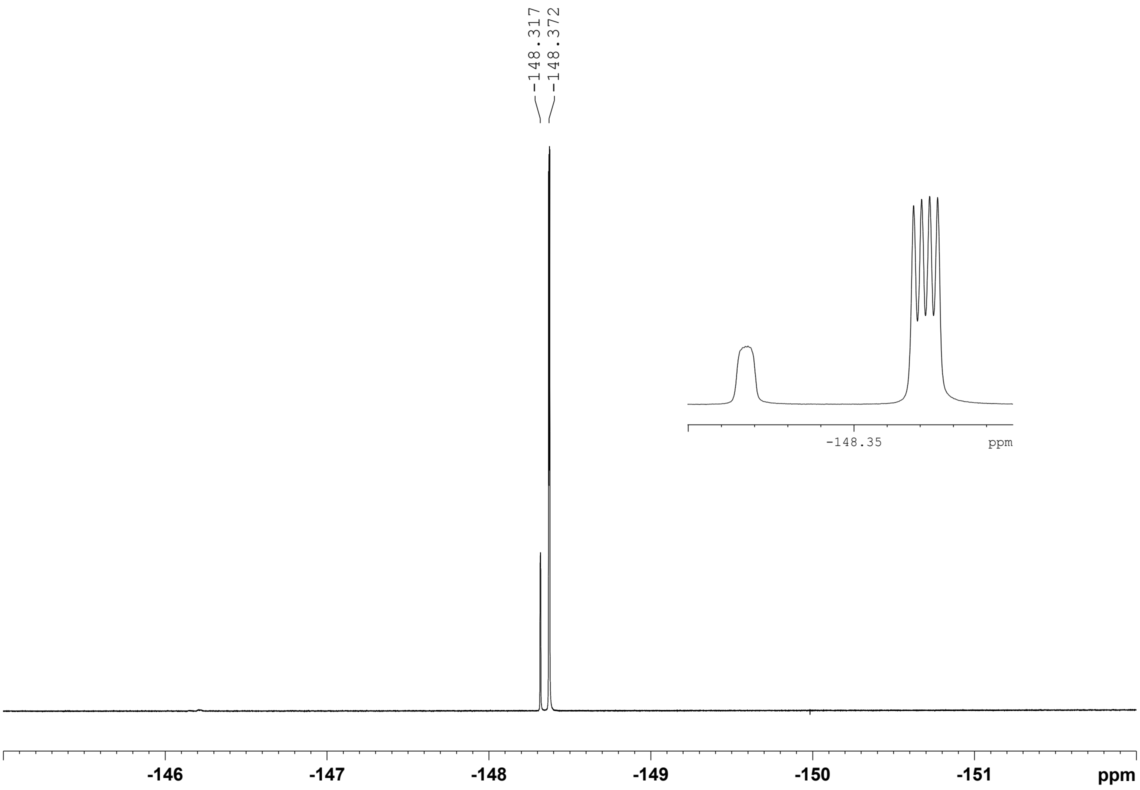


Fig. S36. Compound **14**: ^{19}F NMR spectrum (470 MHz)

