Photorearrangement of dihetarylethenes as tool for benzannulation of heterocycles

Andrey G. Lvov,[1] Alexey M. Kavun,[1,2] Vadim V. Kachala,[1] Konstantin A. Lyssenko,[3]*

Valerii Z. Shirinian[1]

[1] N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky prospect, Moscow, Russian Federation, e-mail: lvov-andre@yandex.ru

[2] Higher Chemical College, D. I. Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, Moscow, Russian Federation

[3] Department of Chemistry, Lomonosov Moscow State University, 119992 Moscow, Russian Federation

Table of contents

I. General methods

General. Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C{^{1}H} NMR) were recorded in deuterated solvents on spectrometers working at 300.13 or 600.13 MHz for ^{1}H and 75.47 or 150.90 MHz for ^{13}C{^{1}H}. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; m, multiplet; br, broad), coupling constant in hertz (Hz), integration, and assignment. Mass spectra were recorded using electron impact ionization (EI, 70 eV, direct inlet probe). High-resolution mass spectra were obtained from a TOF mass spectrometer with an ESI source. All chemicals and solvents were purchased from commercial sources and used without further purification. Silica column chromatography was performed using silica gel 60 (70−230 mesh); TLC analysis was conducted on silica gel 60 F_{254} plates.

Photochemical synthesis. Photochemical reactions were performed with stirring in commercial 12 mL flat-bottomed glass vessels (borosilicate glass). The irradiation was carried out by two 365 nm UV lamps (8W; Vilber Lourmat, model VL-8.LC) without additional filters. The distance between two UV lamps was 3.5 cm, and the vessels were located midway between them.

^{1}H NMR monitoring. Experiments were performed by irradiation with one or two 8W 365 nm UV lamps.

X-ray crystallography. Suitable for X-ray crystallography single crystals were obtained by slow recrystallization from DMSO-d_6/DCM solutions. X-ray diffraction data for all studied complexes were collected on a SMART APEX II area-detector diffractometer (graphite monochromator, ω-scan technique), using $Mo_{K\alpha}$-radiation (0.71073 Å). The intensity data were integrated by the SAINT program[1] and were corrected for absorption and decay using SADABS.[2] All structures were solved by direct methods using SHELXS[3], and were refined on F^2 using SHELXL-2014/2017.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H hydrogen atoms were placed in ideal calculated positions while NH and OH ones were located from the Fourier density synthesis. All hydrogen atoms were refined as riding atoms. Crystal data, data collection and structure refinement details are summarized in Tables S1-7. Crystal structures were analyzed by OLEX2 program.[5]

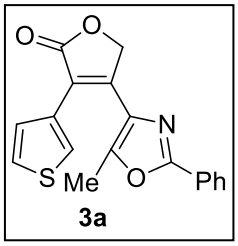
II. Synthesis

II.1. Synthesis of dihetarylethenes

Dihetarylethene 24 were synthesized according literature method[6] from ethyl 3-oxo-4-(thiophen-3-yl)butanoate.

Synthesis of dihetarylethenes 3, 6-12. To the solution of 3-hetarylacetic acid **1** (4.3 mmol) in DMF (7 ml) potassium carbonate K_2CO_3 (0.89 g, 6.4 mmol) was added. The suspension was stirred for 10 min and corresponding 2-bromo-1-(hetaryl)ethanone **2** (4.7 mmol) was added. Argon was passed through the reaction mixture for 30 min and then the suspension was heated at 80 °C until reaction completion (TLC control). The reaction mixture was poured into water (150 mL), and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water (2 x 100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography by gradient system petroleum ether/ethyl acetate (3:1 → 1:1).

*4-(5-Methyl-2-phenyloxazol-4-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**3a**).*



3a

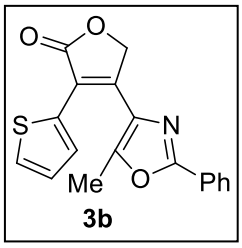
Yellow powder, 59% yield (819 mg); mp 161-163 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 5.20 (s, 2H), 7.30-7.39 (m, 2H), 7.45-7.55 (m, 3H), 7.87-7.92 (m, 1H), 7.99-8.06 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.1, 70.8, 121.0, 125.5, 126.3 (2C), 126.6 (2C), 127.4, 128.9 (2C), 129.1, 130.3, 130.8, 147.2, 148.8, 161.1, 173.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{14}NO_3S$ 324.0689; Found 324.0701.

*4-(5-Methyl-2-phenyloxazol-4-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**3b**).*



3b

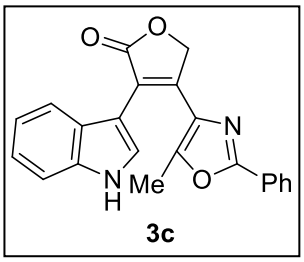
Yellow powder, 73% yield (1.01 g); mp 140-143 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3H), 5.20 (s, 2H), 7.07-7.16 (m, 1H), 7.43 (d, J = 4.8 Hz, 1H), 7.46-7.54 (m, 3H), 7.57-7.63 (m, 1H), 8.00-8.08 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.4, 71.1, 120.2, 126.3 (2C), 126.7, 127.0, 127.7, 128.9 (3C), 129.0, 130.8, 130.9, 146.5, 148.8, 161.2, 172.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{14}NO_3S$ 324.0689; Found 324.0687.

*3-(1H-Indol-3-yl)-4-(5-methyl-2-phenyloxazol-4-yl)furan-2(5H)-one (**3c**).*



3c

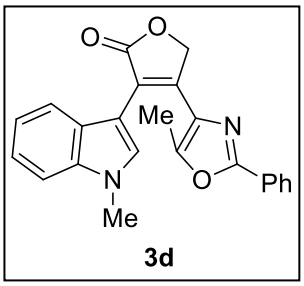
Brown powder, 64% yield (0.98 g); mp 197-199 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.65 (s, 3H), 5.34 (s, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.51-7.57 (m, 3H), 7.75-7.78 (s, 1H), 7.88-7.95 (m, 2H), 11.60 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 11.7, 71.0, 105.3, 112.5, 119.7, 119.8, 119.9, 122.0, 125.6, 126.3 (2C), 126.6, 127.8, 129.6 (2C), 130.0, 131.3, 136.2, 145.2, 149.6, 160.1, 173.8.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_3$ 357.1234; Found 357.1230.

*3-(1-Methyl-1H-indol-3-yl)-4-(5-methyl-2-phenyloxazol-4-yl)furan-2(5H)-one (**3d**).*



3d

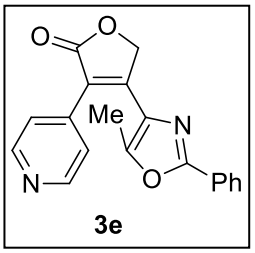
Yellow powder, 35% yield (557 mg); mp 181-182 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3H), 3.89 (s, 3H), 5.32 (s, 2H), 6.98 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.9 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.46-7.54 (m, 3H), 7.73 (s, 1H), 8.00-8.09 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.7, 33.2, 71.3, 105.0, 109.7, 119.6, 120.1, 120.2, 122.1, 125.8, 126.3 (2C), 126.9, 128.9 (2C), 130.0, 130.6, 131.0, 136.6, 144.1, 149.3, 160.8, 174.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{19}N_2O_3$ 371.1390; Found 371.1386.

*4-(5-Methyl-2-phenyloxazol-4-yl)-3-(pyridin-4-yl)furan-2(5H)-one (**3e**).*



3e

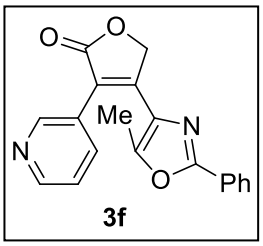
Yellow powder, 34% yield (465 mg); mp 231-234 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 3H), 5.30 (s, 2H), 7.45-7.53 (m, 3H), 7.54-7.63 (m, 2H) 7.94-8.01 (m, 2H), 8.60-8.90 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.7, 70.8, 126.2 (2C), 126.3, 128.5, 129.0 (2C), 131.1, 131.3, 139.5 (2C), 149.1, 149.5, 151.8, 168.8.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1091.

4-(5-Methyl-2-phenyloxazol-4-yl)-3-(pyridin-3-yl)furan-2(5H)-one ***(3f)****.*



3f

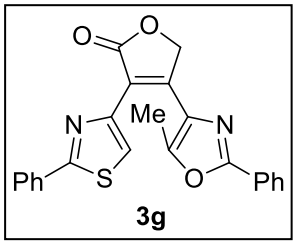
Pale brown powder, 55% yield (752 mg); mp 153-156 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3H), 5.27 (s, 2H), 7.40 (dd, J = 7.8, 5.0 Hz, 1H), 7.43-7.50 (m, 3H), 7.89-8.00 (m, 3H), 8.63 (d, J = 4.1 Hz, 1H), 8.77 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.4, 70.8, 122.1, 123.3, 126.3 (2C), 126.4, 127.0, 128.7, 128.9 (2C), 130.9, 136.7, 148.9, 149.5, 150.1, 150.3, 161.1, 172.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1070.

*4-(5-Methyl-2-phenyloxazol-4-yl)-3-(2-phenylthiazol-4-yl)furan-2(5H)-one (****3g****).*



3g

Pale yellow crystals, 54% yield (929 mg); mp 181-184 °C.

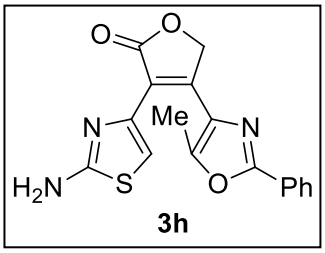
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 5.29 (s, 2H), 7.40-7.45 (m, 3H), 7.48-7.54 (m, 3H), 7.84-7.90 (m, 2H), 8.05-8.10 (m, 2H), 8.27 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.9, 71.3, 118.9, 120.7, 126.3 (2C), 126.4 (2C), 126.9, 128.8 (2C), 129.0 (2C), 129.3, 130.3, 130.6, 133.2, 146.2, 148.9, 150.6, 160.5, 167.2, 172.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{17}N_2O_3S$ 401.0954; Found 401.0943.

Anal. Calcd for $C_{23}H_{16}N_2O_3S$: C, 68.98; H, 4.03; N, 7.00. Found: C, 67.89; H, 3.82; N, 7.08.

*3-(2-Aminothiazol-4-yl)-4-(5-methyl-2-phenyloxazol-4-yl)furan-2(5H)-one (****3h****).*



3h

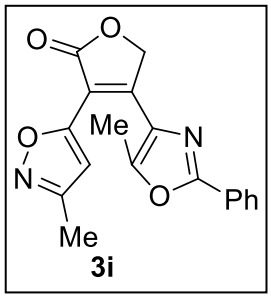
Yellow powder, 23% yield (335 mg); mp 201-202 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 5.19 (s, 2H), 5.41 (br s, 2H), 7.33 (s, 1H), 7.43-7.55 (m, 3H), 7.93-8.08 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.7, 71.0, 111.3, 119.0, 126.2 (2C), 126.8, 128.8 (2C), 129.0, 130.6, 140.7, 147.9, 150.5, 160.5, 167.2, 172.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{14}N_3O_3S$ 340.0750; Found 340.0745.

*4-(5-Methyl-2-phenyloxazol-4-yl)-3-(3-methylisoxazol-5-yl)furan-2(5H)-one (**3i**).*



3i

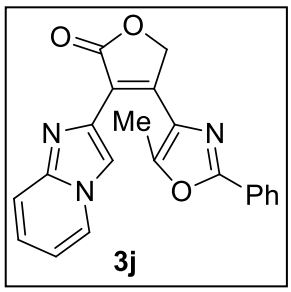
Yellow powder, 39% yield (540 mg); mp 182-184 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 2.39 (s, 3H), 5.39 (s, 2H), 6.91 (s, 1H), 7.43-7.61 (m, 3H), 7.97-8.13 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 11.4, 12.6, 71.7, 106.2, 112.8, 126.4 (2C), 126.5, 128.4, 128.9 (2C), 130.8, 151.5, 151.8, 160.3, 160.5, 161.0, 170.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_4$ 323.1026; Found 323.1026.

*3-(Imidazo[1,2-a]pyridin-2-yl)-4-(5-methyl-2-phenyloxazol-4-yl)furan-2(5H)-one (**3j**).*



3j

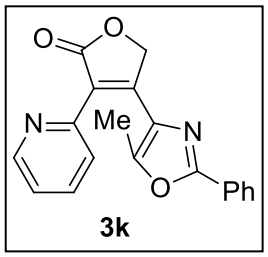
White powder, 21% yield (322 mg); mp 208-209 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 5.30 (s, 2H), 6.81 (t, J = 6.6 Hz, 1H), 7.13-7.24 (m, 1H), 7.40-7.51 (m, 3H), 7.56 (d, J = 9.1 Hz, 1H), 8.00-8.07 (m, 2H), 8.17 (d, J = 6.6 Hz, 1H), 8.41 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 13.5, 71.8, 112.7, 114.0, 117.5, 118.3, 125.1, 126.0, 126.3 (2C), 127.1, 128.8 (2C), 129.2, 130.4, 136.0, 144.9, 148.5, 150.7, 160.5, 173.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{21}H_{16}N_3O_3$ 358.1186; Found 358.1175.

*4-(5-Methyl-2-phenyloxazol-4-yl)-3-(pyridin-2-yl)furan-2(5H)-one (**3k**).*



3k

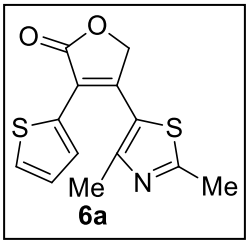
Brown powder, 61% yield (834 mg); mp 155-156 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88 (s, 3H), 5.29 (s, 2H), 7.24-7.34 (m, 1H), 7.41-7.49 (m, 3H), 7.77-7.84 (m, 2H), 7.91-8.00 (m, 2H), 8.69 (d, J = 4.4 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 12.3, 71.0, 123.3, 123.9, 125.1, 126.3 (2C), 126.7, 128.8 (2C), 128.9, 130.6, 136.7, 149.8, 150.0, 150.5, 152.1, 160.6, 172.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1068.

*4-(2,4-Dimethylthiazol-5-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**6a**).*



6a

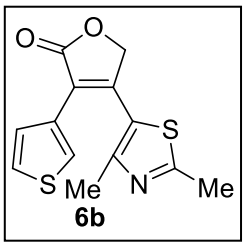
Yellow powder, 56% yield (667 mg); mp 124-125 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.73 (s, 3H), 4.98 (s, 2H), 7.02-7.12 (m, 1H), 7.40 (d, J = 4.6 Hz, 1H), 7.55-7.64 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 16.8, 19.4, 72.0, 120.2, 122.8, 127.2, 128.4, 129.0, 130.4, 145.2, 152.1, 167.9, 171.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{12}NO_2S_2$ 278.0304; Found 278.0305.

*4-(2,4-Dimethylthiazol-5-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**6b**).*



6b

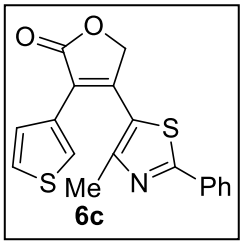
Yellow powder, 26% yield (310 mg); mp 119-122 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 2.72 (s, 3H), 5.00 (s, 2H), 7.14 (d, J = 4.9 Hz, 1H), 7.32 (dd, J = 4.9, 2.5 Hz, 1H), 7.92 (d, J = 2.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 16.8, 19.3, 71.6, 121.0, 122.9, 125.9, 126.7, 127.1, 129.7, 146.2, 152.2, 167.6, 172.2.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{12}NO_2S_2$ 278.0304; Found 278.0310.

*4-(4-Methyl-2-phenylthiazol-5-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**6c**).*



6c

Yellow powder, 66% yield (962 mg); mp 131-134 °C.

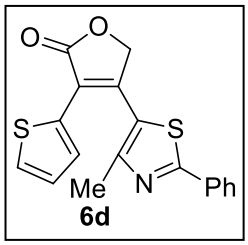
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 5.08 (s, 2H), 7.20 (d, J = 4.8 Hz, 1H), 7.32-7.37 (m, 1H), 7.44-7.53 (m, 3H), 7.89-8.01 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 17.2, 71.6, 121.4, 123.2, 126.0, 126.6 (2C), 126.7, 127.2, 129.1 (2C), 129.7, 130.9, 132.7, 146.0, 153.7, 169.0, 172.2.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{14}NO_2S_2$ 340.0460; Found 340.0449.

Anal. Calcd for $C_{18}H_{13}NO_2S_2$: C, 63.69; H, 3.86; N, 4.13. Found: C, 63.39; H, 3.87; N, 4.11.

*4-(4-Methyl-2-phenylthiazol-5-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**6d**).*



6d

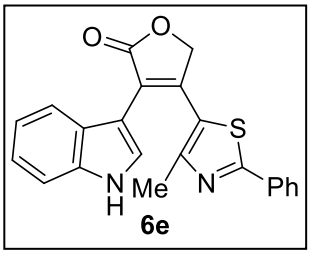
Yellow powder, 55% yield (801 mg); mp 134-136 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 5.06 (s, 2H), 7.02-7.16 (m, 1H), 7.35-7.56 (m, 4H), 7.61-7.71 (m, 1H), 7.89-8.02 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 17.1, 72.0, 120.6, 123.1, 126.7 (2C), 127.3, 128.5, 129.1 (2C), 129.2, 130.5, 130.8, 132.8, 144.8, 153.6, 169.4, 171.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{14}NO_2S_2$ 340.0460; Found 340.0459.

*3-(1H-Indol-3-yl)-4-(4-methyl-2-phenylthiazol-5-yl)furan-2(5H)-one (**6e**).*



Yellow powder, 66% yield (1.06 g); mp 227-230 °C.

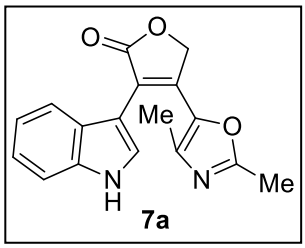
^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.16 (s, 3H), 5.43 (s, 2H), 6.84-6.89 (m, 1H), 6.97 (d, J = 7.9 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.40-7.53 (m, 4H), 7.69-7.83 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 17.6, 71.8, 104.8, 112.5, 119.8, 120.0, 121.2, 122.2, 123.6, 125.5, 126.5 (2C), 128.0, 129.8 (2C), 131.2, 132.7, 136.6, 145.9, 154.6, 167.5, 173.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{22}H_{17}N_2O_2S$ 373.1005; Found 373.1001.

Anal. Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.95; H, 4.33; N, 7.52. Found: C, 70.70; H, 4.03; N, 7.40.

*4-(2,4-Dimethyloxazol-5-yl)-3-(1H-indol-3-yl)furan-2(5H)-one (**7a**).*



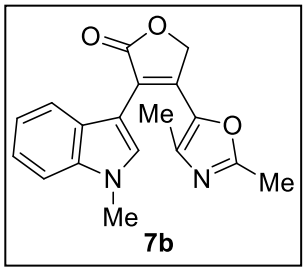
Dark yellow powder, 40% yield (506 mg); mp 213-215 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.82 (s, 3H), 2.22 (s, 3H), 5.35 (s, 2H), 6.90-7.03 (m, 2H), 7.08-7.17 (m, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.68-7.72 (m, 1H), 11.57 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.0, 14.0, 69.6, 105.2, 112.3, 117.6, 119.6, 120.2, 121.9, 126.2, 127.9, 136.2, 139.5, 139.7, 140.2, 162.5, 173.5.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{15}N_2O_3$ 295.1077; Found 295.1084.

*4-(2,4-Dimethyloxazol-5-yl)-3-(1-methyl-1H-indol-3-yl)furan-2(5H)-one (**7b**).*



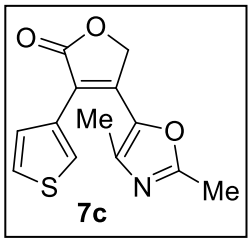
Yellow crystals, 44% yield (583 mg); mp 183-186 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75 (s, 3H), 2.35 (s, 3H), 3.87 (s, 3H), 5.18 (s, 2H), 6.97-7.08 (m, 2H), 7.18-7.27 (m, 1H), 7.36 (d, J = 7.9 Hz, 1H), 7.68 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.9, 14.0, 33.2, 69.5, 104.7, 109.7, 118.5, 120.0, 120.3, 122.1, 126.3, 131.3, 136.6, 137.9, 139.3, 139.6, 162.6, 173.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_3$ 309.1234; Found 309.1226.

*4-(2,4-Dimethyloxazol-5-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**7c**).*



7c

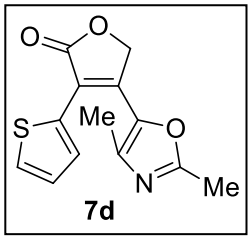
Pale yellow powder, 54% yield (606 mg); mp 177-178 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3H), 2.48 (s, 3H), 5.10 (s, 2H), 7.29 (d, J = 5.5 Hz, 1H), 7.32-7.38 (m, 1H), 7.91-7.86 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.5, 14.0, 69.1, 119.3, 125.1, 127.1, 127.7, 129.9, 138.9, 140.0, 141.0, 163.0, 172.5.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{12}NO_3S$ 262.0532; Found 262.0527.

*4-(2,4-Dimethyloxazol-5-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**7d**).*



7d

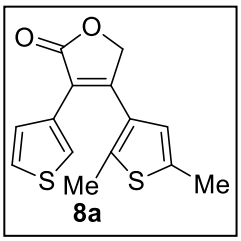
Pale yellow powder, 39% yield (438 mg); mp 115-116 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 2.50 (s, 3H), 5.11 (s, 2H), 7.07-7.14 (m, 1H), 7.46 (d, J = 4.9 Hz, 1H), 7.56 (d, J = 3.2 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.7, 14.0, 69.3, 118.2, 126.9, 128.1, 129.5, 130.6, 138.6, 140.0, 140.2, 163.1, 171.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{12}NO_3S$ 262.0532; Found 262.0529.

*4-(2,5-Dimethylthiophen-3-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**8a**).*



8a

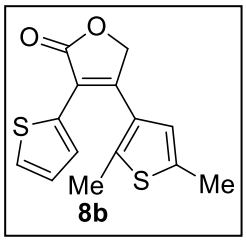
Pale brown powder, 79% yield (938 mg); mp 77-79 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 3H), 2.45 (s, 3H), 4.95 (s, 2H), 6.57 (s, 1H), 7.13 (d, J = 5.0 Hz, 1H), 7.25 (dd, J = 2.4, 5.0 Hz, 1H), 7.95 (d, J = 2.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.3, 15.1, 71.4, 121.5, 124.5, 125.3, 126.0, 126.6, 128.3, 130.5, 136.9, 138.3, 151.5, 173.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{13}O_2S_2$ 277.0351; Found 277.0356.

*4-(2,5-Dimethylthiophen-3-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**8b**).*



8b

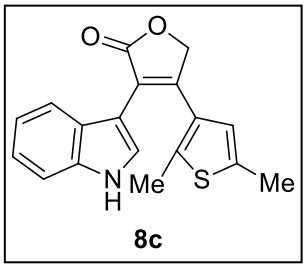
Brown powder, 87% yield (1.03 g); mp 110-112 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (s, 3H), 2.47 (s, 3H), 4.95 (s, 2H), 6.56 (s, 1H), 7.01-7.06 (m, 1H), 7.34 (d, J = 5.0 Hz, 1H), 7.61 (d, J = 3.6 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.3, 15.1, 71.7, 121.2, 124.3, 126.9, 127.4, 127.8, 128.0, 131.3, 137.0, 138.6, 150.6, 172.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{13}O_2S_2$ 277.0351; Found 277.0355.

*4-(2,5-Dimethylthiophen-3-yl)-3-(1H-indol-3-yl)furan-2(5H)-one (**8c**).*



8c

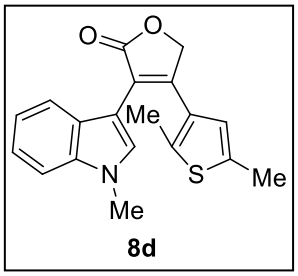
Pale yellow powder, 51% yield (678 mg); mp 201-203 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.74 (s, 3H), 2.37 (s, 3H), 5.22 (s, 2H), 6.72-6.83 (m, 2H), 6.87 (s, 1H), 7.02-7.11 (m, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 2.5 Hz, 1H), 11.49 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 14.6, 15.2, 71.7, 105.9, 112.2, 119.6, 119.9 (2C), 121.9, 125.5, 126.0, 127.3, 130.1, 136.3, 137.0, 137.3, 149.7, 174.1.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{16}NO_2S$ 310.0896; Found 310.0895.

*4-(2,5-Dimethylthiophen-3-yl)-3-(1-methyl-1H-indol-3-yl)furan-2(5H)-one (**8d**).*



8d

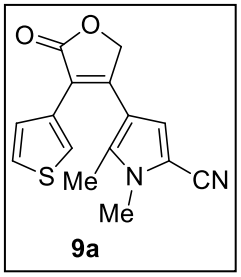
Red powder, 58% yield (806 mg); mp 142-143 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 3H), 2.45 (s, 3H), 3.85 (s, 3H), 5.08 (s, 2H), 6.69 (s, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.87-6.93 (m, 1H), 7.16-7.23 (m, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.79 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.6, 15.1, 33.1, 71.5, 105.5, 109.3, 119.9, 120.4, 120.5, 121.9, 124.9, 125.8, 129.6, 131.0, 136.7, 137.6, 137.7, 147.4, 174.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{18}NO_2S$ 324.1053; Found 324.1056.

*1,5-Dimethyl-4-(5-oxo-4-(thiophen-3-yl)-2,5-dihydrofuran-3-yl)-1H-pyrrole-2-carbonitrile (**9a**).*



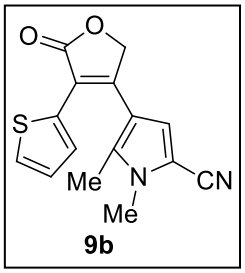
9a

Yellow powder, 64% yield (782 mg); mp 147-150 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (s, 3H), 3.69 (s, 3H), 4.95 (s, 2H), 6.81 (s, 1H), 7.12 (d, J = 4.9 Hz, 1H), 7.28-7.33 (m, 1H), 7.81-7.87 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.9, 33.0, 71.2, 105.5, 113.0, 113.6, 117.9, 120.4, 125.6, 126.1, 126.6, 130.5, 134.5, 149.6, 173.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found 285.0699.



*1,5-Dimethyl-4-(5-oxo-4-(thiophen-2-yl)-2,5-dihydrofuran-3-yl)-1H-pyrrole-2-carbonitrile (**9b**).*

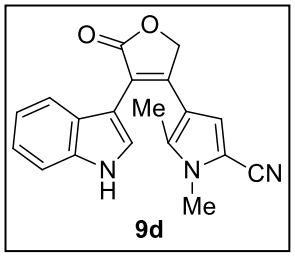
Yellow powder, 83% yield (1.01 g); mp 175-177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3H), 3.70 (s, 3H), 4.93 (s, 2H), 6.81 (s, 1H), 7.02-7.07 (m, 1H), 7.34 (d, J = 5.0 Hz, 1H), 7.53 (d, J = 3.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.0, 33.0, 71.6, 105.5, 113.1 (2C), 118.0, 120.1, 127.1, 127.2, 128.2, 131.2, 134.5, 149.1, 172.1.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found 285.0701.

Anal. Calcd for $C_{15}H_{12}N_2O_2S$: C, 63.36; H, 4.25; N, 9.85. Found: C, 62.98; H, 3.97; N, 9.83.

*4-(4-(1H-Indol-3-yl)-5-oxo-2,5-dihydrofuran-3-yl)-1,5-dimethyl-1H-pyrrole-2-carbonitrile (**9d**).*



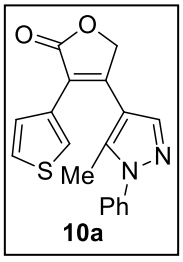
Yellow powder, 72% yield (981 mg); mp 243-246 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.72 (s, 3H), 3.52 (s, 3H), 5.24 (s, 2H), 6.77-6.90 (m, 2H), 7.05 (s, 1H), 7.06-7.13 (m, 1H), 7.44 (d, J = 8.1 Hz, 1H), 7.64 (d, J = 2.5 Hz, 1H), 11.49 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 11.9, 33.1, 71.4, 104.0, 105.7, 112.3, 114.0, 114.9, 117.9, 118.9, 119.5, 120.1, 121.9, 125.5, 127.1, 136.3, 136.6, 149.1, 174.2.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{16}N_3O_2$ 318.1237; Found 318.1244.

*4-(5-Methyl-1-phenyl-1H-pyrazol-4-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**10a**).*



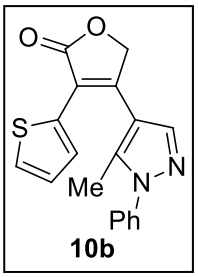
Yellow powder, 75% yield (1.04 g); mp 135-137 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 3H), 5.07 (s, 2H), 7.23-7.28 (m, 1H), 7.32-7.38 (m, 1H), 7.39-7.55 (m, 5H), 7.70 (s, 1H), 7.83-7.89 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.3, 70.9, 112.7, 120.1, 125.1 (2C), 125.7, 126.1, 126.8, 128.6, 129.3 (2C), 130.6, 137.9, 138.9 (2C), 148.5, 173.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_2S$ 323.0849; Found 323.0849.

*4-(5-Methyl-1-phenyl-1H-pyrazol-4-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**10b**).*



10b

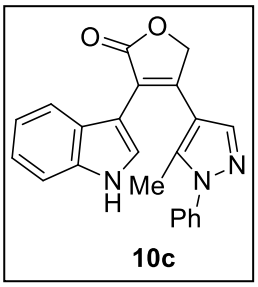
Pale yellow powder, 78% yield (1.08 g); mp 122-123 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3H), 5.06 (s, 2H), 7.04-7.14 (m, 1H), 7.31-7.66 (m, 7H), 7.73 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 12.1, 71.2, 104.8, 112.0, 119.7, 125.0 (2C), 126.9, 127.1, 128.1, 128.4, 129.1 (2C), 131.1, 137.8, 138.7, 147.7, 172.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_2S$ 323.0849; Found 323.0852.

*3-(1H-Indol-3-yl)-4-(5-methyl-1-phenyl-1H-pyrazol-4-yl)furan-2(5H)-one (**10c**).*



10c

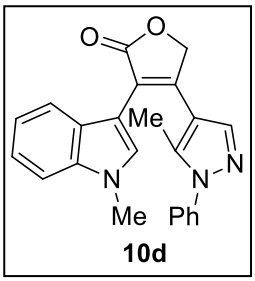
Pale brown powder, 55% yield (840 mg); mp 227-229 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.77 (s, 3H), 5.38 (s, 2H), 6.87-6.94 (m, 2H), 7.10-7.18 (m, 1H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.41-7.55 (m, 4H), 7.71 (d, *J* = 2.5 Hz, 1H), 7.75 (s, 1H), 11.54 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6): δ = 12.2, 71.1, 105.6, 112.5, 114.1, 117.8, 119.4, 120.1, 122.0, 125.4 (2C), 127.2, 128.8, 129.7 (2C), 136.3 (2C), 138.6, 139.1, 139.6, 147.9, 174.1.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{22}H_{18}N_3O_2$ 356.1394; Found 356.1392.

*4-(5-Methyl-1-phenyl-1H-pyrazol-4-yl)-3-(1-methyl-1H-indol-3-yl)furan-2(5H)-one (**10d**).*



10d

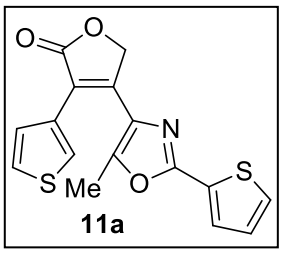
Pale yellow powder, 62% yield (1.04 g); mp 169-170 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.64 (s, 3H), 3.88 (s, 3H), 5.19 (s, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.93-7.00 (m, 1H), 7.21-7.28 (m, 3H), 7.34-7.47 (m, 4H), 7.75 (s, 1H), 7.76 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 12.2, 33.2, 71.1, 105.2, 109.6, 114.2, 118.9, 119.7, 120.6, 122.0, 125.2 (2C), 125.7, 128.4, 129.2 (2C), 130.9, 136.7, 138.4, 138.7, 139.0, 144.7, 174.4.

HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{23}H_{19}N_3O_2Na$ 392.1369; Found 392.1359.

*4-(5-Methyl-2-(thiophen-2-yl)oxazol-4-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**11a**).*



11a

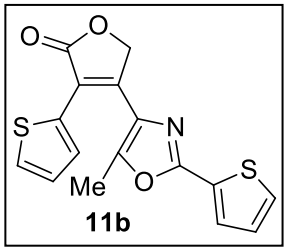
Light brown power, 40% yield (566 mg); mp 153-155 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3H), 5.18 (s, 2H), 7.10-7.20 (m, 1H), 7.24-7.40 (m, 2H), 7.48 (d, J = 4.4 Hz, 1H), 7.63-7.70 (m, 1H), 7.88 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.0, 70.9, 121.2, 125.6, 126.7, 127.3, 128.1 (2C), 128.9, 129.0 (2C), 130.2, 146.9, 148.3, 157.3, 173.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{12}NO_3S_2$ 330.0253; Found 330.0253.

*4-(5-Methyl-2-(thiophen-2-yl)oxazol-4-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**11b**).*



11b

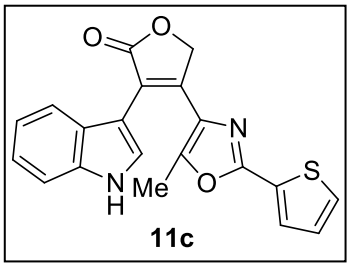
Yellow powder, 37% yield (523 mg); mp 146-148 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (s, 3H), 5.18 (s, 2H), 7.08-7.18 (m, 2H), 7.43 (d, J = 5.1 Hz, 1H) 7.48 (d, J = 4.9 Hz, 1H), 7.58 (d, J = 3.4 Hz, 1H), 7.69 (d, J = 3.3 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.3, 71.1, 120.4, 127.1, 127.8, 128.1, 128.2, 128.7, 128.9, 129.0, 129.1, 130.8, 146.1, 148.2, 157.4, 172.2.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{12}NO_3S_2$ 330.0253; Found 330.0244.

*3-(1H-Indol-3-yl)-4-(5-methyl-2-(thiophen-2-yl)oxazol-4-yl)furan-2(5H)-one (**11c**).*



11c

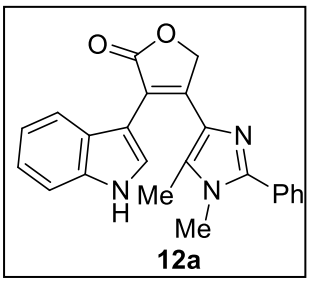
Pale orange powder, 50% yield (778 mg); mp 206-208 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56 (s, 3H), 5.31 (s, 2H), 7.00 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 7.13-7.18 (m, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 5.0 Hz, 1H), 7.67 (d, J = 3.4 Hz, 1H), 7.71-7.77 (m, 1H), 8.83 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.5, 71.3, 106.4, 111.7, 119.8, 119.9, 120.4, 122.6, 125.1, 126.6, 128.0 (2C), 128.6, 129.3, 129.7, 135.7, 145.0, 149.0, 157.0, 174.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{20}H_{15}N_2O_3S$ 363.0798; Found 363.0795.

*4-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-3-(1H-indol-3-yl)furan-2(5H)-one (**12a**).*



12a

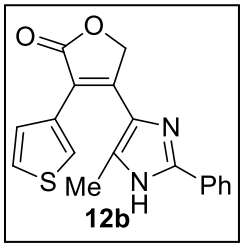
Yellow powder, 34% yield (539 mg); mp 242-243 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.49 (s, 3H), 3.45 (s, 3H), 5.29 (s, 2H), 6.83-6.96 (m, 2H), 7.10 (d, J = 7.4 Hz, 1H), 7.41-7.54 (m, 4H), 7.62-7.70 (m, 3H), 11.48 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 10.4, 32.4, 71.5, 106.4, 112.2, 116.5, 119.4, 120.1, 121.8, 126.0, 127.0, 129.0 (2C), 129.1 (2C), 129.2, 130.3, 130.7, 131.5, 136.2, 147.8, 149.9, 174.6.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1540.

*4-(5-Methyl-2-phenyl-1H-imidazol-4-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**12b**).*



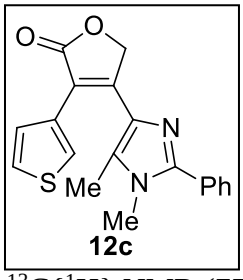
12b

White powder, 46% (637 mg); mp 230-233 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.15 (s, 3H), 5.32 (s, 2H), 7.08-7.20 (m, 1H), 7.33-7.54 (m, 3H), 7.58-7.68 (m, 1H), 7.83-8.01 (m, 3H), 12.87 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 11.8, 71.1, 114.8, 125.3 (2C), 127.0, 127.8, 129.1, 129.3 (3C), 129.9, 130.2, 131.9, 132.5, 145.9, 151.2, 173.3.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{18}H_{15}N_2O_2S$ 323.0849; Found 323.0843.



12c

*4-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-3-(thiophen-3-yl)furan-2(5H)-one (**12c**).*

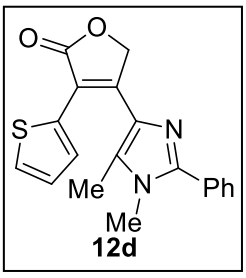
Yellow powder, 48% (694 mg); mp 130-131 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85 (s, 3H), 3.60 (s, 3H), 5.23 (s, 2H), 7.28-7.35 (m, 2H), 7.45-7.55 (m, 3H), 7.57-7.65 (m, 2H), 7.81-7.89 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 10.9, 32.2, 71.5, 118.3, 125.2, 125.7, 127.5, 128.8 (2C), 128.9 (2C), 129.3, 129.7, 129.9, 130.2, 131.4, 148.8, 151.2, 173.9.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{19}H_{17}N_2O_2S$ 337.1005; Found 337.1003.

*4-(1,5-Dimethyl-2-phenyl-1H-imidazol-4-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**12d**).*



12d

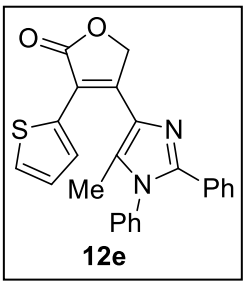
Yellow powder, 58% (838 mg); mp 193-195 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 3.61 (s, 3H), 5.23 (s, 2H), 7.05-7.11 (m, 1H), 7.37 (d, J = 4.5 Hz, 1H), 7.45-7.53 (m, 4H), 7.60-7.68 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.2, 32.2, 71.7, 117.5, 126.8 (2C), 128.2, 128.8 (2C), 128.9 (2C), 129.3, 129.4, 130.0, 130.2, 132.1, 149.0, 150.8, 173.1.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{17}N_2O_2S$ 337.1005; Found 337.0993.

*4-(5-Methyl-1,2-diphenyl-1H-imidazol-4-yl)-3-(thiophen-2-yl)furan-2(5H)-one (**12e**).*



12e

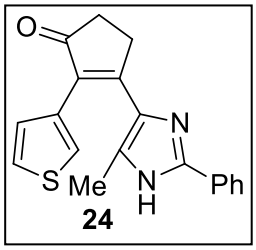
Yellow powder, 51% (873 mg); mp 187-189 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (s, 3H), 5.32 (s, 2H), 7.00-7.77 (m, 13H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.6, 71.7, 118.1, 126.9, 127.0, 127.7, 127.8 (2C), 128.2 (2C), 128.3 (2C), 128.5 (2C), 128.7, 129.4, 129.9 (2C), 131.3, 132.0, 136.5, 148.1, 150.4, 173.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{24}H_{19}N_2O_2S$ 399.1162; Found 399.1154.

*3-(5-Methyl-2-phenyl-1H-imidazol-4-yl)-2-(thiophen-3-yl)cyclopent-2-enone (**24**).*



24

Yellow powder, 62% (992 mg); mp 234-236 °C.

^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ = 1.60 (s, 3H), 2.36-2.41 (m, 2H), 2.88-2.92 (m, 2H), 6.85 (d, J = 4.7, 1H), 7.02-7.18 (m, 4H), 7.32-7.36 (m, 1H), 7.70-7.75 (m, 2H).

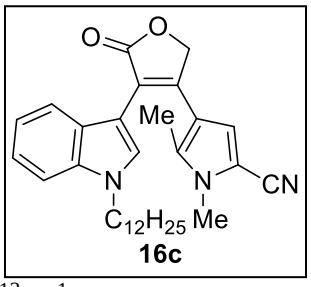
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ = 11.9, 29.4, 34.4, 124.1, 124.3 (2C), 125.1 (2C), 127.9, 128.3, 128.4 (2C), 129.8, 130.0, 131.4, 132.8, 133.9, 146.5, 206.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{17}N_2OS$ 321.1056; Found 321.1053.

Anal. Calcd for $C_{19}H_{16}N_2OS$: C, 71.22; H, 5.03; N, 8.74. Found: C, 70.09; H, 5.05; N, 8.41.

Synthesis of dihetarylethene 16c. Compound **16d** (500 mg, 1.6 mmol) was dissolved in dry DMF (10 mL) and cooled by crushed ice. Then sodium hydride NaH (45 mg, 1.9 mmol) was added portionwise and dodecyl bromide (438 mg, 1.8 mmol) was was added. The reaction mixture was stirred 12 h at ambient temperature, was poured into water (100 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography by petroleum ether/ethyl acetate.

*4-(4-(1-Dodecyl-1H-indol-3-yl)-5-oxo-2,5-dihydrofuran-3-yl)-1,5-dimethyl-1H-pyrrole-2-carbonitrile (**16c**).*



16c

Yellow amorphous powder, 30% yield (230 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.4 Hz, 3H), 1.19-1.40 (m, 18H), 1.60 (s, 3H), 1.83-1.97 (m, 2H), 3.53 (s, 3H), 4.17 (t, J = 7.1 Hz, 2H), 5.06 (s, 2H), 6.70 (d, J = 8.0 Hz, 1H), 6.87 (s, 1H), 6.87-6.93 (m, 1H), 7.14-7.22 (m, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.75 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 11.7, 14.1, 22.7, 26.9, 29.2, 29.3, 29.5 (2C), 29.6 (2C), 30.0, 31.9, 32.7, 46.7, 71.2, 104.9, 105.1, 109.8, 113.4, 115.2, 117.6, 119.2, 119.6, 120.4, 121.8, 125.7, 129.9, 135.4, 136.0, 145.7, 174.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{31}H_{40}N_3O_2$ 486.3115; Found 486.3103.

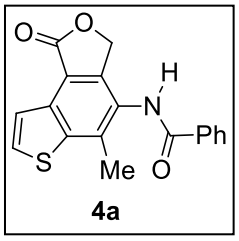
II.2. Photoreactions of dihetarylethenes

Preparative photoreactions of dihetarylethenes. Method A (general). Dihetarylethene (100 mg) was dissolved in 10 mL of appropriate solvent, and the reaction mixture was irradiated (λ = 365 nm, two 8W lamps) with stirring in a 12 mL flat-bottomed glass vessel. After completion of the reaction (TLC control), the mixture was poured into water (100 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography by gradient system petroleum ether/ethyl acetate (6:1 → 1:1).

Method B (*in situ* alkylation method). To the solution of dihetarylethene (100 mg) in DMF (10 mL) potassium carbonate K_2CO_3 (1.5 equiv) and alkyl halogenide (5 equiv of methyl iodide MeI or 2 equiv of benzyl chloride BnCl or 2 equiv of *n*-dodecyl bromide $C_{12}H_{25}Br$) were added. The reaction mixture was irradiated (λ = 365 nm, two 8W lamps) with stirring in a 12 mL flat-bottomed glass vessel. After completion of the reaction (TLC control), the solution was poured into water (100 mL), and extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with water (100 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by column chromatography by gradient system petroleum ether/ethyl acetate (10:1 → 2:1).

Method C (for pyrazole-based dihetarylethenes 10). Dihetarylethene (100 mg) was dissolved in 10 mL of appropriate solvent (toluene or DMF) and DABCO (1 equiv) was added (in the case of DHE's **10c,d**). The reaction mixture was irradiated (λ = 365 nm, two 8W lamps) with stirring. After completion of the reaction (TLC control), the precipitate was fitered off, washed with DCM (5 mL) and dried on air.

*N-(5-methyl-1-oxo-1,3-dihydrothieno[3,2-e]isobenzofuran-4-yl)benzamide (**4a**).*



4a

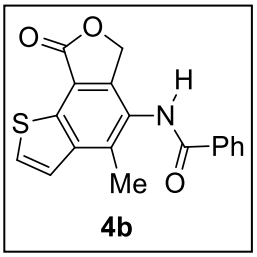
Dihetarylethene: **3a**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 11 h. White crystals, 79% yield (79 mg); 219-222 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.61 (s, 3H), 5.42 (s, 2H), 7.53-7.68 (m, 3H), 7.95 (d, J = 5.4 Hz, 1H), 8.06 (d, J = 7.2 Hz), 8.17 (d, J = 5.4 Hz, 1H), 10.36 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 17.3, 69.7, 117.3, 121.2, 127.1, 128.3 (2C), 129.0 (2C), 132.4, 132.9, 133.4, 134.1, 135.9, 142.6, 144.8, 166.0, 170.5.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{14}NO_3S$ 324.0689; Found 324.0696.

*N-(4-methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl)benzamide (**4b**).*



4b

Dihetarylethene: **3b**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 4 h.

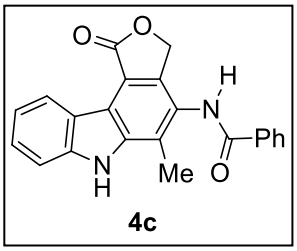
White crystals, 91% yield (91 mg); 147-149 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.65 (s, 3H), 5.44 (s, 2H), 7.52-7.66 (m, 3H), 7.78 (d, J = 5.4 Hz, 1H), 8.01 (d, J = 5.4 Hz, 1H), 8.05 (d, J = 7.3 Hz, 2H), 10.31 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 16.0, 70.4, 117.7, 123.4, 127.9, 128.3 (2C), 128.9 (2C), 129.7, 132.4, 132.5, 134.2, 137.3, 142.2, 143.8, 165.9, 170.4.

HRMS (ESI-TOF) *m/z* [M+Na]$^{+}$ Calcd for $C_{18}H_{13}NO_3SNa$ 346.0508; Found 346.0507.

*N-(5-methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)benzamide (**4c**).*



4c

Dihetarylethene: **3c**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 8 h.

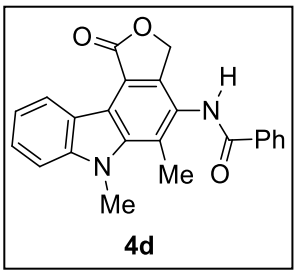
White powder, 89% yield (89 mg); mp > 300 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.64 (s, 3H), 5.46 (s, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.47-7.72 (m, 5H), 8.09 (d, J = 7.0 Hz, 2H), 8.86 (d, J = 7.8 Hz, 1H), 10.34 (s, 1H), 10.85 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.7, 70.3, 112.0, 116.4, 116.7, 119.9, 121.4, 124.8, 125.7, 127.3, 127.6, 128.3 (2C), 129.0 (2C), 132.3, 134.3, 138.6, 140.6, 141.3, 165.9, 171.9.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{22}H_{17}N_2O_3$ 357.1234; Found 357.1232.

*N-(5,6-dimethyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)benzamide (**4d**).*



4d

Dihetarylethene: **3d**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 7 h.

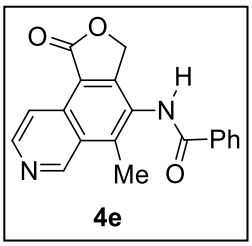
White crystals, 87% yield (87 mg); 246-249 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.84 (s, 3H), 4.21 (s, 3H), 5.44 (s, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.51-7.76 (m, 5H), 8.09 (d, J = 6.9 Hz, 2H), 8.97 (d, J = 7.7 Hz, 1H), 10.33 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 15.0, 33.5, 70.1, 110.2, 116.8, 117.6, 120.0, 120.3, 124.8, 126.8, 127.5, 128.3 (2C), 128.5, 129.0 (2C), 132.4, 134.3, 139.0, 140.8, 142.9, 166.0, 171.8.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{23}H_{19}N_2O_3$ 371.1390; Found 371.1383.