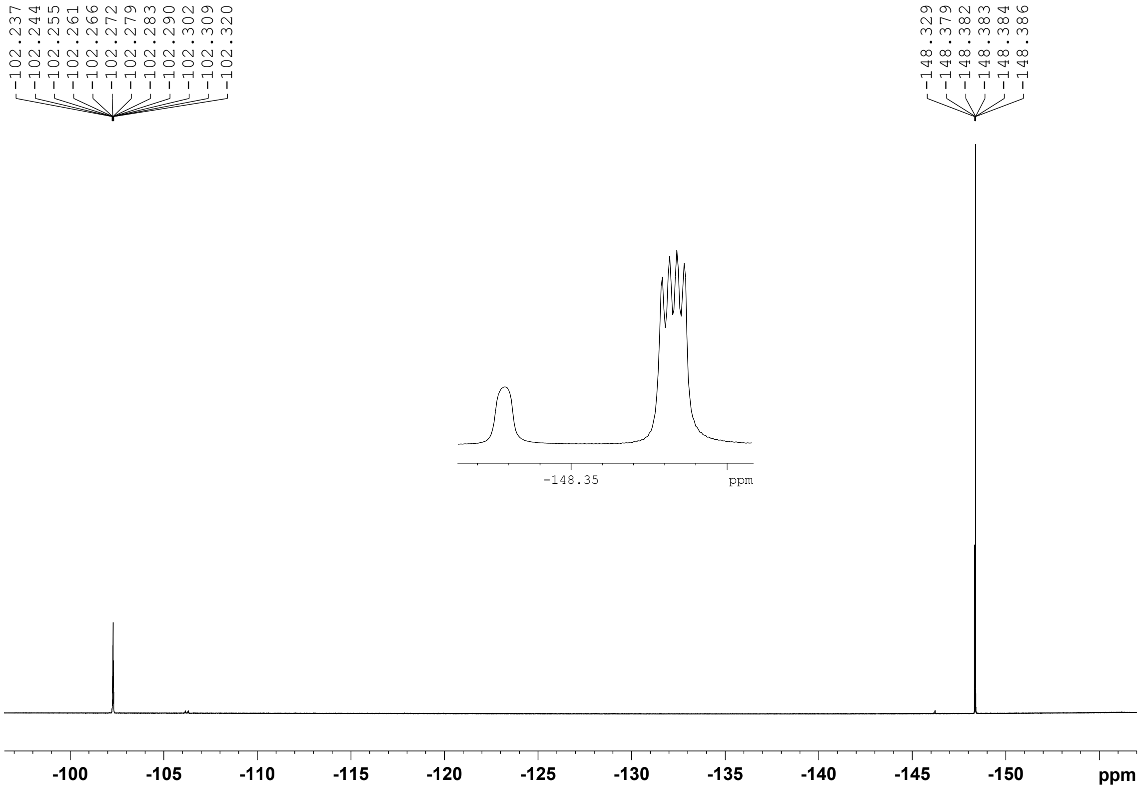


Fig. S37. Compound **15**: ^{19}F NMR spectrum (470 MHz)