Anal. Calcd for $C_{23}H_{18}N_2O_3$: C, 74.58; H, 4.90; N, 7.56. Found: C, 74.44; H, 5.04; N, 7.48.

*N-(5-methyl-1-oxo-1,3-dihydrofuro[3,4-f]isoquinolin-4-yl)benzamide (**4e**).*



4e

Dihetarylethene: **3e**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 3 h.

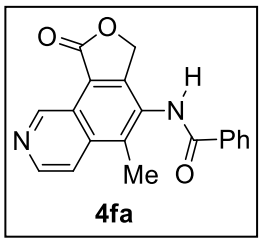
White powder, 90% yield (90 mg); mp 235-238 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (s, 3H), 5.49 (s, 2H), 7.54-7.70 (m, 3H), 8.08 (d, J = 7.1 Hz, 2H), 8.59 (d, J = 5.4 Hz, 1H), 8.80 (d, J = 5.7 Hz, 1H), 9.72 (s, 1H), 10.54 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.2, 69.5, 115.5, 117.6, 128.1, 128.4 (2C), 129.0 (2C), 129.8, 130.5, 132.6, 133.9, 140.2, 145.8, 150.7, 152.5, 166.2, 170.5.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1090.

*N-(5-methyl-1-oxo-1,3-dihydrofuro[3,4-h]isoquinolin-4-yl)benzamide (**4fa**).*



4fa

Dihetarylethene: **3f**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 8 h.

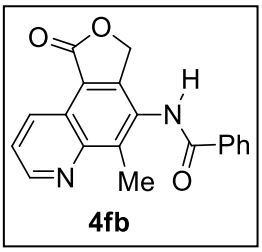
Yellow powder, 35% yield (35 mg); 212-213 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.69 (s, 3H), 5.52 (s, 2H), 7.54-7.73 (m, 3H), 8.09 (d, J = 6.8 Hz, 2H), 8.17 (d, J = 5.8 Hz, 1H), 8.78 (d, J = 5.8 Hz, 1H), 10.12 (s, 1H), 10.61 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.5, 69.9, 118.9, 122.2, 128.4 (2C), 129.0 (2C), 129.1, 132.3, 132.6, 133.9, 136.5, 137.9, 145.2, 147.4, 149.4, 166.1, 170.4.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1050.

*N-(5-methyl-1-oxo-1,3-dihydrofuro[3,4-f]quinolin-4-yl)benzamide (**4fb**).*



4fb

Dihetarylethene: **3f**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 8 h.

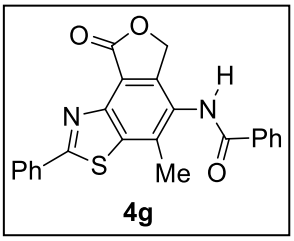
Yellow powder, 54% yield (54 mg); mp 195-198 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.81 (s, 3H), 5.48 (s, 2H), 7.55-7.69 (m, 3H), 7.80 (dd, J = 8.3, 4.2 Hz, 1H), 8.05-8.12 (m, 2H), 9.10-9.17 (m, 2H), 10.52 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.9, 69.4, 117.8, 122.9, 123.7, 128.4 (2C), 129.0 (2C), 131.0, 131.5, 132.5, 134.0, 141.0, 147.6, 148.2, 151.2, 166.0, 170.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1074.

*N-(4-methyl-8-oxo-2-phenyl-6,8-dihydroisobenzofuro[4,5-d]thiazol-5-yl)benzamide (**4g**).*



4g

Dihetarylethene: **3g**. Method: A. Solvent: DCM. Dopant: none or DABCO (1 equiv). Reaction time: 19 h.

Yellow crystals, 35% yield (35 mg, without DABCO), 90% (90 mg, 1 equiv of DABCO); mp 245-248 °C.

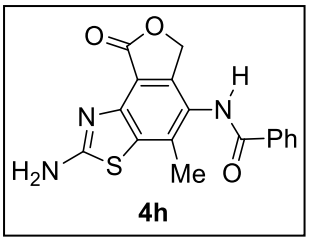
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.62 (s, 3H), 5.44 (s, 2H), 7.53-7.66 (m, 6H), 8.09 (d, J = 7.3 Hz, 2H), 8.14-8.20 (m, 2H), 10.57 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 18.9, 69.1, 116.2, 127.9 (2C), 128.1, 128.4 (2C), 129.0 (2C), 129.9 (2C), 132.5 (2C), 132.8, 134.0, 135.9, 138.4, 146.8, 147.2, 166.0, 168.4, 171.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{17}N_2O_3S$ 401.0954; Found 401.0941.

Anal. Calcd for $C_{23}H_{16}N_2O_3S$: C, 68.98; H, 4.03; N, 7.00. Found: C, 68.71; H, 4.57; N, 6.89.

*N-(2-amino-4-methyl-8-oxo-6,8-dihydroisobenzofuro[4,5-d]thiazol-5-yl)benzamide (**4h**).*



4h

Dihetarylethene: **3h**. Method: A (filtration instead of chromatography). Solvent: DCM. Dopant: DABCO (1 equiv). Reaction time: 40 h.

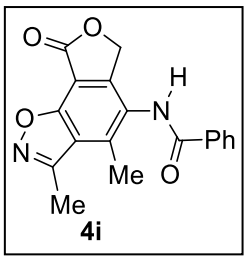
Yellow crystals, 44% yield (44 mg); mp > 300 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 5.24 (s, 2H), 7.48-7.73 (m, 3H), 7.91-8.12 (m, 2H), 8.22 (s, 2H), 10.12 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 18.7, 68.5, 123.3, 126.5, 128.2 (2C), 128.9 (2C), 129.1, 132.3, 134.2, 134.6, 144.2, 148.3, 165.9, 169.0, 170.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{14}N_3O_3S$ 340.0750; Found 340.0750.

*N-(3,4-dimethyl-8-oxo-6,8-dihydroisobenzofuro[5,4-d]isoxazol-5-yl)benzamide (**4i**).*



4i

Dihetarylethene: **3i**. Method: A. Solvent: DCM. Dopant: DABCO (1 equiv). Reaction time: 45 h.

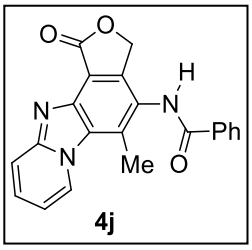
Pale yellow powder, 77% yield (77 mg); mp 224-225 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.66 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 5.47 (s, 2H, CH_2), 7.55-7.61 (m, 2H, H^{arom}), 7.64-7.68 (m, 1H, H^{arom}), 8.05 (d, *J* = 7.4 Hz, 2H, H^{arom}), 10.30 (s, 1H, NH).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 12.4, 14.8, 70.3, 107.0, 123.6, 127.1, 128.3 (2C), 129.0 (2C), 132.5, 134.0, 139.9, 150.1, 156.3, 156.5, 166.1, 167.6.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{15}N_2O_4$ 323.1026; Found 323.1020.

*N-(5-methyl-1-oxo-1,3-dihydroisobenzofuro[4',5':4,5]imidazo[1,2-a]pyridin-4-yl)benzamide (**4j**).*



4j

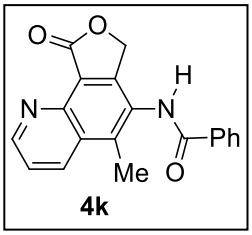
Dihetarylethene: **3j**. Method: A. Solvent: DCM. Dopant: DABCO (1 equiv). Reaction time: 51 h. White powder, 60% yield (60 mg); mp 284-286 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.91 (s, 3H, CH_3), 5.42 (s, 2H, CH_2), 7.13-7.18 (m, 1H, $H^{imidazopyridine}$), 7.57-7.61 (m, 2H, H^{arom}), 7.64-7.68 (m, 1H, H^{arom}), 7.71-7.76 (m, 1H, $H^{imidazopyridine}$), 7.88 (d, *J* = 9.0 Hz, 1H, $H^{imidazopyridine}$), 8.10 (d, *J* = 7.4 Hz, 2H, H^{arom}), 9.24 (d, *J* = 6.8 Hz, 1H, $H^{imidazopyridine}$), 10.41 (s, 1H, NH).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 15.1, 69.1, 111.7, 112.4, 117.9, 123.4, 128.3 (2C), 129.0 (2C), 129.3, 129.6, 130.2, 131.5, 132.4, 134.2, 139.6, 145.9, 150.9, 166.3, 169.5.

HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{21}H_{15}N_3O_3Na$ 380.1006; Found 380.1001.

*N-(5-methyl-9-oxo-7,9-dihydrofuro[3,4-h]quinolin-6-yl)benzamide (**4k**).*



4k

Dihetarylethene: **3k**. Method: A. Solvent: MeOH. Dopant: DABCO (1 equiv). Reaction time: 16 h.

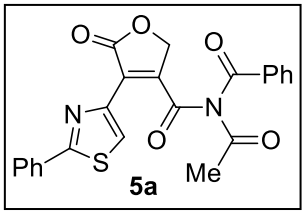
Gray powder, 37% yield (37 mg); mp 210-212 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.70 (s, 3H, CH_3), 5.42 (s, 2H, CH_2), 7.60 (t, J = 7.4 Hz, 2H, H^{arom}), 7.67 (t, J = 7.4 Hz, 1H, H^{arom}), 7.77 (dd, J = 8.6, 4.2 Hz, 1H, $H^{pyridine}$), 8.08 (d, J = 7.4 Hz, 2H, H^{arom}), 8.75 (dd, J = 8.6, 1.6 Hz, 1H, $H^{pyridine}$), 9.12 (dd, J = 4.2, 1.6 Hz, 1H, $H^{pyridine}$).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.6, 68.1, 118.9, 122.7, 128.3 (2C), 128.6, 128.9 (2C), 129.0, 132.5, 134.0, 134.6, 140.1, 143.2, 152.1, 152.2, 166.2, 168.6.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{15}N_2O_3$ 319.1077; Found 319.1077.

*N-acetyl-N-benzoyl-5-oxo-4-(2-phenylthiazol-4-yl)-2,5-dihydrofuran-3-carboxamide (**5a**).*



5a

Dihetarylethene: **3g**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 19 h.

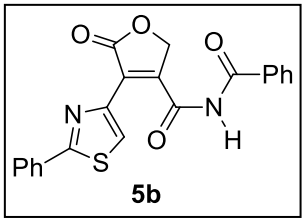
Yellow amorphous powder, 18% yield (19 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.58 (s, 3H), 5.21 (s, 2H), 7.07-7.21 (m, 2H), 7.40-7.59 (m, 4H), 7.63-7.76 (m, 2H), 7.90-8.03 (m, 2H), 8.23 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 26.0, 70.7, 106.9, 122.3, 127.0 (2C), 128.6 (2C), 129.2 (2C), 130.1 (2C), 130.9, 131.6, 132.9, 134.4, 144.4, 148.9, 165.6, 168.9, 170.5, 171.9, 172.8.

HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{23}H_{16}N_2O_5SNa$ 455.0672; Found 455.0662.

*N-benzoyl-5-oxo-4-(2-phenylthiazol-4-yl)-2,5-dihydrofuran-3-carboxamide (**5b**).*



5b

Dihetarylethene: **3g**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 19 h.

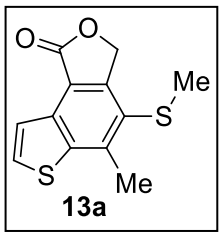
Yellow amorphous powder, 15% yield (15 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.27 (s, 2H), 6.94-7.75 (m, 10H), 8.96 (s, 1H), 14.06 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 70.8, 122.8, 126.3, 127.0 (2C), 128.1 (2C), 128.4 (2C), 128.9 (2C), 131.0, 131.2, 132.9, 133.5, 144.5, 146.9, 160.4, 167.4, 170.0, 171.8.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{21}H_{15}N_2O_4S$ 391.0747; Found 391.0745.

*5-Methyl-4-(methylthio)thieno[3,2-e]isobenzofuran-1(3H)-one (**13a**).*



13a

Dihetarylethene: **6b** and **6c**. Method: B. Reaction time: 8 h.

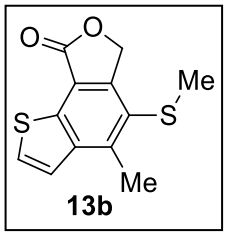
Yellow powder, 85% yield (77 mg, from **6c**), 27% (24 mg, from **6b**); mp 193-196 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 2.92 (s, 3H), 5.44 (s, 2H), 7.78 (d, J = 5.4 Hz, 1H), 8.06 (d, J = 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 19.0 (2C), 70.1, 118.0, 122.0, 124.4, 131.6, 135.4, 142.9, 143.2, 150.3, 170.8.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}O_2S_2$ 251.0195; Found 251.0194.

*4-Methyl-5-(methylthio)thieno[2,3-e]isobenzofuran-8(6H)-one (**13b**).*



13b

Dihetarylethene: **6d**. Method: B. Reaction time: 8 h.

Pale yellow powder, 78% yield (58 mg); mp 195-197 °C.

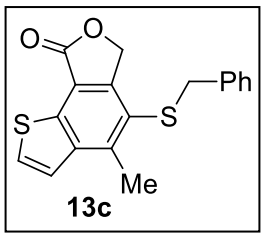
^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.34 (s, 3H), 2.87 (s, 3H), 5.54 (s, 2H), 7.72 (d, J = 5.4 Hz, 1H), 7.96 (d, J = 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 18.0, 18.6, 71.1, 117.9, 123.6, 125.5, 129.5, 134.6, 142.0, 144.6, 150.1, 170.5.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}O_2S_2$ 251.0195; Found 251.0198.

Anal. Calcd for $C_{12}H_{10}O_2S_2$: C, 57.57; H, 4.03. Found: C, 58.98; H, 4.10.

*5-(Benzylthio)-4-methylthieno[2,3-e]isobenzofuran-8(6H)-one (**13c**).*



13c

Dihetarylethene: **6d**. Method: B. Reaction time: 8 h.

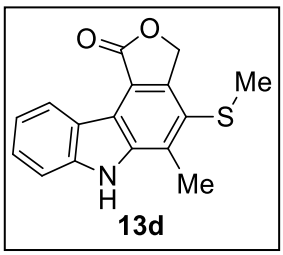
Yellow amorphous powder, 81% yield (78 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.86 (s, 3H), 3.86 (s, 2H), 4.87 (s, 2H), 6.88-6.97 (m, 2H), 7.13-7.23 (m, 3H), 7.55 (d, J = 5.5 Hz, 1H), 7.67 (d, J = 5.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 17.7, 40.4, 70.7, 118.2, 122.4, 122.5, 127.5, 128.5 (3C), 128.6 (2C), 135.8, 137.9, 141.9, 145.6, 150.7, 170.5.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{15}O_2S_2$ 327.0508; Found 327.0514.

*5-Methyl-4-(methylthio)-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**13d**).*



13d

Dihetarylethene: **6e**. Method: B. Reaction time: 8 h.

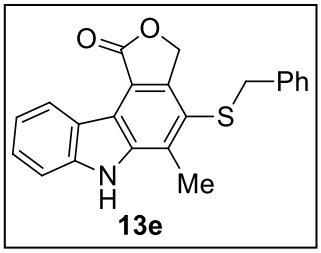
Yellow powder, 71% yield (54 mg); mp 265-268 °C.

^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 2.36 (s, 3H, CH$_3$), 2.86 (s, 3H, CH$_3$), 5.56 (s, 2H, CH$_2$), 7.23-7.29 (m, 1H, H^{carbazole}), 7.49-7.54 (m, 1H, H^{carbazole}), 7.62 (d, J = 8.2 Hz, 1H, H^{carbazole}), 8.80 (d, J = 8.0 Hz, 1H, H^{carbazole}), 11.80 (s, 1H, NH).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d$_6$): δ = 15.7, 18.9, 71.0, 112.0, 117.0, 117.9, 120.0, 121.2, 124.9, 125.0, 127.7, 132.7, 140.3, 141.3, 145.0, 172.1.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for C$_{16}$H$_{14}$NO$_2$S 284.0740; Found 284.0747.

*4-(Benzylthio)-5-methyl-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**13e**).*



13e

Dihetarylethene: **6e**. Method: B. Reaction time: 8 h.

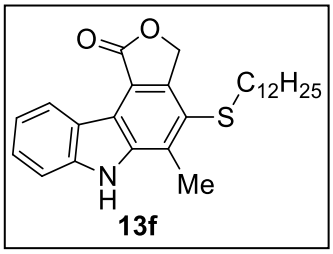
Yellow powder, 64% yield (62 mg); mp 217-218 °C (decomp.).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.65 (s, 3H), 3.98 (s, 2H), 5.12 (s, 2H), 6.96-7.01 (m, 2H), 7.15-7.18 (m, 3H), 7.23-7.29 (m, 1H), 7.49-7.54 (m, 1H), 7.62 (d, J = 8.2 Hz, 1H), 8.79 (d, J = 8.0 Hz, 1H), 11.76 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 15.5, 39.7, 71.0, 112.1, 120.0, 121.1, 122.0, 125.0, 127.5, 127.8, 128.2, 128.6 (2C), 129.3 (2C), 130.5, 134.1, 138.7, 140.1, 141.3, 146.2, 172.0.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for C$_{22}$H$_{18}$NO$_2$S 360.1053; Found 360.1044.

*(Dodecylthio)-5-methyl-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**13f**).*



13f

Dihetarylethene: **6e**. Method: B. Reaction time: 8 h.

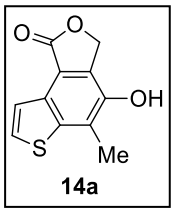
Pale yellow powder, 47% yield (55 mg); mp 200-203 °C.

^{1}H NMR (300 MHz, CDCl$_3$+DMSO-d$_6$): δ = 0.81 (t, J = 6.6 Hz, 3H), 1.13-1.34 (m, 18H), 1.42-1.52 (m, 2H), 2.72 (t, J = 7.1 Hz, 2H), 2.84 (s, 3H), 5.42 (m, 2H), 7.13-7.20 (m, 1H), 7.38-7.45 (m, 1H), 7.54 (d, J = 8.1 Hz, 1H), 8.80 (d, J = 7.9 Hz, 1H), 11.45 (br s, 1H).

^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$+DMSO-d$_6$): δ = 14.3, 15.8, 22.6, 28.6, 29.0, 29.2, 29.4 (2C), 29.5 (2C), 30.0, 31.8, 35.9, 70.9, 111.7, 117.1, 118.2, 119.6, 121.3, 123.3, 125.1, 127.3, 132.8, 140.4, 141.2, 144.8, 171.9.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for C$_{27}$H$_{36}$NO$_2$S 438.2461; Found 438.2456.

*4-Hydroxy-5-methylthieno[3,2-e]isobenzofuran-1(3H)-one (**14a**).*



Dihetarylethene: **7c**. Method: A. Solvent: DMF. Dopant: none. Reaction time:25 h.

Pale yellow powder, 32% yield (27 mg); mp 267-269 °C (decomp.).

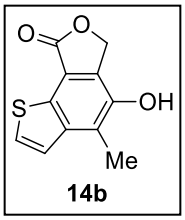
^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.47 (s, 3H), 5.38 (s, 2H), 7.76 (d, J = 5.4 Hz, 1H), 7.83 (d, J = 5.4 Hz, 1H), 9.90 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 14.9, 69.0, 117.3, 120.9, 124.1, 128.4, 128.8, 135.4, 143.5, 146.2, 179.8.

MS (EI) *m/z* (%) = 220 (100) $[M]^+$.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_9O_3S$ 221.0267; Found 221.0271.

*5-Hydroxy-4-methylthieno[2,3-e]isobenzofuran-8(6H)-one (**14b**).*



Dihetarylethene: **7d**. Method: A. Solvent: DMF. Dopant: none. Reaction time: 25 h.

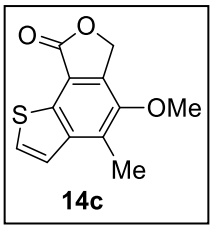
Yellow powder, 54% yield (45 mg); mp 229-233 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.53 (s, 3H), 5.43 (s, 2H), 7.58 (d, J = 5.4 Hz, 1H), 7.86 (d, J = 5.4 Hz, 1H), 9.66 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.6, 69.6, 117.6, 122.6, 125.6, 126.0, 129.0, 134.8, 142.8, 146.8, 170.6.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_9O_3S$ 221.0267; Found 221.0276.

*5-Methoxy-4-methylthieno[2,3-e]isobenzofuran-8(6H)-one (**14c**).*



Dihetarylethene: **7d**. Method: B (alkylation agent was added after completion of first step of reaction). Solvent: DMF. Dopant: none. Reaction time: 25 + 12 h (without irradiation).

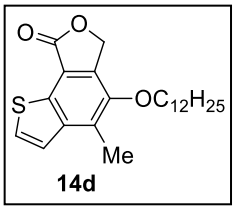
Pale gray powder, 35% yield (31 mg).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.65 (s, 3H), 3.92 (s, 3H), 5.50 (s, 2H), 7.48 (d, J = 5.4 Hz, 1H), 7.65 (d, J = 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.4, 60.5, 68.7, 118.7, 121.7, 128.9, 130.5, 131.3, 136.7, 142.8, 149.5, 170.1.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}O_3S$ 235.0423; Found 235.0428.

*5-(Dodecyloxy)-4-methylthieno[2,3-e]isobenzofuran-8(6H)-one (**14d**).*



14d

Dihetarylethene: **7d**. Method: B (alkylation agent was added after completion of first step of reaction). Solvent: DMF. Dopant: none. Reaction time: 25 + 12 h (without irradiation).

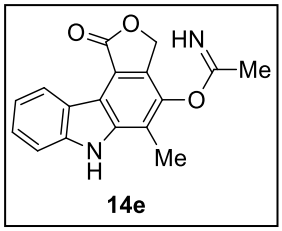
Pale yellow powder, 34% yield (50 mg); mp 75-78 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.1 Hz, 3H), 1.25-1.37 (m, 16H), 1.45-1.55 (m, 2H), 1.78-1.88 (m, 2H), 2.64 (s, 3H), 3.98 (t, J = 6.4 Hz, 3H), 5.46 (s, 2H), 7.47 (d, J = 5.4 Hz, 1H), 7.64 (d, J = 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.6, 14.1, 22.7, 26.0, 29.3, 29.4, 29.6 (4C), 30.3, 31.9, 68.9, 73.5, 118.6, 121.7, 128.8, 130.3, 131.4, 137.1, 142.8, 148.7, 170.2.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{33}O_3S$ 389.2145; Found 389.2136.

*5-Methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl acetimidate (**14e**).*



14e

Dihetarylethene: **7a**. Method: A. Solvent: DMF. Dopant: DABCO (3 equiv). Reaction time: 7 h.

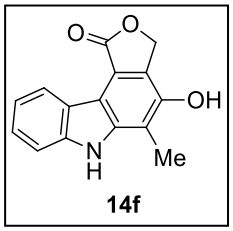
Brown powder, 50% yield (50 mg); mp >300 °C (decomp.).

^{1}H NMR (600 MHz, DMSO-d_6): δ = 2.16 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 5.37 (s, 2H, CH_2), 7.24-7.28 (m, 1H, $H^{carbazole}$), 7.48-7.52 (m, 1H, $H^{carbazole}$), 7.63 (d, J = 8.1 Hz, 1H, $H^{carbazole}$), 8.82 (d, J = 7.9 Hz, 1H, $H^{carbazole}$), 9.85 (s, 1H, NH), 11.75 (s, 1H, NH).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.6, 23.2, 70.4, 111.9, 116.0, 116.6, 119.8, 121.4, 124.5, 124.7, 127.1, 127.7, 138.0, 140.5, 141.2, 168.8, 172.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{17}H_{15}N_2O_3$ 295.1077; Found 295.1074.

*4-Hydroxy-5-methyl-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**14f**).*



14f

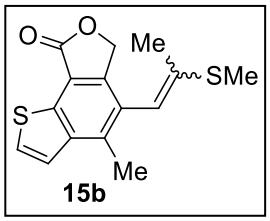
Dihetarylethene: **7a**. Method: A. Solvent: DMF. Dopant: DABCO (3 equiv). Reaction time: 7 h. Pale orange powder, 29% yield (25 mg); mp 295-298 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.52 (s, 3H), 5.44 (s, 2H), 7.13-7.21 (m, 1H), 7.34-7.43 (m, 1H), 7.53 (d, J = 8.1 Hz, 1H), 8.69 (d, J = 7.8 Hz, 1H), 9.61 (s, 1H), 11.44 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 11.3, 69.6, 111.4, 116.4, 113.8, 116.8, 119.4, 122.0, 123.9, 125.7, 129.2, 140.7, 141.8, 147.1, 172.1.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{12}NO_3$ 254.0812; Found 254.0811.

*4-Methyl-5-(2-(methylthio)prop-1-en-1-yl)thieno[2,3-e]isobenzofuran-8(6H)-one (**15b**, E- and Z-isomers in ratio ≈ 2:1).*



15b

Dihetarylethene: **8b**. Method: B. Reaction time: 8 h.

Yellow powder, 90% yield (95 mg); mp 154-157 °C.

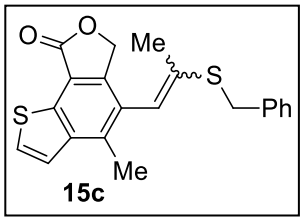
Isomer 1. ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ = 1.36 (s, 3H), 2.03 (s, 3H), 2.20 (s, 3H), 4.81 (s, 2H), 5.65 (s, 1H), 7.13-7.19 (m, 1H), 7.24-7.31 (m, 1H).

Isomer 2. ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ = 1.82 (s, 3H), 1.87 (s, 3H), 2.18 (s, 3H), 4.93 (s, 2H), 5.98 (s, 1H), 7.13-7.19 (m, 1H), 7.24-7.31 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ = 13.4, 14.5, 16.9, 17.0, 18.8, 22.5, 113.3, 116.8, 116.9, 118.6, 122.1, 127.2, 127.4, 127.6, 133.0, 133.2, 138.2, 138.3, 138.7, 139.4, 141.0, 141.2, 144.5, 144.7, 170.3, 170.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{15}O_2S_2$ 291.0508; Found 291.0506.

*5-(2-(Benzylthio)prop-1-en-1-yl)-4-methylthieno[2,3-e]isobenzofuran-8(6H)-one (**15c**, E- and Z-isomers in ratio ≈ 93:7).*



15c

Dihetarylethene: **8b**. Method: B. Reaction time: 8 h.

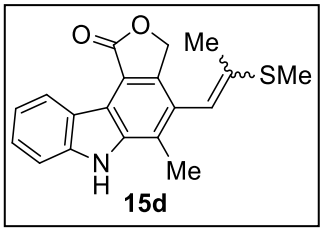
Pale yellow powder, 55% yield (73 mg); mp 190-193 °C.

Major isomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.55 (s, 3H), 3.90 (s, 2H), 5.05 (s, 2H), 6.40 (s, 1H), 7.16-7.30 (m, 5H), 7.52 (d, *J* = 5.4 Hz, 1H), 7.61 (d, *J* = 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 17.2, 17.3, 19.2, 23.6, 35.2, 36.1, 70.1, 70.4, 119.1, 121.8, 122.1 (2C), 127.3, 127.4, 127.8, 128.1, 128.5, 128.6, 128.7, 133.8, 136.7, 137.3, 137.7, 138.0, 138.2, 138.5, 141.3, 141.5, 144.8, 170.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{21}H_{19}O_2S_2$ 367.0821; Found 367.0828.

*5-Methyl-4-(2-(methylthio)prop-1-en-1-yl)-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**15d**, E- / Z-isomers in ratio ≈ 52:48).*



15d

Dihetarylethene: **8c**. Method: B. Reaction time: 10 h.

Yellow powder, 91% yield (95 mg); mp 271-274 °C.

Isomer 1. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.21 (s, 3H), 2.42 (s, 3H), 2.53 (s, 3H), 5.33 (s, 2H), 6.42 (s, 1H), 7.18-7.30 (m, 1H), 7.44-7.53 (m, 1H), 7.55-7.65 (m, 1H), 8.75-8.85 (m, 1H), 11.65 (s, 1H).

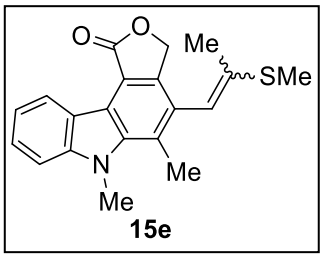
Isomer 2. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.72 (s, 3H), 2.21 (s, 3H), 2.53 (s, 3H), 5.26 (s, 2H), 6.12 (s, 1H), 7.18-7.30 (m, 1H), 7.44-7.53 (m, 1H), 7.55-7.65 (m, 1H), 8.75-8.85 (m, 1H), 11.65 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.2, 14.3, 14.7, 14.8, 19.0, 22.5, 70.3, 70.5, 111.4, 114.4, 115.7, 115.8, 116.0, 116.2, 119.1, 119.3, 121.0, 124.2, 126.3, 126.4, 126.6, 127.6 (2C), 138.4 (2C), 139.7, 139.8, 140.2, 140.5, 171.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{18}NO_2S$ 324.1053; Found 324.1056.

Anal. Calcd for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.30; N, 4.33. Found: C, 69.53; H, 5.85; N, 4.04.

*5,6-Dimethyl-4-(2-(methylthio)prop-1-en-1-yl)-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**15e**, E- / Z- isomers in ratio ≈ 63:37).*



15e

Dihetarylethene: **8d**. Method: B. Reaction time: 8 h.

Yellow powder, 81% yield (84 mg); mp 205-207 °C.

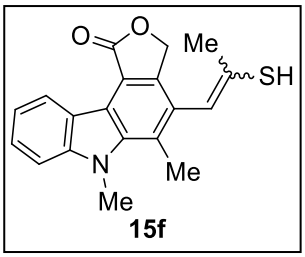
Isomer 1. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.73 (s, 3H), 2.46 (s, 3H), 2.75 (s, 3H), 4.13 (s, 3H), 4.99 (s, 2H), 5.94 (s, 1H), 7.30-7.41 (m, 2H), 7.49-7.58 (m, 1H), 9.09 (d, *J* = 7.9 Hz, 1H).

Isomer 2. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 2.26 (s, 3H), 2.78 (s, 3H), 4.11 (s, 3H), 5.17 (s, 2H), 6.28 (s, 1H), 7.30-7.41 (m, 2H), 7.49-7.58 (m, 1H), 9.10 (d, *J* = 7.9 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.9, 15.0, 16.7, 16.8, 19.0, 22.8, 33.1, 70.1, 70.4, 108.4, 108.5, 114.9, 116.7, 118.7, 119.7, 119.8, 120.1, 121.0, 121.1, 125.7 (2C), 126.4, 126.8, 126.9, 128.6, 128.9, 138.4, 139.1, 139.7, 139.8, 140.6, 142.4, 172.0.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{20}H_{20}NO_2S$ 338.1209; Found 338.1197.

*4-(2-Mercaptoprop-1-en-1-yl)-5,6-dimethyl-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**15f**, E- / Z-isomers in ratio ≈ 81:19).*



15f

Dihetarylethene: **8d**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 14 h.

Brown powder, 52% yield (52 mg); mp 174-176 °C.

Isomer 1. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.75 (s, 3H), 4.07 (s, 3H), 5.10 (s, 2H), 6.21 (s, 1H), 7.24-7.40 (m, 2H), 7.47-7.57 (m, 1H), 9.06 (d, *J* = 7.8 Hz, 1H).

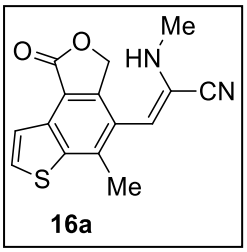
Isomer 2. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80 (s, 3H), 2.75 (s, 3H), 4.07 (s, 3H), 5.00 (s, 2H), 6.32 (s, 1H), 7.24-7.40 (m, 2H), 7.47-7.57 (m, 1H), 9.06 (d, *J* = 7.8 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 16.5, 16.8, 22.3, 26.4, 33.0, 70.1, 70.3, 108.5, 117.0, 119.0, 119.2, 119.8, 120.9, 125.6, 126.6, 127.0, 128.5, 132.5, 134.1, 139.5, 140.4, 142.4, 172.0.

MS (EI) *m/z* (%) = 323 (100) $[M]^+$.

HRMS (ESI-TOF) *m/z* $[M+Na]^+$ Calcd for $C_{19}H_{17}NO_2SNa$ 346.0872; Found 346.0867.

*(Z)-3-(5-Methyl-1-oxo-1,3-dihydrothieno[3,2-e]isobenzofuran-4-yl)-2-(methylamino)acrylonitrile (**16a**).*



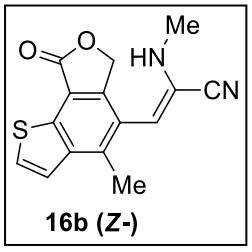
Dihetarylethene: **9a**. Method: A. Solvent: DCM / NMP (9:1). Dopant: none. Reaction time: 7 h. Pale yellow powder, 67% yield (67 mg); mp 196-199 °C.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.57 (s, 3H), 2.67 (d, J = 4.8 Hz, 3H), 5.32 (s, 2H), 5.52-5.57 (m, 1H), 6.00 (s, 1H), 7.91 (d, J = 5.4 Hz, 1H), 8.13 (d, J = 5.4 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 19.0, 32.3, 70.3, 104.9, 116.7, 120.7, 121.2, 123.6, 124.0, 131.7, 132.5, 137.5, 138.4, 146.7, 169.0.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found 285.0696.

*(Z)-3-(4-Methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl)-2-(methylamino)acrylonitrile (**16b**, Z-isomer).*



Dihetarylethene: **9b**. Method: A. Solvent: DCM / NMP (9:1). Dopant: none. Reaction time: 7 h.

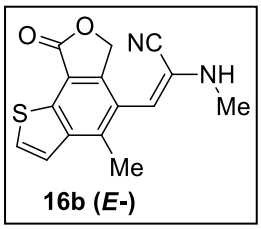
Yellow powder, 47% yield (47 mg); mp 212-215 °C.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.62 (s, 3H, CH_3), 2.66 (d, J = 4.8 Hz, 3H, CH_3), 5.36 (s, 2H, CH_2), 5.45-5.49 (m, 1H, NH), 6.01 (s, 1H, CH), 7.77 (d, J = 5.4 Hz, 1H, H^{thiophene}), 7.97 (d, J = 5.4 Hz, 1H, H^{thiophene}).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 17.9, 32.3, 71.0, 105.4, 116.8, 117.2, 123.4 (2C), 124.7, 129.1, 133.4, 139.1, 141.7, 145.7, 170.7.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found 285.0690.

*(E)-3-(4-Methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl)-2-(methylamino)acrylonitrile (**16b**, E-isomer).*



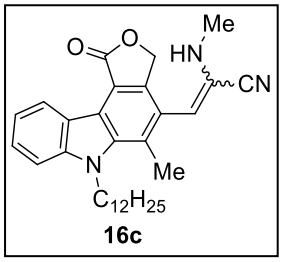
Dihetarylethene: **9b**. Method: A. Solvent: DCM / NMP (9:1). Dopant: none. Reaction time: 7 h. Yellow powder, 44% yield (44 mg); mp 203-205 °C.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.69 (s, 3H, CH_3), 2.73 (d, J = 4.9 Hz, 3H, CH_3), 5.26 (s, 2H, CH_2), 5.86 (s, 1H, CH), 6.54 (q, J = 4.9 Hz, 1H, NH), 7.76 (d, J = 5.4 Hz, 1H, H^{thiophene}), 7.99 (d, J = 5.4 Hz, 1H, H^{thiophene}).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 18.1, 30.9, 70.8, 102.2, 116.2, 117.1, 123.5, 124.9, 126.5, 129.3, 133.0, 139.3, 141.9, 146.6, 170.6.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{15}H_{13}N_2O_2S$ 285.0692; Found 285.0698.

*3-(6-Dodecyl-5-methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)-2-(methylamino)acrylonitrile (**16c**, isomer 1).*



16c

Dihetarylethene: **9c**. Method: A. Solvent: DMF. Dopant: DABCO (2 equiv) + imidazole (2 equiv). Reaction time: 6 h.

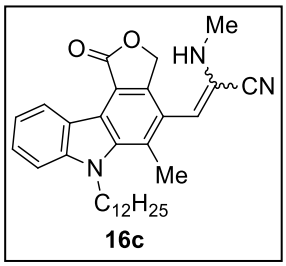
Yellow amorphous powder, 32% yield (32 mg).

^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ = 0.83 (t, J = 6.4, 3H), 1.15-1.30 (m, 18H), 1.64-1.79 (m, 2H), 2.50 (s, 3H), 2.74 (s, 3H), 4.52-4.62 (m, 2H), 5.30 (s, 2H), 5.74 (s, 1H), 7.19-7.26 (m, 1H), 7.45-7.53 (m, 1H), 7.58 (d, J = 8.0 Hz, 1H), 8.96 (d, J = 7.7 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ = 14.2, 17.1, 22.5, 26.5, 29.1 (2C), 29.3, 29.4 (3C), 30.6 (2C), 31.7, 45.3, 70.3, 102.6, 109.8, 110.0, 115.8, 119.9, 121.0, 125.1, 127.2, 127.3, 127.7, 140.0, 141.3, 142.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{31}H_{40}N_3O_2$ 486.3115; Found 486.3105.

*3-(6-Dodecyl-5-methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)-2-(methylamino)acrylonitrile (**16c**, isomer 2).*



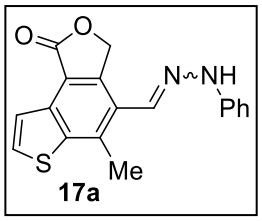
16c

Dihetarylethene: **9c**. Method: A. Solvent: DMF. Dopant: DABCO (2 equiv) + imidazole (2 equiv). Reaction time: 6 h.

Yellow amorphous powder, 30% yield (30 mg).

^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.85 (t, J = 6.4 Hz, 3H), 1.14-1.31 (m, 18H), 1.67-1.85 (m, 2H), 2.66 (s, 3H), 2.75 (s, 3H), 4.54-4.63 (m, 2H), 5.29 (s, 2H), 5.94 (s, 1H), 7.21-7.28 (m, 1H), 7.48-7.55 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 8.98 (d, J = 7.8 Hz, 1H). HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{31}H_{40}N_3O_2$ 486.3115; Found 486.3105.

*5-Methyl-4-((2-phenylhydrazono)methyl)thieno[3,2-e]isobenzofuran-1(3H)-one (**17a**).*



17a

Dihetarylethene: **10a**. Method: C. Solvent: toluene. Dopant: none. Reaction time: 34 h.

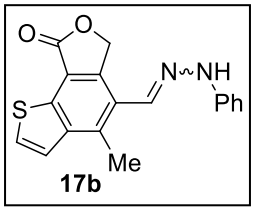
Light green powder, 40% yield (40 mg); mp 245-246 °C.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.74 (s, 3H), 5.64 (s, 2H), 6.78-6.85 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.26-7.33 (m, 2H), 7.91 (d, *J* = 5.4 Hz, 1H), 8.11 (d, *J* = 5.4 Hz, 1H), 8.39 (s, 1H), 10.70 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 18.3, 72.9, 112.6 (2C), 117.8, 119.8, 121.6, 124.8, 129.8 (2C), 132.5, 133.5, 133.8, 135.0, 142.9, 144.0, 145.1, 170.7.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{18}H_{15}N_2O_2S$ 323.0849; Found 323.0833.

*4-Methyl-5-((2-phenylhydrazono)methyl)thieno[2,3-e]isobenzofuran-8(6H)-one (**17b**).*



17b

Dihetarylethene: **10b**. Method: C. Solvent: toluene. Dopant: none. Reaction time: 33 h.

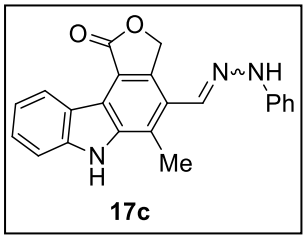
Yellow powder, 70% yield (70 mg); mp 225-226 °C.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.76 (s, 3H), 5.63 (s, 2H), 6.77-6.90 (m, 1H), 6.99-7.14 (m, 2H), 7.24-7.37 (m, 2H), 7.69-7.82 (m, 1H), 7.86-7.97 (m, 1H), 8.39 (s, 1H), 10.59 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 16.8, 73.6, 112.5 (2C), 118.3, 119.7, 123.4, 125.8, 129.3, 129.8 (2C), 132.9, 134.4, 136.6, 142.1, 143.0, 145.2, 170.6.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{18}H_{15}N_2O_2S$ 323.1; Found 323.1.

*5-Methyl-4-((2-phenylhydrazono)methyl)-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**17c**).*



17c

Dihetarylethene: **10c**. Method: C. Solvent: DMF. Dopant: DABCO (1 equiv). Reaction time: 56 h.

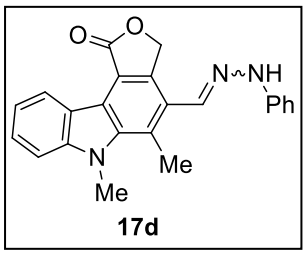
Green powder, 73% yield (73 mg); mp 275-277 °C (decomp.).

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.75 (s, 3H), 5.61 (s, 2H), 6.76-6.86 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.17-7.37 (m, 3H), 7.40-7.49 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 8.46 (s, 1H), 8.82 (d, *J* = 7.6 Hz, 1H), 10.79 (s, 1H), 11.87 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 14.2, 73.5, 111.8, 112.5, 119.4, 119.7, 121.6, 124.8, 124.9, 125.2, 127.0, 128.7 (4C), 129.7, 134.8, 137.9, 140.4, 141.4, 145.4, 172.0.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{22}H_{18}N_3O_2$ 356.1394; Found 356.1371.

*5,6-Dimethyl-4-((2-phenylhydrazono)methyl)-3,6-dihydro-1H-furo[3,4-c]carbazol-1-one (**17d**).*



17d

Dihetarylethene: **10d**. Method: C. Solvent: DMF. Dopant: DABCO (1 equiv). Reaction time: 29 h.

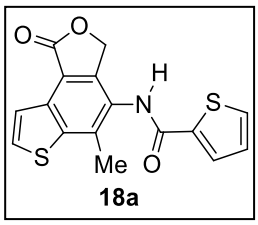
Yellow powder, 45% yield (45 mg); mp > 300 °C.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.04 (s, 3H), 4.22 (s, 3H), 5.72 (s, 2H), 6.80-6.85 (m, 1H), 7.08 (d, J = 7.6 Hz, 2H), 7.27-7.32 (m, 3H), 7.56 (ddd, J = 1.1, 7.1, 8.3 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 8.55 (s, 1H), 9.02 (d, J = 7.8 Hz, 1H), 10.66 (s, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ = 15.9, 34.2, 73.4, 110.3, 112.5 (2C), 117.7, 118.1, 119.6, 120.1, 120.7, 125.1, 126.0, 126.5, 127.6, 129.8 (2C), 131.2, 135.2, 138.6, 141.1, 145.2, 171.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1547.

*N-(5-methyl-1-oxo-1,3-dihydrothieno[3,2-e]isobenzofuran-4-yl)thiophene-2-carboxamide (**18a**).*



18a

Dihetarylethene: **11a**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 7 h.

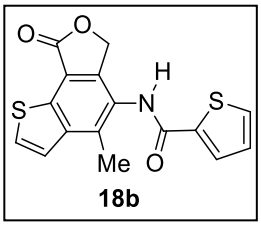
Yellow powder, 85% yield (85 mg); mp 139-142 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 5.09 (s, 2H), 7.10-7.19 (m, 1H), 7.56-7.65 (m, 2H), 7.76 (d, J = 5.4 Hz, 1H), 7.89 (d, J = 3.2 Hz, 1H), 8.55 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 16.7, 69.5, 117.5, 121.5, 124.7, 128.1, 129.8, 131.1, 131.7, 133.8, 134.9, 137.4, 142.7, 143.4, 160.6, 170.7.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{12}NO_3S_2$ 330.0253; Found 330.0254.

*N-(4-Methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl)thiophene-2-carboxamide (**18b**).*



18b

Dihetarylethene: **11b**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 8 h.

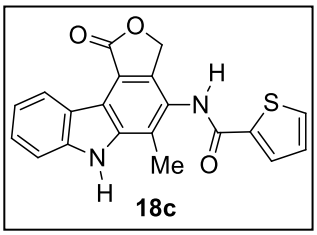
Yellow powder, 75% yield (75 mg); mp 221-223 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52 (s, 3H), 5.03 (s, 2H), 7.15 (t, J = 4.3 Hz, 1H), 7.34 (d, J = 5.4 Hz, 1H), 7.54 (d, J = 5.4 Hz, 1H), 7.60 (d, J = 4.9 Hz, 1H), 7.88 (d, J = 3.2 Hz, 1H), 8.38 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 15.4, 70.1, 117.9, 122.0, 125.6, 128.1, 128.7, 129.8, 131.6, 133.3, 135.8, 137.5, 141.6, 142.3, 160.5, 170.4.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{16}H_{12}NO_3S_2$ 330.0253; Found 330.0250.

*N-(5-Methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)thiophene-2-carboxamide (**18c**).*



18c

Dihetarylethene: **11c**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 5 h.

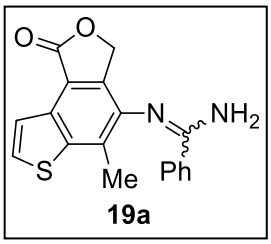
Pale yellow crystals, 84% yield (84 mg); mp > 300 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.62 (s, 3H), 5.45 (s, 2H), 7.18-7.38 (m, 2H), 7.45-7.70 (m, 2H), 7.85-7.95 (m, 1H), 8.03-8.14 (m, 1H), 8.80-8.90 (m, 1H), 10.35 (s, 1H), 11.84 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.7, 70.3, 112.0, 116.5, 116.7, 119.9, 121.3, 124.8, 125.7, 127.0, 127.3, 128.6, 130.0, 132.4, 138.5, 139.3, 140.6, 141.3, 160.4, 171.9.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{20}H_{15}N_2O_3S$ 363.0798; Found 363.0789.

*N'-(5-Methyl-1-oxo-1,3-dihydrothieno[3,2-e]isobenzofuran-4-yl)benzimidamide (**19a**).*



19a

Dihetarylethene: **12b**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 18 h.

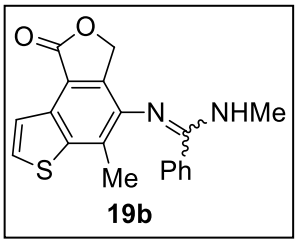
Gray powder, 83% yield (83 mg); mp 227-228 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.48 (s, 3H), 5.15-5.35 (m, 2H), 6.64 (br s, 2H), 7.43-7.60 (m, 3H), 7.63-7.74 (m, 1H), 7.84-7.94 (m, 1H), 7.97-8.13 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 15.0, 70.1, 117.8, 123.0, 127.8 (2C), 128.3, 128.5 (2C), 128.7, 130.6, 130.8, 135.8, 139.7 (2C), 140.4, 142.7, 171.0.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{18}H_{15}N_2O_2S$ 323.0849; Found 323.0864.

*N-Methyl-N'-(5-methyl-1-oxo-1,3-dihydrothieno[3,2-e]isobenzofuran-4-yl)benzimidamide (**19b**).*



19b

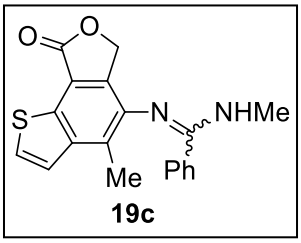
Dihetarylethene: **12c**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 11 h.

Dark yellow powder, 75% yield (75 mg); mp 124-127 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.28 (s, 3H), 2.92 (s, 3H), 5.11 (s, 2H), 7.18-7.35 (m, 5H), 7.69-7.83 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 16.7, 29.1, 69.7, 116.5, 121.0, 128.0 (2C), 128.7 (2C), 129.0, 129.3, 129.9, 130.1, 135.6, 140.4, 141.8, 142.9, 159.2, 171.2.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{19}H_{17}N_2O_2S$ 337.1005; Found 337.1000.

*N-Methyl-N'-(4-methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl)benzimidamide (**19c**).*



19c

Dihetarylethene: **12d**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 12 h.

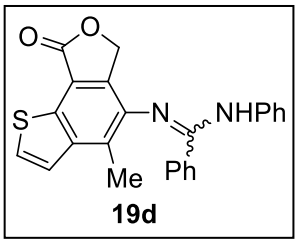
Yellow powder, 87% yield (87 mg); mp 190-193 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 3H), 3.12 (s, 3H), 5.02 (s, 2H), 5.09 (s, 1H), 7.04-7.60 (m, 7H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 15.3, 29.2, 70.0, 117.4, 122.0 (2C), 127.1, 127.5, 128.7 (2C), 129.0 (2C), 130.1, 133.4, 134.8, 138.7, 142.2, 158.6, 171.2.

HRMS (ESI-TOF) *m/z* [M+H]$^{+}$ Calcd for $C_{19}H_{17}N_2O_2S$ 337.1005; Found 337.0993.

*N'-(4-Methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl)-N-phenylbenzimidamide (**19d**).*



19d

Dihetarylethene: **12e**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 18 h.

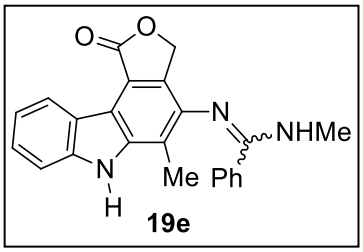
Gray powder, 94% yield (94 mg); mp 185-187 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.42 (s, 3H), 5.26 (s, 2H), 6.96-7.10 (m, 1H), 7.23-7.44 (m, 7H), 7.50-7.59 (m, 1H), 7.78-7.87 (m, 1H), 7.89-8.00 (m, 2H), 9.52 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 15.8, 70.4, 120.5 (2C), 122.5, 130.0, 124.0, 124.4, 128.4, 128.7 (4C), 128.8 (2C), 129.3, 130.1, 130.2, 135.6, 139.2, 141.4, 142.3, 156.6, 170.8.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{24}H_{19}N_2O_2S$ 399.1162; Found 399.1151.

*N-Methyl-N'-(5-methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)benzimidamide (**19e**).*



19e

Dihetarylethene: **12a**. Method: A. Solvent: DCM. Dopant: DABCO (3 equiv). Reaction time: 9 h.

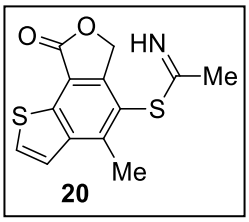
Pale brown powder, 76% yield (76 mg); mp 251-252 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.30 (s, 3H), 2.94 (s, 3H), 5.16 (s, 2H), 7.12-7.22 (m, 1H), 7.20-7.30 (m, 5H), 7.33-7.40 (m, 1H), 7.46-7.51 (m, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 11.29 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 13.2, 29.1, 70.3, 111.4, 112.5, 116.1, 119.3, 119.4, 120.4, 122.0, 123.8, 125.7, 128.0 (2C), 128.6 (2C), 128.9, 129.0, 129.9, 134.3, 140.5, 141.3, 172.5.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{23}H_{20}N_3O_2$ 370.1550; Found 370.1543.

*4-Methyl-8-oxo-6,8-dihydrothieno[2,3-e]isobenzofuran-5-yl ethanimidothioate (**20**).*



20

Dihetarylethene: **6a**. Method: A (without chromatography). Solvent: DCM. Dopant: none. Reaction time: 5 h.

Yellow powder, 84% yield (84 mg); mp 259-260 °C.

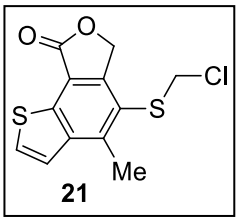
^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.77 (s, 3H), 2.42 (s, 3H), 5.16 (s, 2H), 7.68 (d, *J* = 5.5 Hz, 1H), 8.01 (d, *J* = 5.5 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 17.8, 22.7, 70.6, 118.5, 120.6, 123.8, 124.6, 130.4, 136.1, 142.0, 145.1, 149.7, 170.0.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{13}H_{12}NO_2S_2$ 278.0304; Found 278.0297.

Anal. Calcd for $C_{13}H_{11}NO_2S_2$: C, 56.29; H, 4.00; N, 5.05. Found: C, 57.12; H, 3.95; N, 4.81.

*5-((Chloromethyl)thio)-4-methylthieno[2,3-e]isobenzofuran-8(6H)-one (**21**).*



21

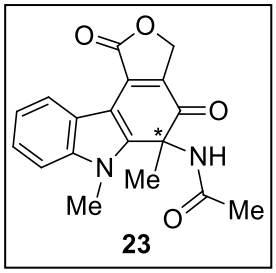
Dihetarylethene: **6a**. Method: A. Solvent: DCM. Dopant: DABCO (1 equiv). Reaction time: 7 h.

Colorless crystals, 27% yield (28 mg); mp 147-149 °C.

^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 2.96 (s, 3H), 5.23 (s, 2H), 5.62 (s, 2H), 7.84 (d, *J* = 5.5 Hz, 1H), 8.06 (d, *J* = 5.5 Hz, 1H).

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{12}H_{10}ClO_2S_2$ 284.9805; Found 284.9805.

*Syn- 3a-hydroxy-2,11,11b-trimethyl-11,11b-dihydro-3aH-furo[3,4-c]oxazolo[4,5-a]carbazol-6(4H)-one (**23**).*



23

Dihetarylethene: **7a** or **7b**. Method: B (for **7a**) or A (for **7b**). Solvent: DMF (for **7a**) or DCM (for **7b**). Reaction time: 7 h (for **7a**) or 6 h (for **7b**).

Orange powder, 73% yield (80 mg, from **7b**), 30% yield (33 mg, from **7a**); mp > 300 °C.

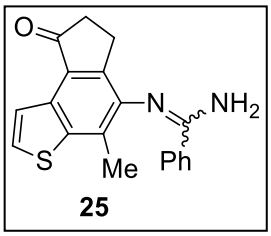
^{1}H NMR (300 MHz, DMSO-d$_6$): δ = 1.54 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 5.17 (d, *J* = 17.5 Hz, 1H, ½CH_2), 5.26 (d, *J* = 17.5 Hz, 1H, ½CH_2), 7.21-7.30 (m, 2H, H^{indole}), 7.53-7.58 (m, 1H, H^{indole}), 8.46-8.51 (m, 1H, H^{indole}), 9.52 (s, 1H, OH).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d$_6$): δ = 21.7, 23.2, 31.5, 60.3, 69.7, 101.6, 110.8, 122.2 (2C), 122.6, 122.9, 136.0, 137.1, 138.3, 148.2, 169.3, 172.0, 194.5.

MS (EI) *m/z* (%) = 324 (100) [M]$^+$.

HRMS (ESI-TOF) *m/z* [M+H]$^+$ Calcd for $C_{18}H_{17}N_2O_4$ 325.1183; Found 325.1185.

*N'-(4-Methyl-8-oxo-7,8-dihydro-6H-indeno[5,4-b]thiophen-5-yl)benzimidamide (**25**).*



25

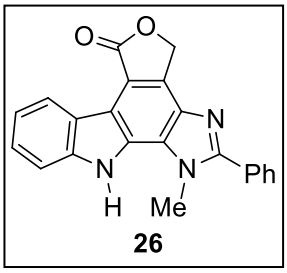
Dihetarylethene: **24**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 8 h.

Yellow powder, 46% yield (46 mg); mp 228-231 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.38 (s, 3H), 2.59-2.68 (m, 2H), 2.84-2.94 (m, 2H), 6.49 (br s, 2H), 7.45-7.53 (m, 3H), 7.81 (d, J = 5.4 Hz, 1H), 7.99 (d, J = 5.4 Hz, 1H), 8.06 (d, J = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 16.5, 24.5, 36.6, 122.0, 127.7 (2C), 128.3, 128.5 (2C), 129.2, 129.5, 130.0, 130.7, 136.0, 141.8, 143.5, 149.1, 154.8, 206.3.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{19}H_{17}N_2OS$ 321.1056; Found 321.1067.

*1-Methyl-2-phenyl-4,11-dihydrofuro[3,4-c]imidazo[4,5-a]carbazol-6(1H)-one (**26**).*



26

Dihetarylethene: **12a**. Method: A. Solvent: DCM. Dopant: none. Reaction time: 20 h.

Yellow powder, 52% yield (50 mg); mp 285-283 °C.

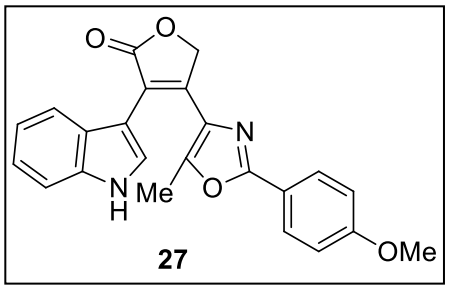
^{1}H NMR (300 MHz, DMSO-d_6): δ = 4.35 (s, 3H), 5.77 (s, 2H), 7.22-7.33 (m, 1H), 7.42-7.51 (m, 1H), 7.57-7.77 (m, 4H), 7.87-7.95 (m, 2H), 8.95-9.05 (m, 1H), 12.14 (s, 1H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ = 34.9, 69.3, 112.1, 114.0, 118.4, 120.0, 122.0, 124.0, 125.6, 126.4, 129.0, 129.2 (2C), 129.5, 129.8, 130.0 (2C), 130.4, 134.2, 140.2, 141.0, 154.2.

MS (EI) *m/z* (%) = 353 (100) $[M]^+$.

HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{22}H_{16}N_3O_2$ 354.1237; Found 354.1232.

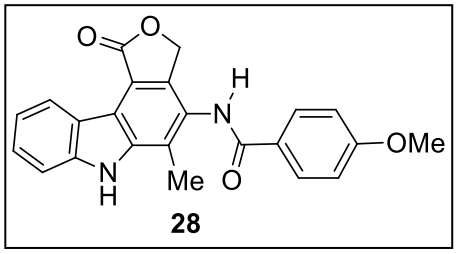
II.3. Gram-scale experiments



27

Synthesis of dihetarylethene 27. 2-(Indol-3-yl)acetic acid **1a** (2 g, 11.43 mmol) was dissolved in DMF (25 ml) and potassium carbonate K_2CO_3 (2.37 g, 17.14 mmol) was added. After 5 minutes of stirring, 2-bromo-1-(2-(4-methoxyphenyl)-5-methyloxazol-4-yl)ethanone (bromoketone **2a**, 3.53 g, 11.43 mmol) was added. Argon was bubbled through this solution for 30 min. The reaction mixture was stirred for 4 h at 80 °C. The resulting mixture was poured in water (300 ml), extracted with ethyl acetate (5 × 50 ml). The combined organic phases were washed with brine (2 × 200 ml), dried over under $MgSO_4$ and evaporated in vacuum. The residue was recrystallized form acetone to give 2.51 g (57%) of DHE **27**. Additional quantity of **27** (0.35 g, 8%) was isolated by column chromatography of filtrate solution.

*3-(1H-indol-3-yl)-4-(2-(4-methoxyphenyl)-5-methyloxazol-4-yl)furan-2(5H)-one (**27**).* Pale yellow powder, 65% yield (2.86 g); mp 249-252 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.62 (s, 3H), 3.82 (s, 3H), 5.32 (s, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.04-7.14 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.72-7.78 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 11.58 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 11.7, 55.8, 71.1, 105.3, 112.5, 115.0 (2C), 119.3, 119.6, 119.8, 122.0, 125.6, 127.7, 128.1 (2C), 129.8, 130.7, 136.2, 145.4, 148.9, 160.2, 161.7, 173.9. HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{19}N_2O_4$ 387.1339; Found 387.1344.



28

Synthesis of carbazole 28. Each of five 12 mL glass vessels were charged by solution of 200 mg of dihetarylethene **27** in mixture DCM / NMP 10:1 (11 mL). The solutions were irradiated with stirring by two 8W UV lamps (365 nm) for 6.5 h. The precipitate was filtred off, washed by 5 ml of DCM and dried on air. These manipulations afforded 580 mg (58%) of desired carbazole **28** as white powder. The filtrate was evaporated and dissolved in ethyl acetate (50 mL). The solution was washed with water (3 x 150 mL), dried with magnesium sulfate, and evaporated in vacuum. The residue was purified by recrystallization from EtOH. These manipulations gave us additional 170 mg (17%) of desired carbazole **28** as white powder. The crystallization filtrate was purified by flash chromatography by petroleum ether/ethyl acetate (2:1) to give additional 80 mg (8%) of carbazole **28**.

4-Methoxy-N-(5-methyl-1-oxo-3,6-dihydro-1H-furo[3,4-c]carbazol-4-yl)benzamide ***(28)***. White powder, 75% yield (750 mg); mp > 300 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.61 (s, 3H), 3.86 (s, 3H), 5.43 (s, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 2H), 8.84 (d, *J* = 7.8 Hz, 1H), 10.16 (s, 1H), 11.82 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 13.7, 55.9, 70.3, 111.9, 114.2 (2C), 116.3, 116.6, 119.9, 121.4, 124.8, 125.6, 126.4, 127.2, 127.9, 130.2 (2C), 138.6, 140.6, 141.2, 162.6, 165.3, 172.0. HRMS (ESI-TOF) *m/z* $[M+H]^+$ Calcd for $C_{23}H_{19}N_2O_4$ 387.1339; Found 387.1338.

III. Photochemical equipment and gram-scale benzannulation

Figure S1. Device for preparative photochemical reactions, used in our work.

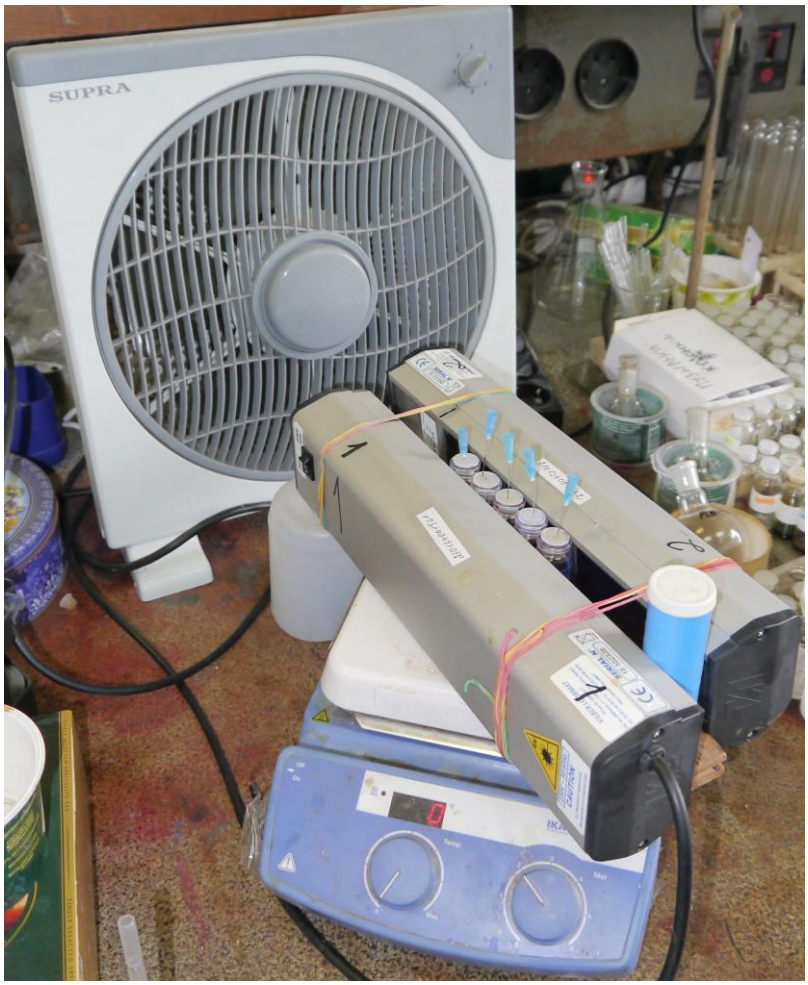
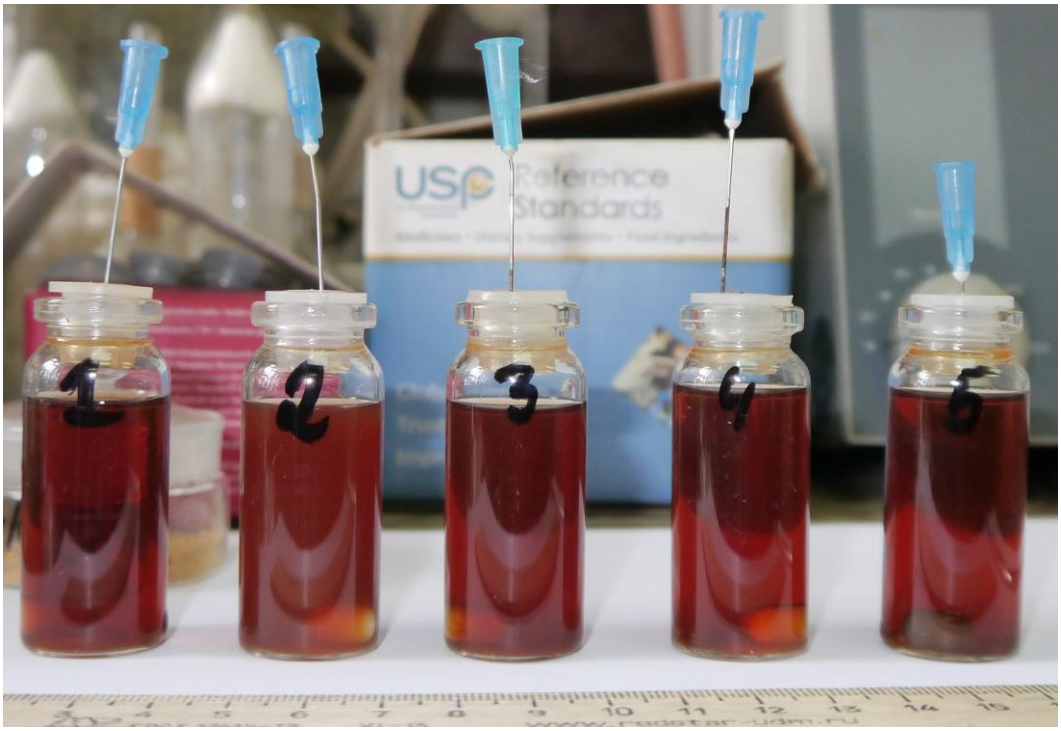
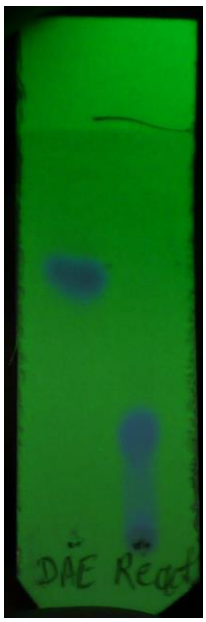


Figure S2. Photochemical reactors, used in our work.

Figure S3. Synthesis of carbazole **28** (photochemical step of benzannulation). Reaction mixtures before and after photoreaction (+ TLC of the mixture).

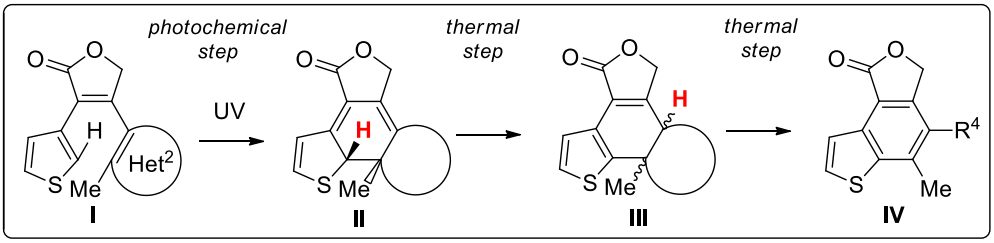




IV. Proposed mechanism for photorearrangement of dihetarylethenes

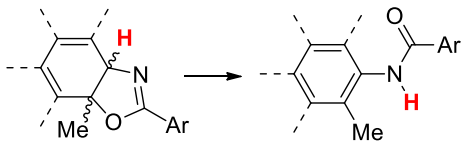
Based on the previous mechanistic studies[7] as well as experimental works[8] we can propose the following general mechanism of the rearrangement (Scheme S1). The key step is hydrogen migration (red in the photogenerated intermediate **II**). The driving force of the photorearrangement is the stepwise restoration of aromaticity of annulating heterocycle (thiophene on Scheme S1) and benzene ring. According to literature data,[6,7] mechanism of the hydrogen migration is concerted [1,n]-H migration or proton elimination. Last step of the proposed mechanism (**III** → **IV**) is spontaneous cycloreversion of heterocycle due to C-heteroatom bond cleavage and restoration of aromaticity. For clearance we have depicted a specific frameworks of this step for all used transforming heterocycles (Het^2).

Scheme S1. General mechanism (for simplicity thiophene was depicted as annulating moiety)

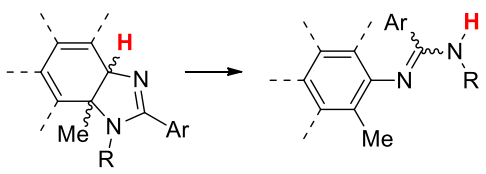


Frameworks of step **III** → **IV** for different heterocycles from the present work:

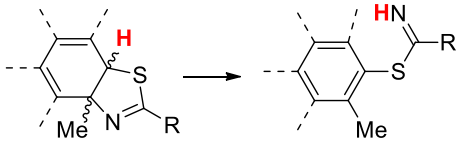
*Oxazole as transforming moiety (DHEs **3, 11**)*



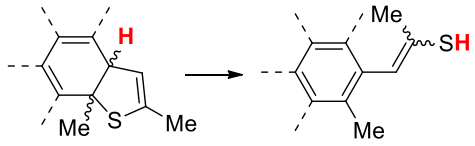
*Imidazole as transforming moiety (DHEs **12**)*



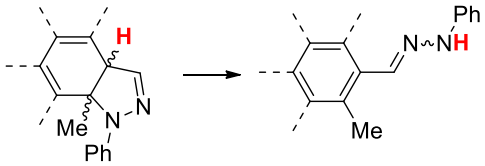
*Thiazole as transforming moiety (DHEs **6**)*



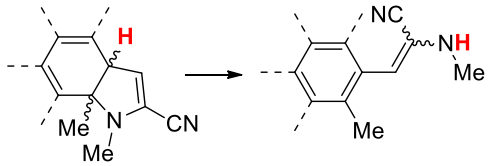
*Thiophene as transforming moiety (DHEs **8**)*



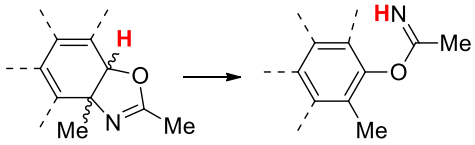
*Pyrazole as transforming moiety (DHEs **10**)*



*Pyrrole as transforming moiety (DHEs **9**)*

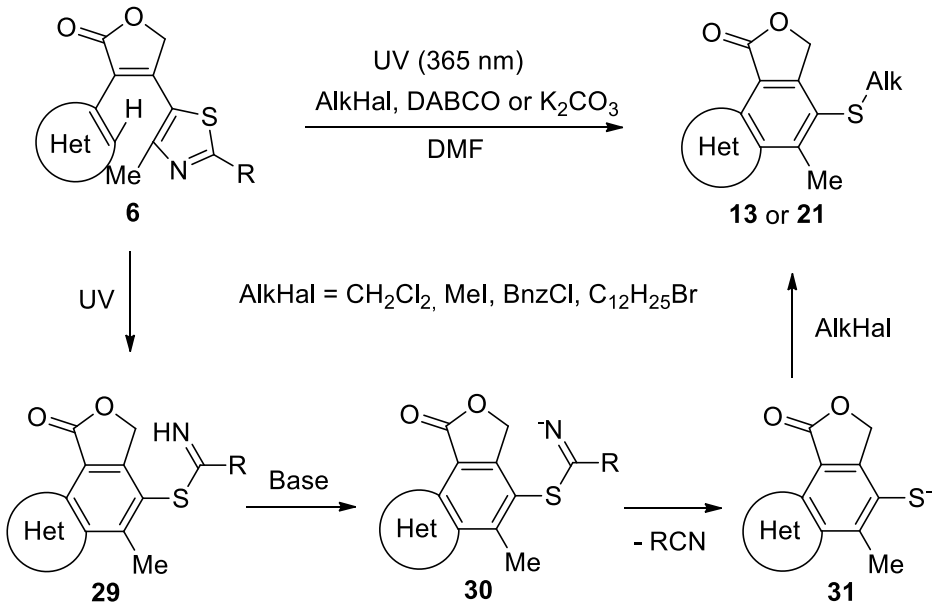


*Oxazole as transforming moiety (DHEs **7**)*



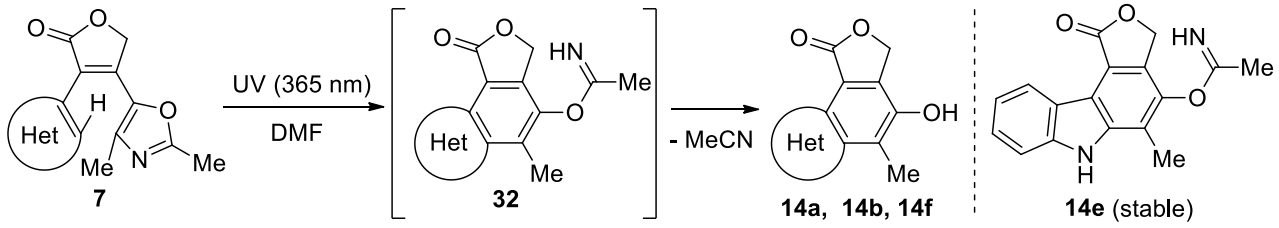
For the photoreaction of thiazole-based dihetarylethenes **6** we propose the mechanism on Scheme S2. The key step after the photorearrangement is base-induced (base = DABCO or K_2CO_3) elimination of acetonitrile (R = Me) or benzonitrile (R = Ph) from the imidosulfide derivative **28**. A last stage is alkylation of thiophenolate **31** by alkyl halides (CH_2Cl_2, MeI, BnzCl, $C_{12}H_{25}Br$).

Scheme S2. Proposed mechanism of photoreaction of thiazole derivatives (photorearrangement / *in situ* alkylation)



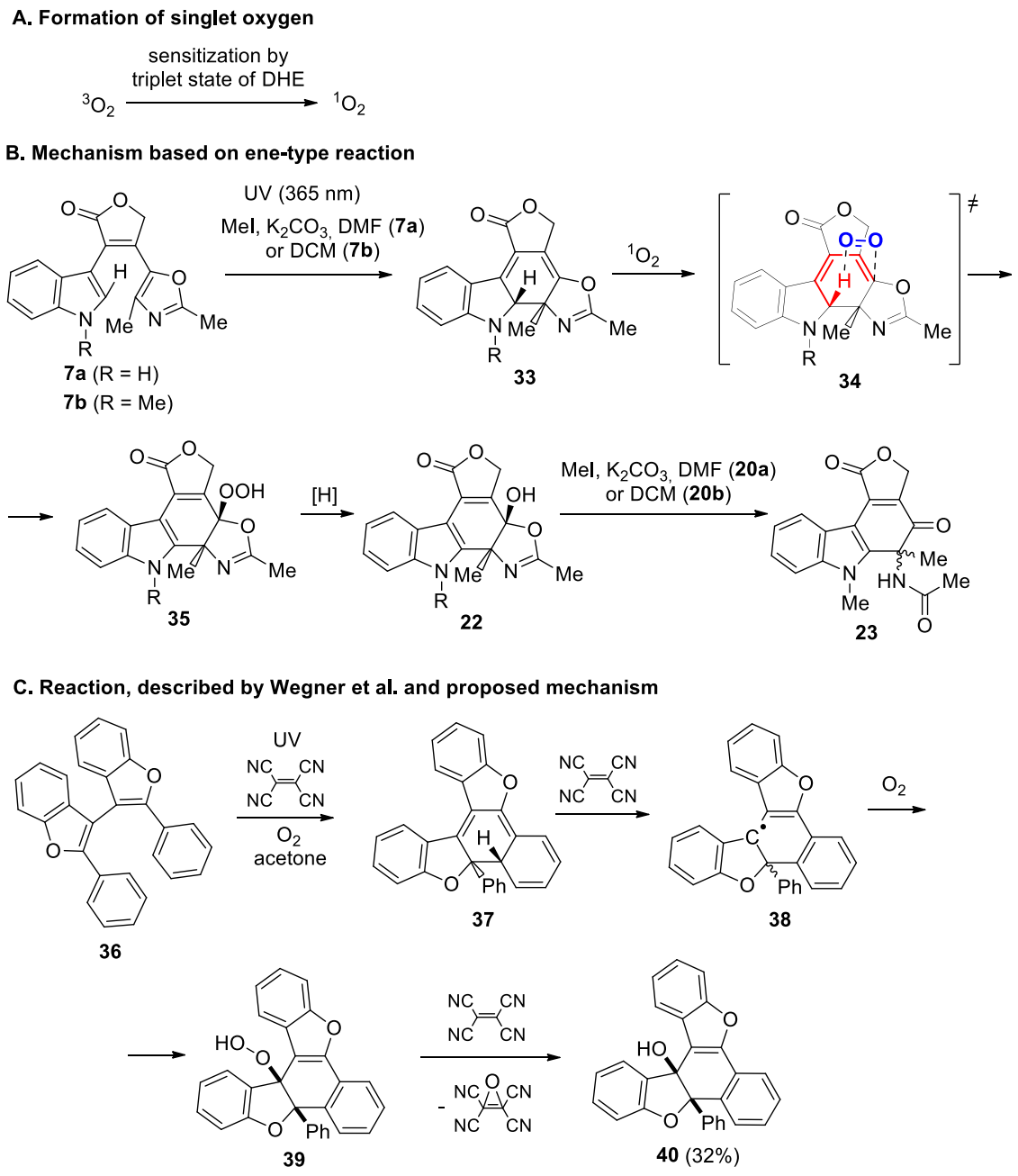
The mechanism of photoreaction of oxazole-based dihetarylethenes **7** (Scheme S3) in general follows the Scheme S2. The key step after photorearrangement is thermal or photochemical elimination of acetonitrile from acetimidate derivative **32**. Apparently, stability of compounds **32** depends on heterocyclic fragment Het. For indole derivative, acetimidate **14e** is stable and was isolated, while in the case of thiophene-based DHEs only benzo[*b*]thiophenoles **14a,b** were obtained.

Scheme S3. Proposed mechanism of photoreaction of oxazole derivatives **7**.



The formation of photoproduct **23** from dihetarylethenes **7a** and **7b** is rather unclear, and we propose the following mechanism (Scheme S4B). The key step is ene-type[9] reaction between intermediate **33** with singlet oxygen, formed after sensitization (Scheme S4A). This results in intermediate **35** with peroxide function. Subsequent reduction and cycloreversion of heterocyclic ring of **22** leads to stable product **23**. Under *in situ* alkylation conditions (for **7b**) additional alkylation of indole takes place. This mechanism is rather speculative and requires comprehensive exploration, but the benefit of the key step (**33** → **35**) is restoration of indole ring aromaticity.

Scheme S4. Proposed mechanism of formation for photoproduct **23**.



It sould be noted, that related transformation was described by Wegner et al. for terarylene **36** (Scheme S4C). [10] It was found, that **36** undergoes oxidative rearrangement towards **40** in aerobic conditions the presence of oxygen and tetracyanoethylene (TCNE) as a sensitizer. Importantly, several sensitizers were employed, but only TCNE provides formation of **40**. The authors suggested the following mechanism (Scheme S4C). Formation of cation-radical of **36** in the presence of TCNE results in formation of radical **38** after deprotonation. Subsequent reaction with oxygen and trapping of the peroxo by tetracyanoethylene provides **39** in 32% yield.

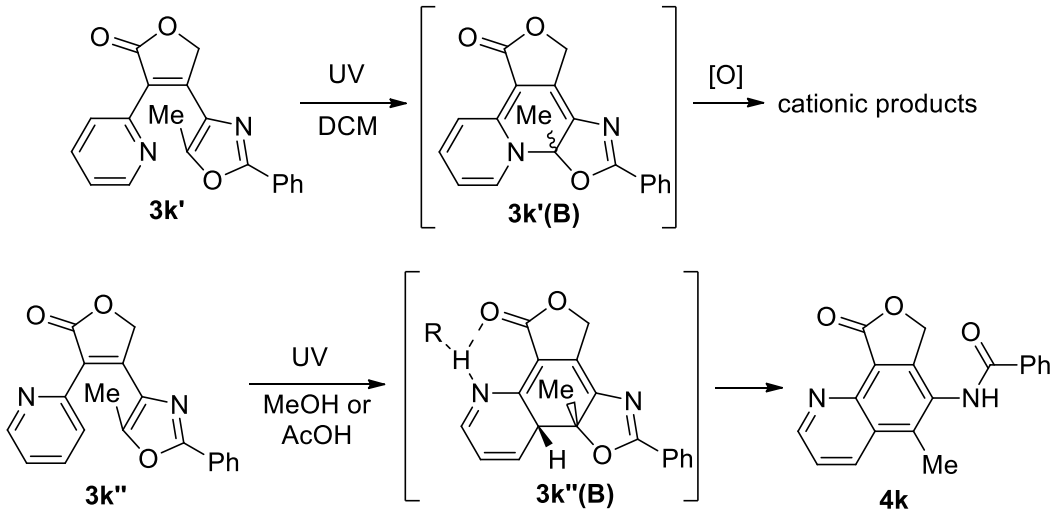
V. Specific aspects of the photorearrangement

V.1. Role of conformation for α-pyridine derivative

More complex results were obtained for dihetarylethene **3k** based on α-substituted pyridine. Upon irradiation (with or without DABCO) in DCM we have observed gradual conversion of **3k**, however, we did not fix any products. It is known, that intra- or intermolecular noncovalent interactions lead to loss of photoactivity of some photochromic diarylethenes.[11] We suppose that DHE **3k** exists mainly in the photoinactive conformation, which prevents cyclization (nitrogen atom of pyridine is turned towards oxazole), and protonation of pyridine should return the desired photoactivity. This assumption was supported by DFT calculation. Actually, photolysis in protic solvents (MeOH or AcOH) let us to detect and isolate desired quinoline **4k** in 37% yield (in MeOH); the structure of the latter was proved by 2D NMR spectroscopy methods.

We observed the formation of water-soluble precipitate after irradiation of DHE **3k** in DCM, wherein we did not fix any products by TLC. This result was explained by stabilization of conformer **3k'** (Scheme S5). Photocyclization of **3k'** should lead to formation of C-N bond (structure **3k'(B)**). Fedorova et al. demonstrated, that air oxygen oxidizes related intermediates towards corresponding cationic polyheteroaromatics.[12,13] Apparently, in the protic solvents (MeOH and AcOH) conformation **3k''** is more stable due to protonation of pyridine / hydrogen bonding with carbonyl. Kawai et al. described similar impact of methanol on terarylene conformation.[14] Thus, photocyclization of **3k** in MeOH and AcOH gave us target quinoline **4k**.

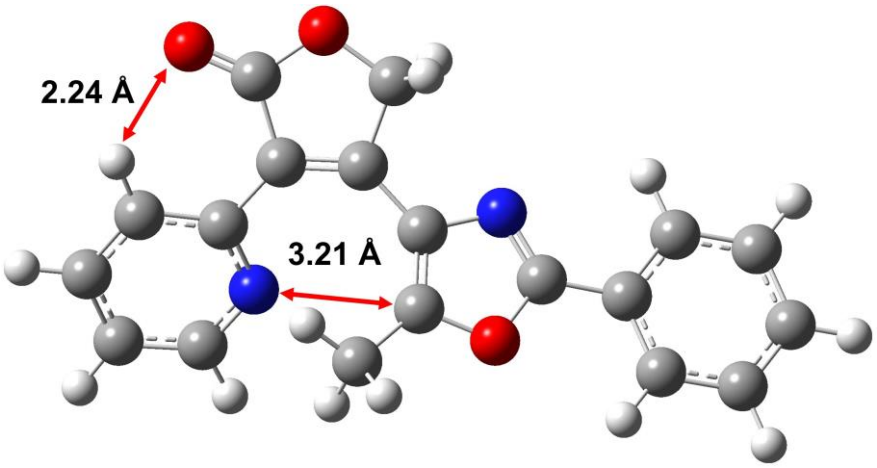
Scheme S5. Proposed phototransformation of



To support this hypothesis, we optimized structures **3k** and **3kH**$^+$ by the DFT method on B3LYP/6-31G (d) level of theory (Figures S4,S5). It was previously reported that this method quite

accurately describes the structure of photoactive terarylenes[15,16] and diarylethenes.[17] Generally, DFT calculations are in consistence with our conclusions (*vide supra*). For **3k** and **3kH**$^+$ the antiparallel photoactive conformations are stable and the distance between the reaction centers is less than 4.2 Å, that is necessary for cyclization.[18] We can conclude, that carbonyl group of furan-2(5*H*)-one bridge play important role in stabilization of conformers **3k'** and **3k''**. As can be seen form Figures S3,S4, the distances between oxygen of carbonyl and hydrogens of pyridine (protonated pyridine) rings are shortened (2.24 Å and 1.75 Å).

Figure S4. Optimized structure of dihetarylethene **3k**.



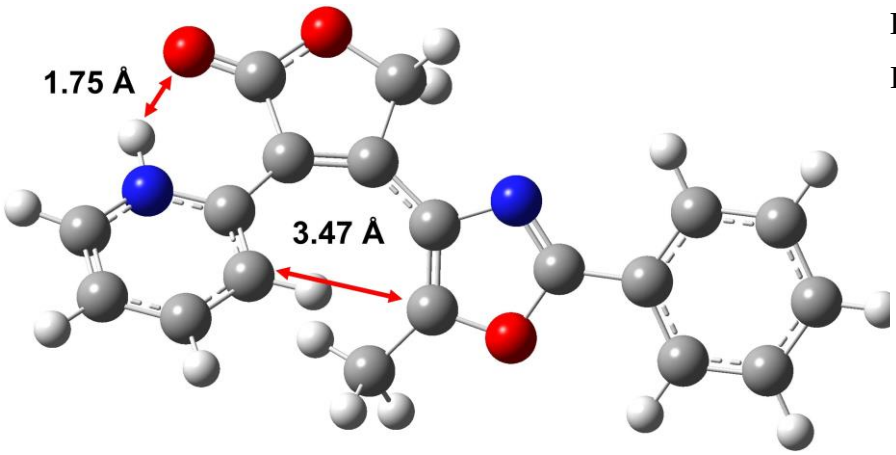
E = -1067.638737 Hartree

Imaginary Freq = 0

Cartesian coordinates of the optimized structure of structure 3k:

1	C	-3.0331110	2.2241650	0.0815990
2	O	-2.0987240	3.2189470	0.1819790
3	C	-2.3282910	0.9048140	0.0566720
4	C	-0.7956170	2.6466210	0.2491550
5	C	-0.9990050	1.1524700	0.2008170
6	C	0.1821260	0.3190900	0.3259470
7	N	1.4091630	0.8132240	-0.1223650
8	C	0.3882800	-0.8893610	0.9436240
9	C	2.2811210	-0.0970910	0.1918570
10	O	1.7259740	-1.1615380	0.8527220
11	C	-3.0488290	-0.3530230	-0.2225480
12	C	-4.4380460	-0.4560580	-0.0288930
13	N	-2.3185850	-1.3748870	-0.7160400
14	C	-5.0764430	-1.6476800	-0.3634950
15	C	-2.9512850	-2.5044190	-1.0386230
16	C	-4.3256320	-2.6986230	-0.8854500
17	C	3.7170840	-0.1114870	-0.0656030
18	C	4.2993210	0.9622280	-0.7596340
19	C	4.5244180	-1.1746140	0.3687790
20	C	5.6677680	0.9693740	-1.0110060
21	C	5.8937740	-1.1597250	0.1123160
22	C	6.4695690	-0.0902080	-0.5765490
23	O	-4.2152380	2.4723560	0.0269210
24	C	-0.4437130	-1.8575580	1.6976590
25	H	-0.1931700	3.0015660	-0.5944290
26	H	-0.3078970	2.9726680	1.1753510
27	H	-4.9914890	0.3925310	0.3513020
28	H	-6.1492180	-1.7479100	-0.2217710
29	H	-2.3258480	-3.2990820	-1.4440830
30	H	-4.7841540	-3.6416570	-1.1674330
31	H	3.6656920	1.7773460	-1.0934420
32	H	4.0764980	-2.0053520	0.9041230
33	H	6.1111350	1.8030030	-1.5485440
34	H	6.5124220	-1.9859470	0.4515950
35	H	7.5377840	-0.0820590	-0.7750330
36	H	-0.6960300	-2.7291560	1.0832510
37	H	0.0937410	-2.2047350	2.5868360
38	H	-1.3805310	-1.3911750	2.0083920

Figure S5. Optimized structure of dihetarylethene **3kH**$^{+}$.



E = -1068.034230 Hartree

Imaginary Freq = 0

Cartesian coordinates of the optimized structure of structure 3kH^{+}:

1	C	2.9505410	2.1646320	0.1715090
2	O	2.0429680	3.1522010	0.2188860
3	C	2.2504980	0.8527730	0.0805840
4	C	0.7220930	2.5952030	0.2121850
5	C	0.9054560	1.0966400	0.1800420
6	C	-0.2713300	0.2750850	0.2830800
7	N	-1.4885020	0.7784800	-0.1738340
8	C	-0.4936180	-0.9199280	0.9421780
9	C	-2.3767330	-0.1087830	0.1633100
10	O	-1.8236980	-1.1676820	0.8593370
11	C	3.0098500	-0.3494580	-0.2236950
12	C	2.4944240	-1.5681290	-0.6890990
13	C	3.3554810	-2.6115640	-1.0063360
14	C	5.2254260	-1.2436320	-0.4257140
15	C	4.7425440	-2.4620120	-0.8602120
16	C	0.3194550	-1.8476510	1.7682030
17	O	4.1542620	2.3613810	0.2053180
18	C	-3.8077050	-0.1235520	-0.0923910
19	C	-4.3784210	0.9325220	-0.8244850
20	C	-4.6192780	-1.1675560	0.3827250
21	C	-5.7462160	0.9403310	-1.0740960
22	C	-5.9874790	-1.1499830	0.1269580
23	C	-6.5525220	-0.0990700	-0.5997580
24	H	0.1942780	2.9321120	1.1097920
25	H	0.1774750	2.9573200	-0.6662090
26	H	1.4255390	-1.6684830	-0.8253270
27	H	2.9490050	-3.5463690	-1.3801060
28	H	6.2792740	-1.0185080	-0.3096930
29	H	5.4295710	-3.2657950	-1.0964710
30	H	-0.2189500	-2.0935620	2.6892650
31	H	0.5201000	-2.7928800	1.2466880
32	H	1.2754290	-1.3921440	2.0362110
33	H	-3.7424120	1.7325560	-1.1886010
34	H	-4.1806260	-1.9825250	0.9488730
35	H	-6.1859560	1.7564660	-1.6392370
36	H	-6.6139150	-1.9564030	0.4957890
37	H	-7.6205080	-0.0893880	-0.7966240
38	N	4.3680330	-0.2468740	-0.1266200
39	H	4.7119310	0.7039550	0.1205690

V.2. Possible competition with 1,2-dyotropic rearrangement

In the photoreactions of DHE **8a** (Scheme S6) under alkylation conditions (UV; iodomethane, K_2CO_3, DMF or benzyl chloride, K_2CO_3, DMF) we detected the formation of two inseparable isomeric photoproducts. Both compounds exist as a mixture of *E*- / *Z*-isomers, and possess different ^{1}H NMR spectra.

Apparently, the first product is a desired benzo[*b*]thiophene **15a**, which forms *via* expected photorearrangement of **8a** throw photocyclization / [1,5]-H shift / cycloreversion cascade sequence (**14a(A)→14a(B)→C→D**) with subsequent alkylation (Scheme S6). As all other target benzo[*b*]thiophenes, **15a** features two doublets in downfield region with J^3 = 5.4 Hz (for Bn-alkylated products, see Figures S6 and S7 below).

The second product has two doublets (J^3 = 3.2 Hz) in downfield region. According to the literature data,[19,20] we assign the structure **G** to the second product (Scheme S6). Probably, DHE **8a** converts to the annulated isomer **F** similar to number of other dithienylethenes with subsequent C-S bond cleavage / hydrogen migration and alkylation towards structure **G**.

Equality of molecular masses of two photoproducts was supported by DOSY NMR spectroscopy (Figure S8) and high-resolution mass-spectrometry (Figure S9).

Scheme S6. Possible pathways for isomeric annulated products from DHE **8a**.

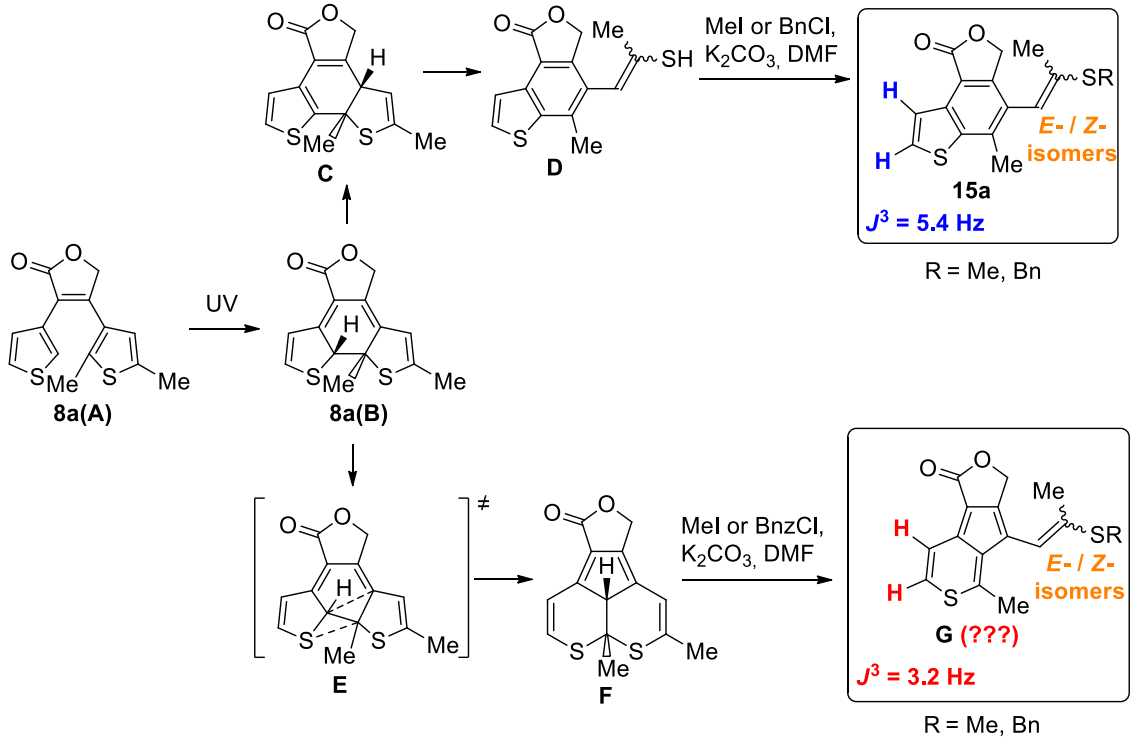


Figure S6. ^{1}H NMR spectra (600.13 MHz, $CDCl_3$) of photoproducts after photoreaction of **8a** in the presence of benzyl chloride and K_2CO_3 in DMF.