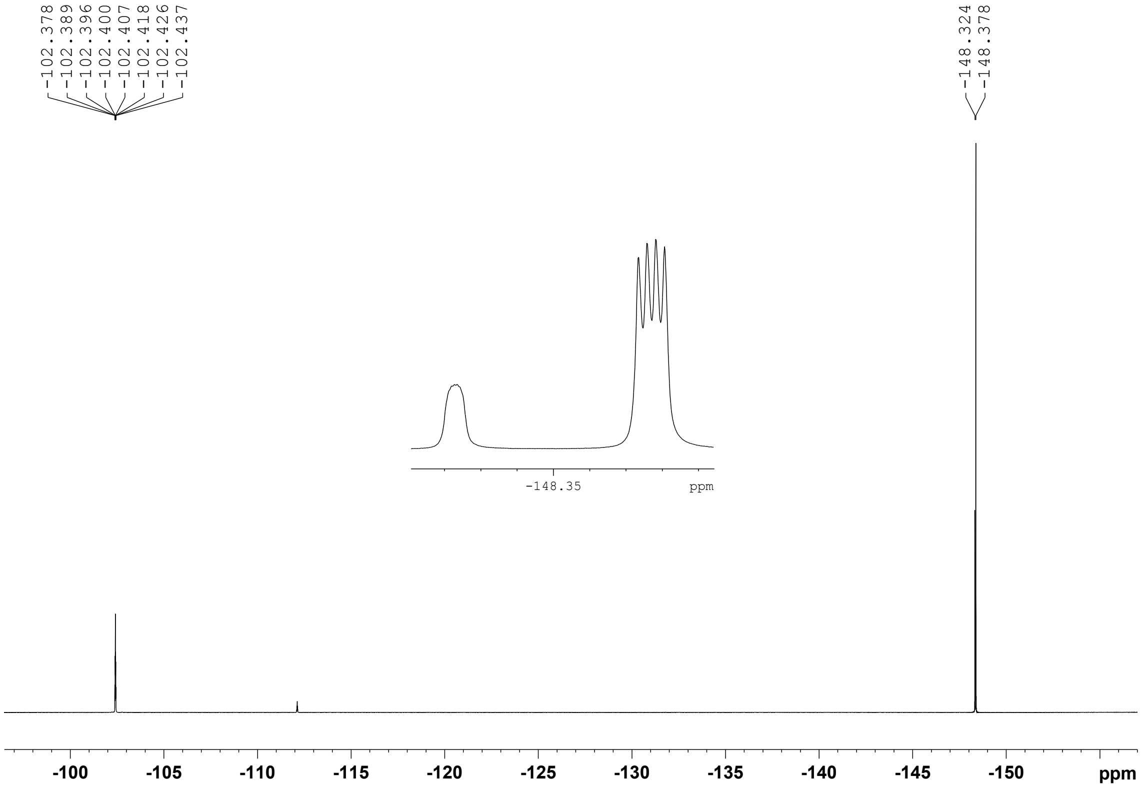


Fig. S38. Compound **16**: ^{19}F NMR spectrum (470 MHz)

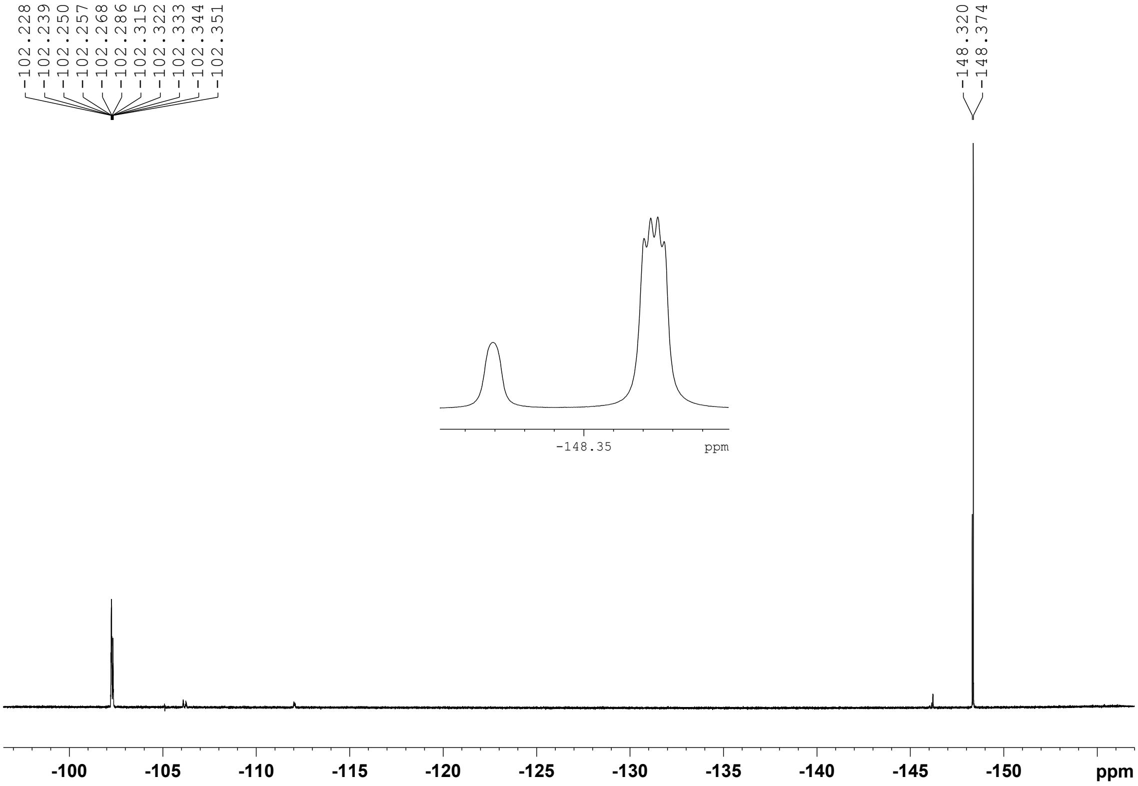


Fig. S39. Compound **17**: ^{19}F NMR spectrum (470 MHz)