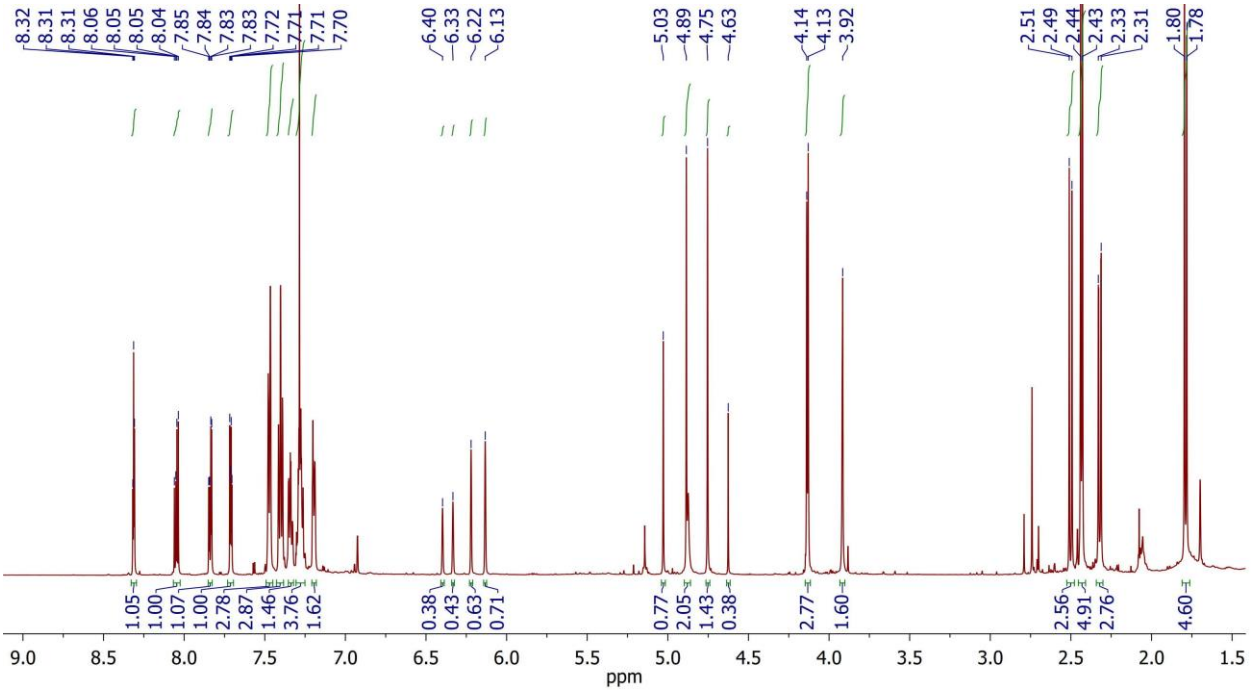


Figure S7. Downfield region of ^{1}H NMR spectra from Figure S6.

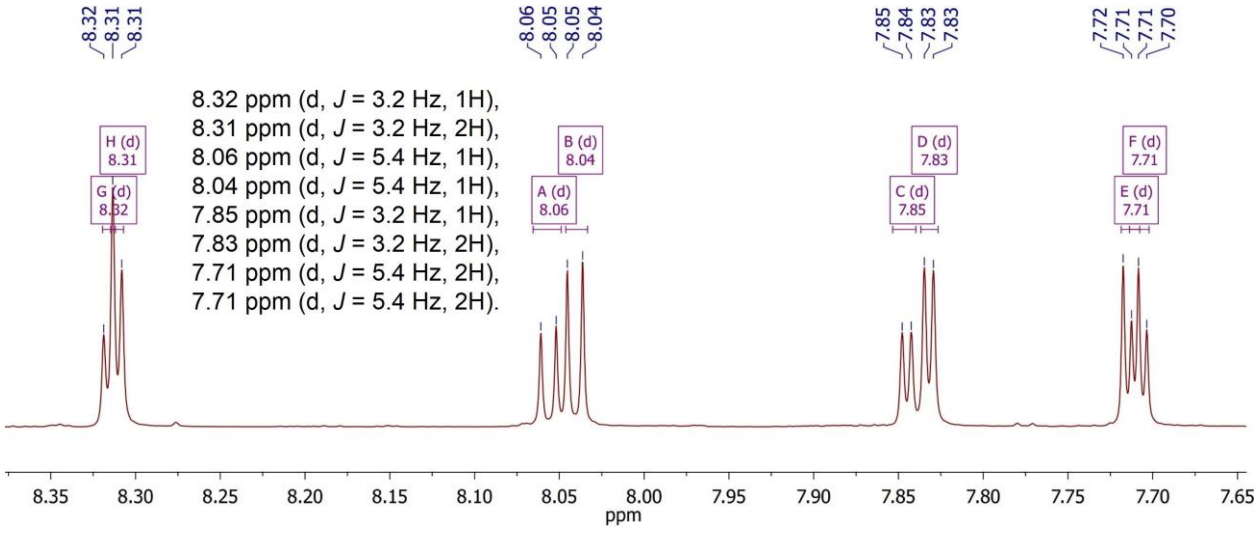


Figure S8. 2D NMR DOSY spectra of mixture after photoreaction of **8a** in the presence of benzyl chloride and K_2CO_3 in DMF. As can be seen from the spectrum, major components of the mixture have equal molecular masses.

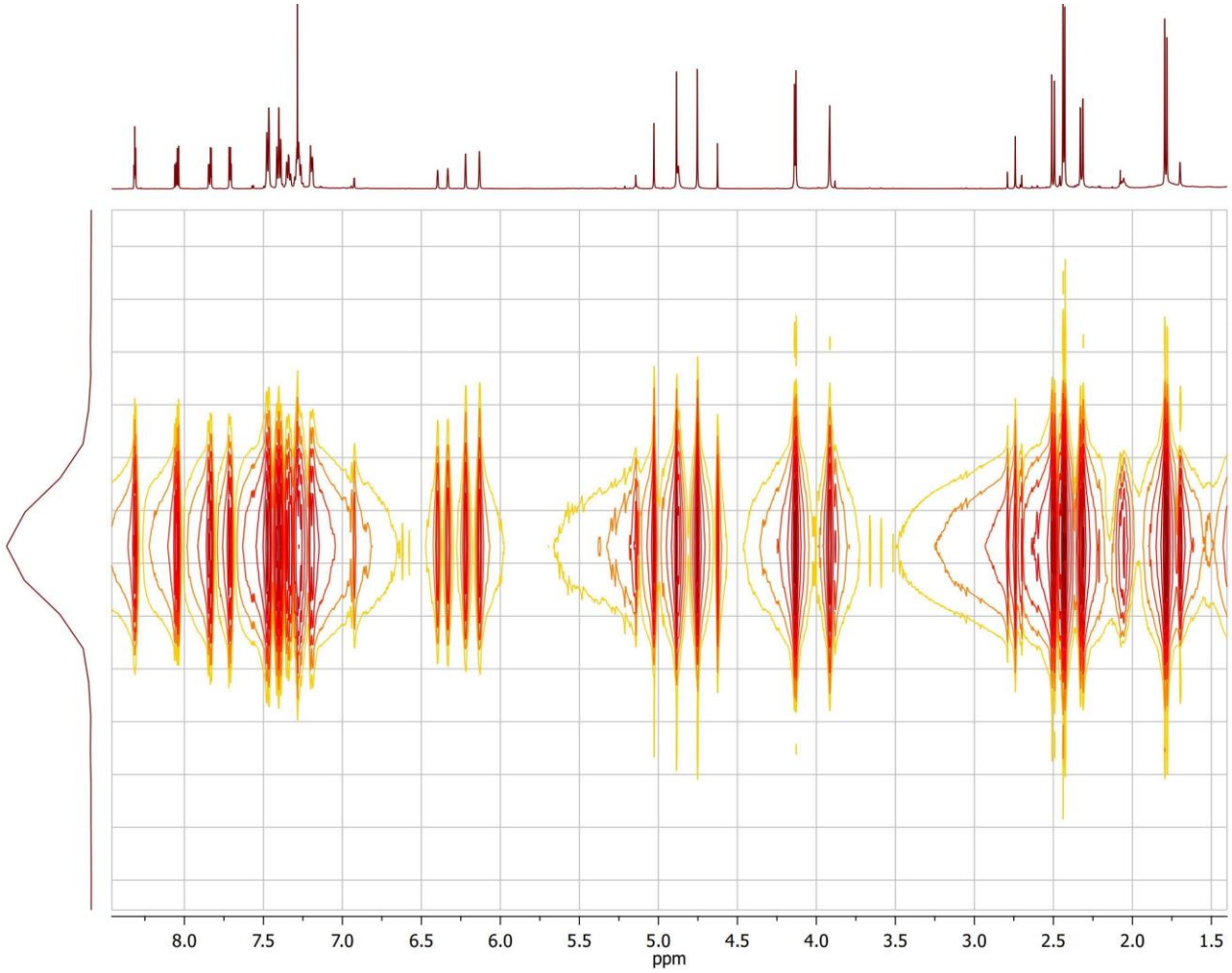
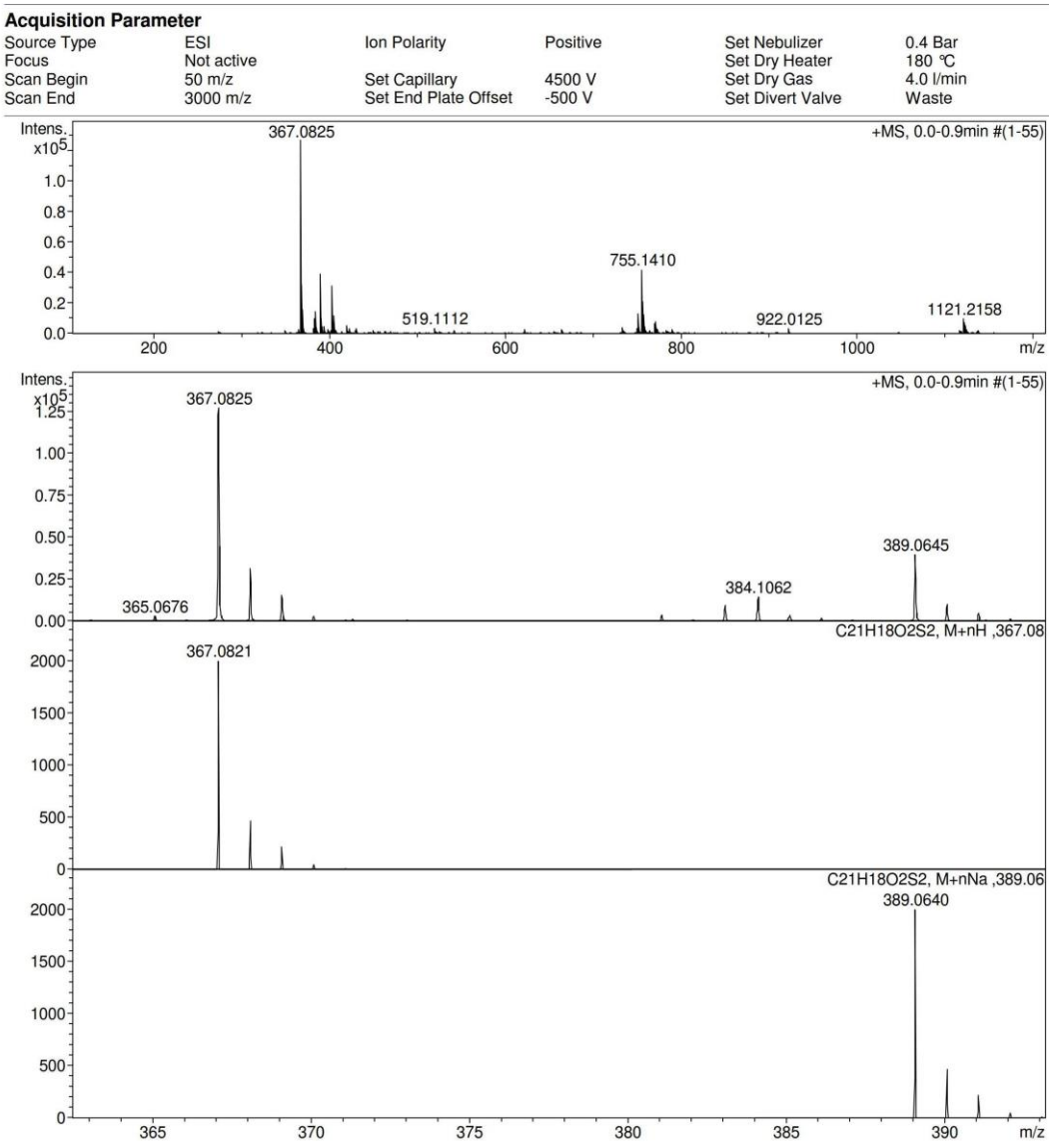


Figure S9. High-resolution mass spectrum (electrospray ionization) of the mixture after photoreaction of **8a** in the presence of benzyl chloride and K_2CO_3 in DMF. The major component of the mixture has molecular mass corresponding to **15a** (or **G** from Scheme S6).



VI. NMR monitoring of photoreactions of dihetarylethenes

Figure S10. ^{1}H NMR monitoring of photoreaction of DHE **3a** before (**A**) and after (**B**-**F**) irradiation ($CDCl_3$, C = 0.04 M) with two 8W UV lamps (365 nm) and after addition of 0.3 ml of DMSO-d_6 (**G**).

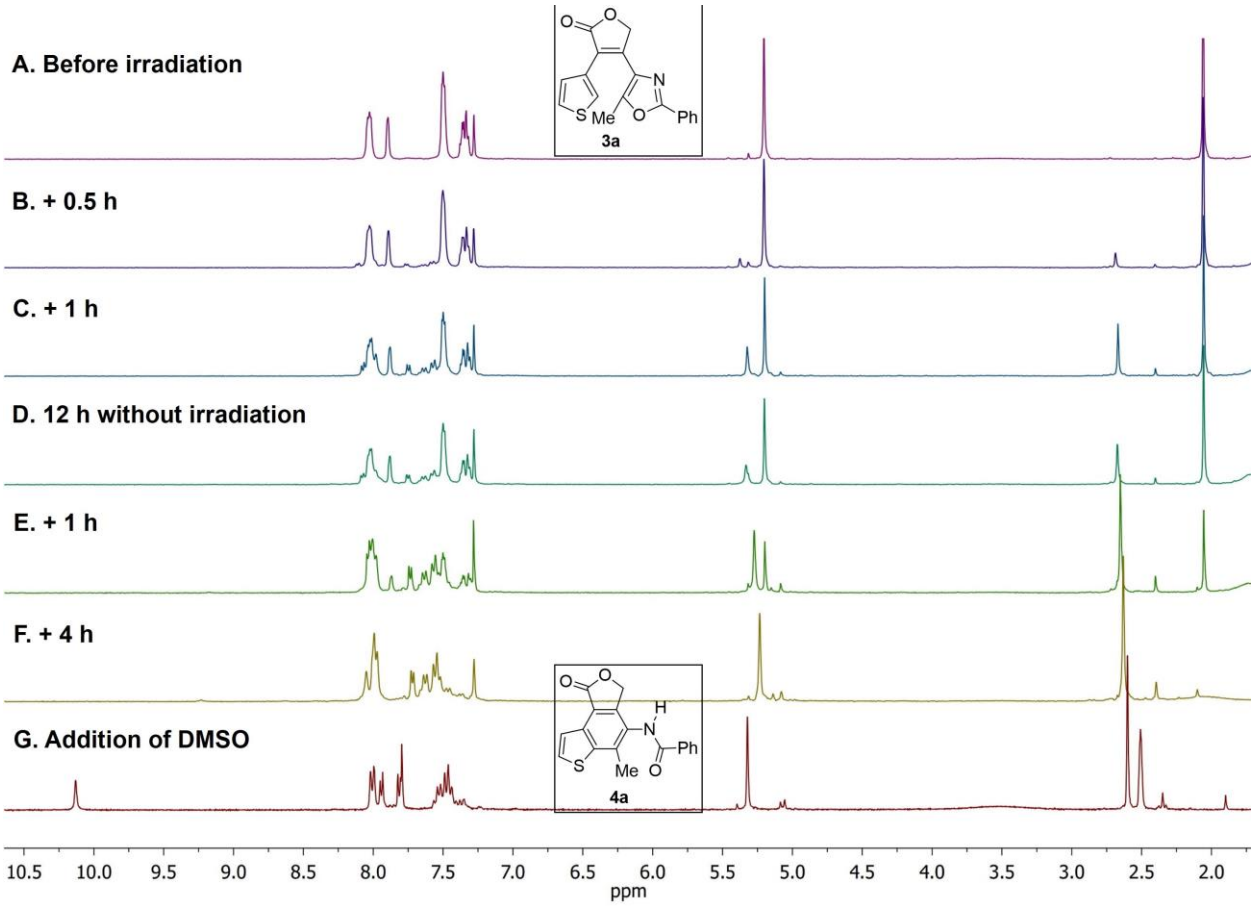


Figure S11. ^{1}H NMR (200 MHz) monitoring of photoreaction of DHE **3b** before (**A**) and after (**B-H**) irradiation ($CDCl_3$, C = 0.1 M) with one 6W UV lamp (365 nm).

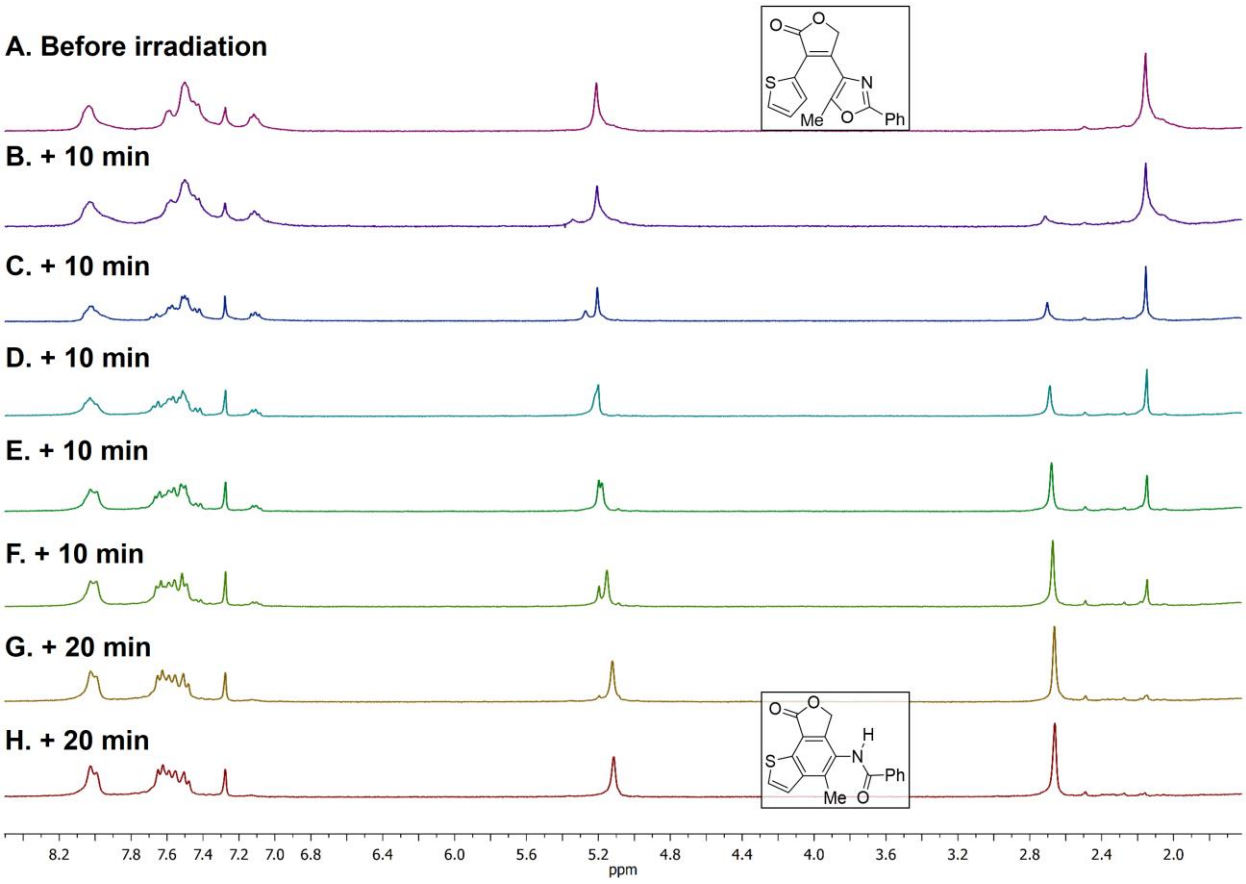


Figure S12. ^{1}H NMR (200 MHz) monitoring of photoreaction of DHE **3c** before (**A**) and after (**B-D**) irradiation (DMSO-d_6, C = 0.05 M) with one 8W UV lamp (365 nm).

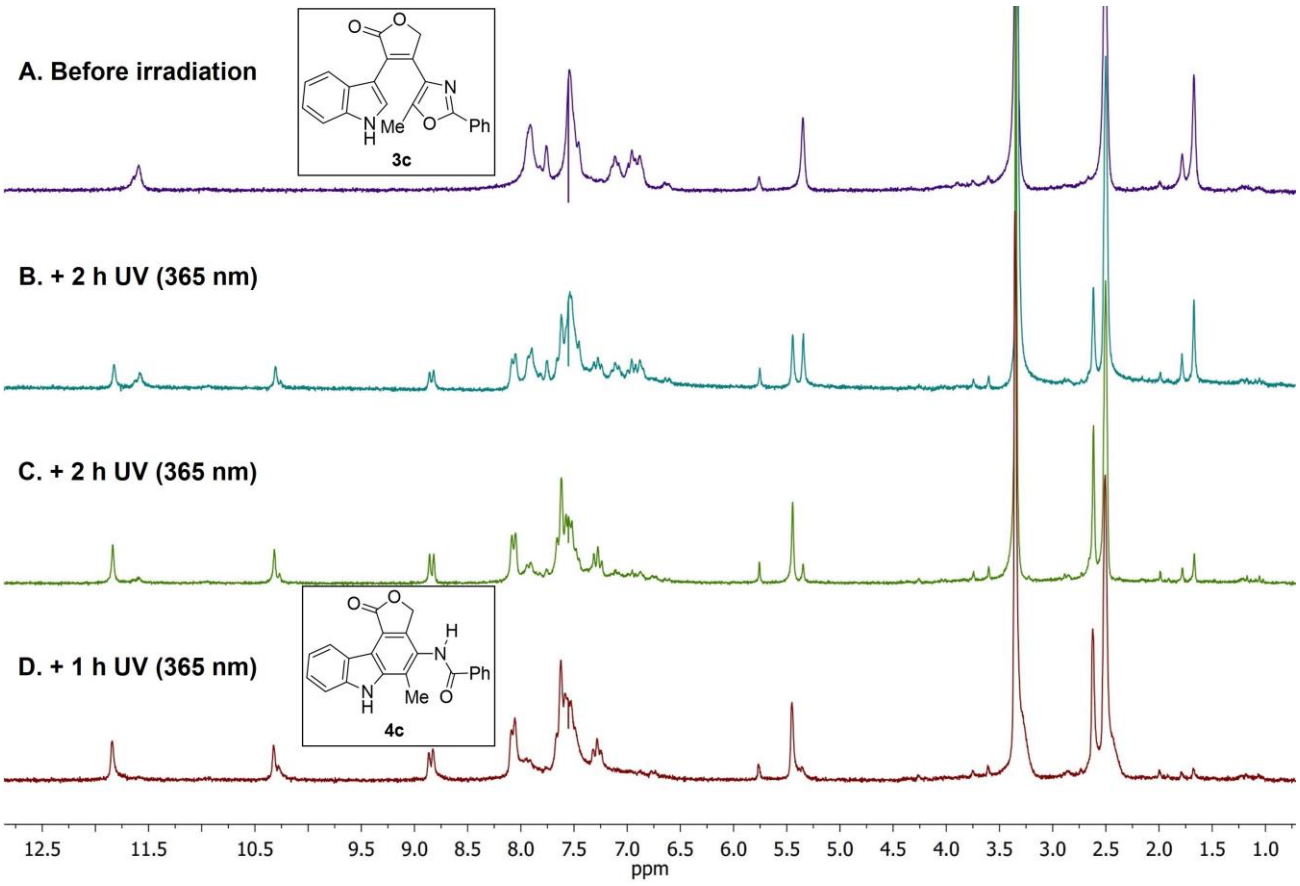


Figure S13. ^{1}H NMR (200 MHz) monitoring of photoreaction of DHE **3d** before (**A**) and after (**B-E**) irradiation ($CDCl_3$, C = 0.12 M) with one 8W UV lamp (365 nm).

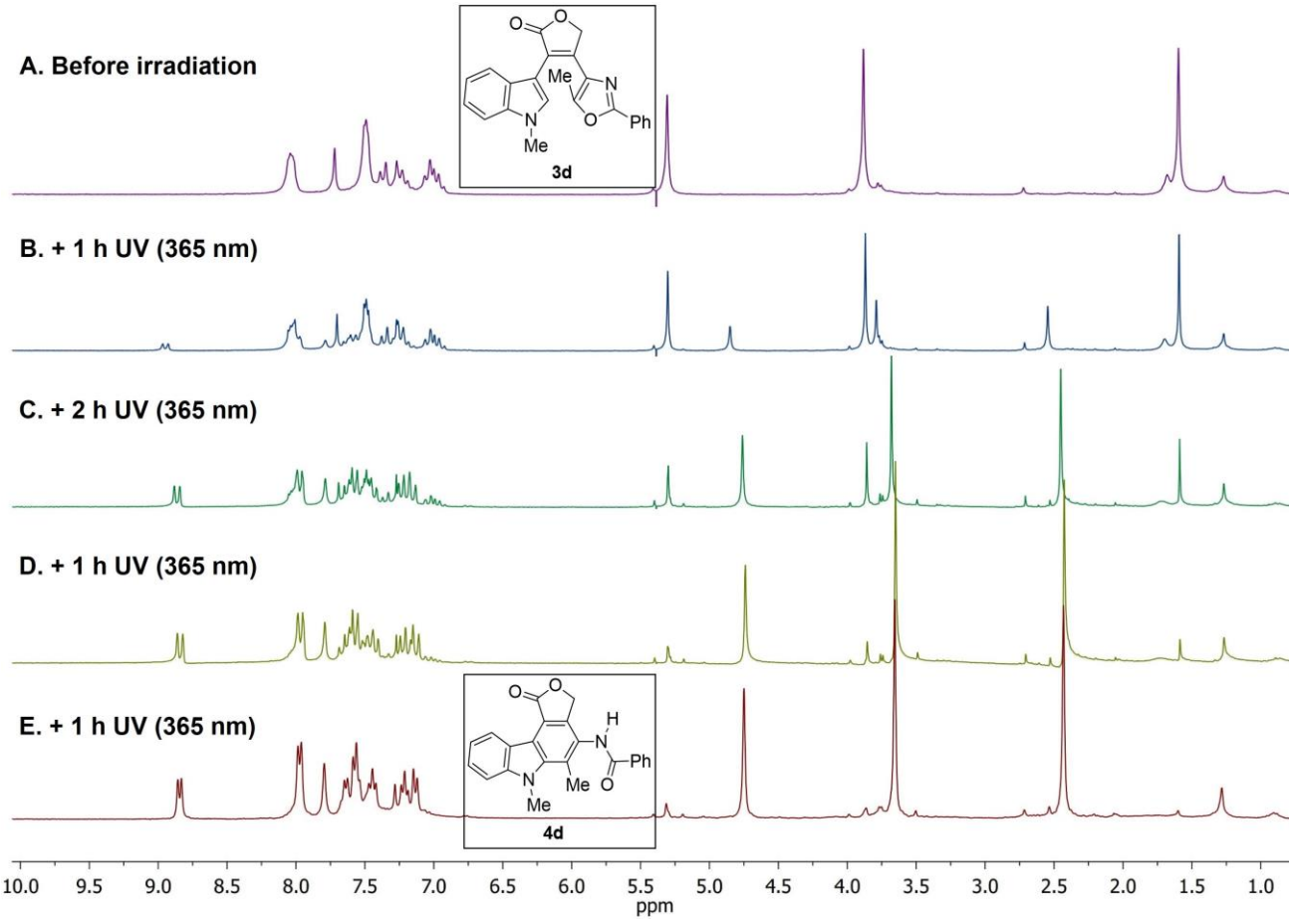


Figure S14. ^{1}H NMR monitoring of photoreaction of DHE **3e** before (**A**) and after (**B**) irradiation ($CDCl_3$, C = 0.05 M) with one 8W UV lamp (365 nm).

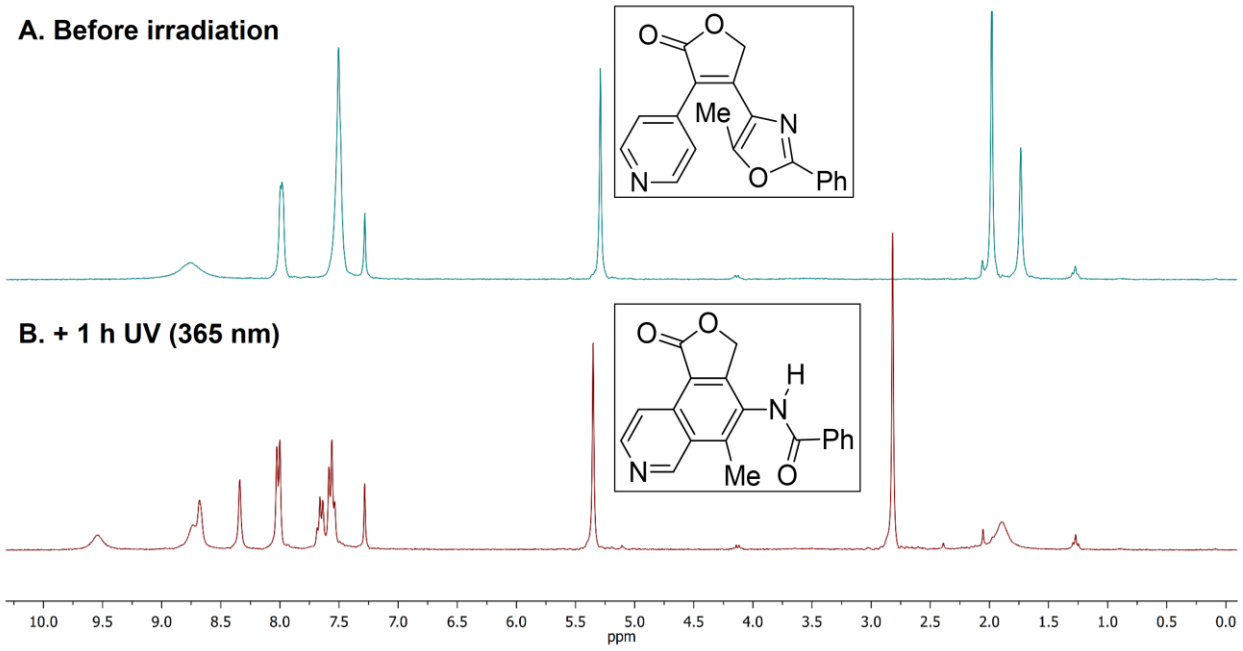


Figure S15. ^{1}H NMR monitoring of photoreaction of DHE **3f** before (**A**) and after (**B-C**) irradiation ($CDCl_3$, C = 0.09 M) with one 8W UV lamp (365 nm).

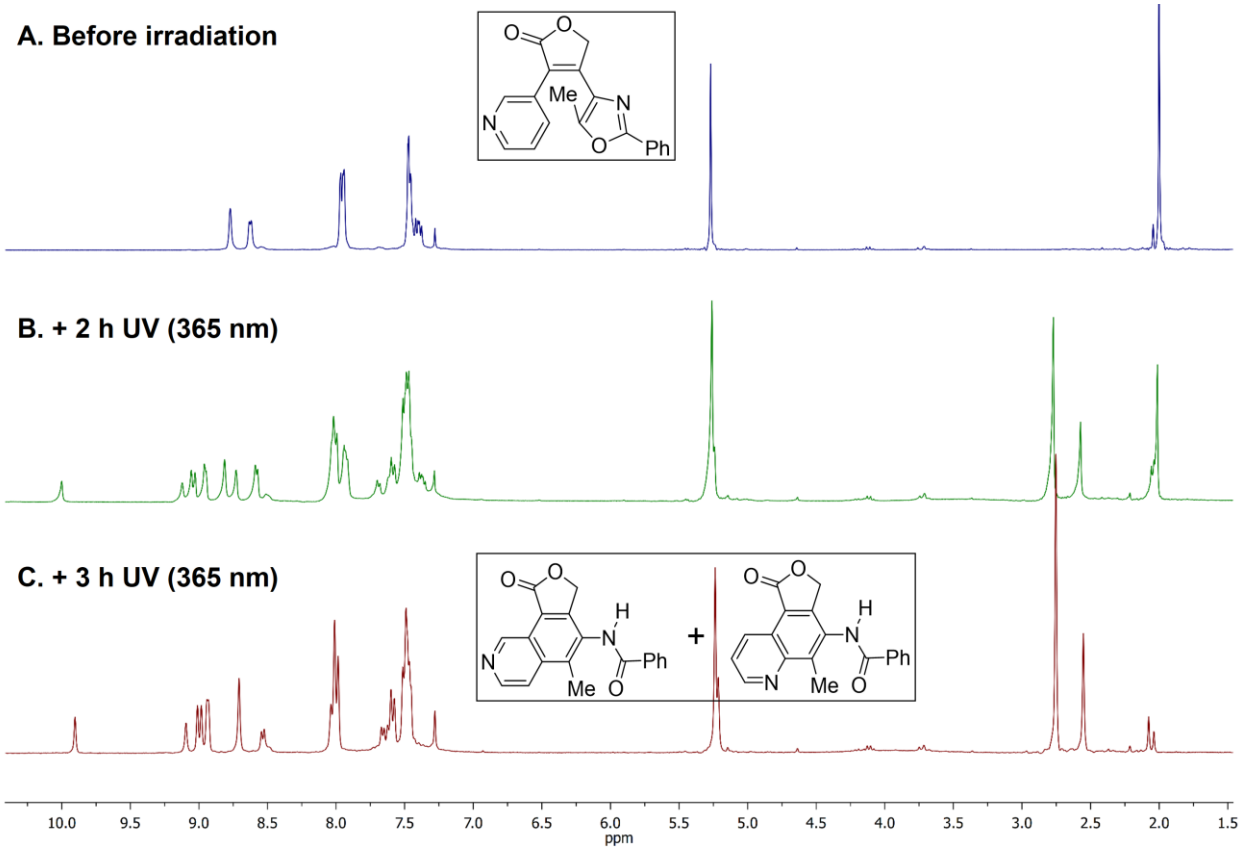


Figure S16. ^{1}H NMR monitoring of photoreaction of DHE **7d** before (**A**) and after (**B-D**) irradiation (DMF-d_7, C = 0.07 M) with two 8W UV lamps (365 nm).

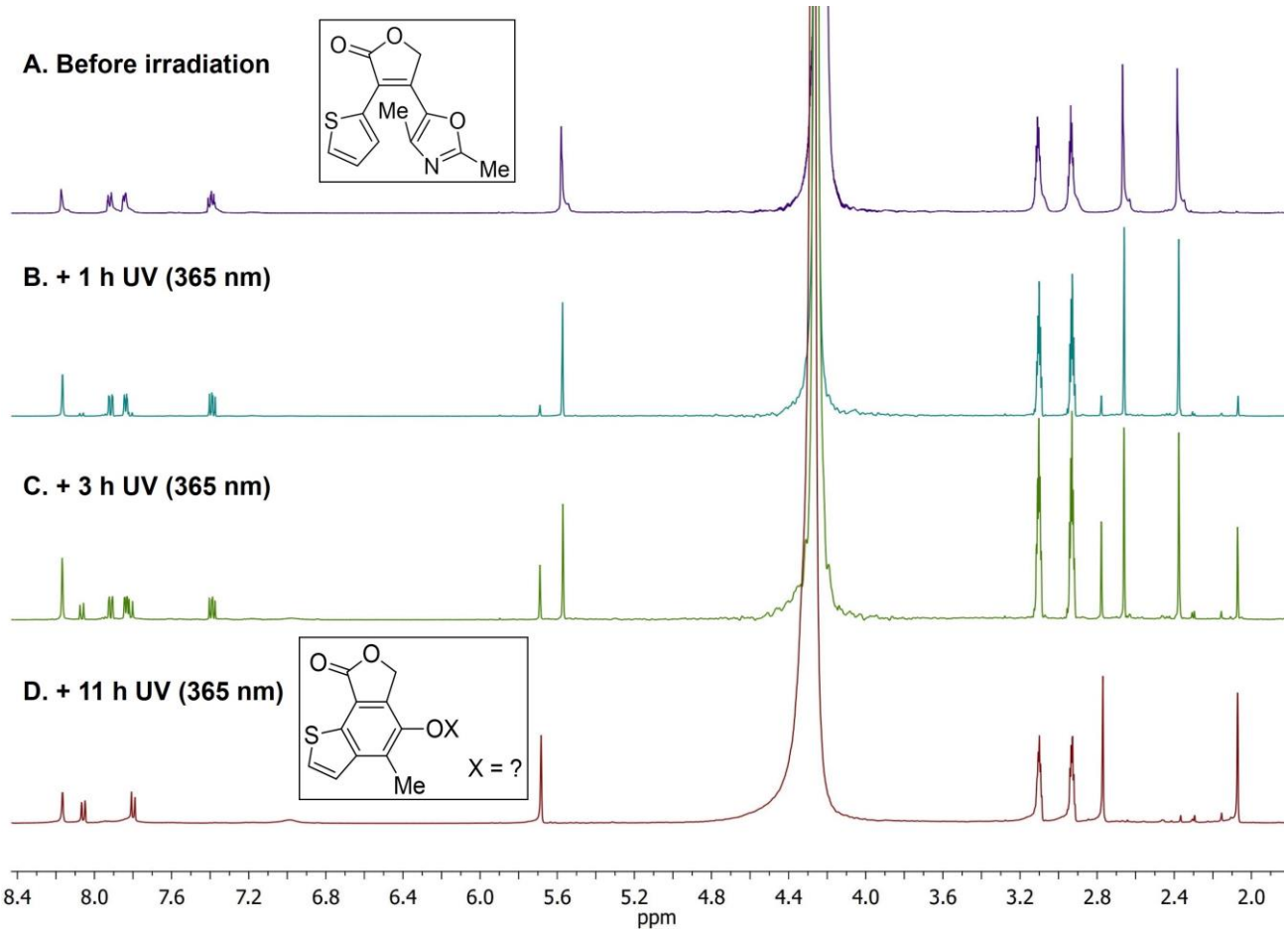


Figure S17. ^{1}H NMR monitoring of photoreaction of DHE **10c** before (**A**) and after (**B**-**E**) irradiation (DMF-d_7, C = 0.05 M) with two 8W UV lamps (365 nm).

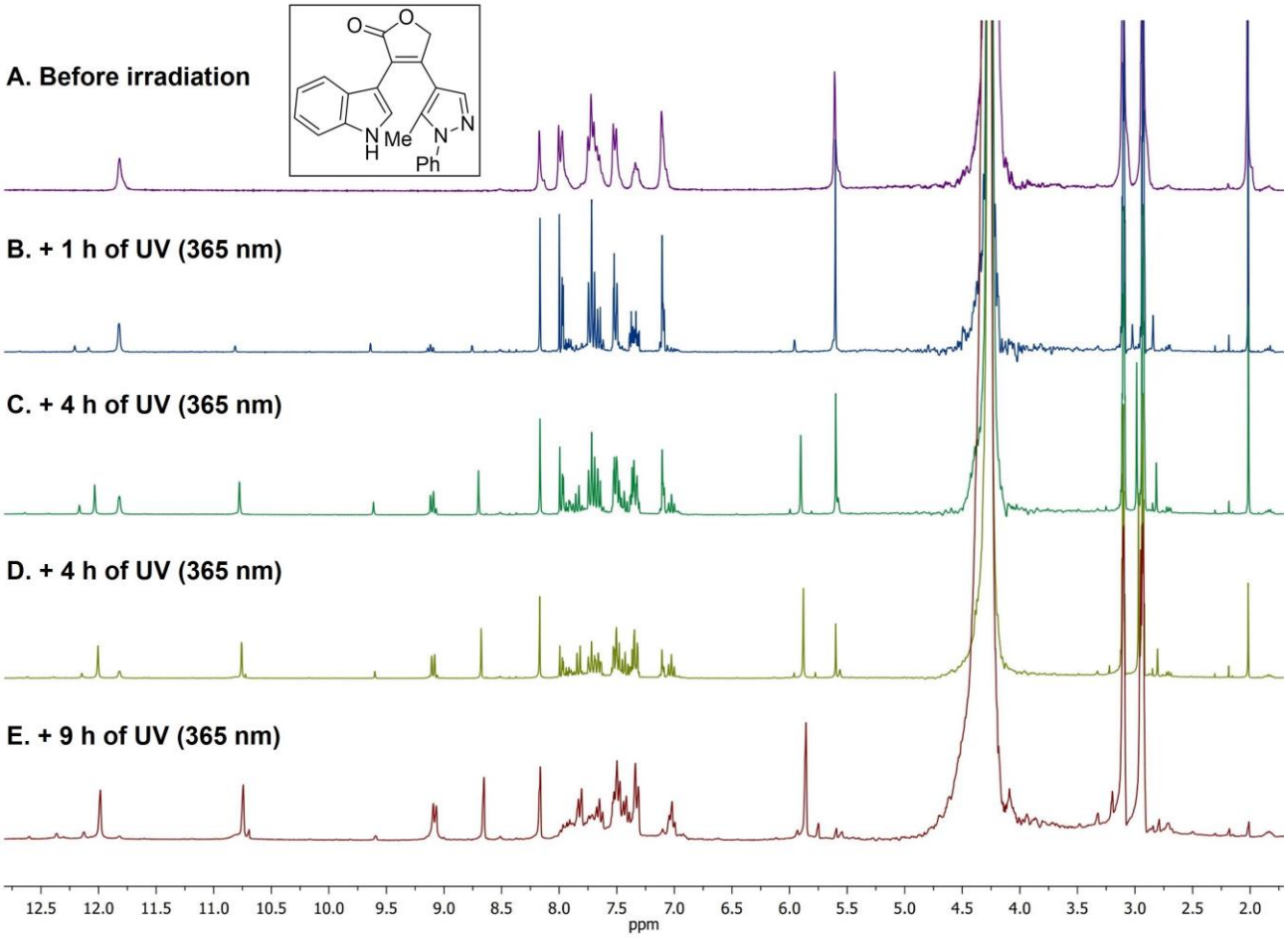


Figure S18. ^{1}H NMR monitoring of photoreaction of DHE **12a** before (**A**) and after (**B**-**E**) irradiation (DMSO-d_6, C = 0.05 M) with two 8W UV lamps (365 nm).

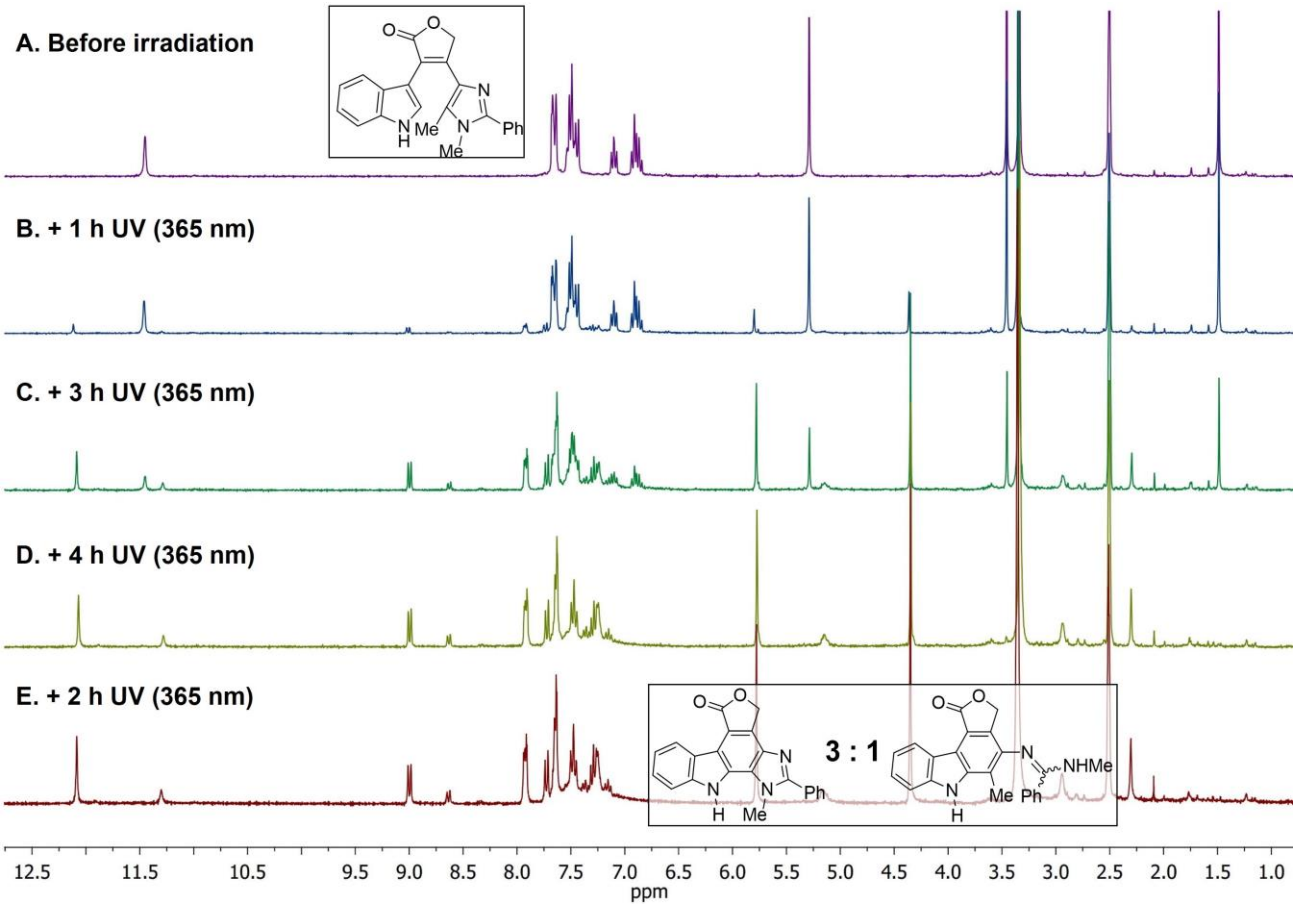


Figure S19. ^{1}H NMR monitoring of photoreaction of DHE **12a** before (**A**) and after (**B**-**E**) irradiation (DMSO-d_6, C = 0.05 M) in the presence of DABCO (1 equiv) with two 8W UV lamps (365 nm).