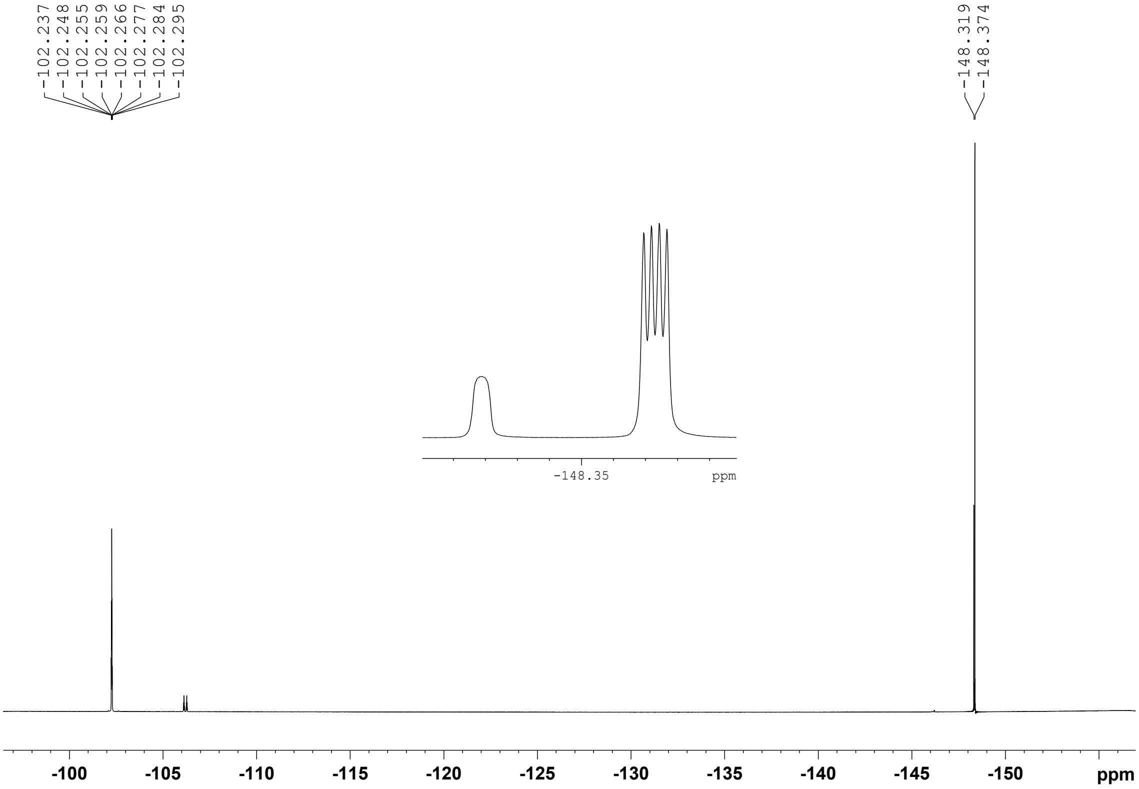


Fig. S40. Compound **18**: ^{19}F NMR spectrum (470 MHz)