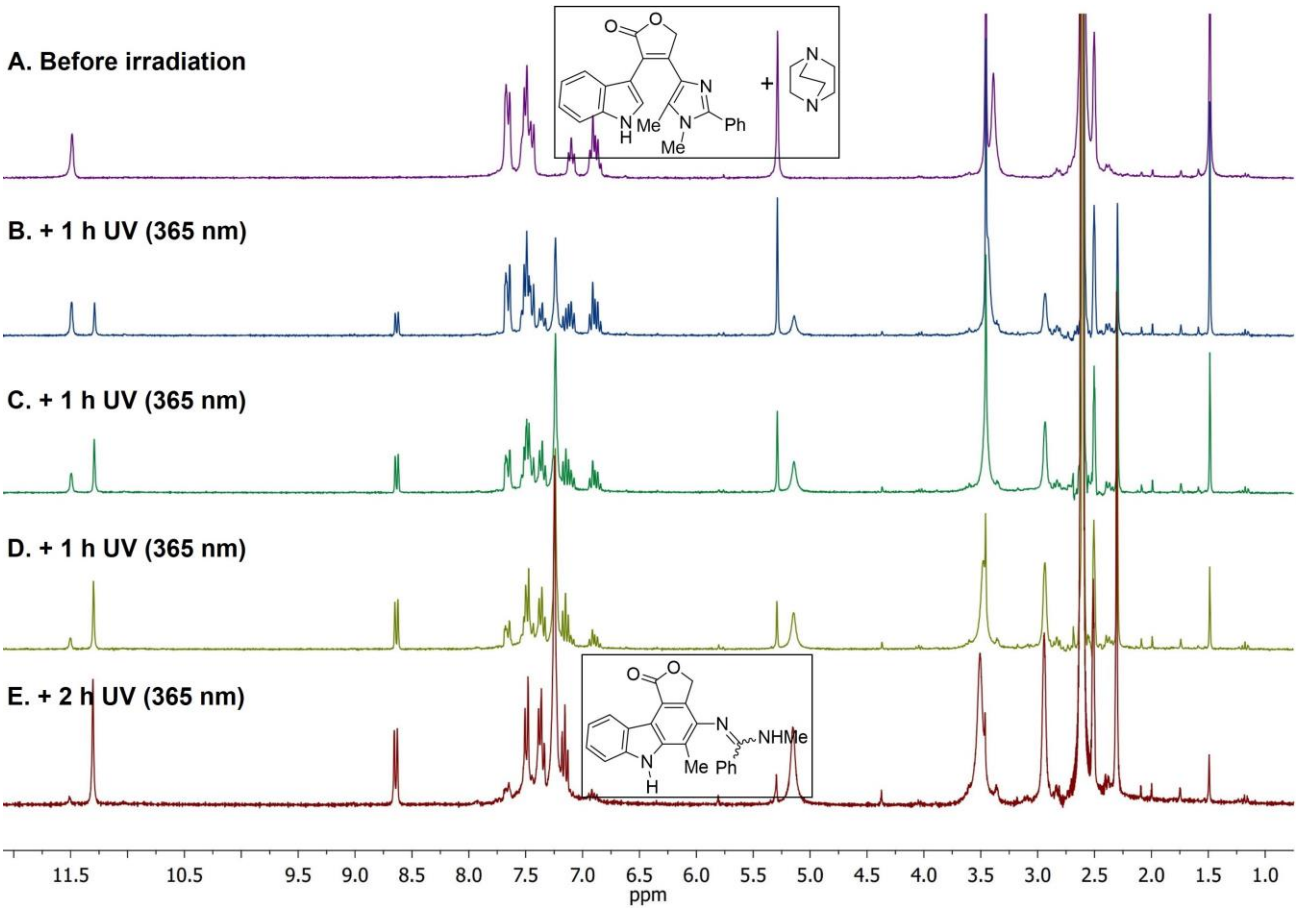
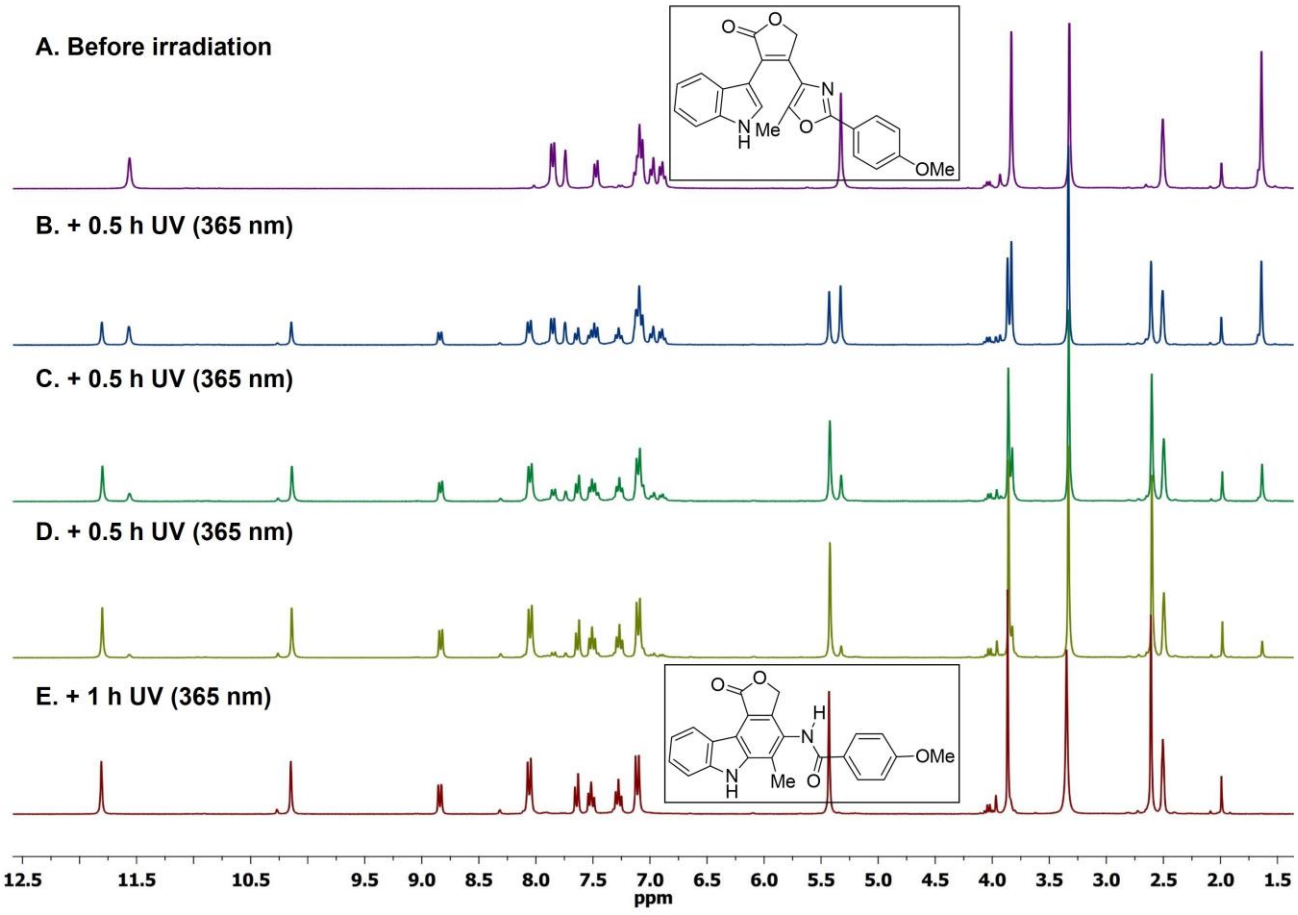
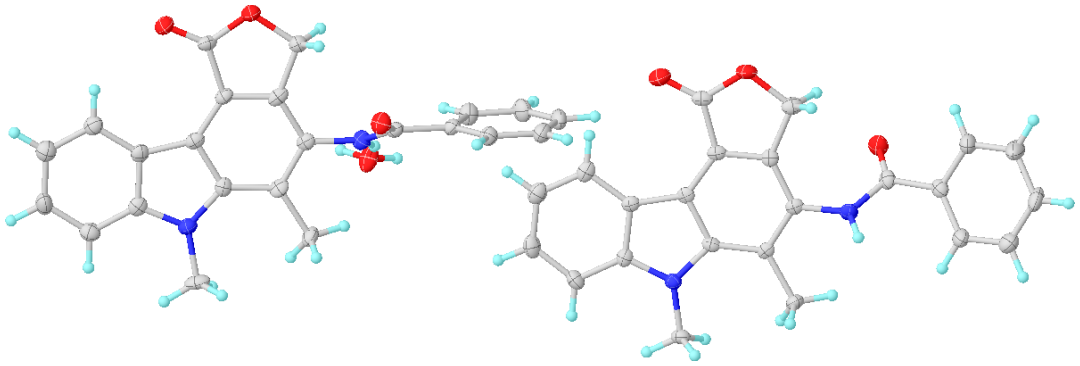


Figure S20. ^{1}H NMR monitoring of photoreaction of DHE **27** before (**A**) and after (**B**-**E**) irradiation (DMSO-d_6, C = 0.065 M) with two 8W UV lamps (365 nm).



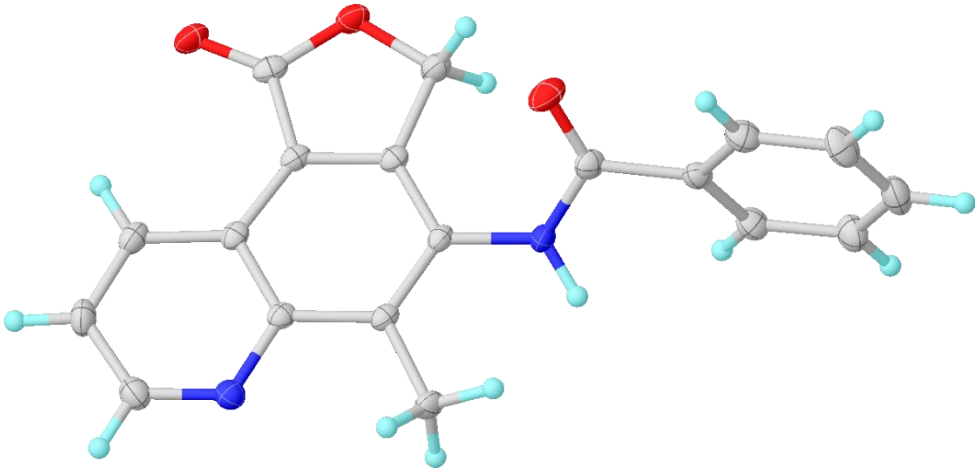
VII. X-ray crystallography

Table S1. Crystal data and structure refinement for carbazole **4d**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



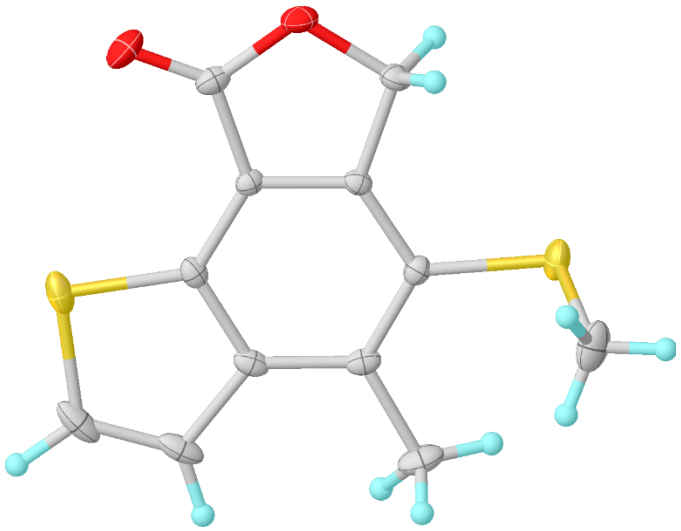
CCDC number	1859659
Empirical formula	$(C_{23}H_{18}N_2O_3)_2*0.5H_2O$
Formula weight	379.40
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a/Å 7.522(2) b/Å 9.502(3) c/Å 26.913(8) α/° 86.186(5) β/° 89.331(5) γ/° 69.408(5)
Volume/$Å^3$	1796.7(10)
Z	4
ρ_{calc} g/cm^3	1.403
μ/mm^{-1}	0.096
F(000)	796.0
Crystal size/mm^3	0.350 × 0.250 × 0.050
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.516 to 53.992
Index ranges	$-9 \leq h \leq 9$ $-12 \leq k \leq 12$ $-34 \leq l \leq 34$
Reflections collected	27572
Independent reflections	7754 [R_{int} = 0.0748, R_{sigma} = 0.0691]
Data/restraints/parameters	7754/0/520
Goodness-of-fit on F^2	1.615
Final R indexes [I>=2σ (I)]	R_1 = 0.1027, wR_2 = 0.2634
Final R indexes [all data]	R_1 = 0.1079, wR_2 = 0.2668
Largest diff. peak/hole / e $Å^{-3}$	0.60/-0.49

Table S2. Crystal data and structure refinement for quinoline **4fb**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



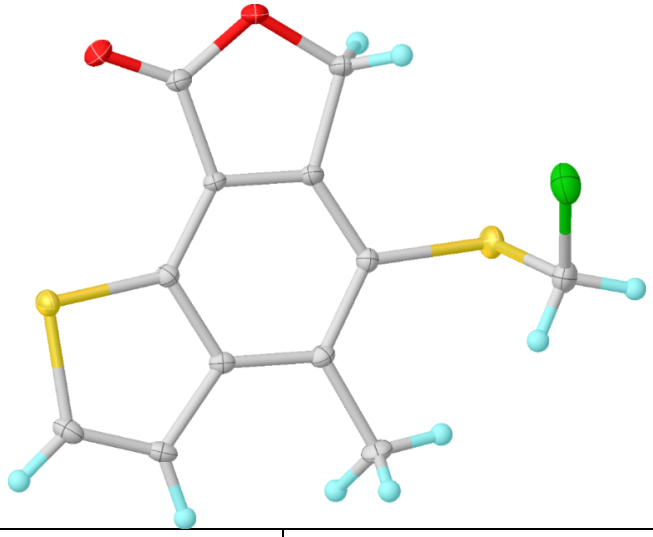
CCDC number	1859658
Empirical formula	$C_{19}H_{14}N_2O_3$
Formula weight	318.32
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a/Å 16.7044(15) b/Å 4.7039(4) c/Å 18.5969(17) α/° 90 β/° 90 γ/° 90
Volume/Å^3	1461.3(2)
Z	4
ρ_{calc} g/cm^3	1.447
μ/mm^{-1}	0.100
F(000)	664.0
Crystal size/mm^3	0.350 × 0.250 × 0.250
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.38 to 57.99
Index ranges	-22 ≤ h ≤ 22 -6 ≤ k ≤ 6 -25 ≤ l ≤ 25
Reflections collected	16893
Independent reflections	3901 [R_{int} = 0.0447, R_{sigma} = 0.0348]
Data/restraints/parameters	3901/1/218
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.0962
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.1007
Largest diff. peak/hole / e Å^{-3}	0.27/-0.24

Table S3. Crystal data and structure refinement for benzo[*b*]thiophene **13b**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



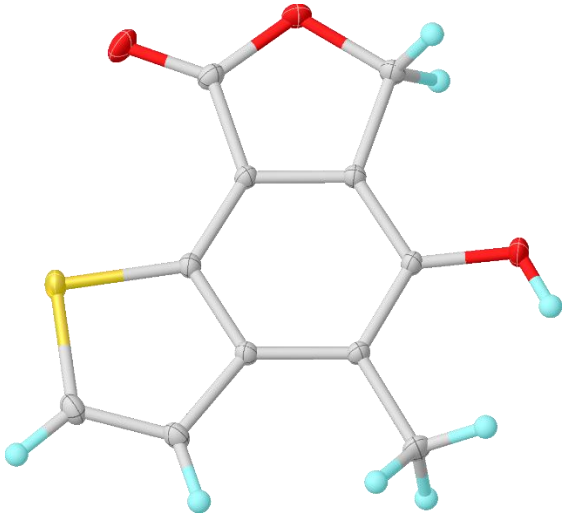
CCDC number	1859655
Empirical formula	$C_{12}H_{10}O_2S_2$
Formula weight	250.32
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a/Å 7.4647(5) b/Å 10.1476(6) c/Å 14.7974(9) α/° 90 β/° 97.6800(10) γ/° 90
Volume/$Å^3$	1110.83(12)
Z	4
ρ_{calc} g/cm^3	1.497
μ/mm^{-1}	0.458
F(000)	520.0
Crystal size/mm^3	0.484 × 0.328 × 0.294
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.882 to 57.984
Index ranges	$-10 \leq h \leq 10$ $-13 \leq k \leq 13$ $-20 \leq l \leq 20$
Reflections collected	13452
Independent reflections	2957 [R_{int} = 0.0207, R_{sigma} = 0.0143]
Data/restraints/parameters	2957/0/185
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0266, wR_2 = 0.0742
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0764
Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.21

Table S4. Crystal data and structure refinement for benzo[*b*]thiophene **21**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



CCDC number	1859654
Empirical formula	$C_{12}H_9ClO_2S_2$
Formula weight	284.76
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a/Å 7.2227(9) b/Å 8.8688(11) c/Å 9.7985(13) α/° 72.745(2) β/° 86.410(3) γ/° 77.000(2)
Volume/$Å^3$	584.04(13)
Z	2
ρ_{calc} g/cm^3	1.619
μ/mm^{-1}	0.668
F(000)	292.0
Crystal size/mm^3	0.400 × 0.200 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.352 to 67.292
Index ranges	-10 ≤ h ≤ 10 -13 ≤ k ≤ 13 -14 ≤ l ≤ 14
Reflections collected	8655
Independent reflections	4201 [R_{int} = 0.0281, R_{sigma} = 0.0443]
Data/restraints/parameters	4201/0/155
Goodness-of-fit on F^2	0.948
Final R indexes [I>=2σ (I)]	R_1 = 0.0422, wR_2 = 0.1267
Final R indexes [all data]	R_1 = 0.0539, wR_2 = 0.1387
Largest diff. peak/hole / e $Å^{-3}$	0.69/-0.41

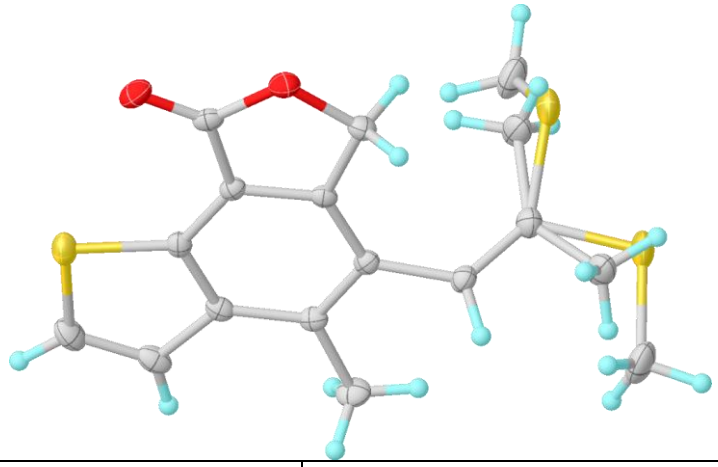
Table S5. Crystal data and structure refinement for benzo[*b*]thiophene **14b**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



CCDC number	1859660
Empirical formula	$C_{11}H_8O_3S$
Formula weight	220.23
Temperature/K	120(2)
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	a/Å 16.1338(3) b/Å 8.52590(10) c/Å 14.3640(2) α/° 90 β/° 114.5437(8) γ/° 90
Volume/$Å^3$	1797.31(5)
Z	8
ρ_{calc} g/cm^3	1.628
μ/mm^{-1}	0.339
F(000)	912.0
Crystal size/mm^3	0.380 × 0.290 × 0.210
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.526 to 79.994
Index ranges	$-29 \leq h \leq 29$, $-15 \leq k \leq 15$, $-25 \leq l \leq 25$
Reflections collected	81008
Independent reflections	5578 [R_{int} = 0.0520, R_{sigma} = 0.0180]
Data/restraints/parameters	5578/0/138
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0887
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0924
Largest diff. peak/hole / e $Å^{-3}$	0.65/-0.47

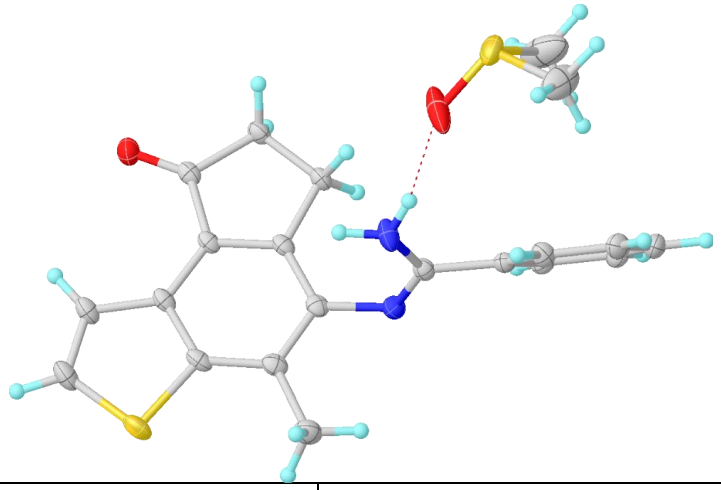
Table S6. Crystal data and structure refinement for benzo[*b*]thiophene **15b**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

Analysis of the Fourier density synthesis in **15b** have revealed the disorder due to superposition of two isomers with occupancies 0.96 and 0.04. The positional and atomic displacement parameters for atoms with minor occupancies were refined with DFIX and EADP instructions.



CCDC number	1859657
Empirical formula	$C_{15}H_{14}O_2S_2$
Formula weight	290.38
Temperature/K	120(2)
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a/Å 7.5548(5) b/Å 8.9850(6) c/Å 11.3559(7) α/° 75.4510(10) β/° 79.4630(10) γ/° 65.9620(10)
Volume/Å^3	678.58(8)
Z	2
ρ_{calc} g/cm^3	1.421
μ/mm^{-1}	0.386
F(000)	304.0
Crystal size/mm^3	0.320 × 0.220 × 0.180
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.72 to 57.998
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	8441
Independent reflections	3608 [R_{int} = 0.0146, R_{sigma} = 0.0183]
Data/restraints/parameters	3608/9/189
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.1001
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.1037
Largest diff. peak/hole / e Å^{-3}	0.47/-0.43

Table S7. Crystal data and structure refinement for benzo[*b*]thiophene **25**. Ellipsoids represent the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.



CCDC number	1859656
Empirical formula	$C_{21}H_{22}N_2O_2S_2$ $C_{19}H_{16}N_2OS*(CH_3)_2SO$
Formula weight	398.52
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a/Å 8.7979(18) b/Å 24.844(5) c/Å 9.4540(19) α/° 90 β/° 111.09(3) γ/° 90
Volume/$Å^3$	1927.9(8)
Z	4
ρ_{calc} g/cm^3	1.373
μ/mm^{-1}	0.295
F(000)	840.0
Crystal size/mm^3	0.400 × 0.220 × 0.180
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.278 to 57.998
Index ranges	$-11 \leq h \leq 11$ $-33 \leq k \leq 33$ $-12 \leq l \leq 12$
Reflections collected	19659
Independent reflections	5117 [R_{int} = 0.0269, R_{sigma} = 0.0244]
Data/restraints/parameters	5117/0/246
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0392, wR_2 = 0.0977
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.1041
Largest diff. peak/hole / e $Å^{-3}$	0.42/-0.37

VIII. 2D NMR data and complete NMR assignment

Compound 4i

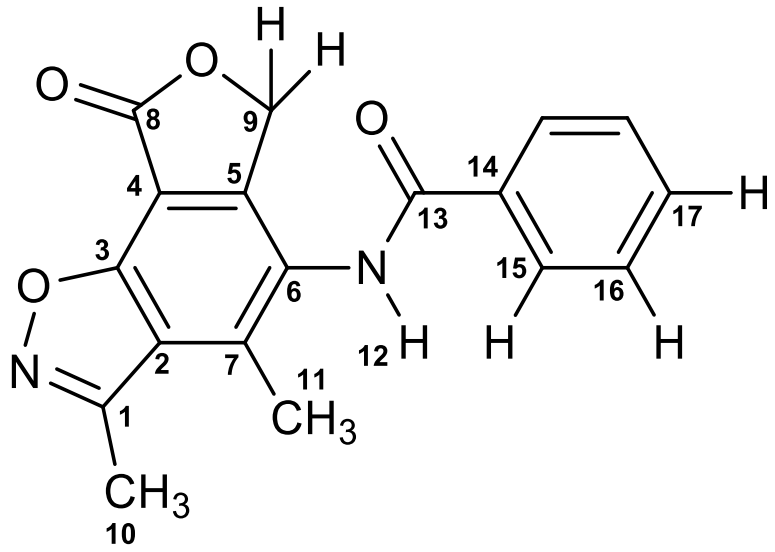
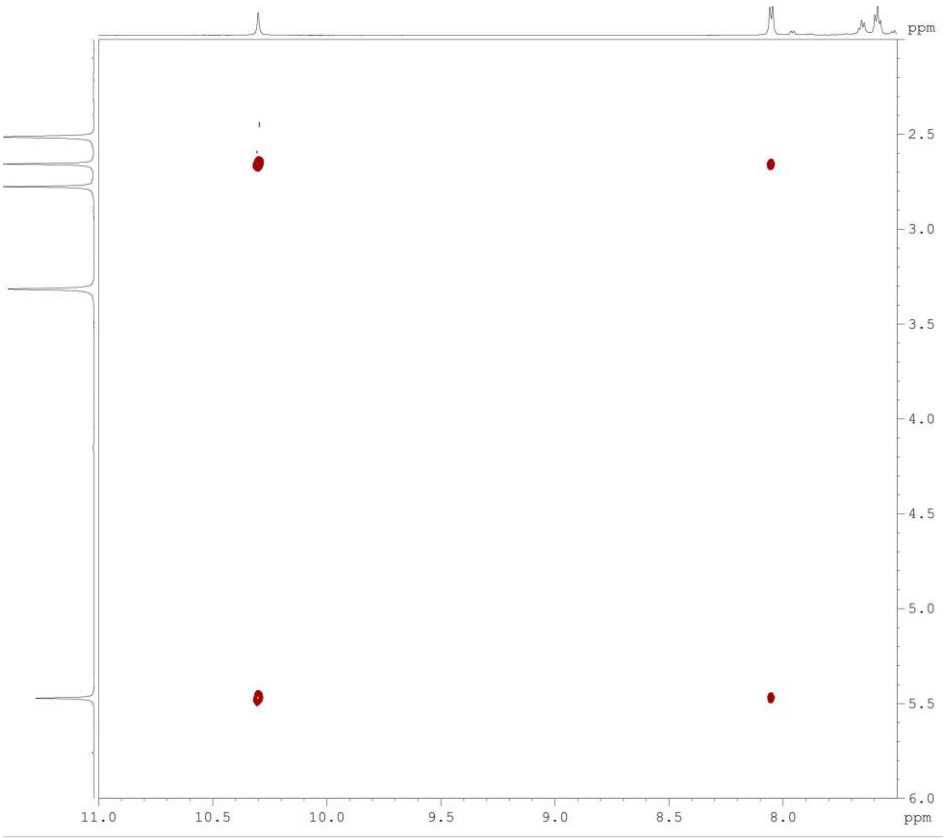
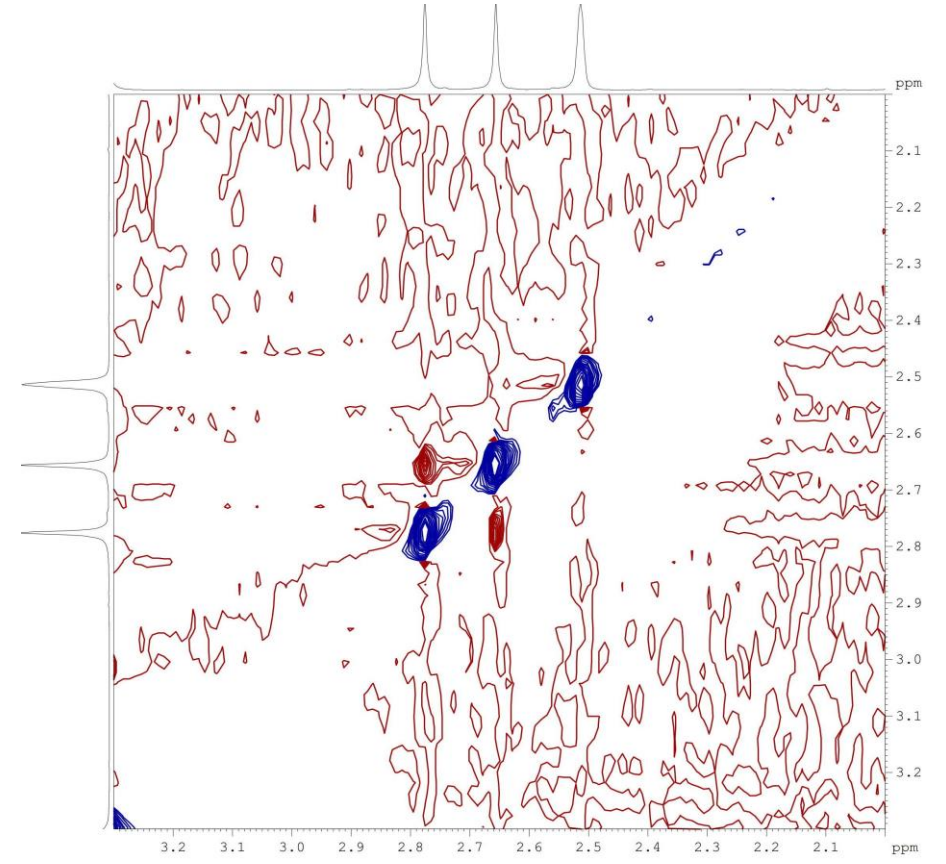


Table S8. Assignment of NMR signals and 2D NMR correlations for compound **4i**.

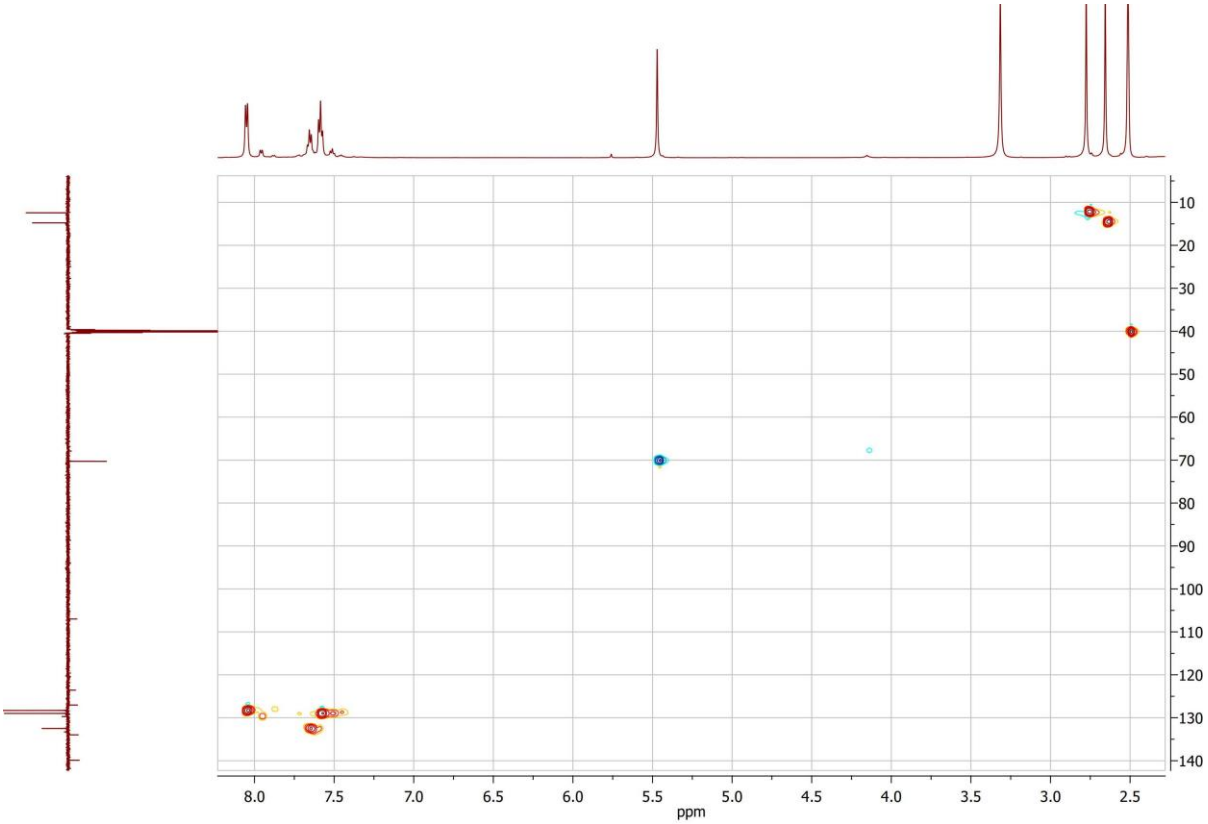
№	^{1}H	^{13}C	NOESY	HMBC
1	-	156.5	-	10
2	-	123.6	-	9, 10, 11
3	-	156.3	-	9, 10
4	-	107.0	-	9, 11
5	-	139.9	-	9, 11, 12
6	-	150.1	-	9, 11, 12
7	-	127.1	-	9, 11, 12
8	-	167.6	-	9
9	5.47 (s)	70.3	12, 15	2, 3, 4, 5, 6, 7, 8
10	2.78	12.4	11	1, 2, 3
11	2.66	14.8	10, 12, 15	2, 4, 5, 6, 7
12	10.30 (s)	-	9, 11	5, 6, 7, 13
13	-	166.1	-	12, 15
14	-	134.0	-	16
15	8.05 (d, *J* = 7.4 Hz)	128.3	9, 11	13, 16, 17
16	7.55-7.61 (m)	129.0	-	14, 15, 17
17	7.64-7.68 (m)	132.5	-	15, 16

$^{1}H-^{1}H$ NOESY spectra

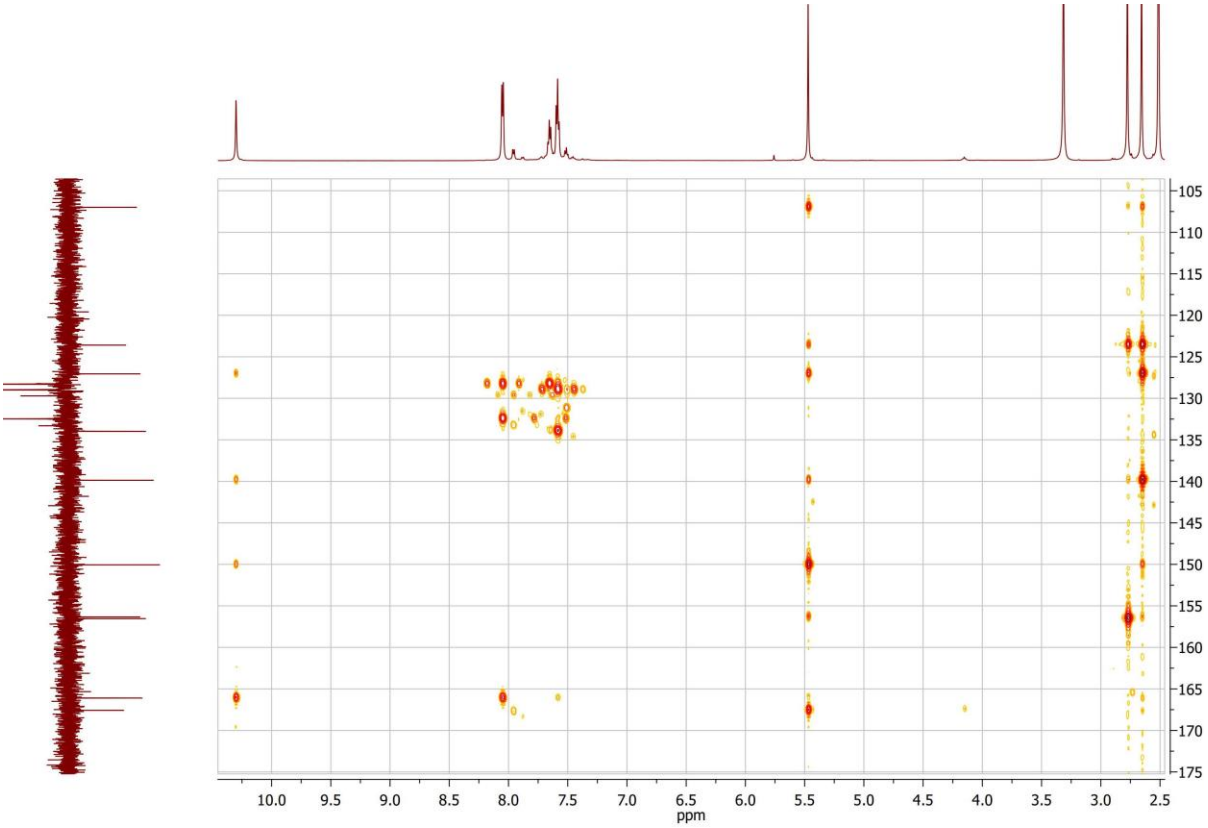




$^{1}H-^{13}C$ HSQC spectrum



$^{1}H-^{13}C$ HMBC spectrum



Compound 4j

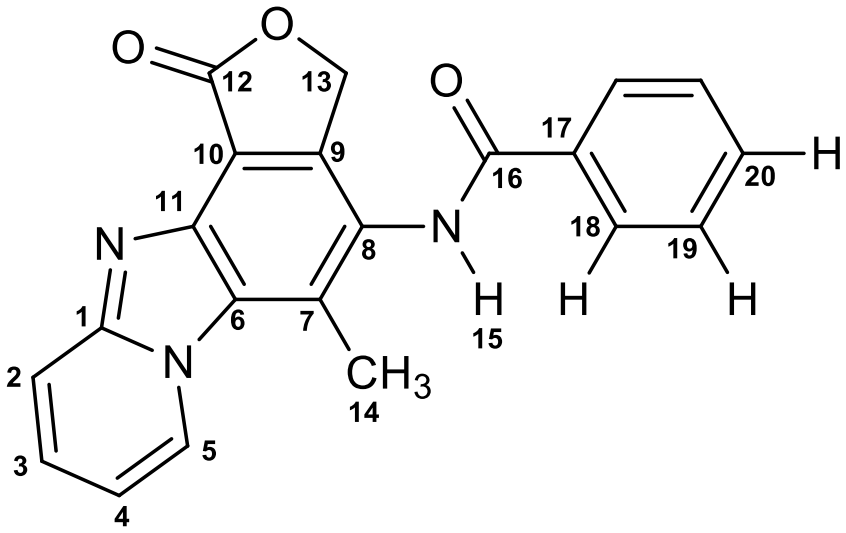
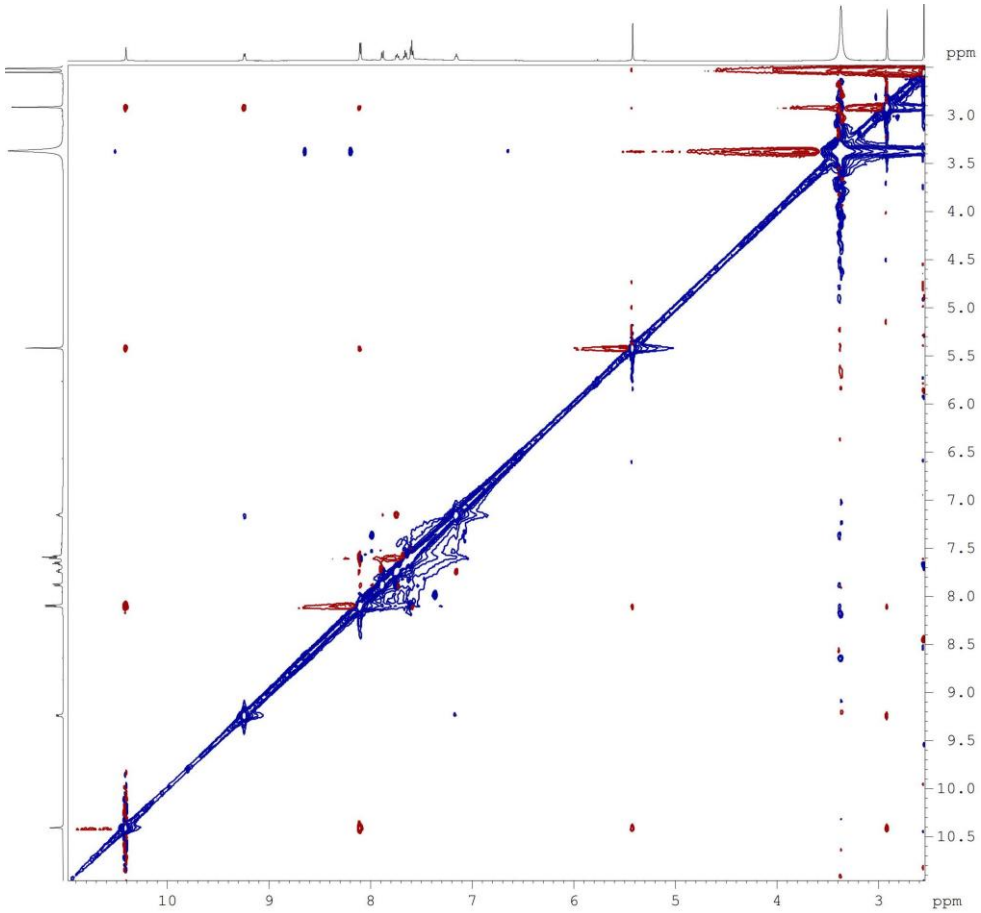


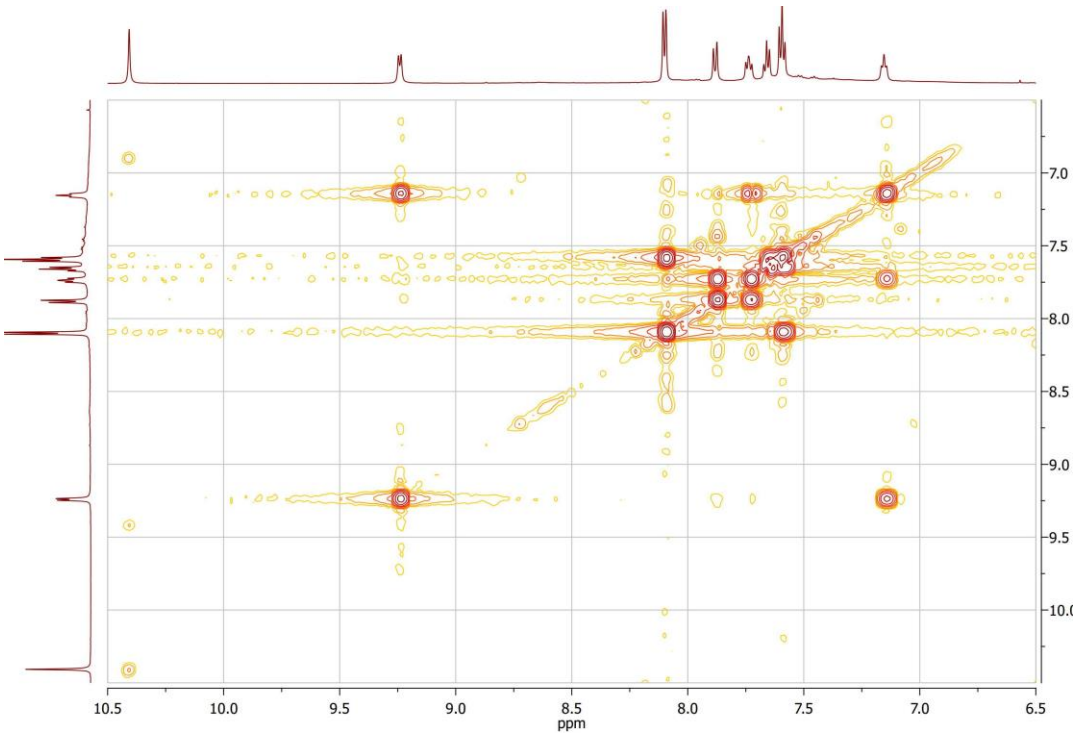
Table S9. Assignment of NMR signals and 2D NMR correlations for compound **4j**.