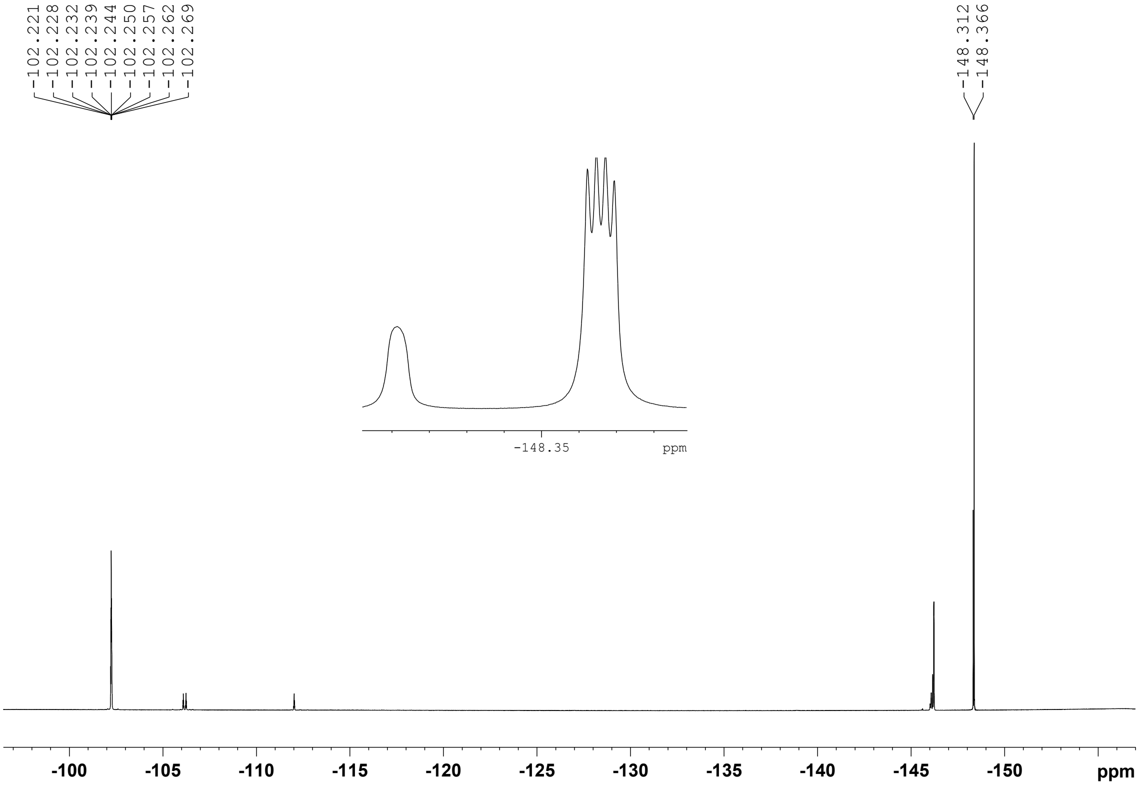


Fig. S41. Compound **19**: ^{19}F NMR spectrum (470 MHz)

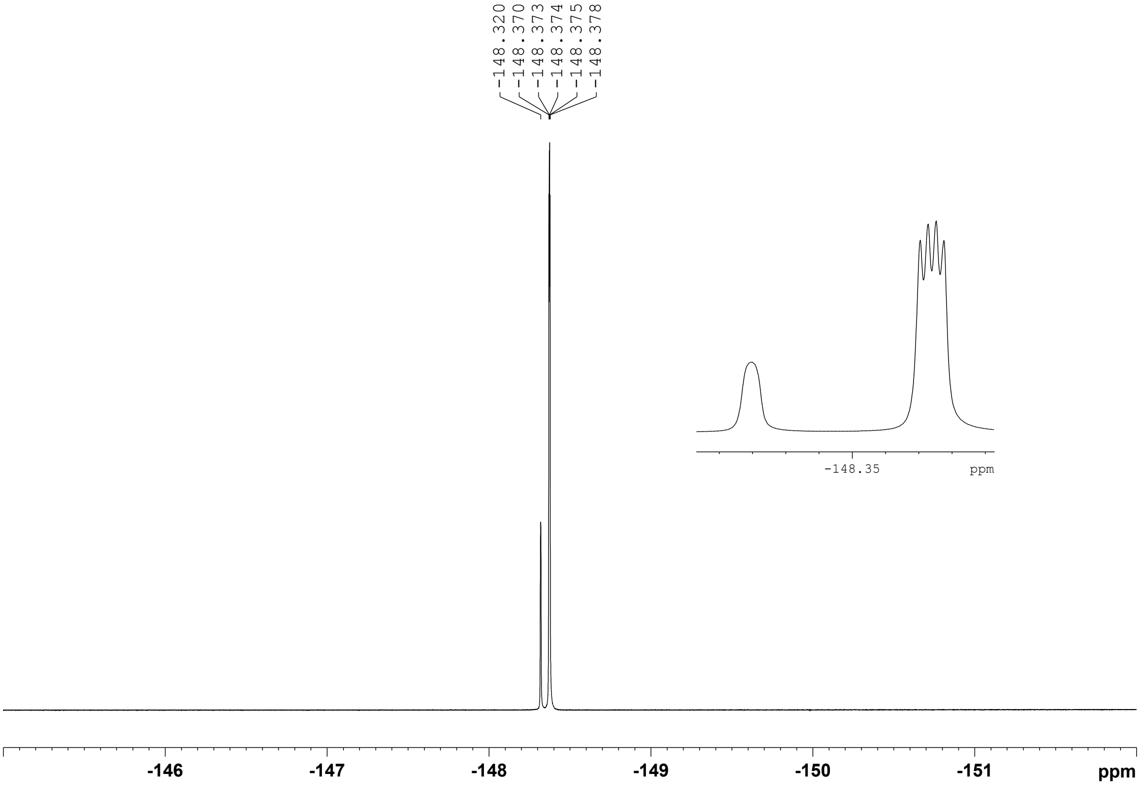


Fig. S42. Compound **22**: ^{19}F NMR spectrum (470 MHz)