№	^{1}H	^{13}C	NOESY	COSY	HMBC
1	-	150.9	-	-	3, 5
2	7.88 (d, *J* = 9.0 Hz)	117.9	-	3	4
3	7.71-7.76 (m)	131.5	4	2, 4	1, 5
4	7.13-7.18 (m)	112.4	3, 5	3, 5	2, 6
5	9.24 (d, *J* = 6.8 Hz)	129.6	4, 14	4	1, 3
6	-	129.3	-	-	4, 13, 14
7	-	130.2	-	-	14, 15
8	-	123.4	-	-	13, 14
9	-	145.9	-	-	13, 15
10	-	111.7	-	-	13
11	-	139.6	-	-	-
12	-	169.5	-	-	13
13	5.42 (s)	69.1	15, 18	-	6, 8, 9, 10, 12
14	2.91 (s)	15.1	5, 15, 18	-	6, 7, 8
15	10.41 (s)	-	13, 14, 18	-	7, 9, 16
16	-	166.3	-	-	15, 18
17	-	134.2	-	-	19
18	8.10 (d, *J* = 7.4 Hz)	128.3	13, 14, 15	19	16, 19, 20
19	7.57-7.61 (m)	129.0	-	18, 20	17, 18
20	7.64-7.68 (m)	132.4	-	19	18

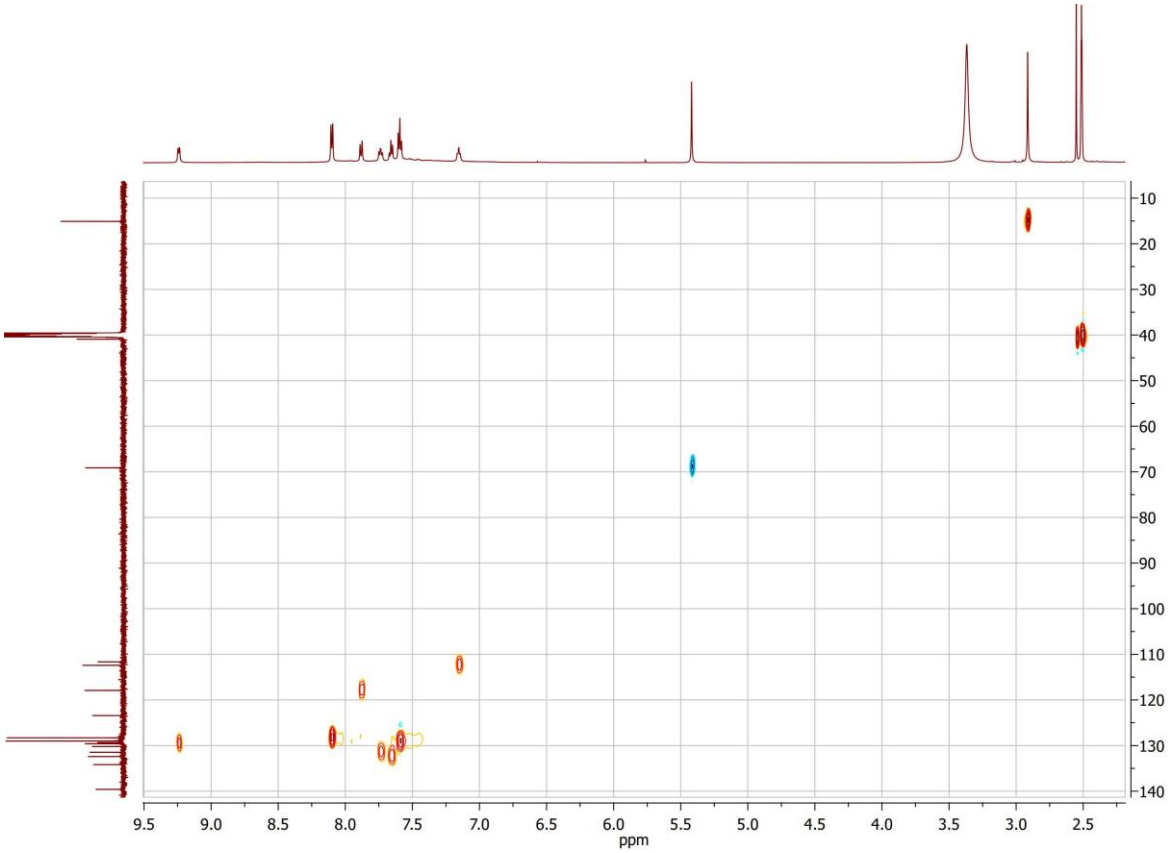
$^{1}H-^{1}H$ NOESY spectrum



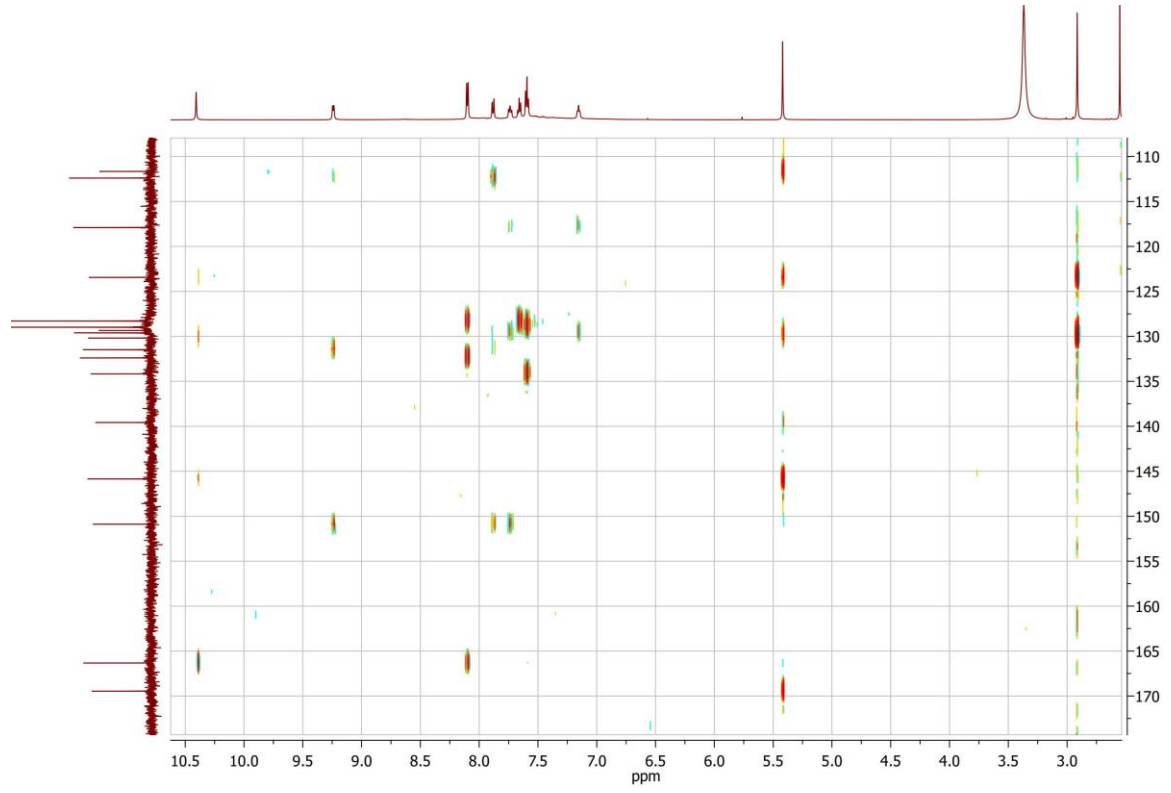
$^{1}H-^{1}H$ COSY spectrum



$^{1}H-^{13}C$ HSQC spectrum



$^{1}H-^{13}C$ HMBC spectrum



Compound 4k

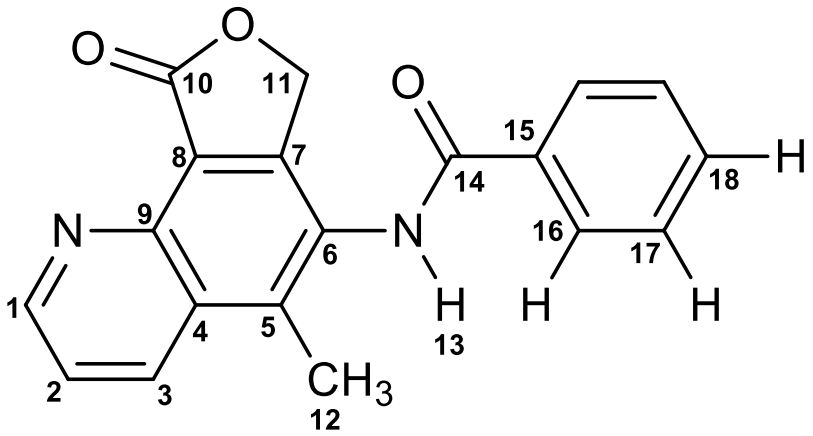
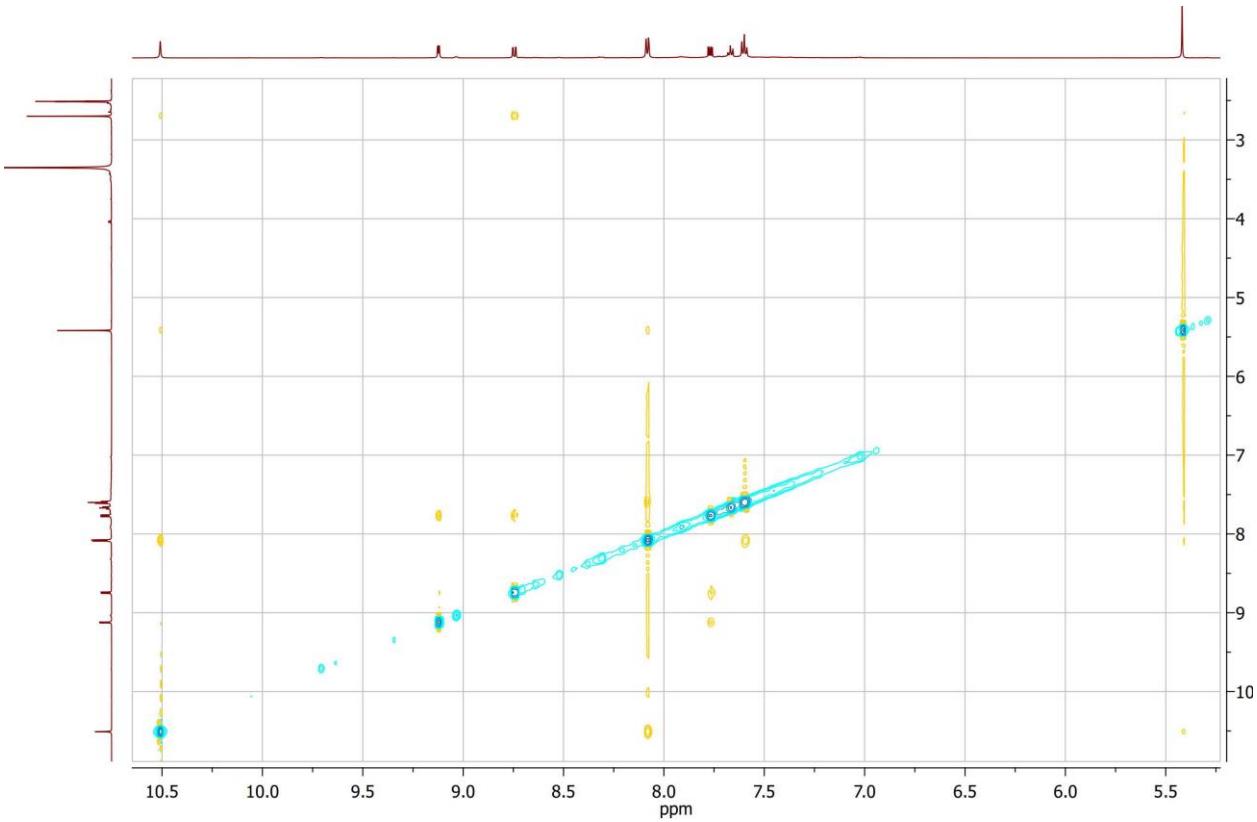


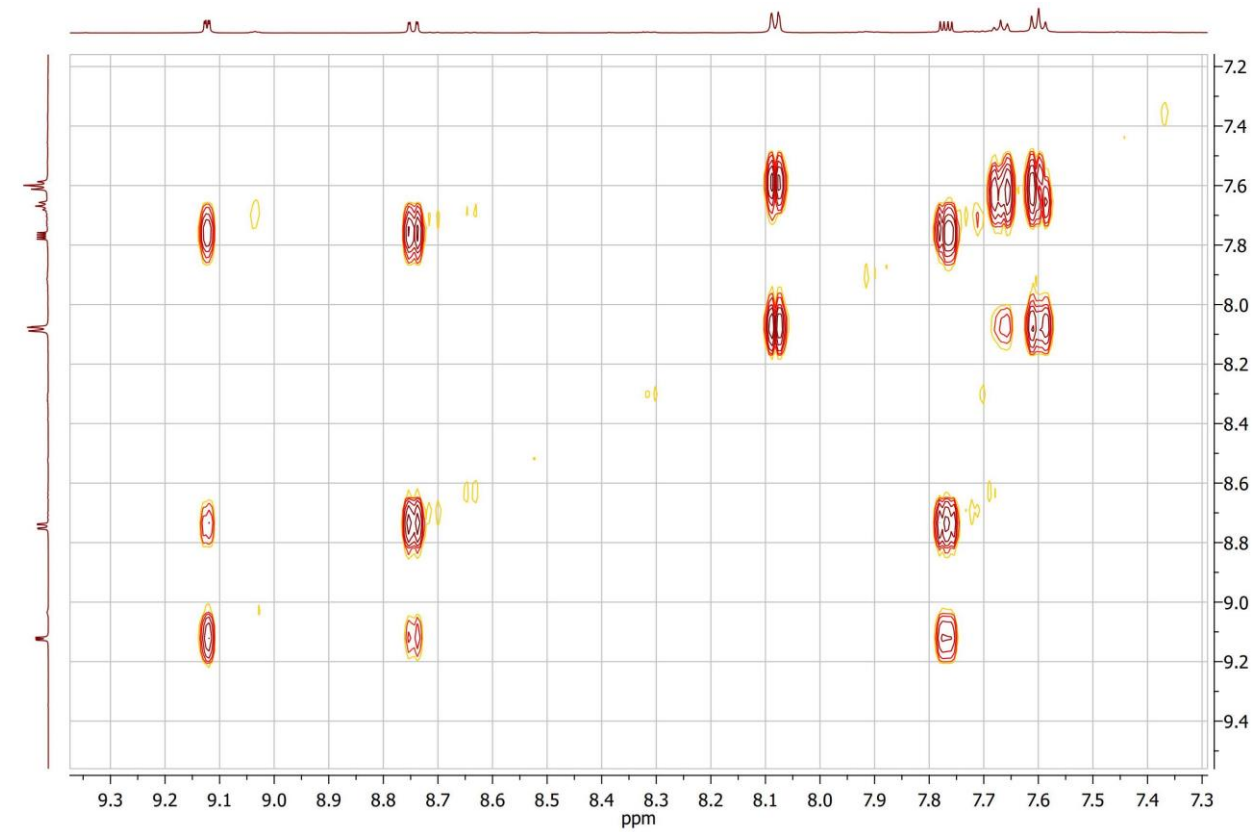
Table S10. Assignment of NMR signals and 2D NMR correlations for compound **4k**.

№	^{1}H	^{13}C	NOESY	COSY	HMBC
1	9.12 (dd, *J* = 4.2, 1.6 Hz)	152.2	2	2, 3	2, 3, 9
2	7.77 (dd, *J* = 8.6, 4.2 Hz)	122.7	1, 3	1, 3	1, 5
3	8.75 (dd, *J* = 8.6, 1.6 Hz)	134.6	2, 12	1, 2	1, 4, 9
4	-	140.1	-	-	3, 11, 12
5	-	128.6	-	-	2, 12
6	-	128.9	-	-	11, 12
7	-	152.1	-	-	11, 12
8	-	118.9	-	-	11, 12
9	-	143.2	-	-	1, 3, 11
10	-	168.6	-	-	11
11	5.42 (s)	68.1	13, 16	-	4, 6, 7, 8, 9, 10
12	2.70 (s)	14.6	3, 13	-	4, 5, 6, 7, 8
13	10.51 (s)	-	11, 12, 16	-	-
14	-	166.2	-	-	16
15	-	134.0	-	-	17
16	8.08 (d, *J* = 7.4 Hz)	128.3	11, 13, 17	17	14, 18
17	7.60 (t, *J* = 7.4 Hz)	129.0	16, 18	16, 18	15
18	7.67 (t, *J* = 7.4 Hz)	132.5	17	17	16

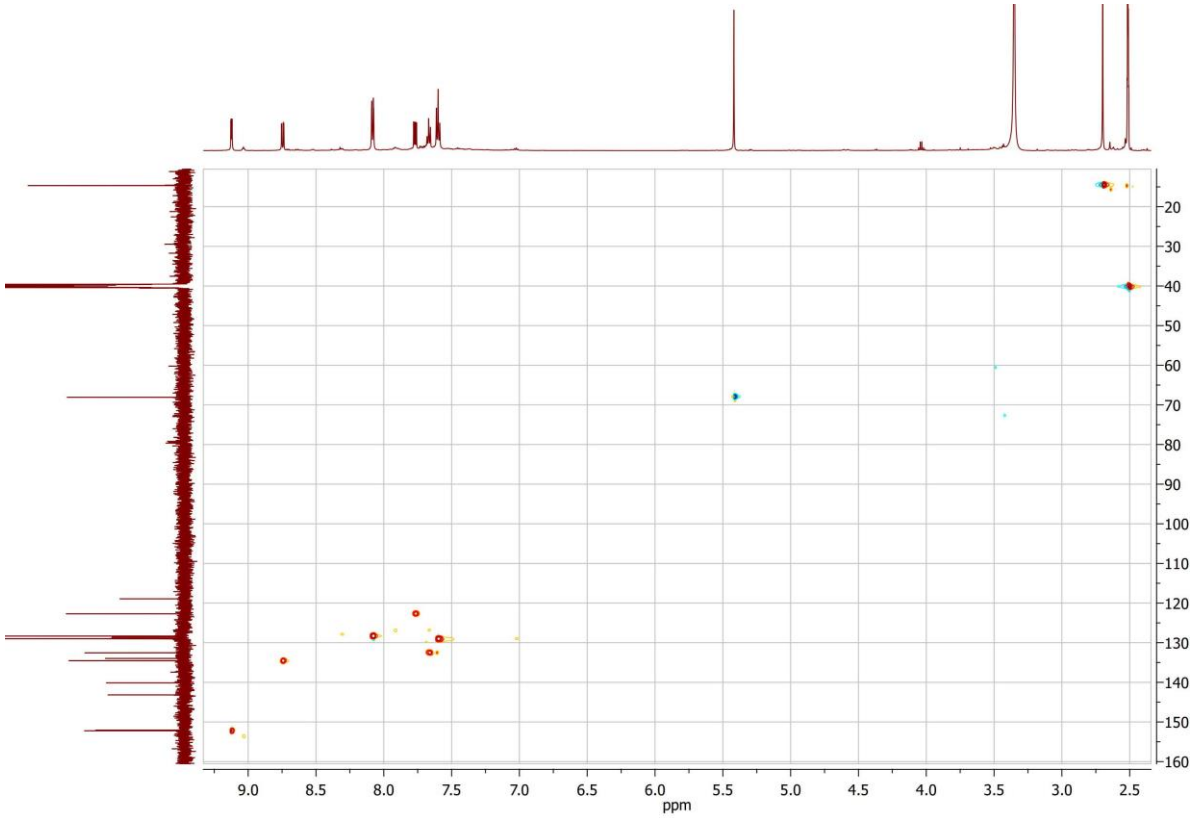
$^{1}H-^{1}H$ NOESY spectrum



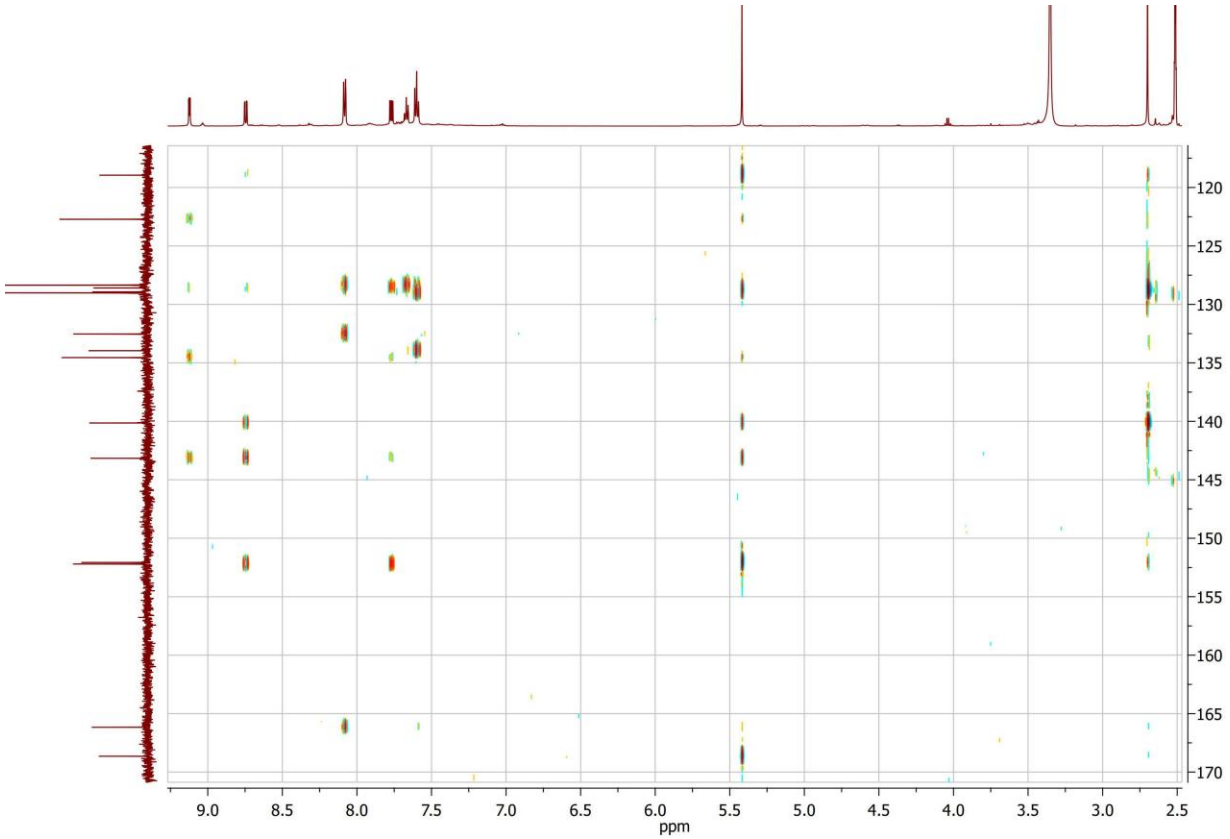
$^{1}H-^{1}H$ COSY spectrum



$^{1}H–^{13}C$ HSQC spectrum



$^{1}H–^{13}C$ HMBC spectrum



Compound 13d

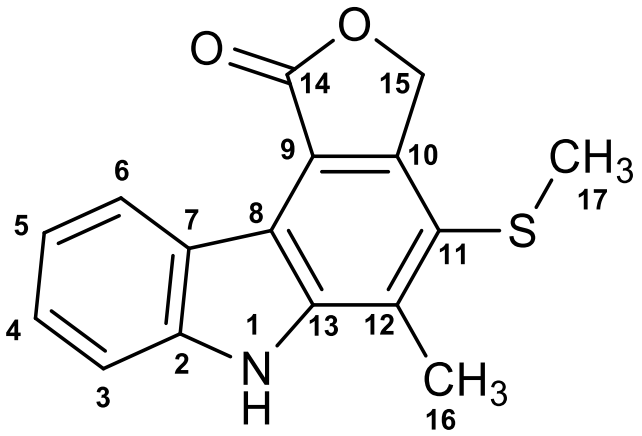
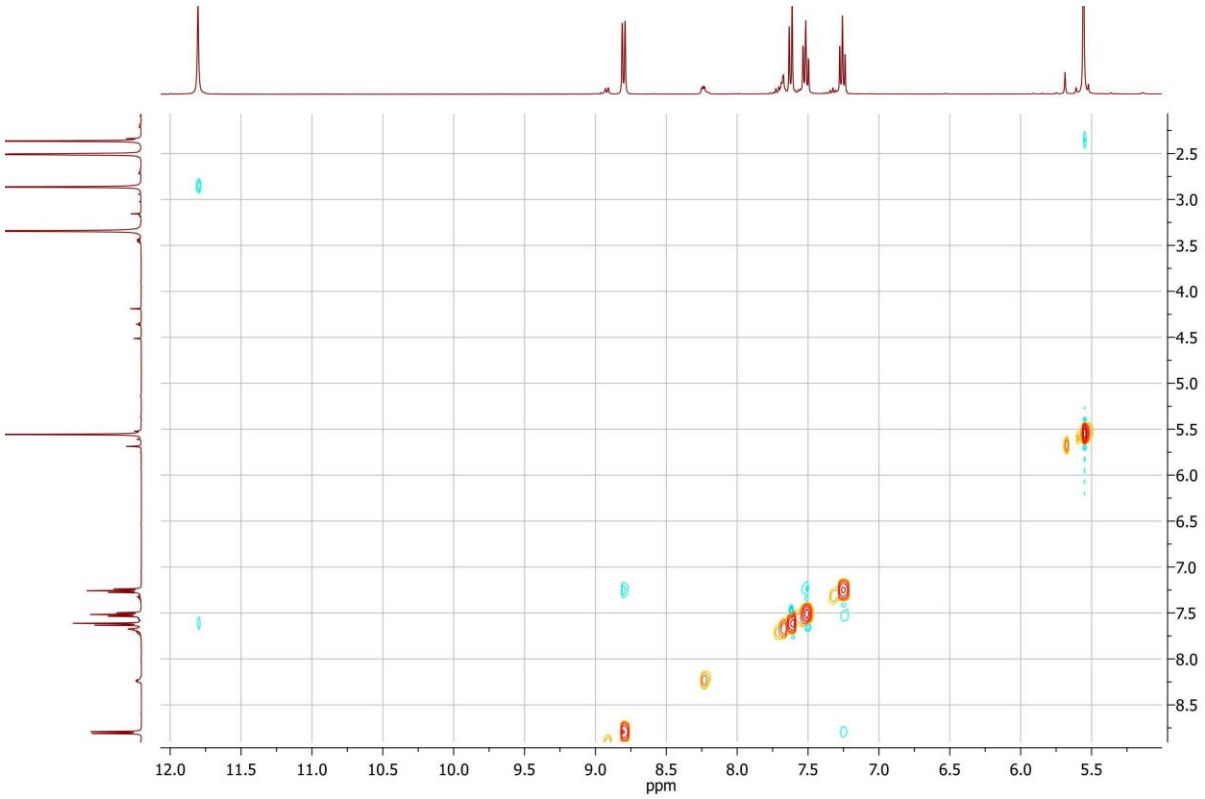


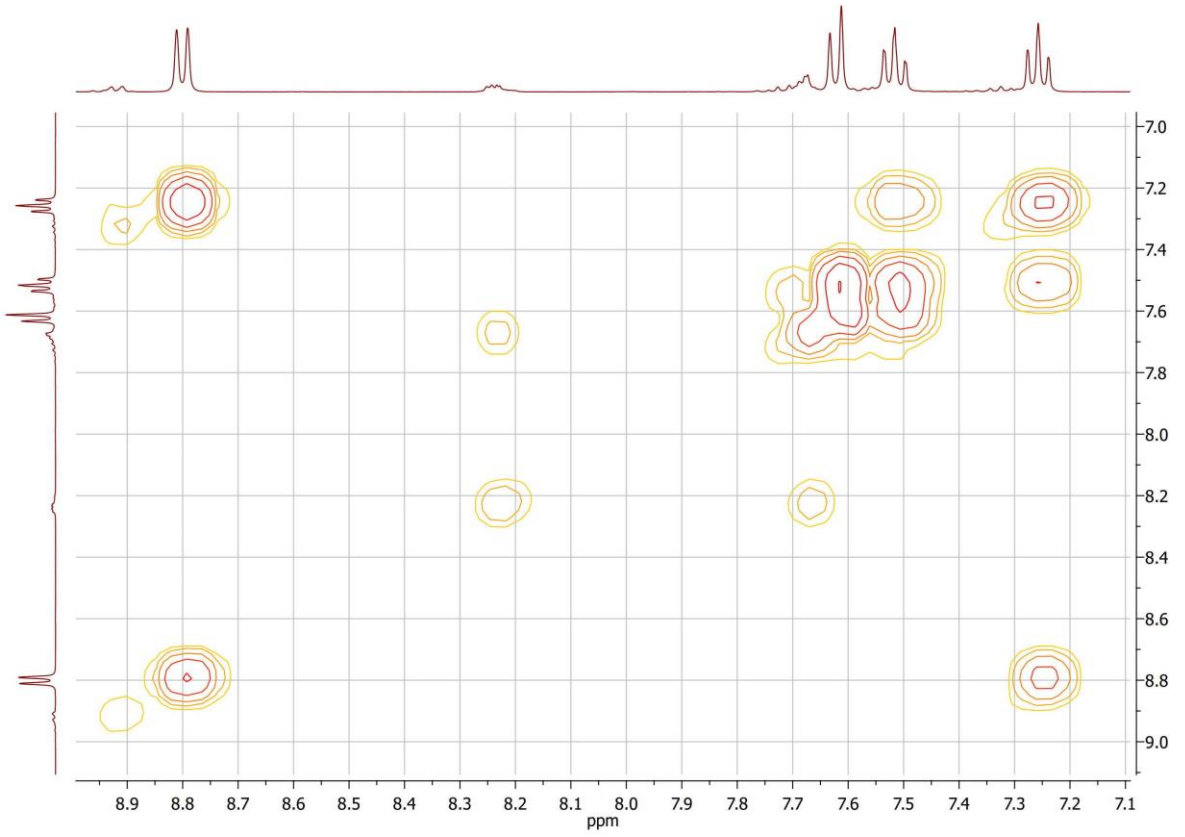
Table S11. Assignment of NMR signals and 2D NMR correlations for compound **13d**.

№	^{1}H	^{13}C	NOESY	HMBC	COSY
1	11.80 (s)	-	3, 16	2, 7, 8, 13	-
2	-	141.3	-	1, 4, 6	-
3	7.62 (d, *J* = 8.2 Hz)	112.0	1	5	4
4	7.49-7.54 (m)	127.7	5	2, 5, 6	3, 5
5	7.23-7.29 (m)	120.0	4, 6	3, 4, 7	4, 6
6	8.80 (d, *J* = 8.0 Hz)	125.0	5	2, 4, 8	5
7	-	121.2	-	1, 5	-
8	-	117.9	-	1, 6	-
9	-	117.0	-	15, 16	-
10	-	145.0	-	15, 16	-
11	-	124.9	-	15, 16, 17	-
12	-	132.7	-	15, 16	-
13	-	140.3	-	1, 15, 16	-
14	-	172.1	-	15	-
15	5.56 (s)	71.0	17	9, 10, 11, 12, 13, 14	-
16	2.86 (s)	15.7	1, 17	9, 10, 11, 12, 13	-
17	2.36 (s)	18.9	15, 16	11	-

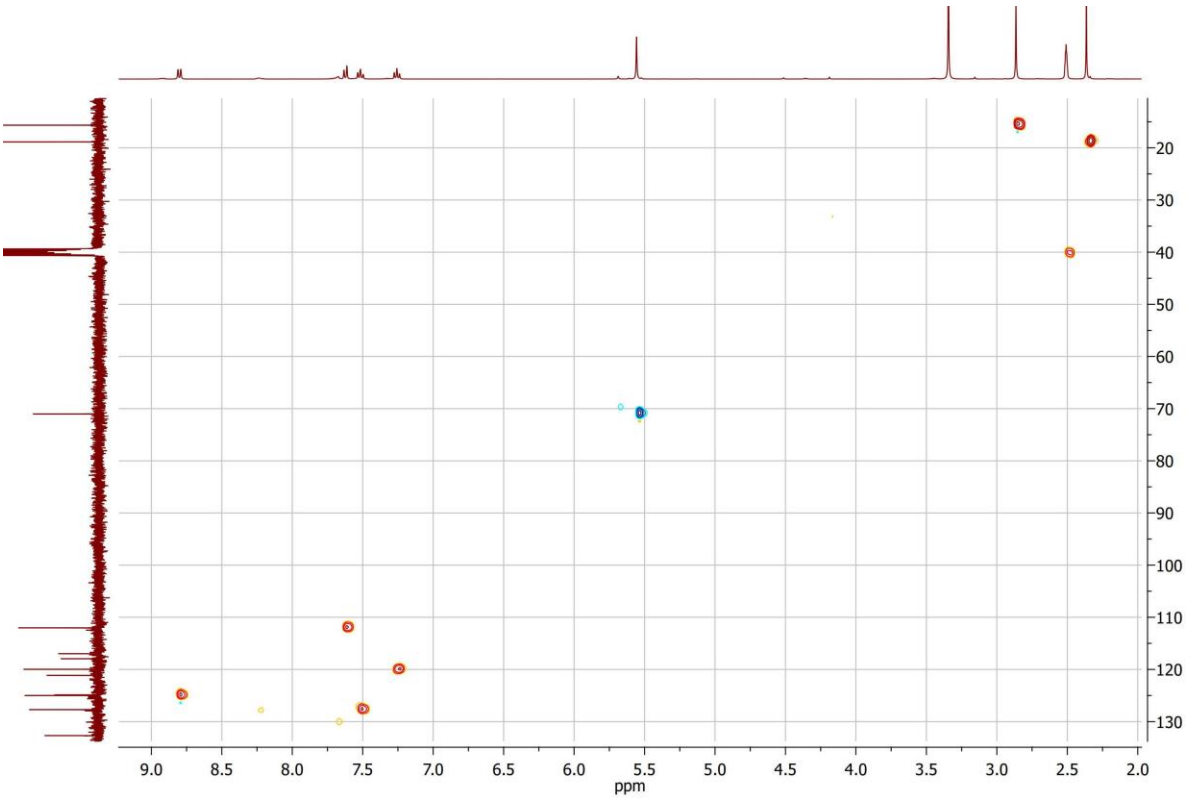
$^{1}H-^{1}H$ NOESY spectrum



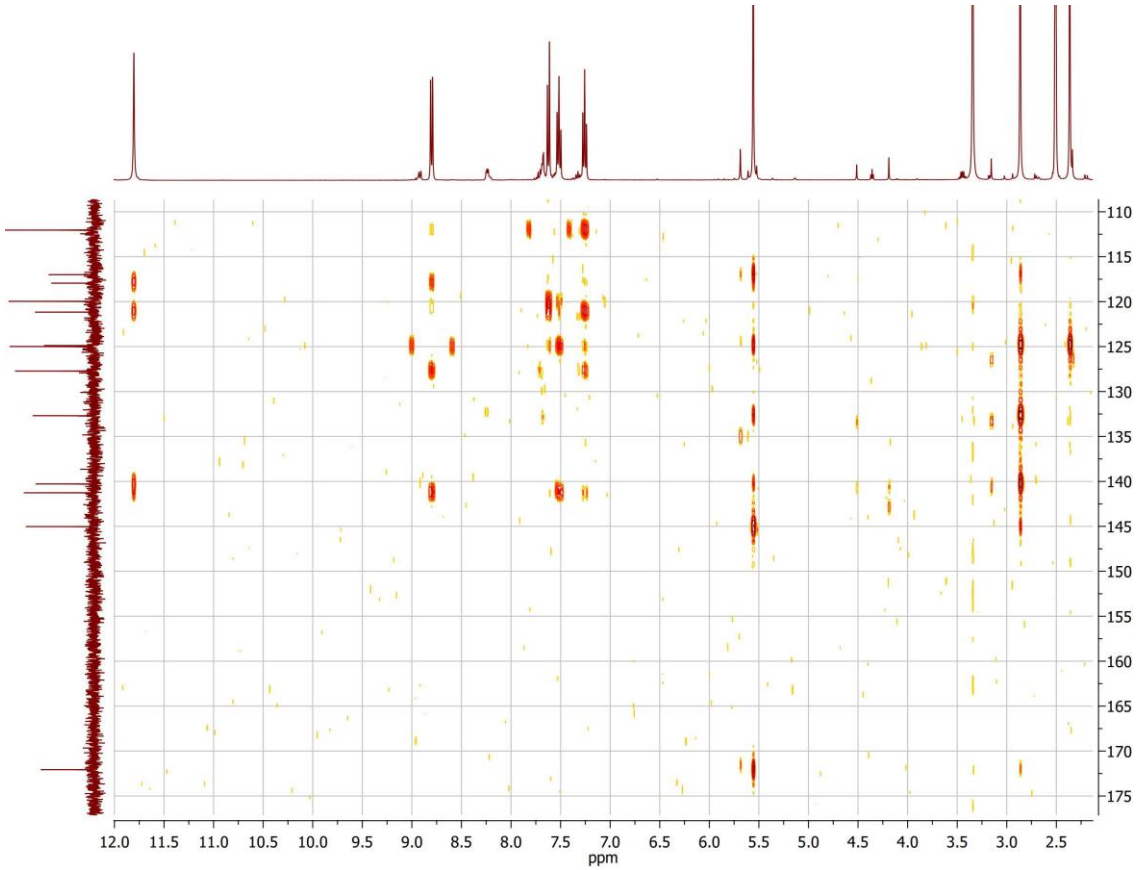
$^{1}H-^{1}H$ COSY spectrum



$^{1}H–^{13}C$ HSQC spectrum



$^{1}H–^{13}C$ HMBC spectrum



Compound 16b (*E*-isomer)

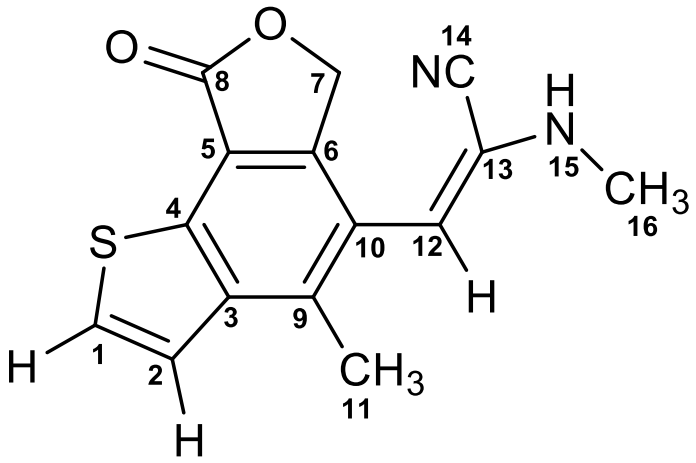
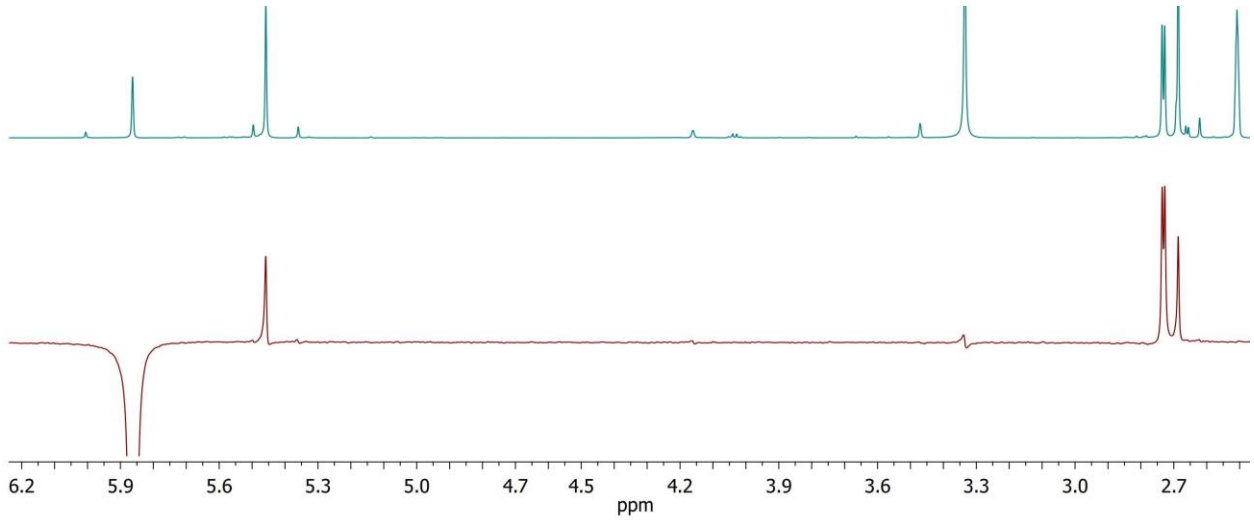


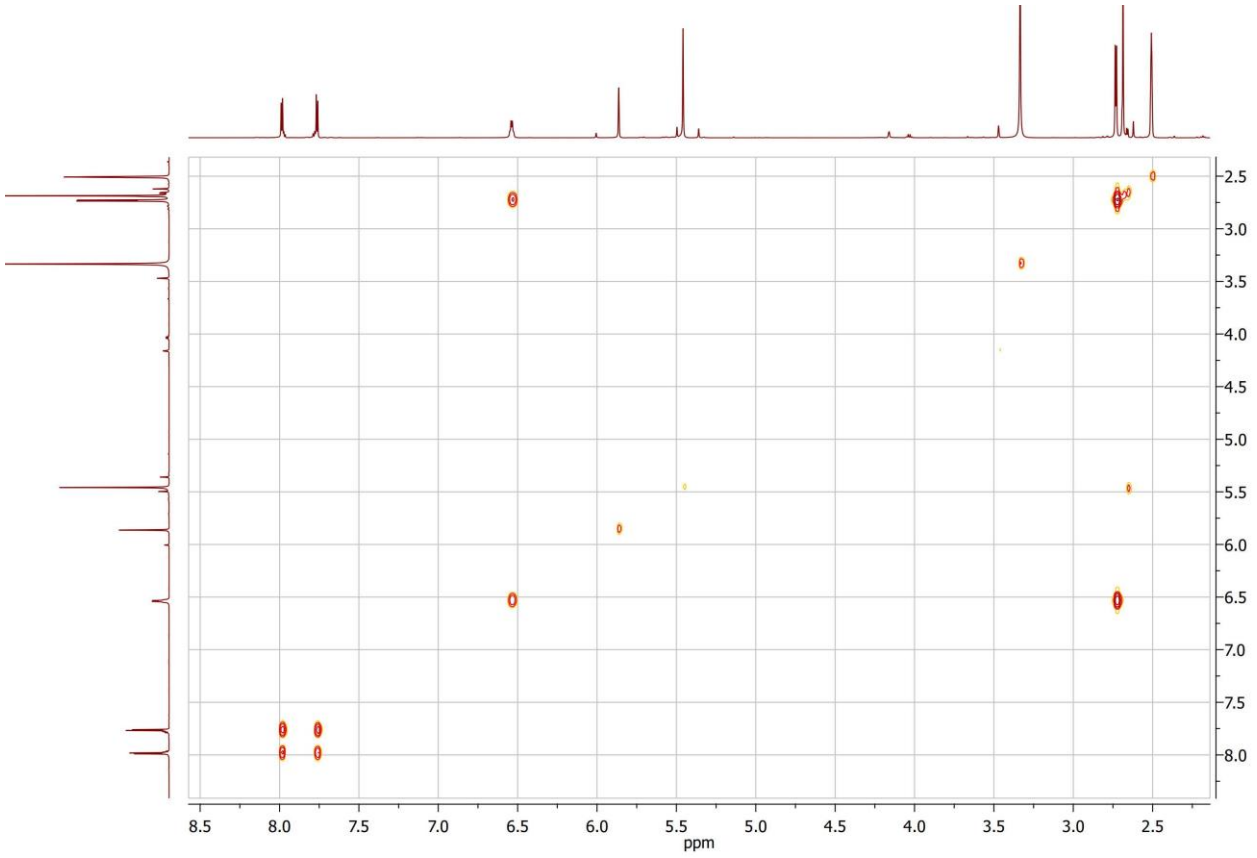
Table S12. Assignment of NMR signals and 2D NMR correlations for compound **16b** (*E*-isomer).

№	^{1}H	^{13}C	NOESY (1D)	COSY	HMBC
1	7.99 (d, *J* = 5.4 Hz)	129.3	-	2	2, 3, 4, 5
2	7.76 (d, *J* = 5.4 Hz)	123.5	-	1	1, 3, 4, 11
3	-	141.9	-	-	1, 2, 11
4	-	133.0	-	-	1, 2
5	-	117.1	-	-	1, 7, 11
6	-	146.6	-	-	7, 12
7	5.46 (s)	70.8	12	-	5, 6, 8
8	-	170.6	-	-	7
9	-	139.3	-	-	11, 12
10	-	126.5	-	-	11
11	2.69 (s)	18.1	12	-	2, 3, 5, 9, 10
12	5.86 (s)	102.2	7, 11, 16	-	6, 9, 14, 15
13	-	124.9	-	-	16
14	-	116.2	-	-	12
15	6.54 (q, *J* = 4.9 Hz)	-	-	16	12
16	2.73 (d, J = 4.9 Hz)	30.9	12	15	13

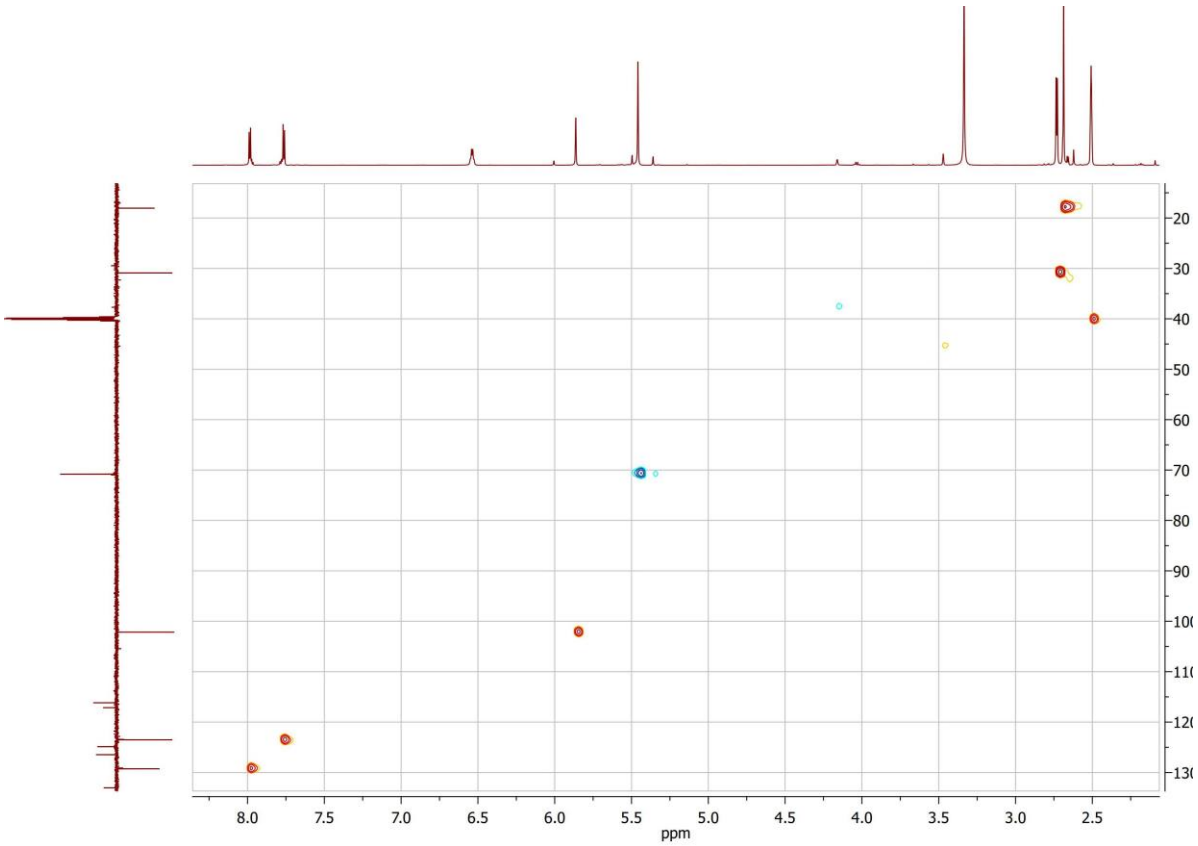
$^{1}H-^{1}H$ 1D NOESY spectra (selective at 5.86 ppm)



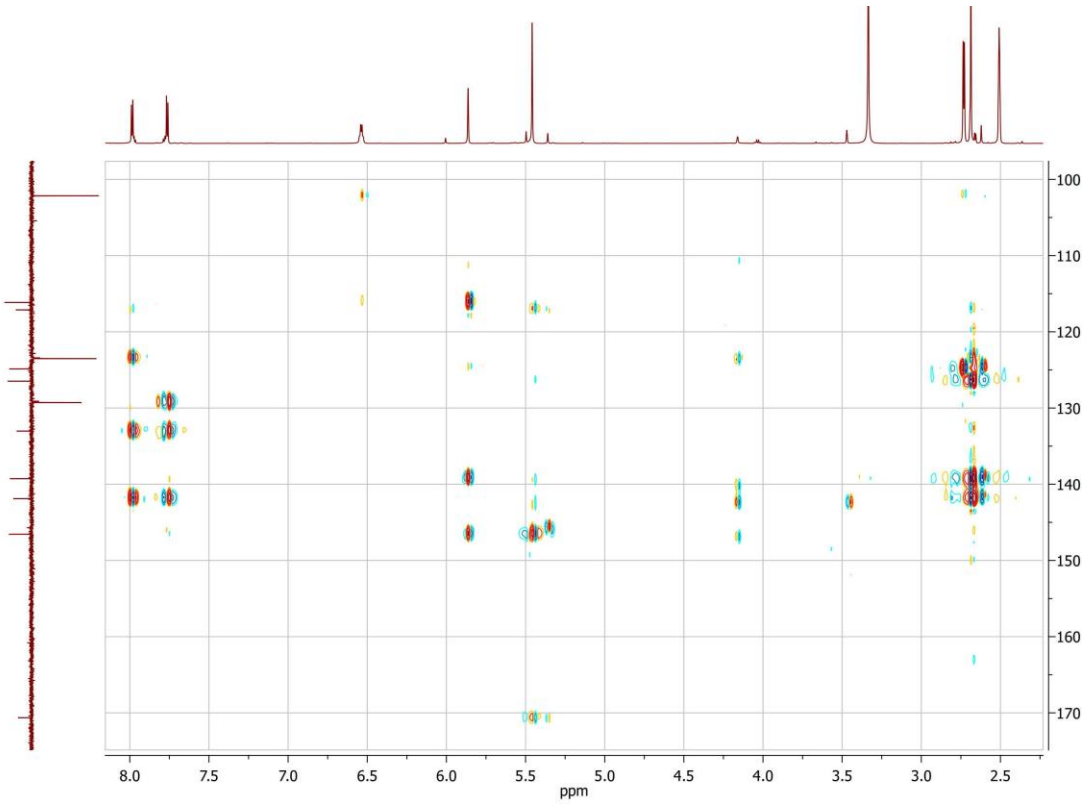
$^{1}H-^{1}H$ COSY spectrum



$^{1}H–^{13}C$ HSQC spectrum



$^{1}H–^{13}C$ HMBC spectrum



Compound 16b (*Z*-isomer)

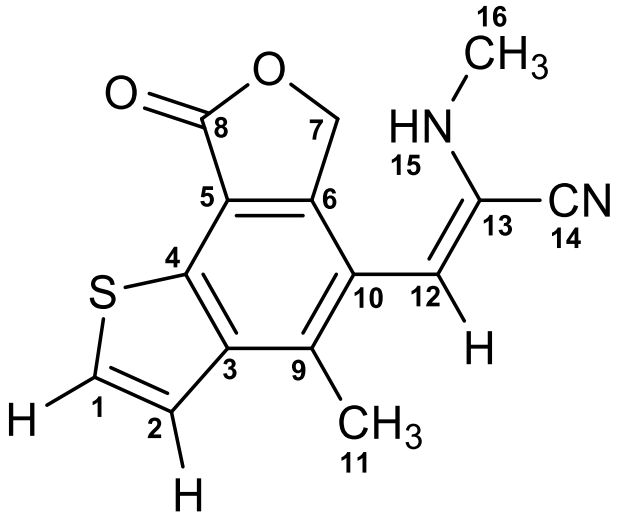
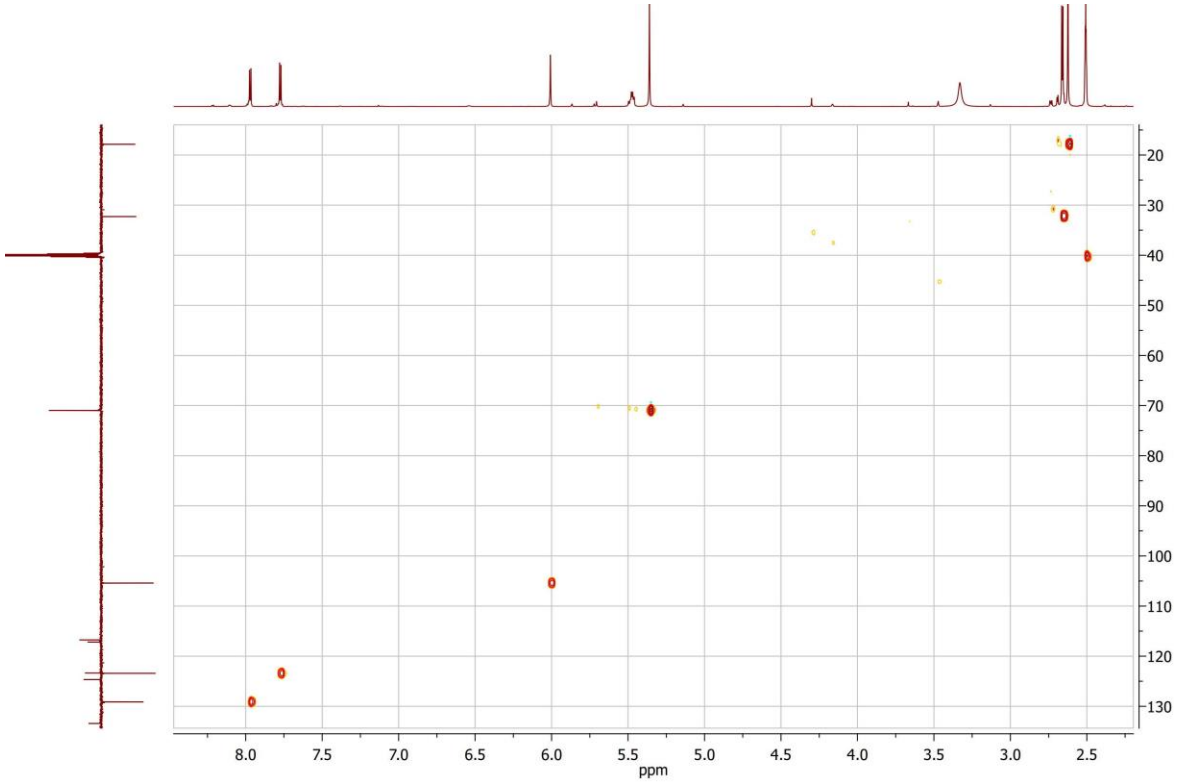


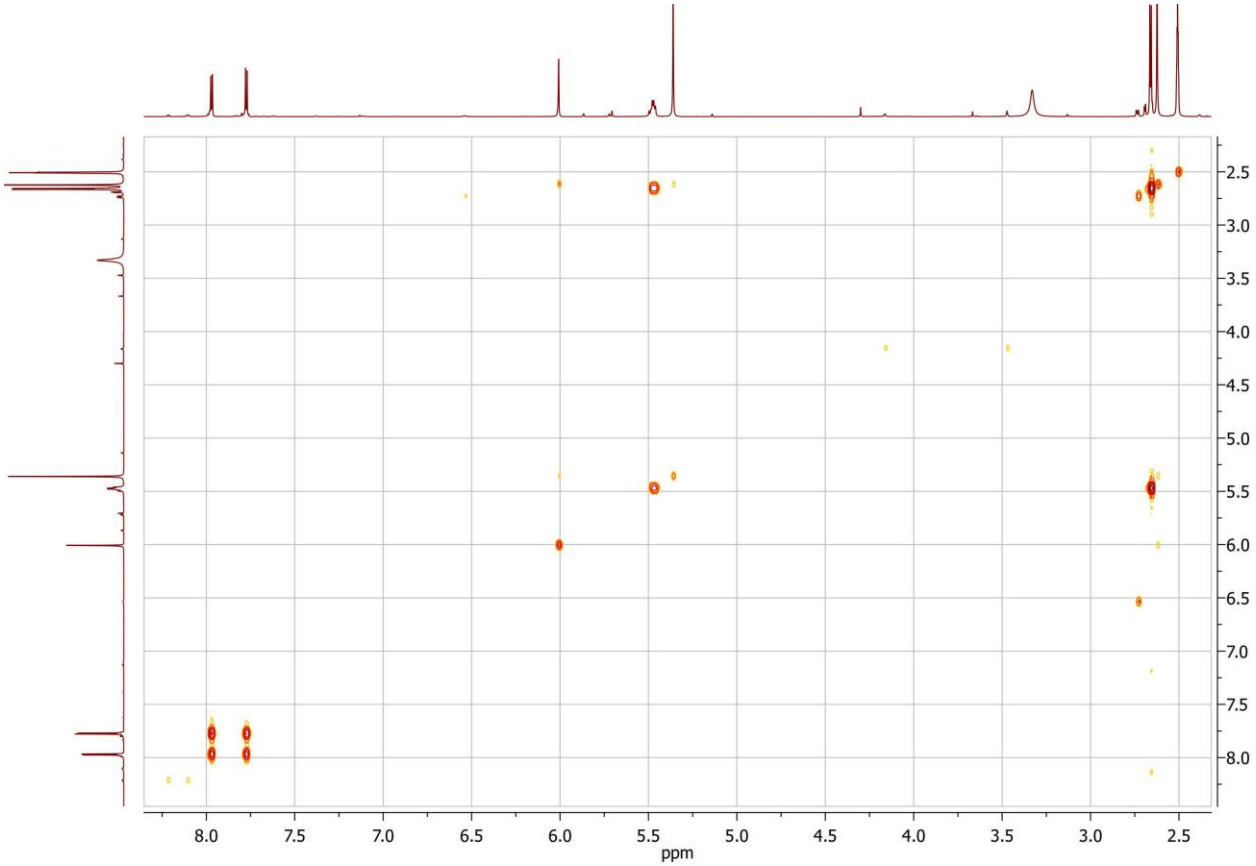
Table S13. Assignment of NMR signals and 2D NMR correlations for compound **16b** (*Z*-isomer).