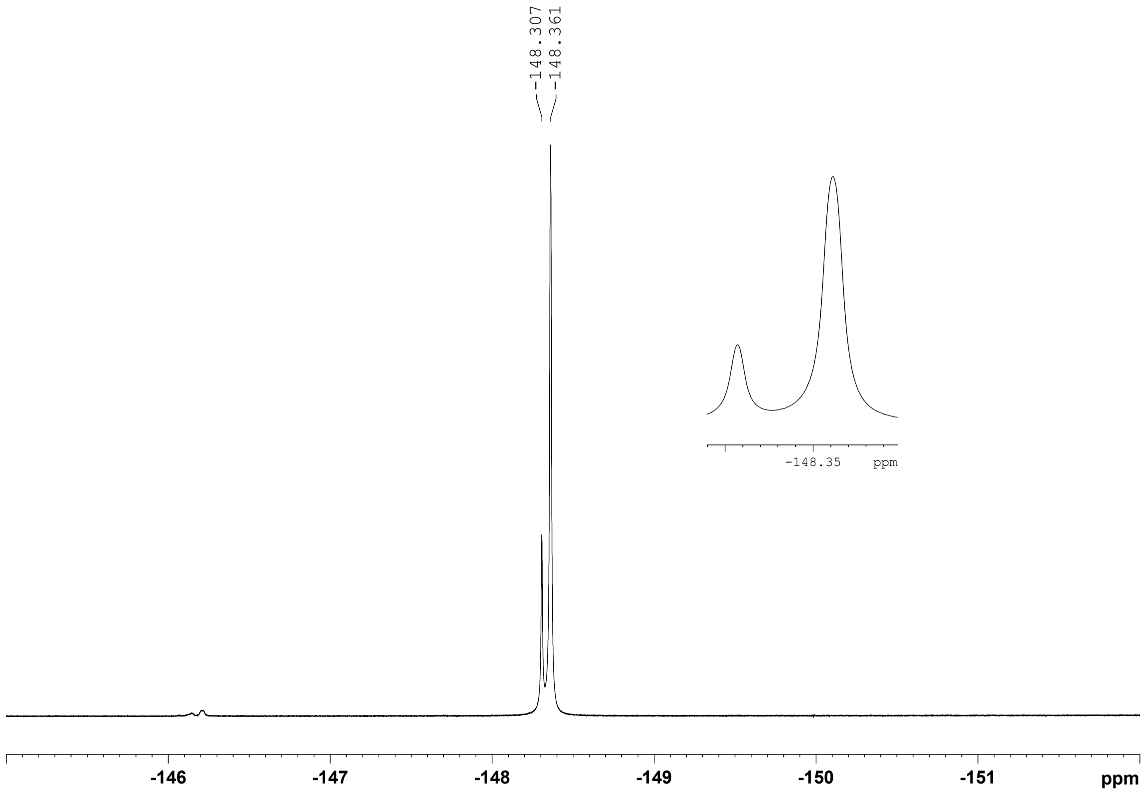


Fig. S43. Compound **23**: ^{19}F NMR spectrum (470 MHz)