№	^{1}H	^{13}C	NOESY (1D)	COSY	HMBC
1	7.97 (d, *J* = 5.4 Hz, 1H)	129.1	-	2	2
2	7.77 (d, *J* = 5.4 Hz, 1H)	123.4	-	1	1
3	-	141.7	-	-	1, 2, 11
4	-	133.4	-	-	1, 2
5	-	117.2	-	-	7
6	-	145.7	-	-	7
7	5.36 (s)	71.0	12	-	5, 6, 8
8	-	170.7	-	-	7
9	-	124.7	-	-	7, 11
10	-	139.1	-	-	7, 11
11	2.62 (s)	17.9	12	-	3, 9, 10
12	6.01 (s)	105.4	7, 11	-	-
13	-	123.4	-	-	16
14	-	116.8	-	-	-
15	5.45-5.49 (m)	-	-	16	-
16	2.66 (d, *J* = 4.8 Hz)	32.3	-	15	13

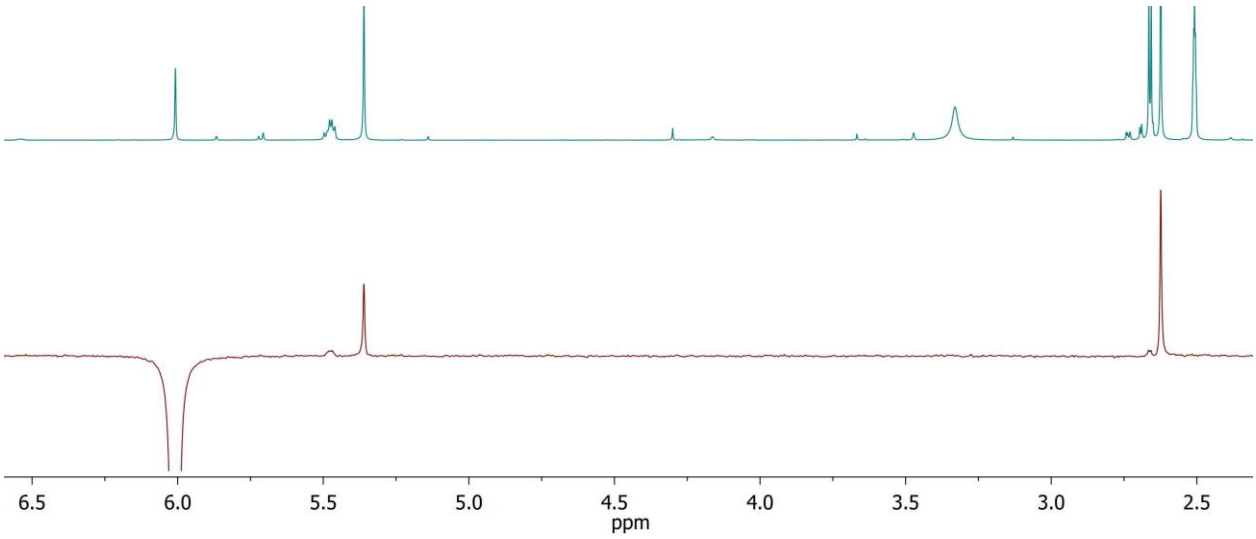
$^{1}H-^{13}C$ HSQC spectrum



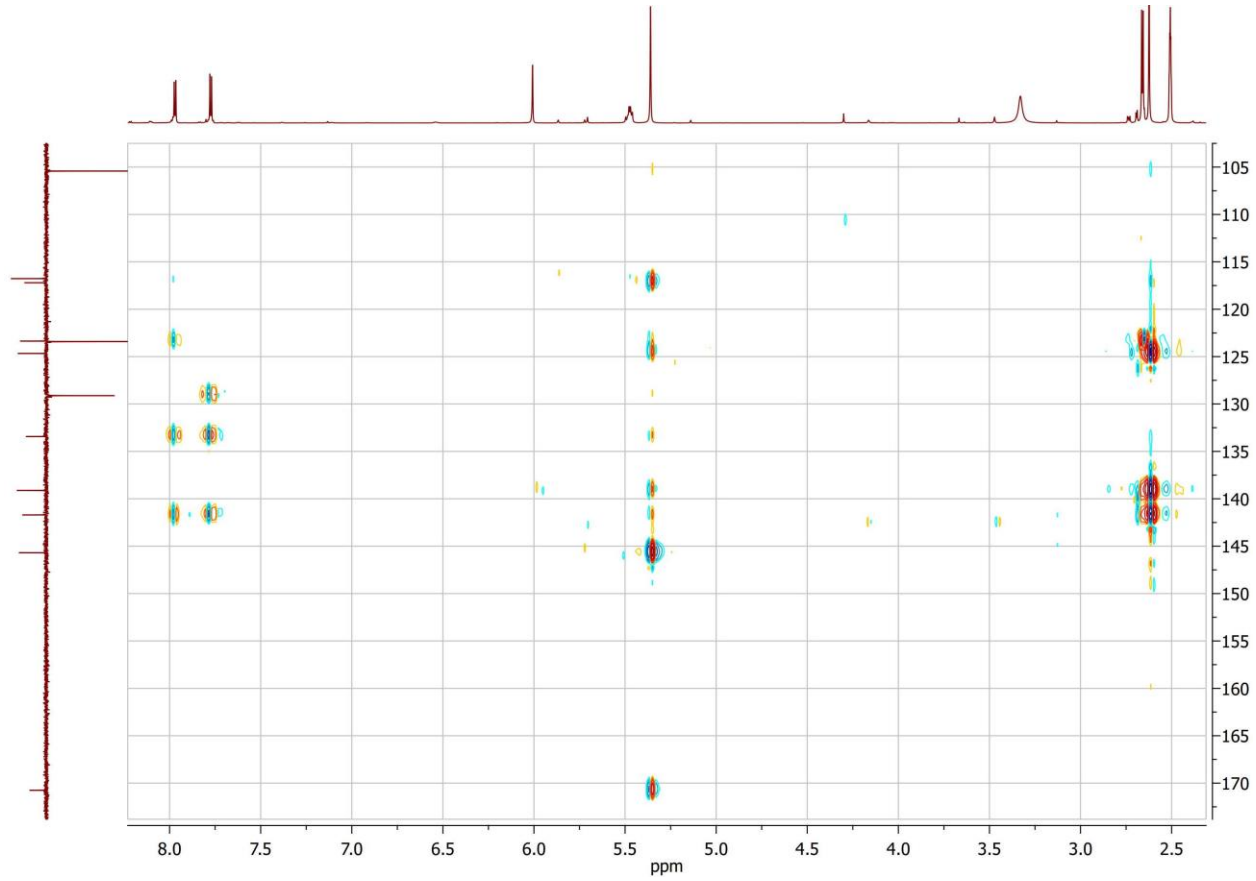
$^{1}H-^{1}H$ COSY spectrum



$^{1}H-^{1}H$ 1D NOESY spectra (selective at 5.86 ppm)



$^{1}H-^{13}C$ HMBC spectrum



Compound 23

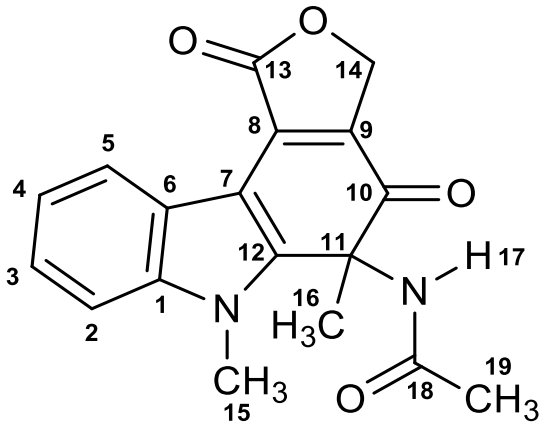
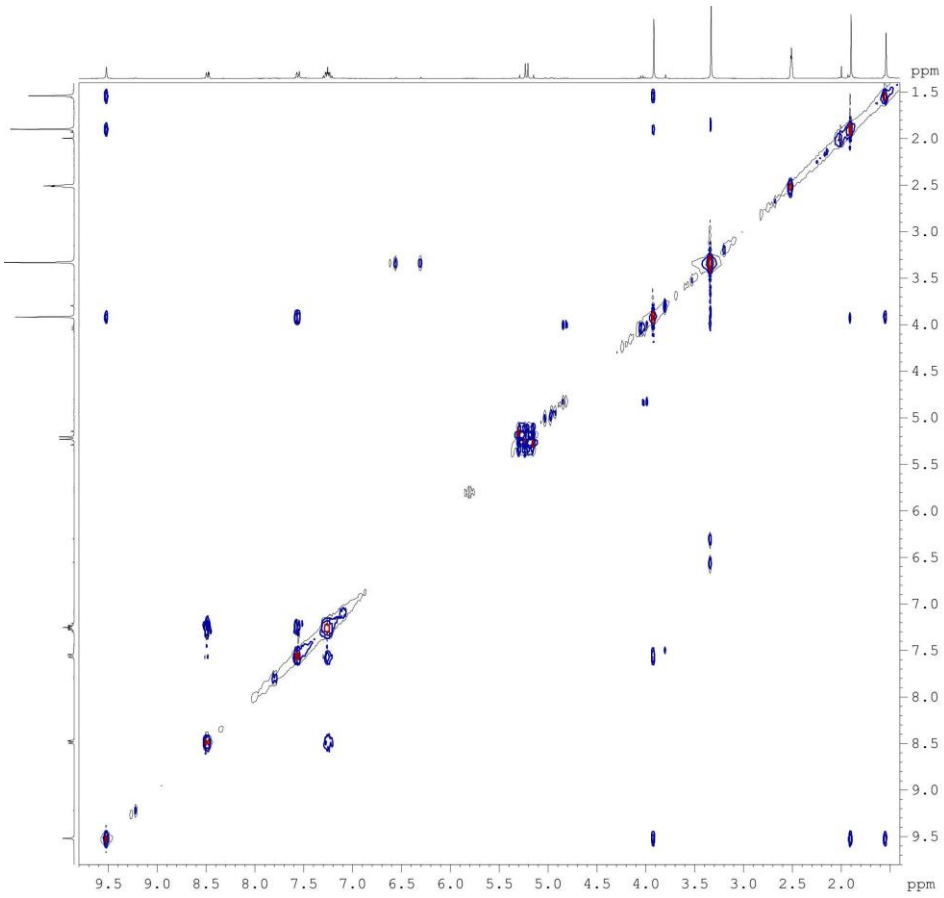


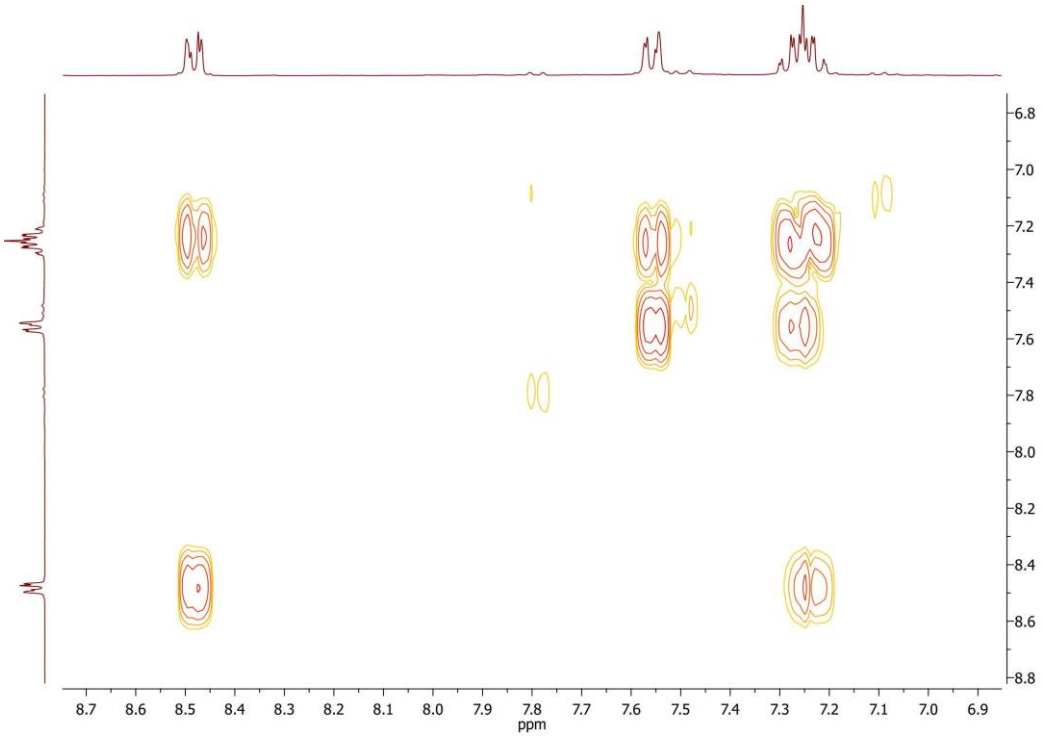
Table S15. Assignment of NMR signals and 2D NMR correlations for compound **23**.

№	^{1}H	^{13}C	NOESY	HMBC	COSY
1	-	138.3	-	2, 3, 5, 15	-
2	7.53-7.58 (m)	110.8	3, 15	1, 4	3
3	7.21-7.30 (m)	122.9	2	1, 4, 5	2
4	7.21-7.30 (m)	122.2	5	2, 3	5
5	8.46-8.51 (m)	122.2	4	1, 3, 6	4
6	-	122.6	-	5	-
7	-	101.6	-	14	-
8	-	136.0	-	14	-
9	-	137.1	-	14	-
10	-	194.5	-	16	-
11	-	60.3	-	16, 17	-
12	-	148.2	-	15, 16	-
13	-	172.0	-	14	-
14	5.17 (d, J = 17.5 Hz, ½CH_2), 5.26 (d, J = 17.5 Hz, ½CH_2)	69.7	-	7, 8, 9, 13	-
15	3.92 (s)	31.5	2, 16, 17, 19	1, 12	-
16	1.54 (s)	23.2	15, 17	10, 11, 12, 17	-
17	9.52 (s)	-	15, 16, 19	11, 16, 18	-
18	-	169.3	-	17, 19	-
19	1.90 (s)	21.7	15, 17	18	-

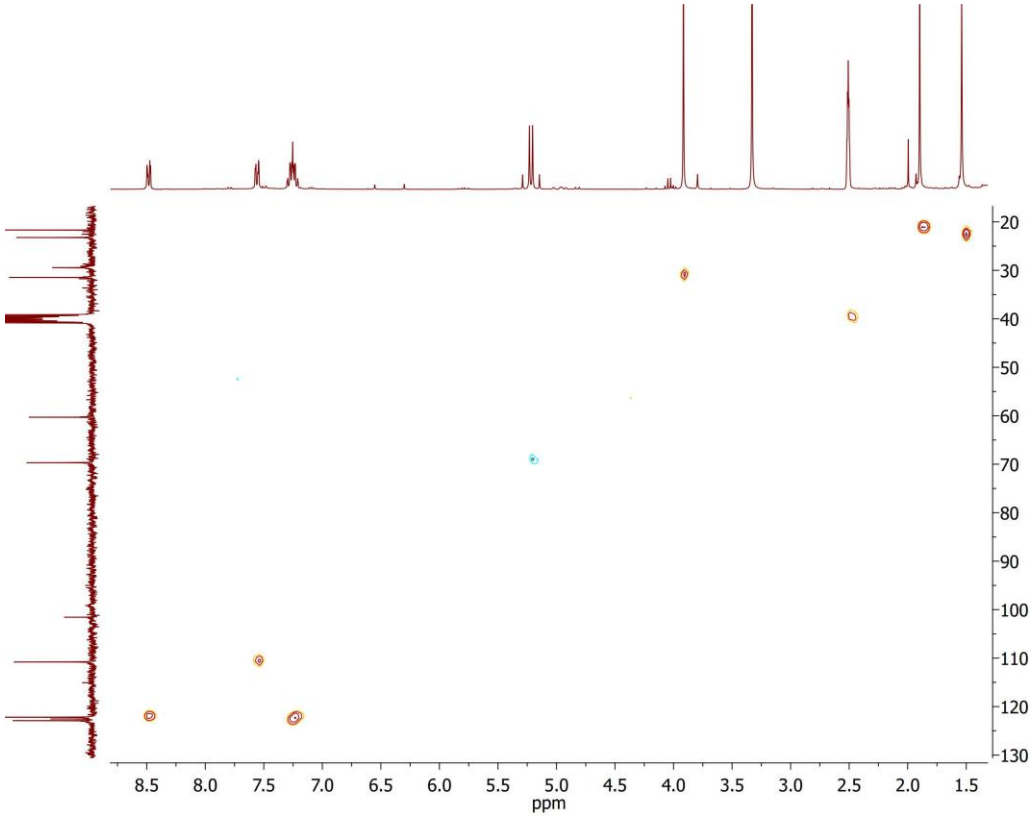
$^{1}H–^{1}H$ NOESY spectrum



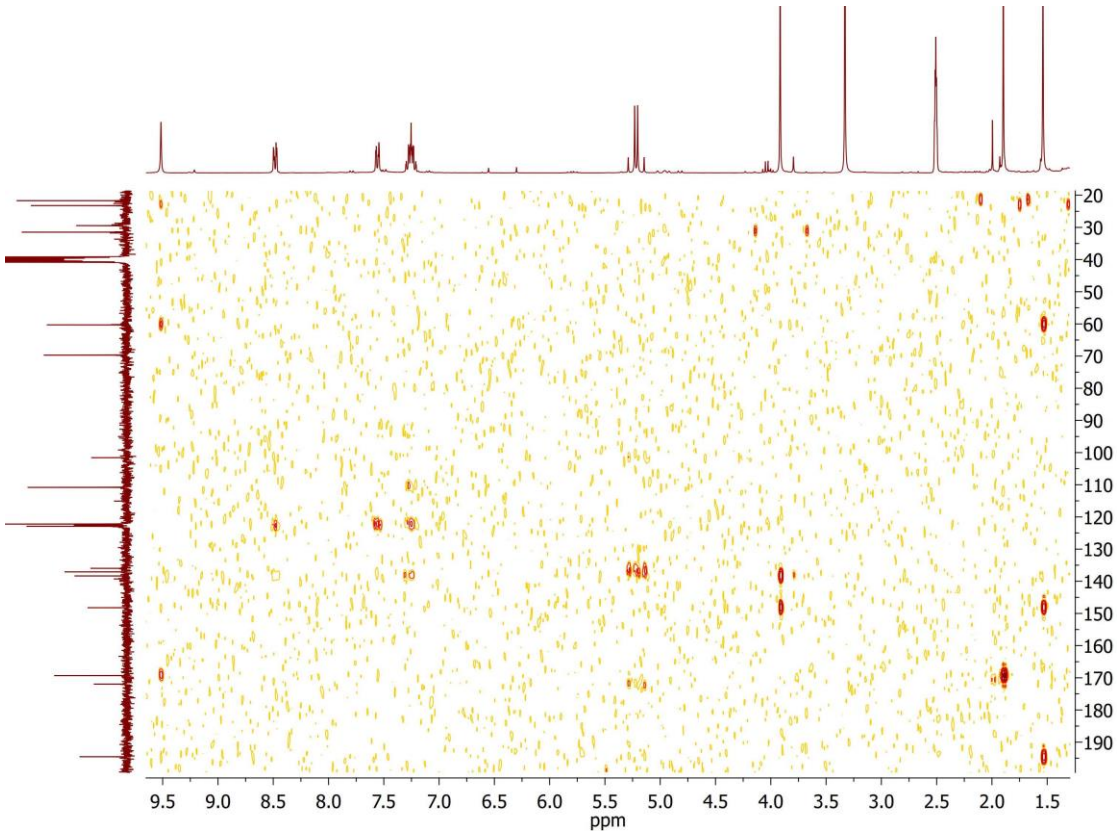
$^{1}H–^{1}H$ COSY spectrum



$^{1}H–^{13}C$ HSQC spectrum



$^{1}H–^{13}C$ HMBC spectrum



Compound 14e

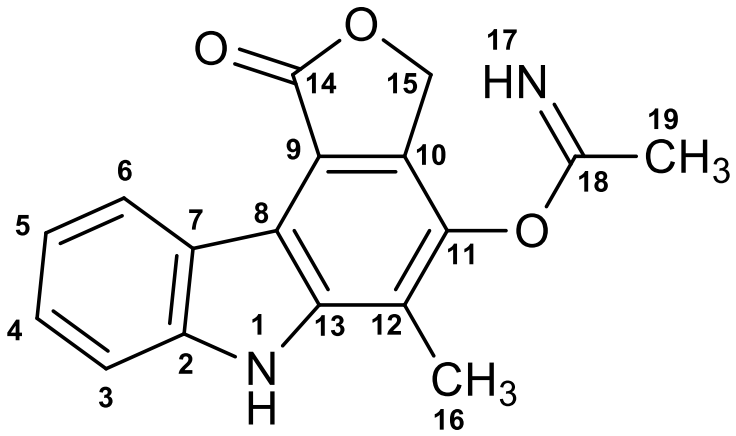
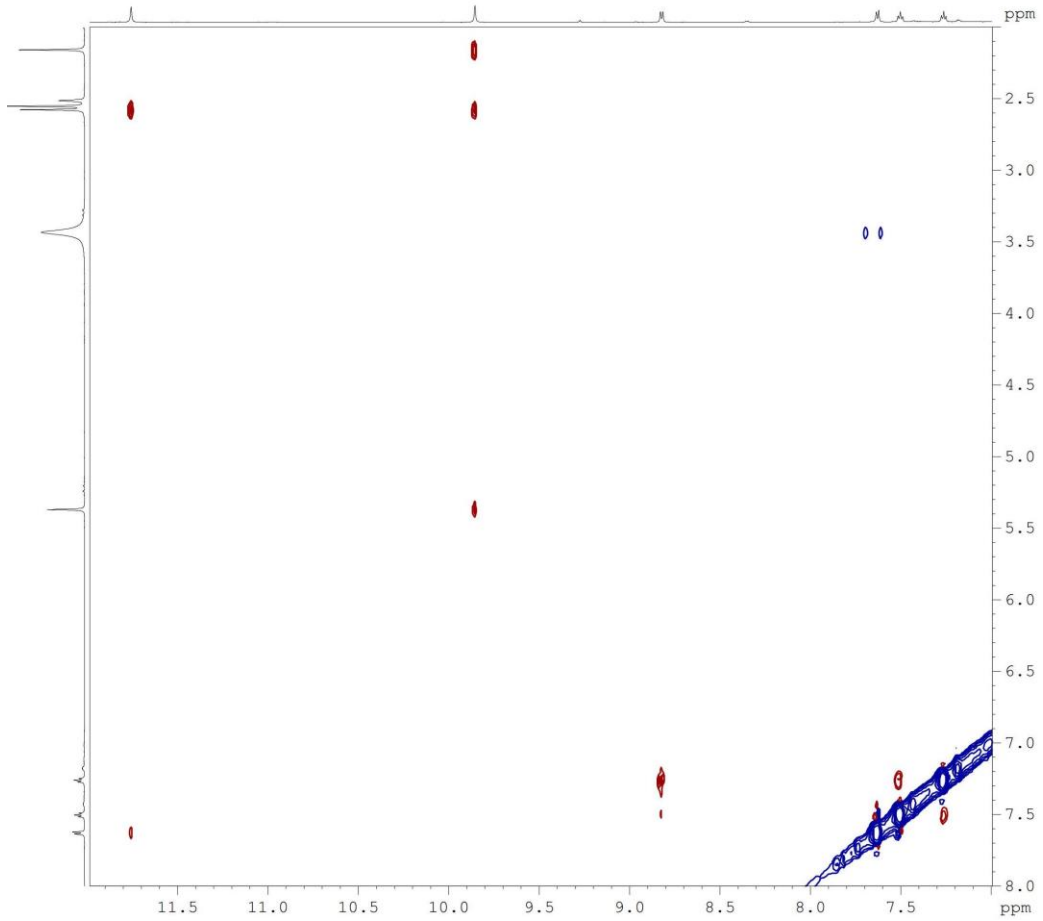


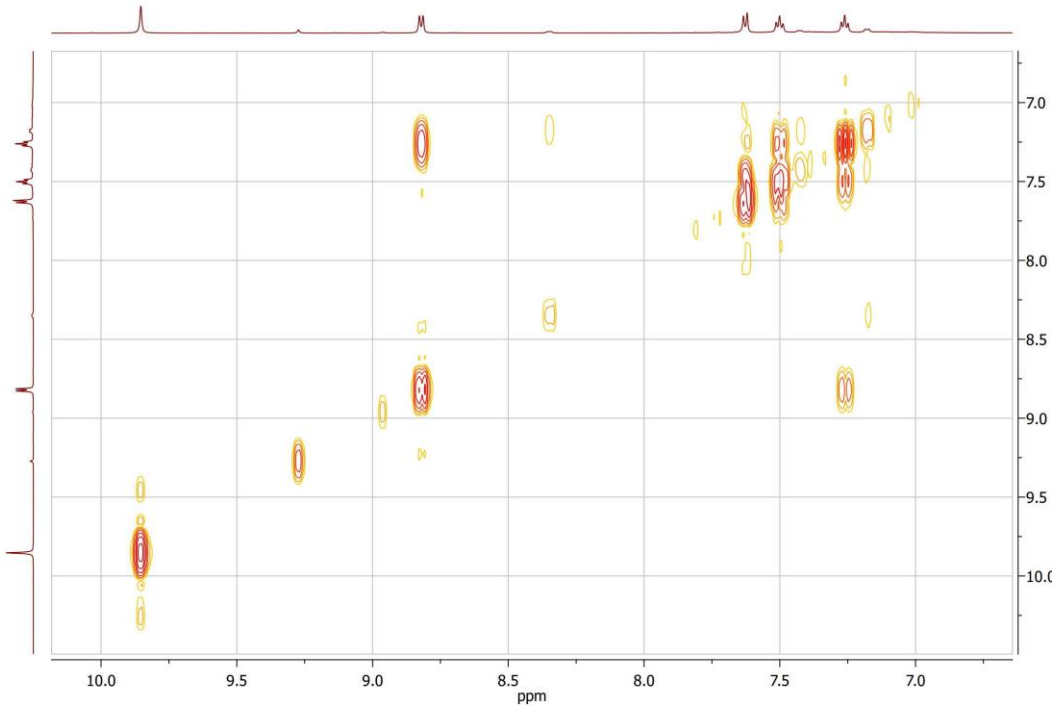
Table S14. Assignment of NMR signals and 2D NMR correlations for compound **14e**.

№	^{1}H	^{13}C	NOESY	HMBC	COSY
1	11.75	-	3, 16	2, 3, 7, 8, 13	-
2	-	141.2	-	1, 4, 6	-
3	7.63 (d, *J* = 8.1 Hz)	111.9	1, 4	1, 4, 5, 6, 8	4
4	7.48-7.52 (m)	127.1	3, 5	2, 3, 6	3, 5
5	7.24-7.28 (m)	119.8	4, 6	3, 8	4, 6
6	8.82 (d, *J* = 7.9 Hz)	124.7	5	2, 3, 4, 7	5
7	-	116.0	-	1, 6	-
8	-	121.4	-	1, 3, 5	-
9	-	116.6	-	15, 16	-
10	-	138.0	-	15, 16, 17	-
11	-	127.7	-	15, 16, 17	-
12	-	124.5	-	15, 16, 17	-
13	-	140.5	-	1, 16	-
14	-	172.0	-	15	-
15	5.37 (s)	70.4	17	9, 10, 11, 12, 14	-
16	2.58 (s)	13.6	1, 17	9, 11, 10, 12, 13	-
17	9.85 (s)	-	15, 16, 19	10, 11, 12, 18	-
18	-	168.8	-	17, 19	-
19	2.16 (s)	23.2	17	18	-

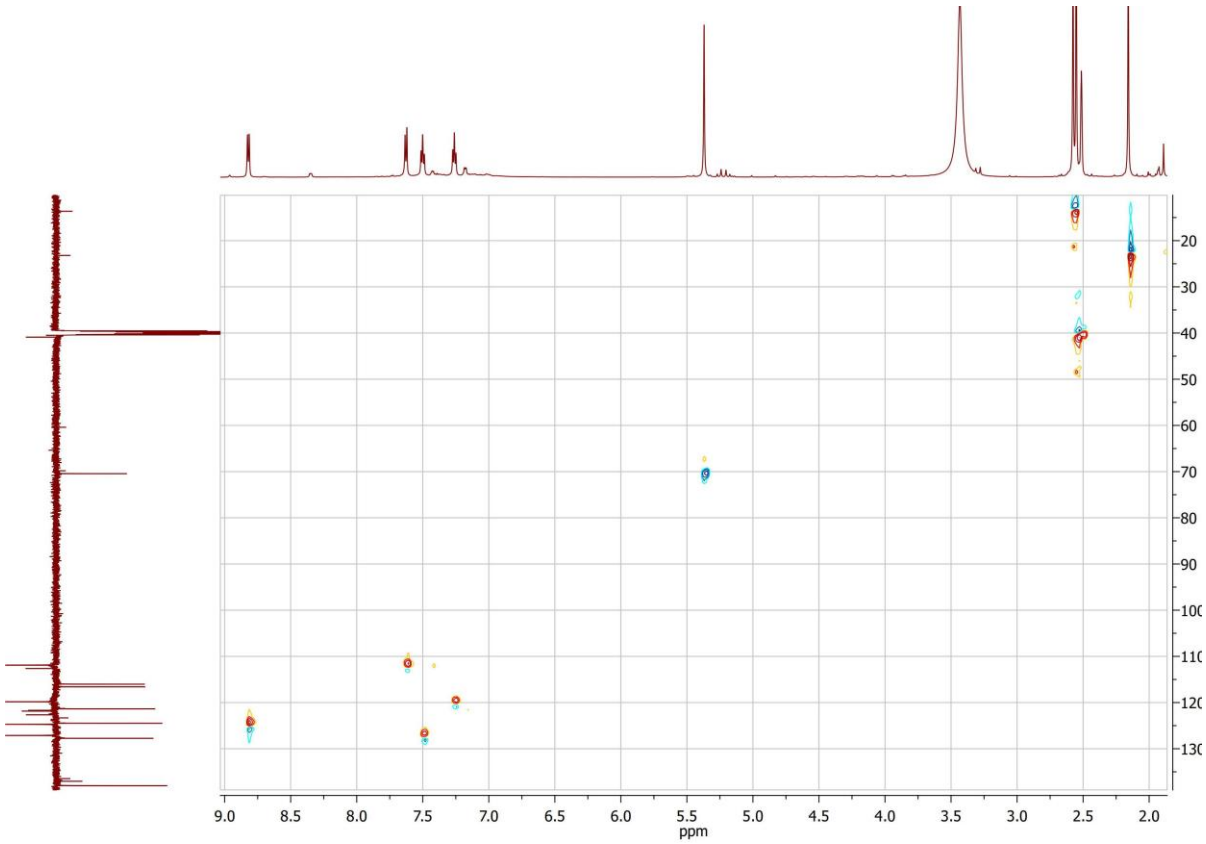
$^{1}H-^{1}H$ NOESY spectrum



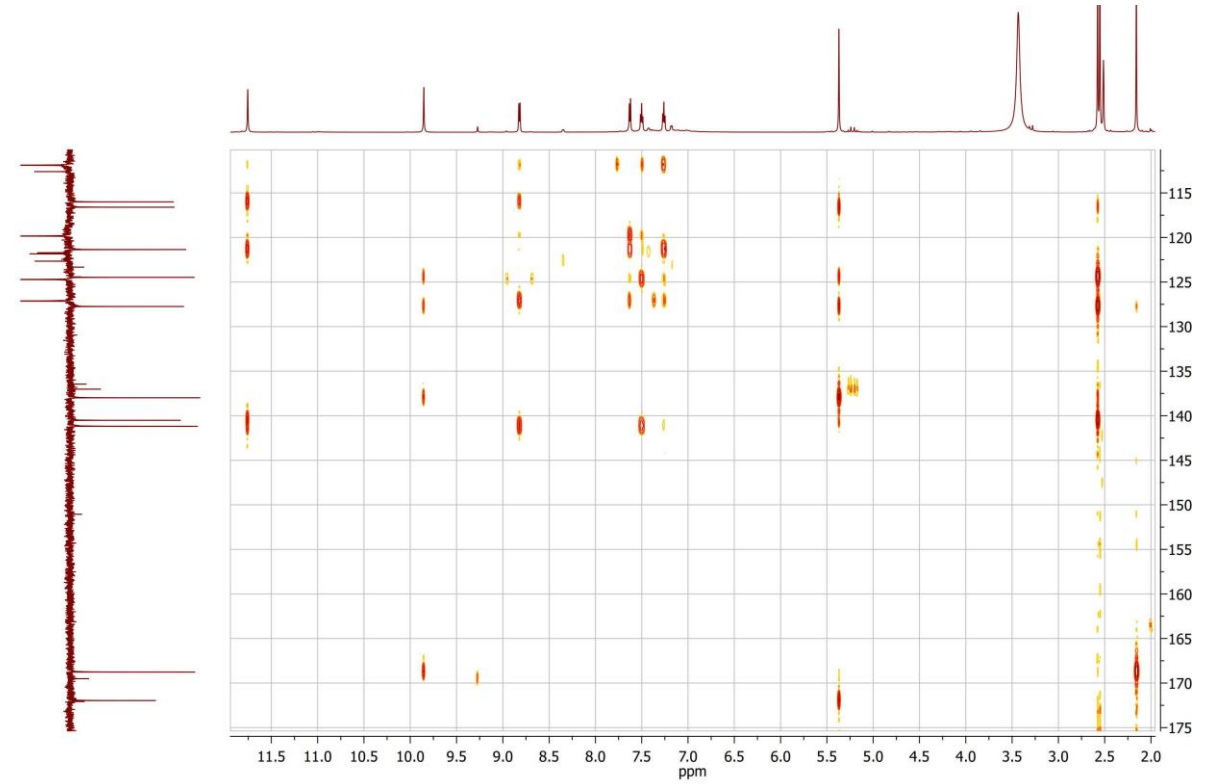
$^{1}H-^{1}H$ COSY spectrum



$^{1}H-^{13}C$ HSQC spectrum

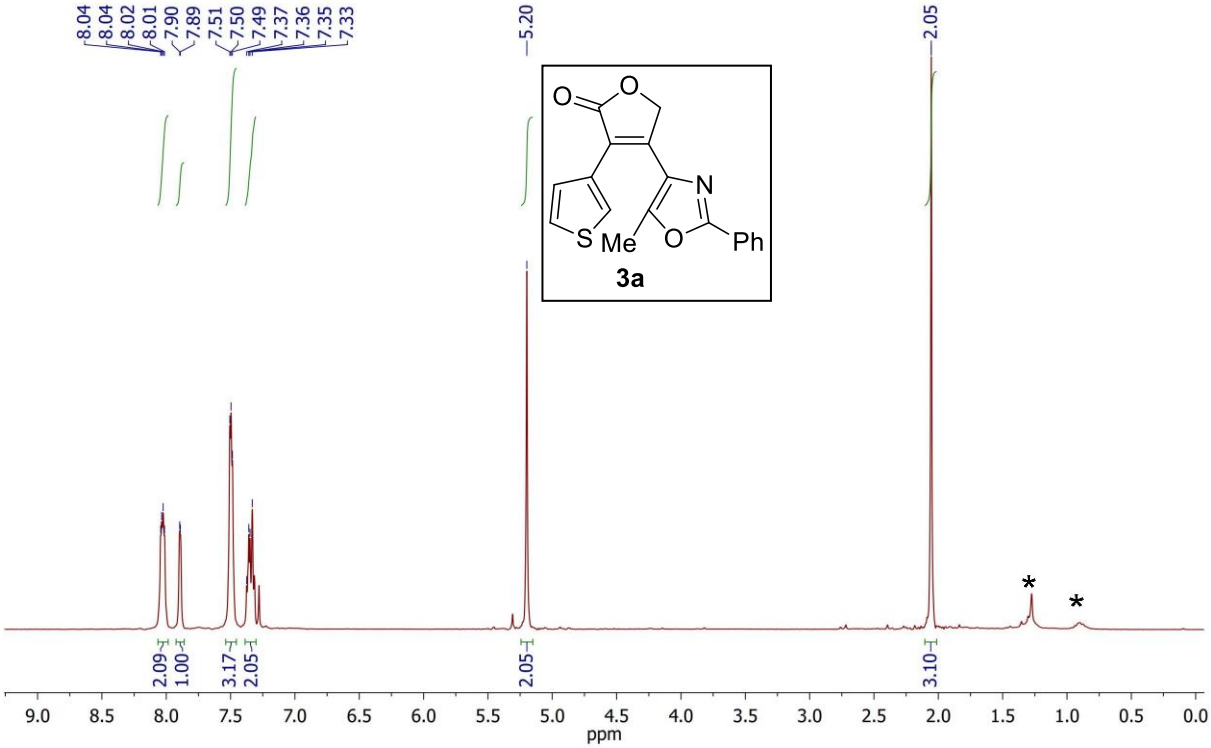


$^{1}H-^{13}C$ HMBC spectrum



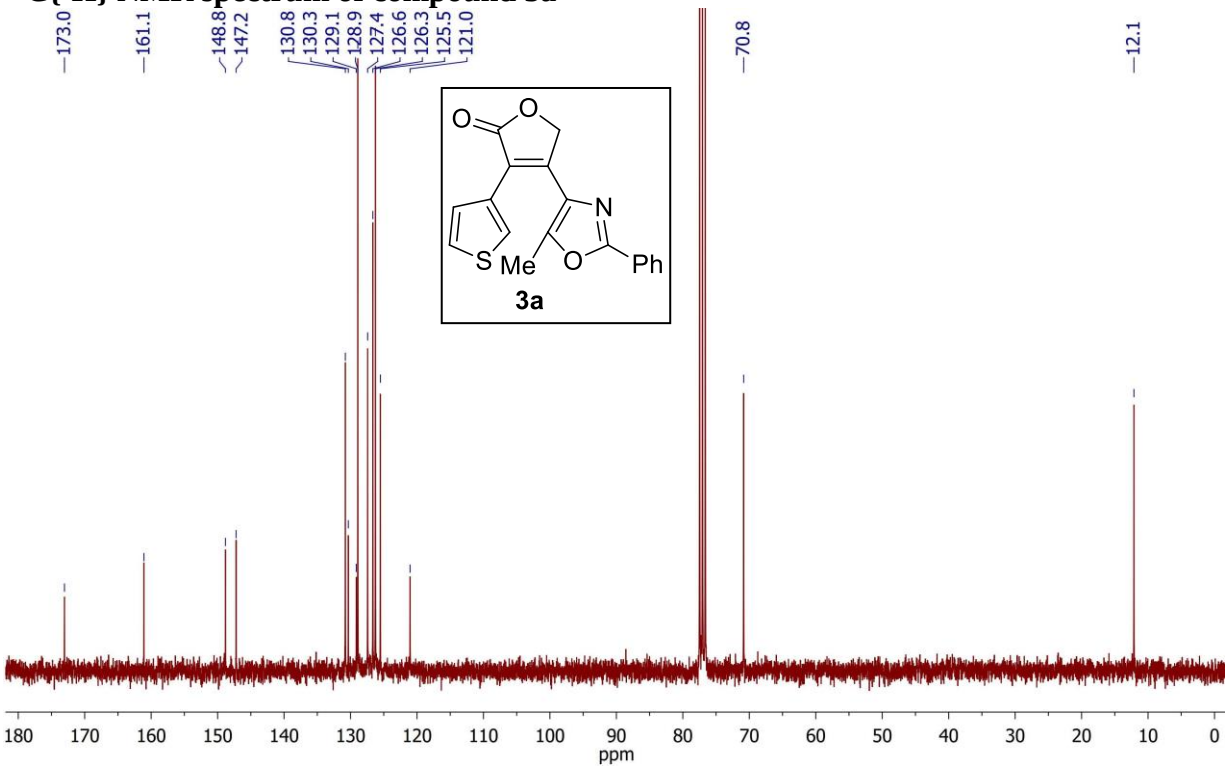
IX. Copies of NMR spectra for all new compounds