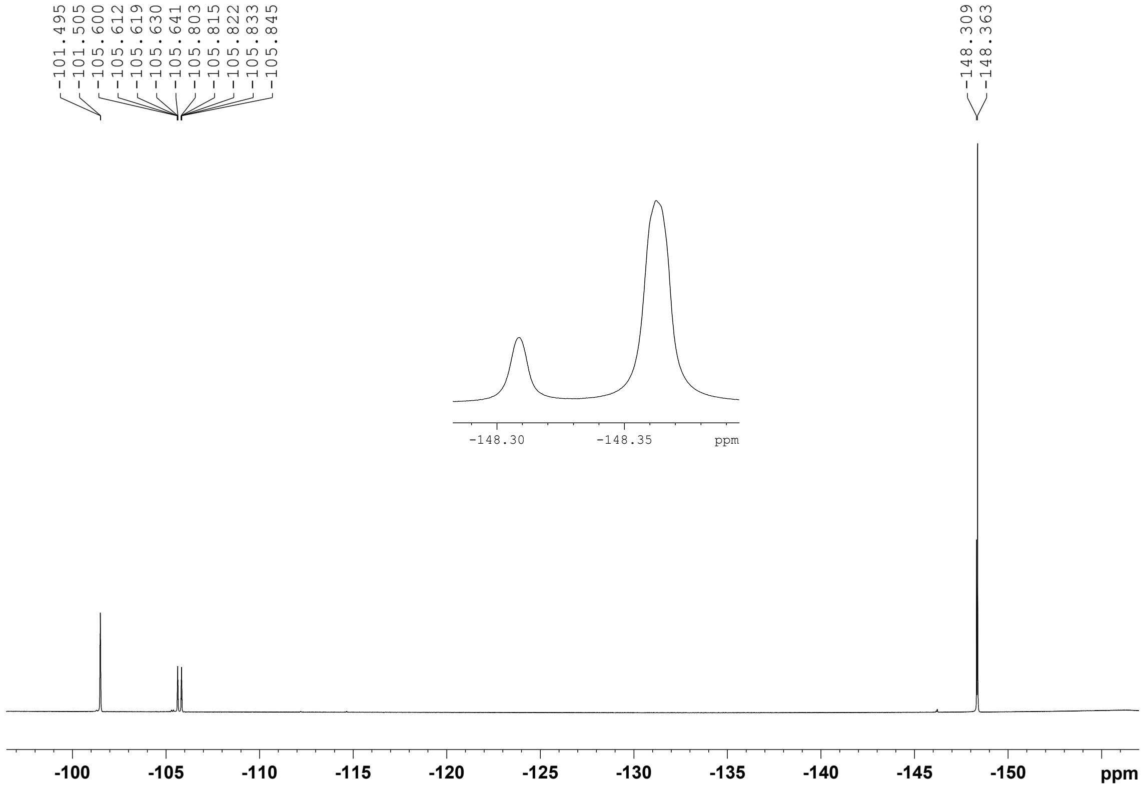


Fig. S44. Compound **25**: ^{19}F NMR spectrum (470 MHz)

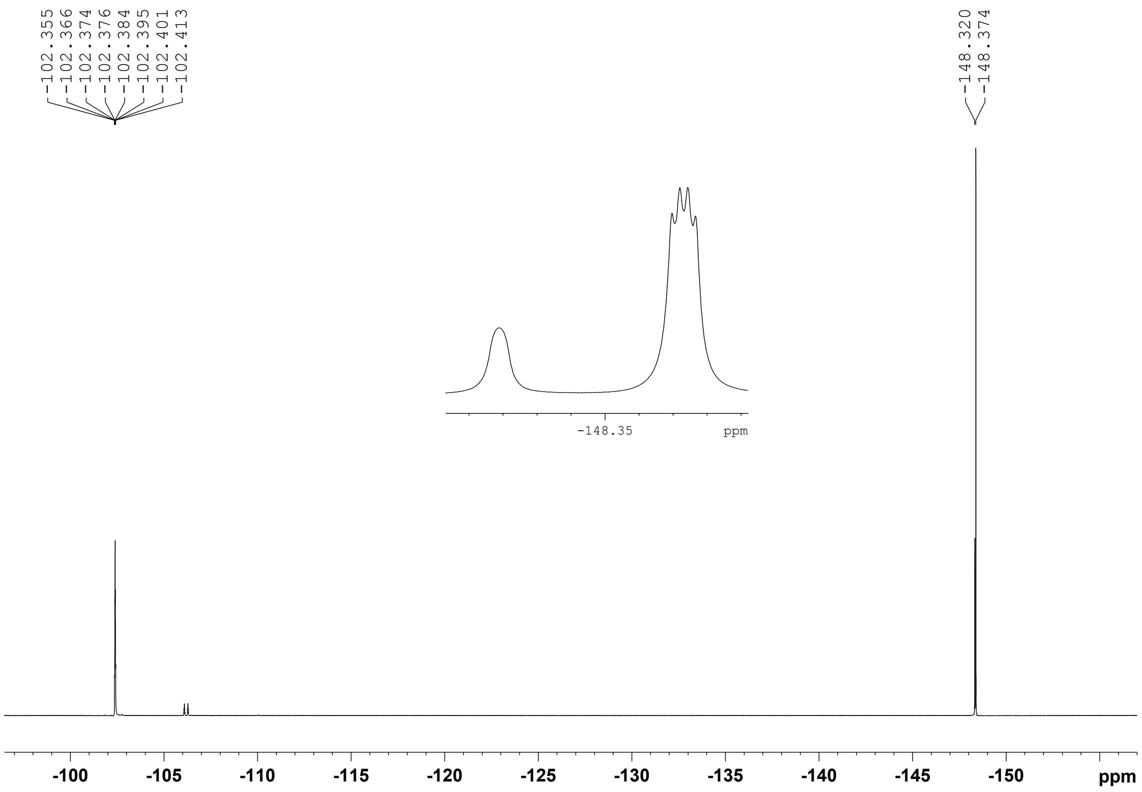


Fig. S45. Compound **26**: ^{19}F NMR spectrum (470 MHz)

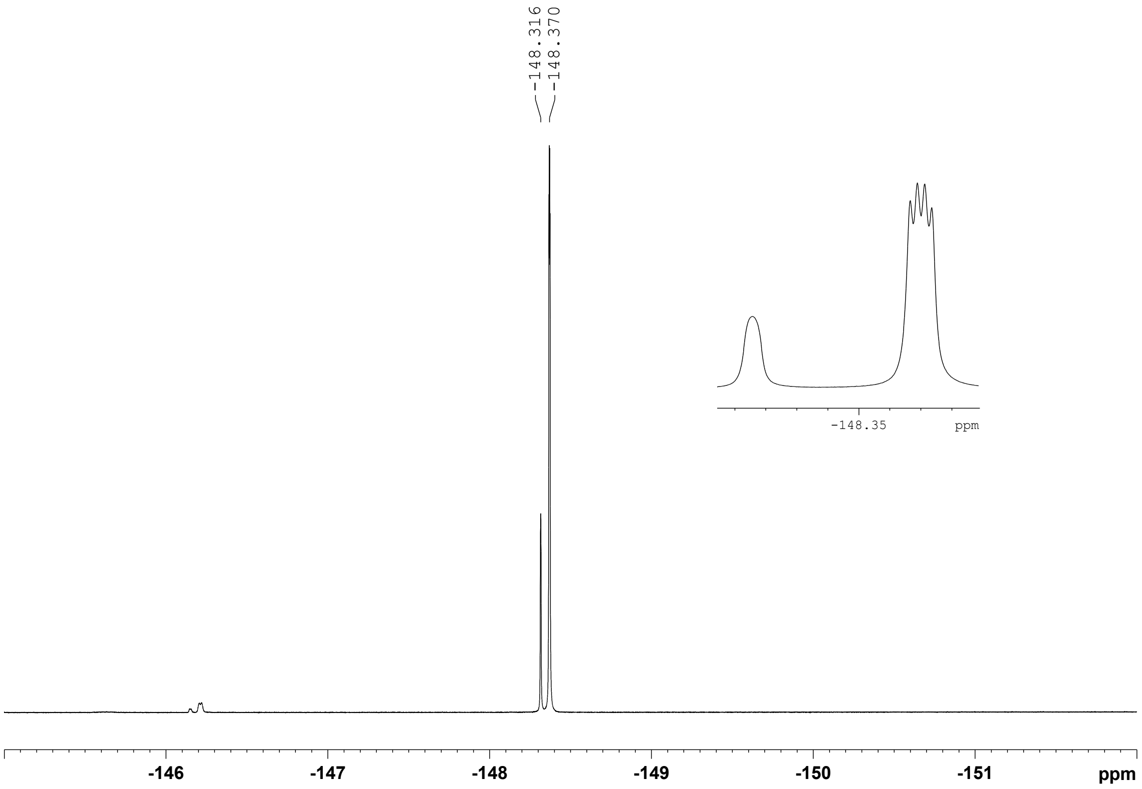


Fig. S46. Compound **27**: ^{19}F NMR spectrum (470 MHz)