^{1}H NMR spectrum of compound 3a

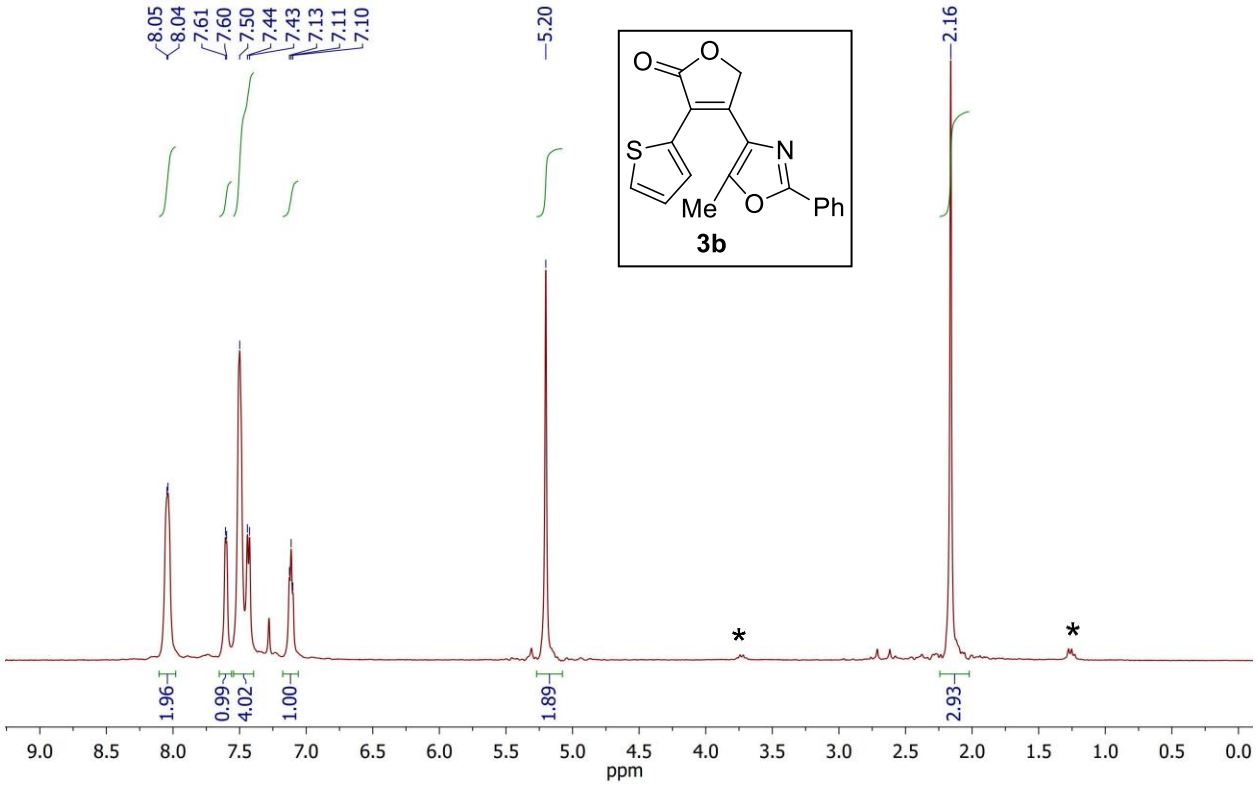


* Grease

^{13}C{^{1}H} NMR spectrum of compound 3a

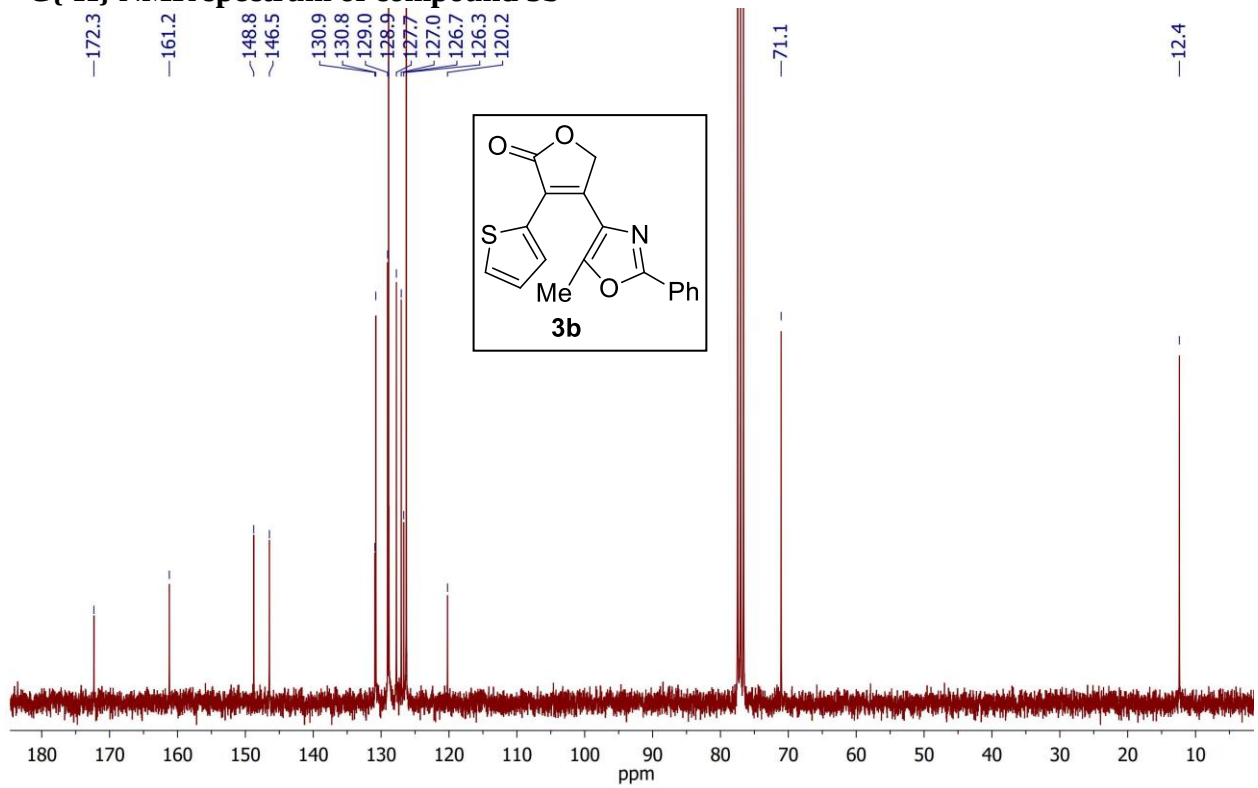


^{1}H NMR spectrum of compound 3b

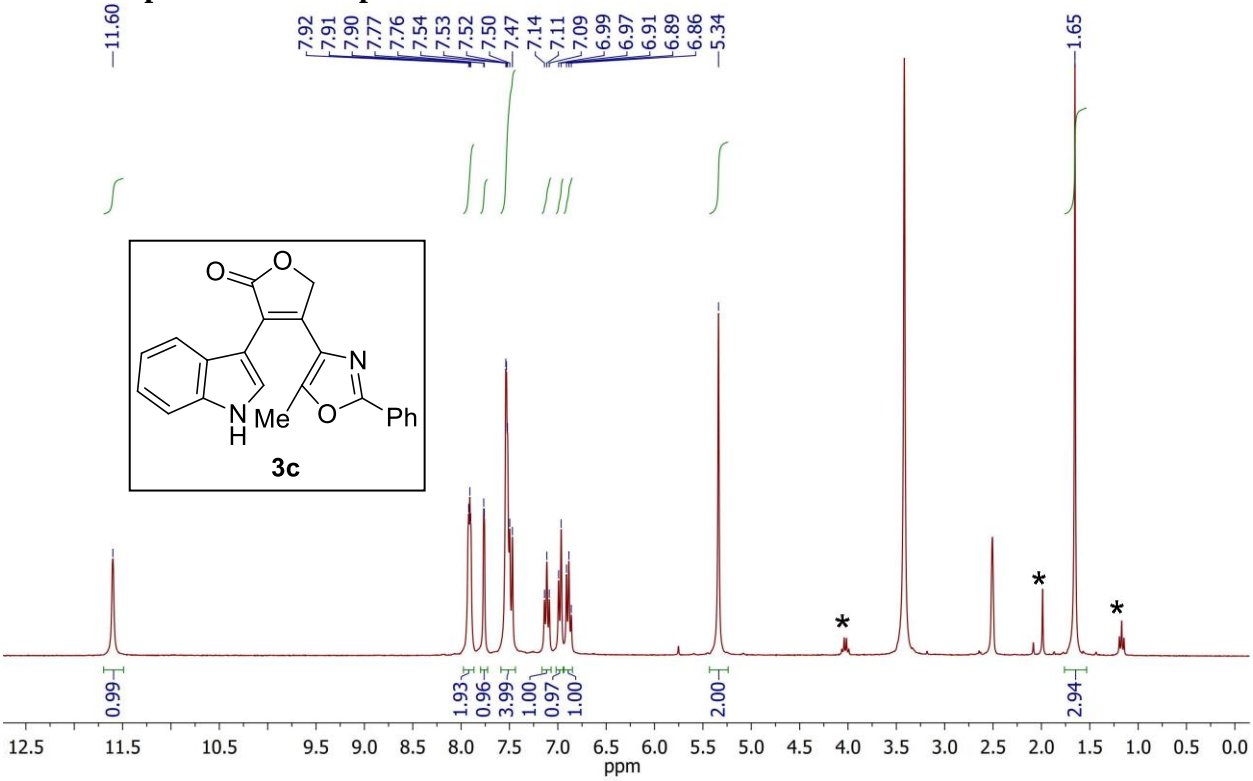


* Ethanol

^{13}C{^{1}H} NMR spectrum of compound 3b

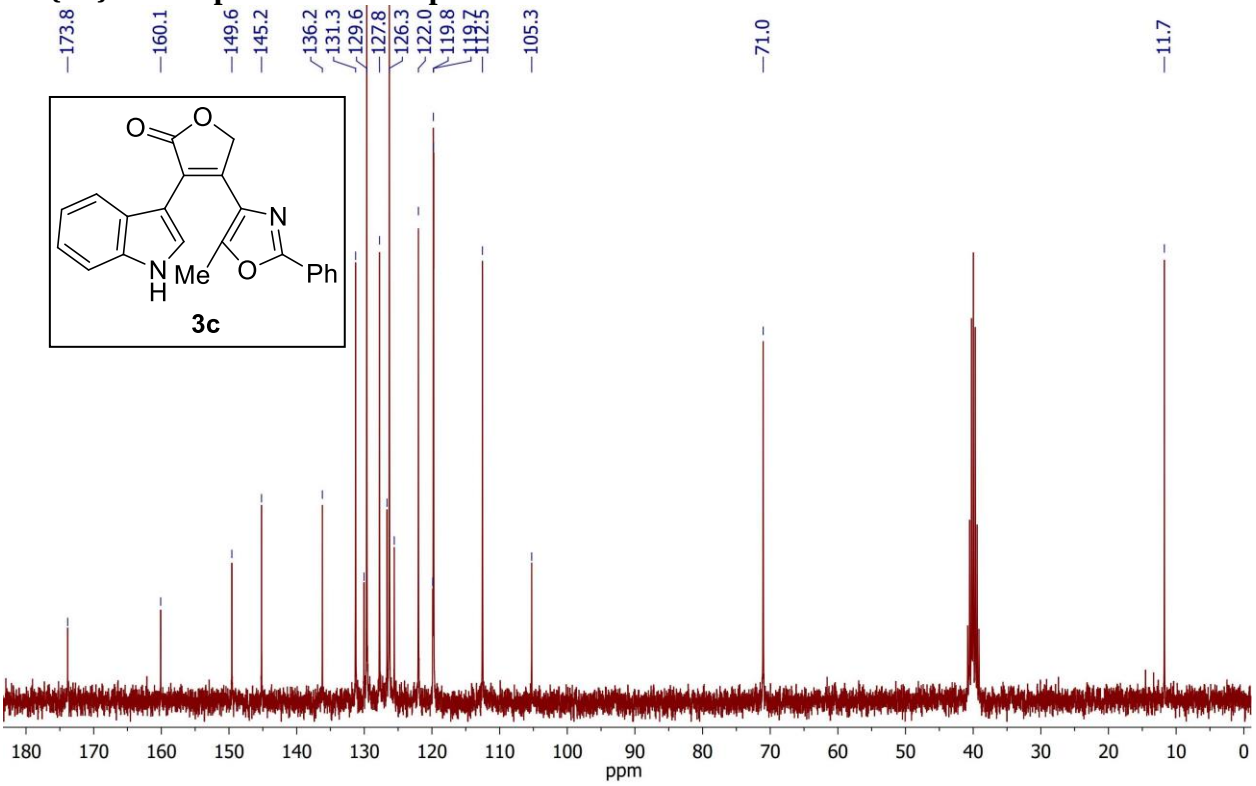


^{1}H NMR spectrum of compound 3c

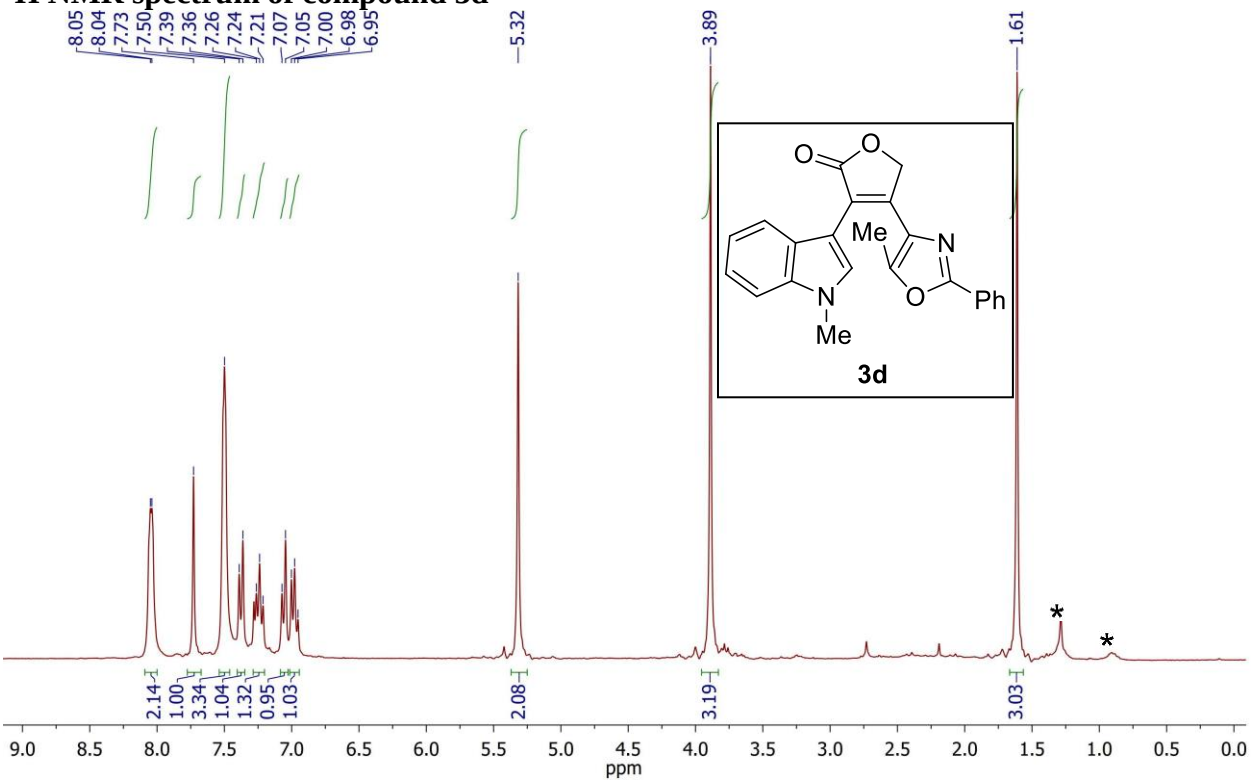


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 3c

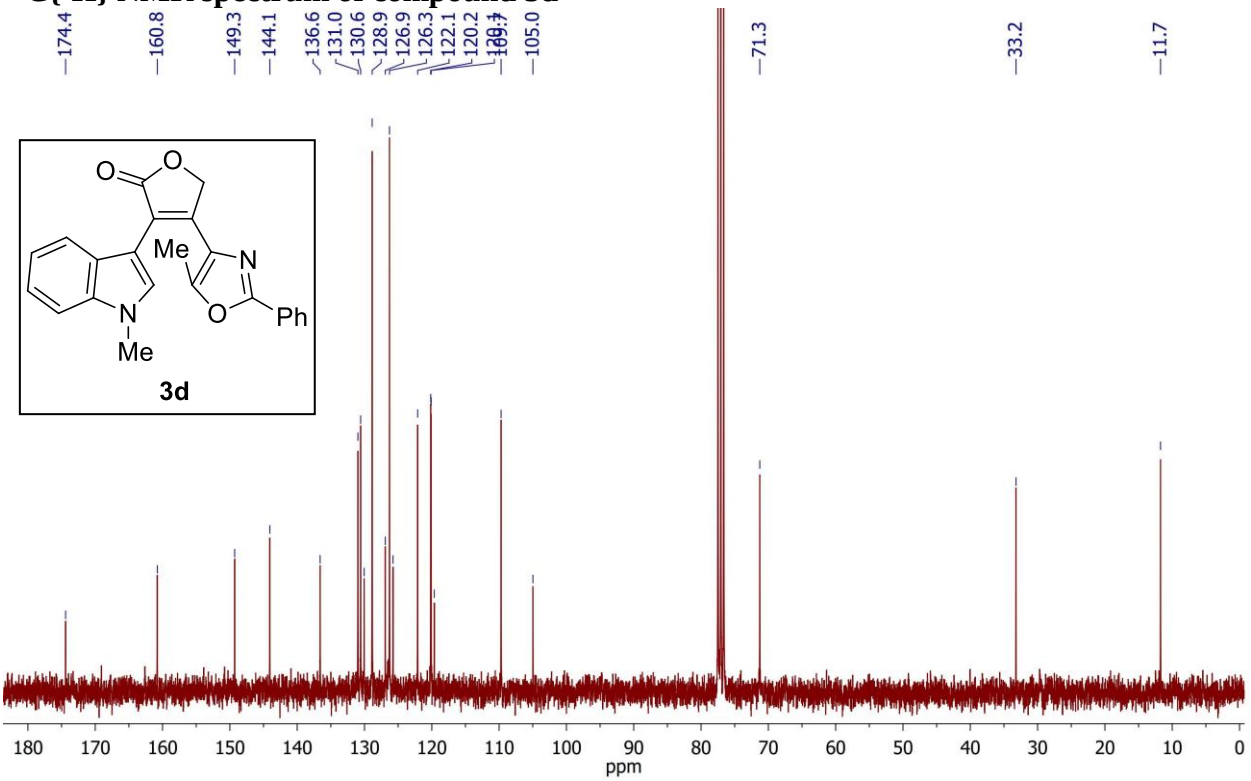


^{1}H NMR spectrum of compound 3d

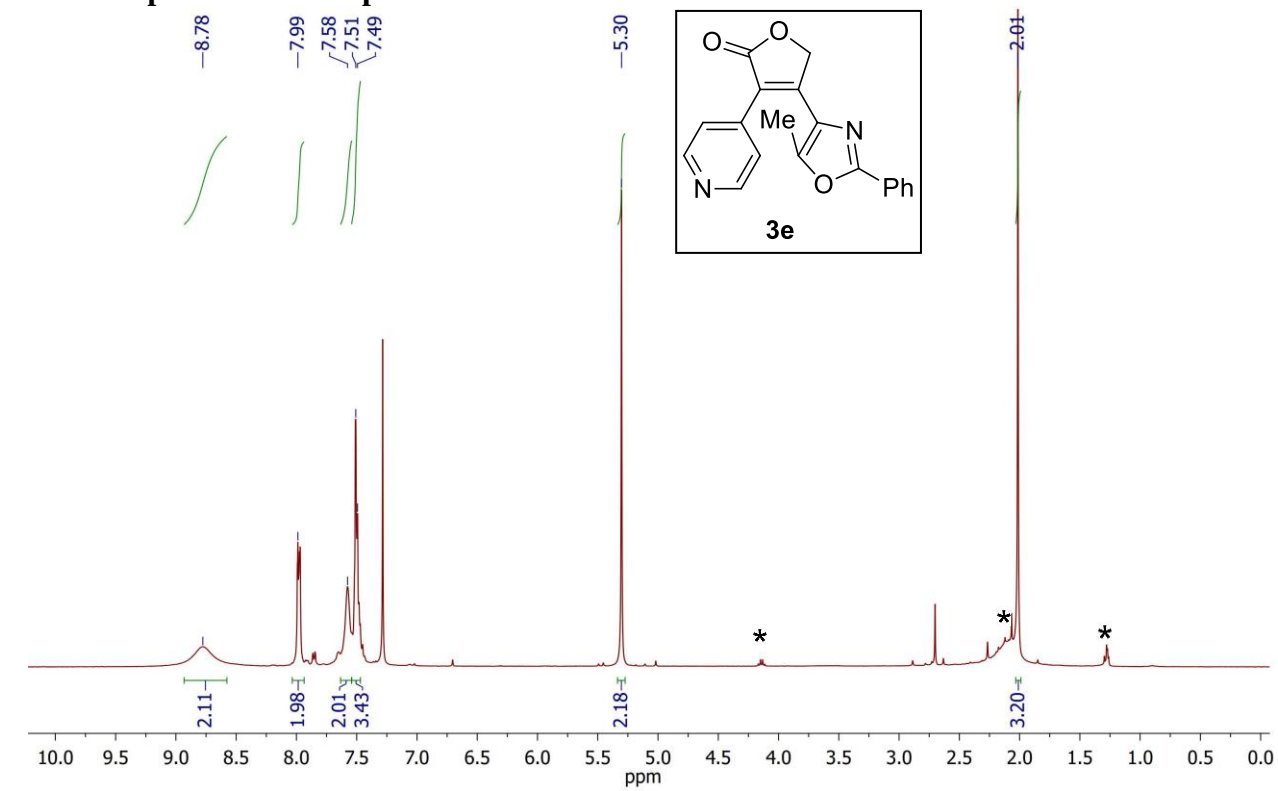


* Grease

^{13}C{^{1}H} NMR spectrum of compound 3d

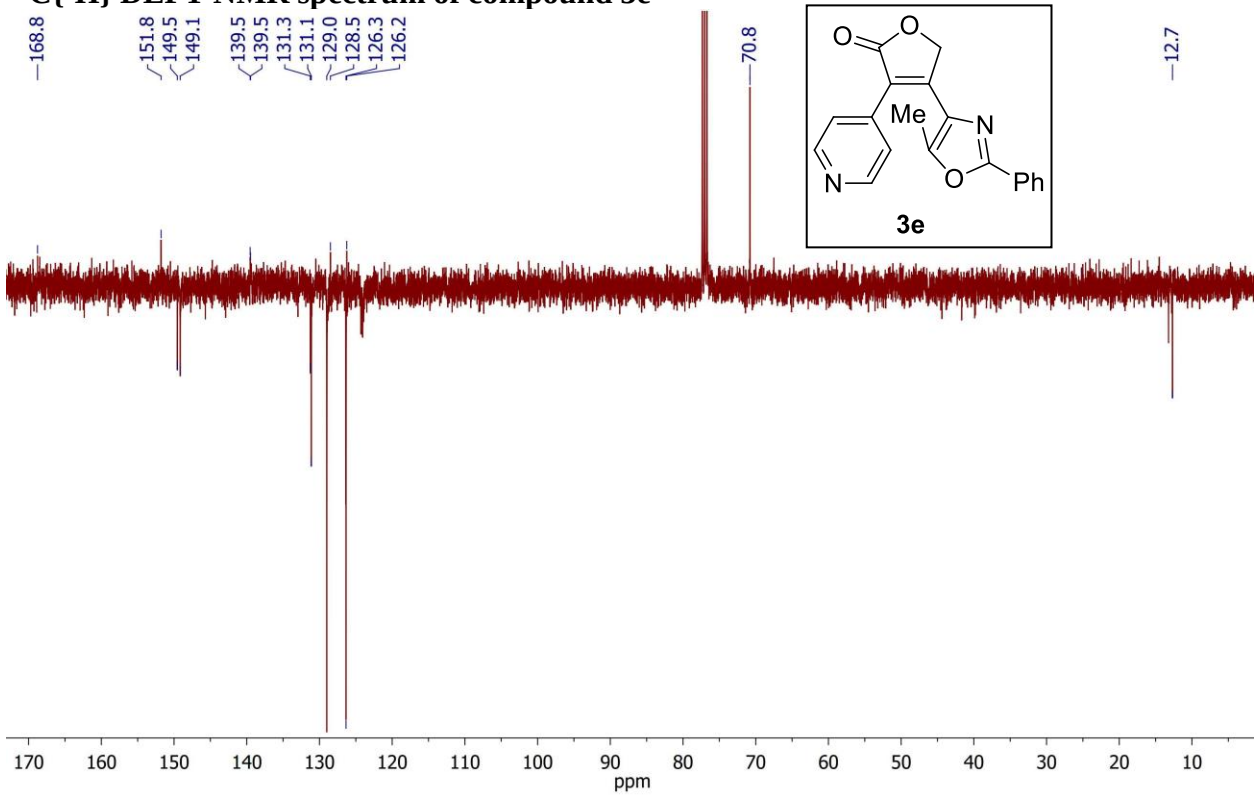


^{1}H NMR spectrum of compound 3e

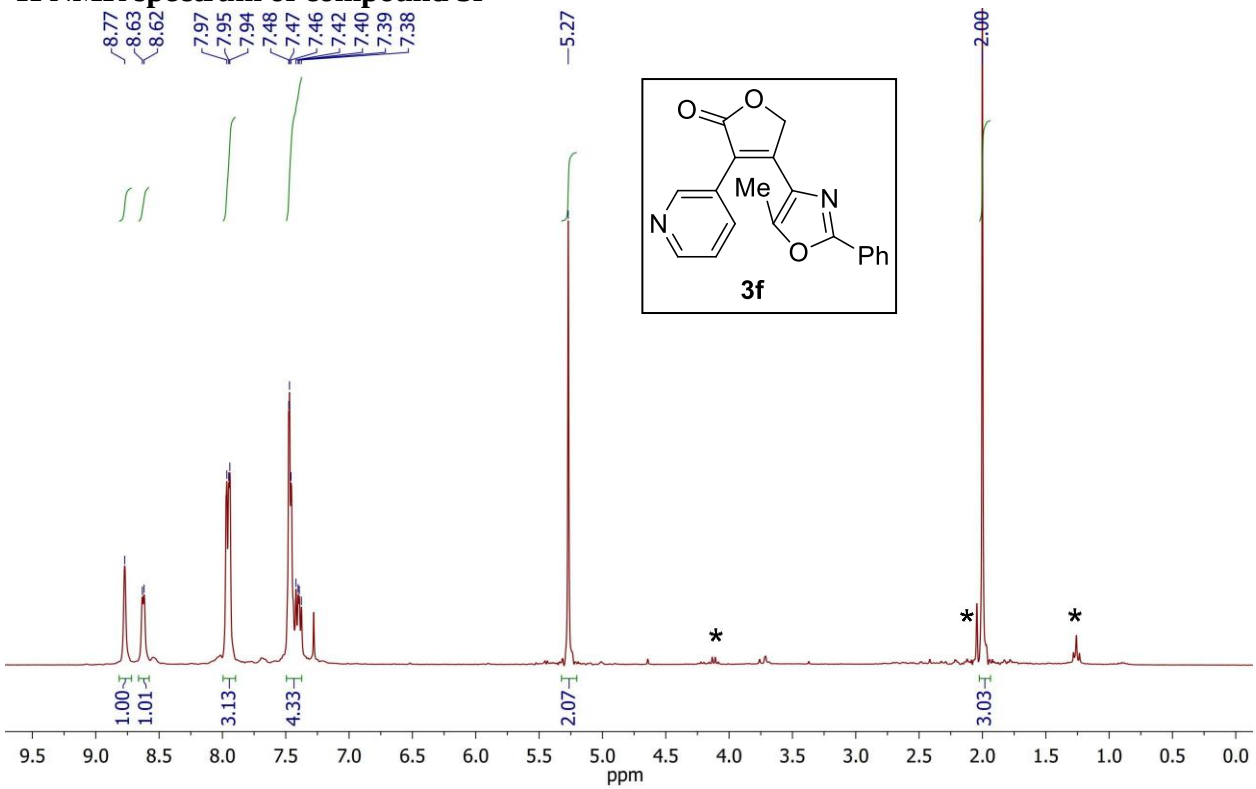


* Ethyl acetate

^{13}C{^{1}H} DEPT NMR spectrum of compound 3e

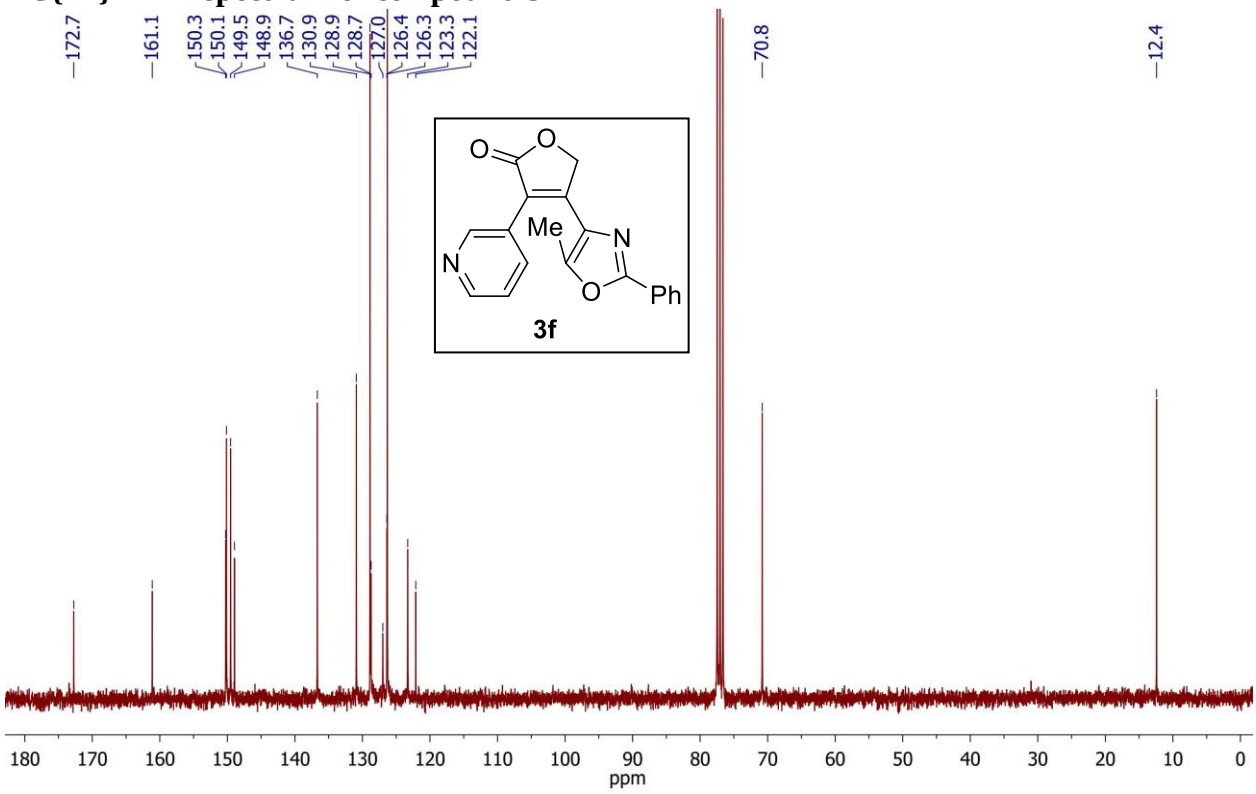


^{1}H NMR spectrum of compound 3f

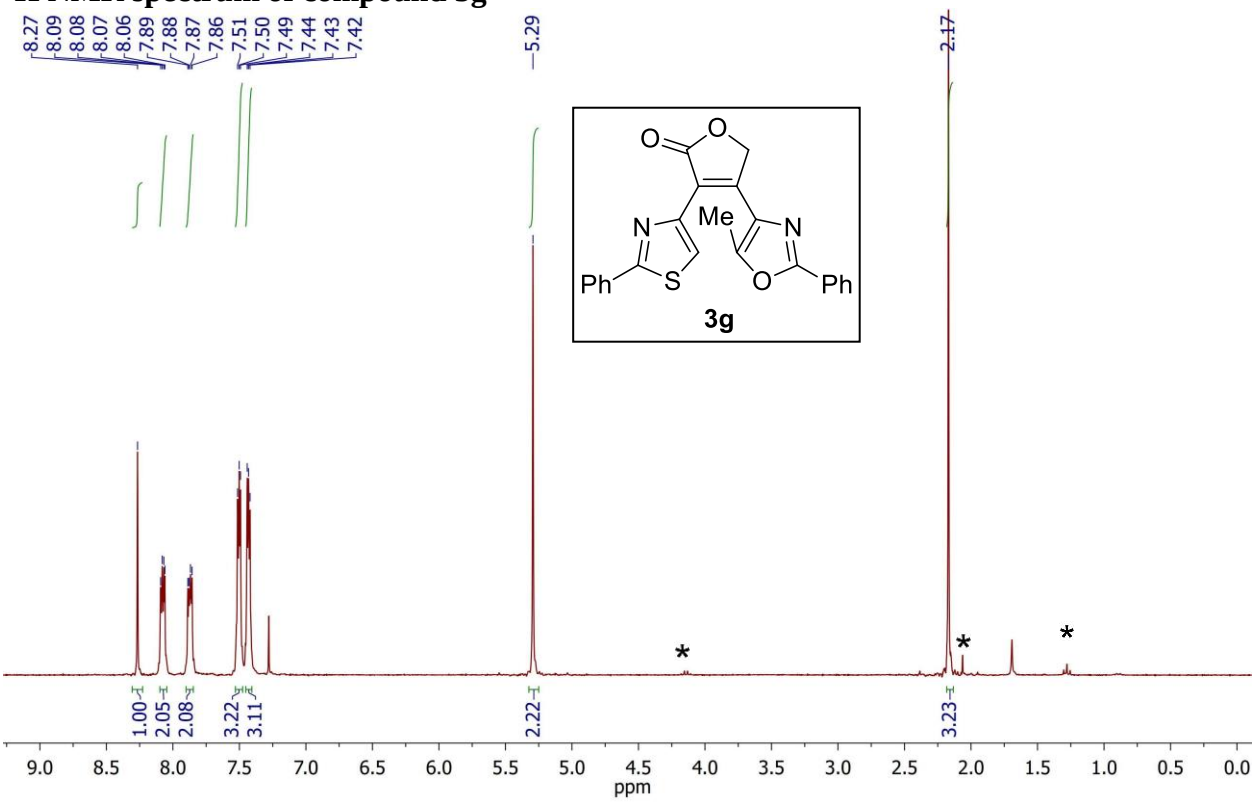


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 3f

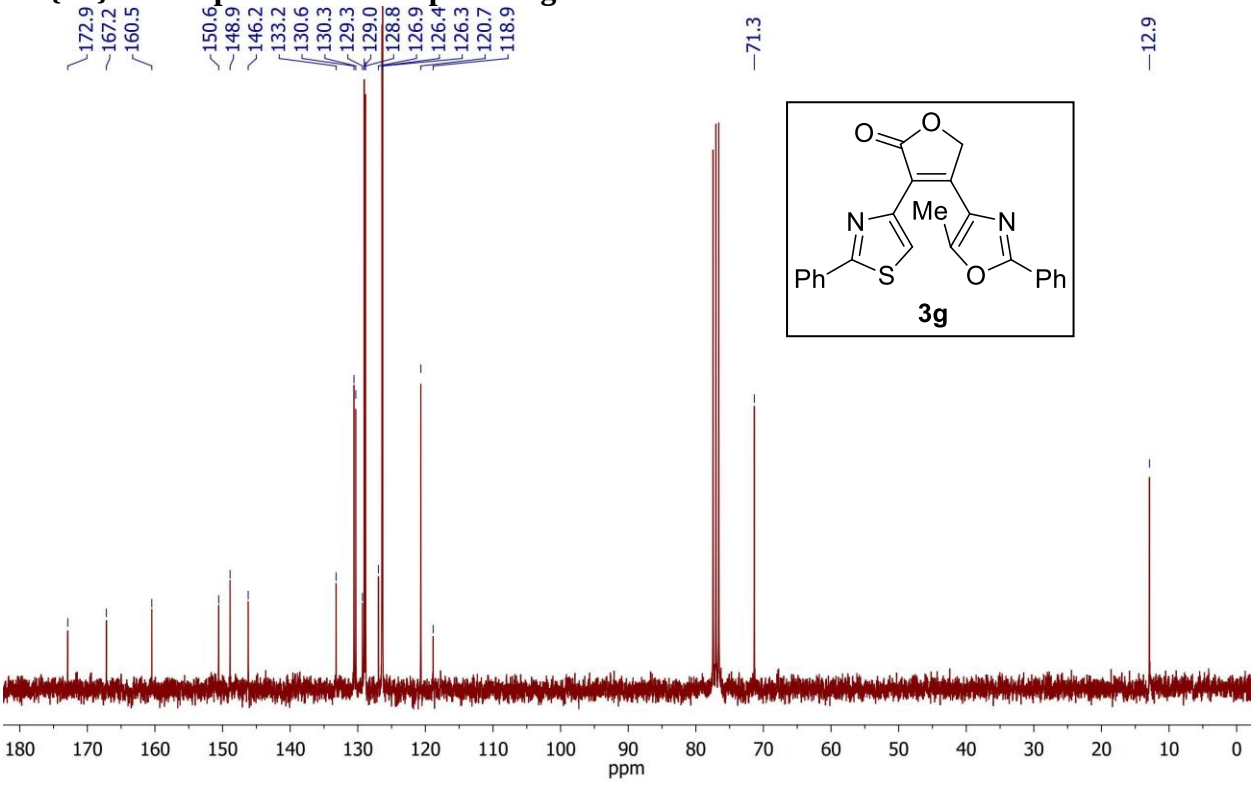


^{1}H NMR spectrum of compound 3g

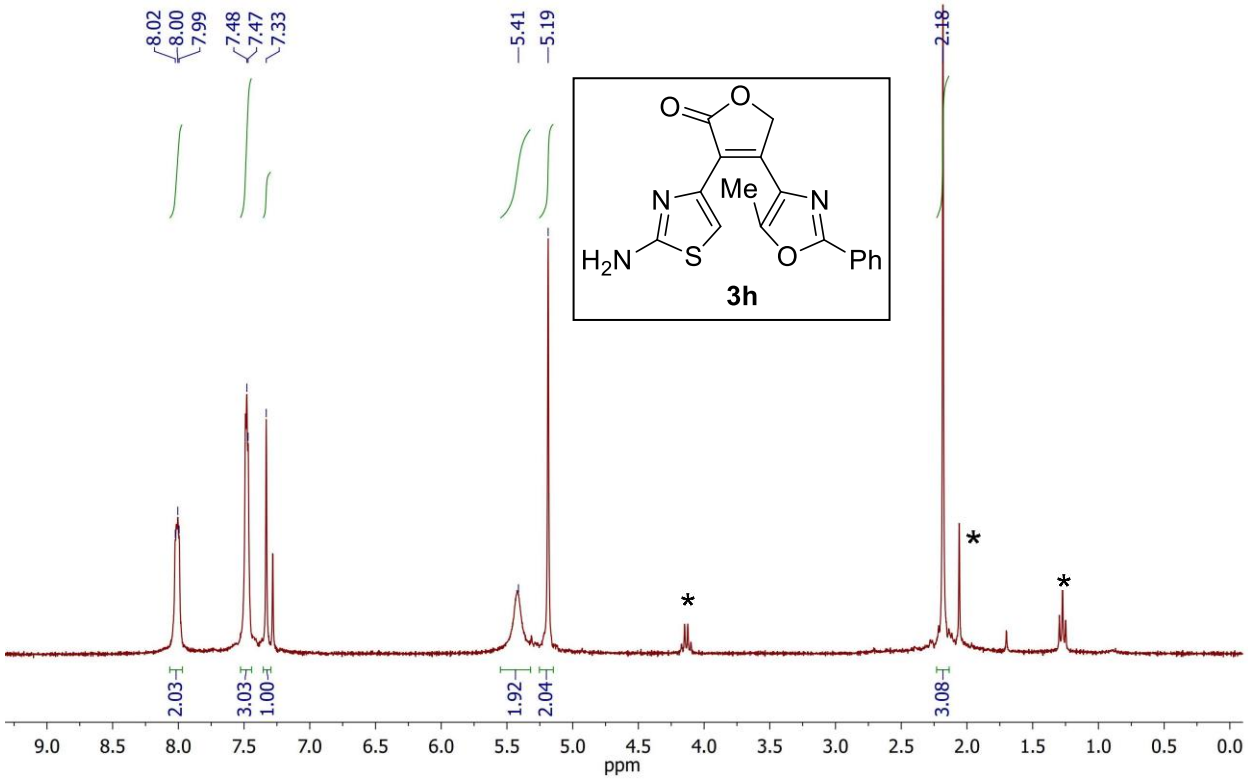


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 3g

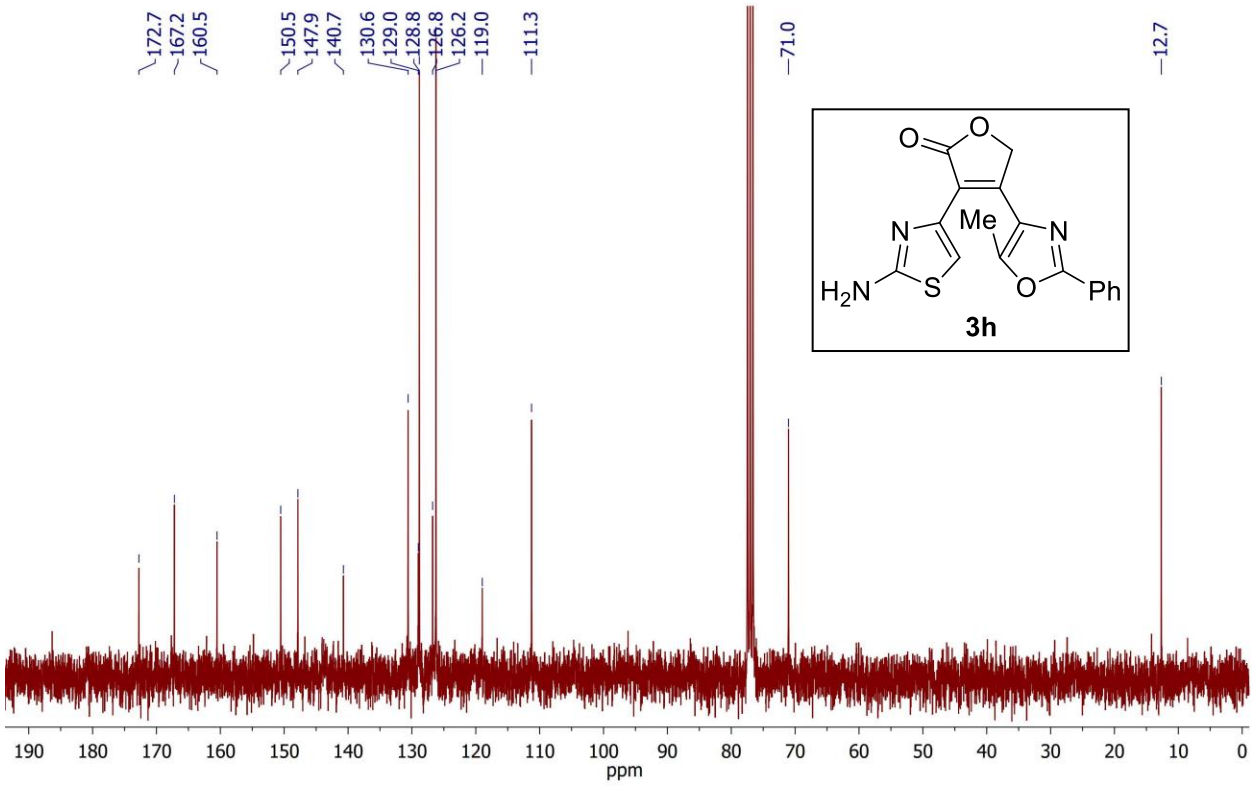


^{1}H NMR spectrum of compound 3h

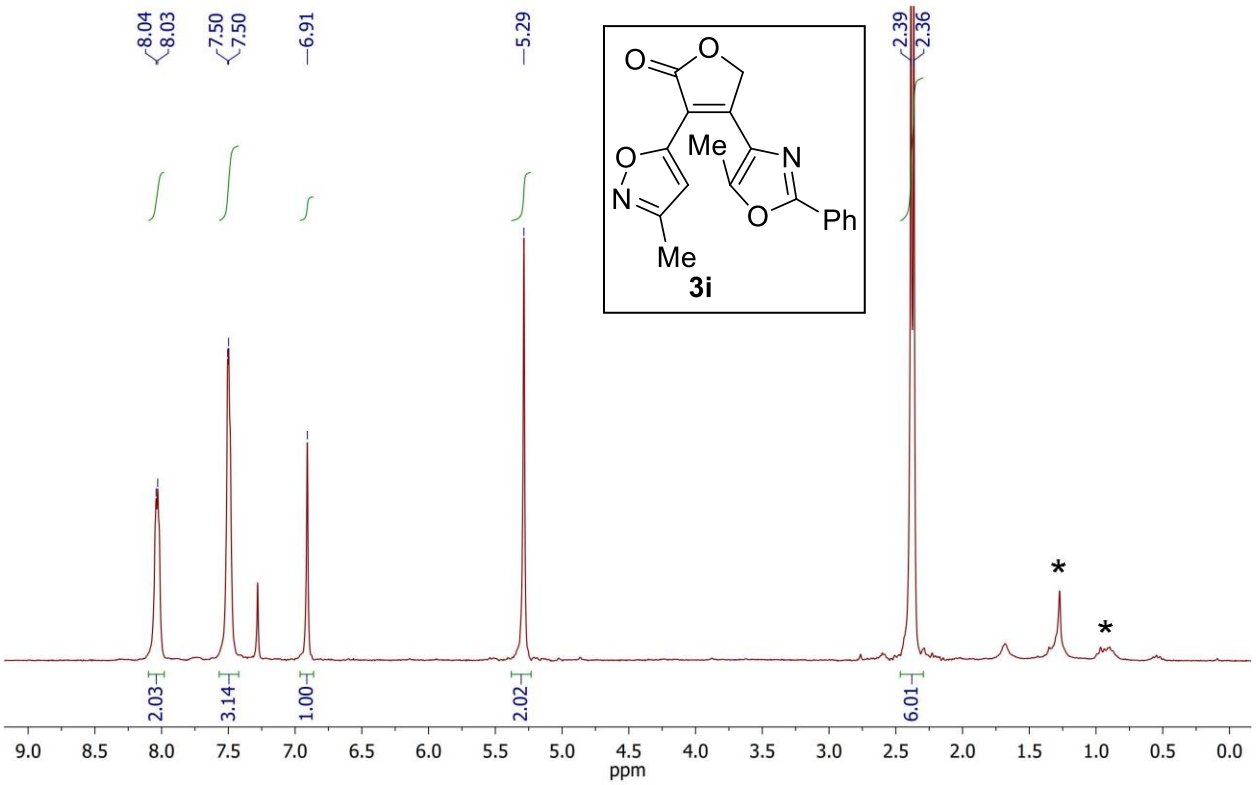


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 3h

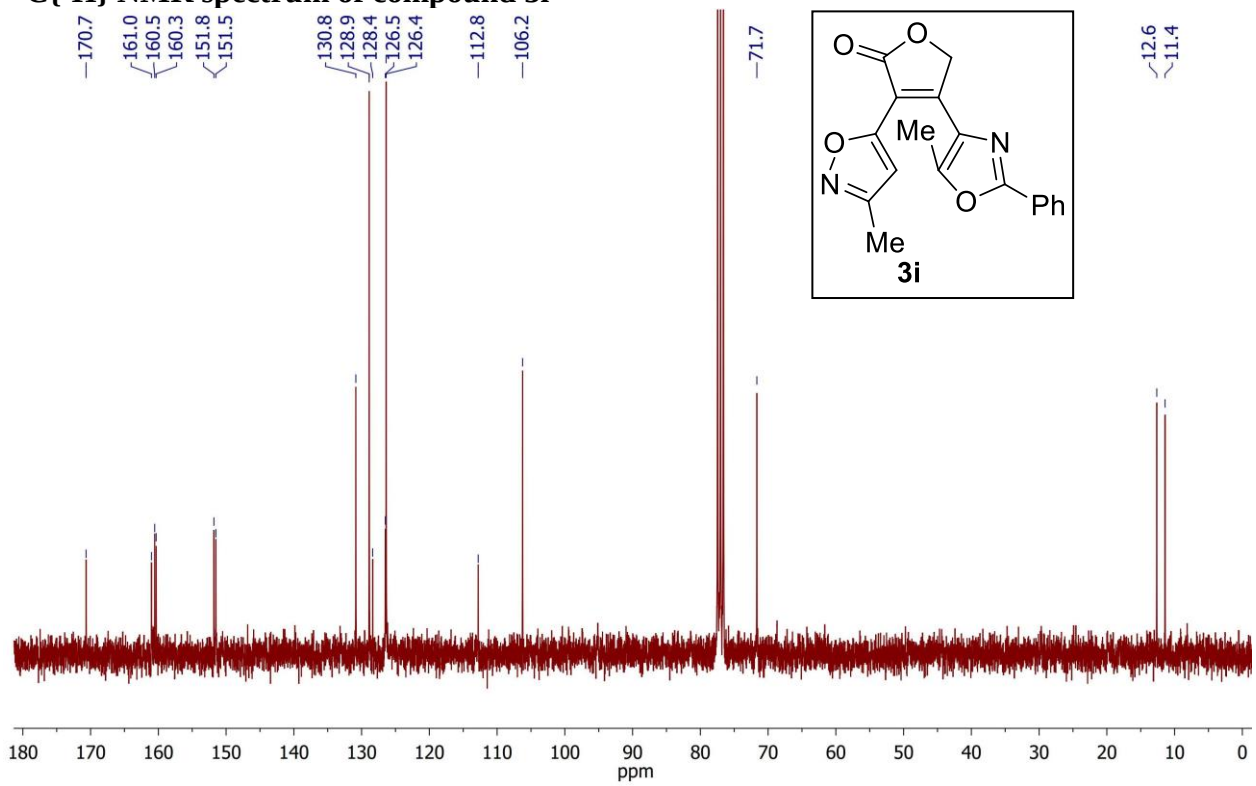


^{1}H NMR spectrum of compound 3i

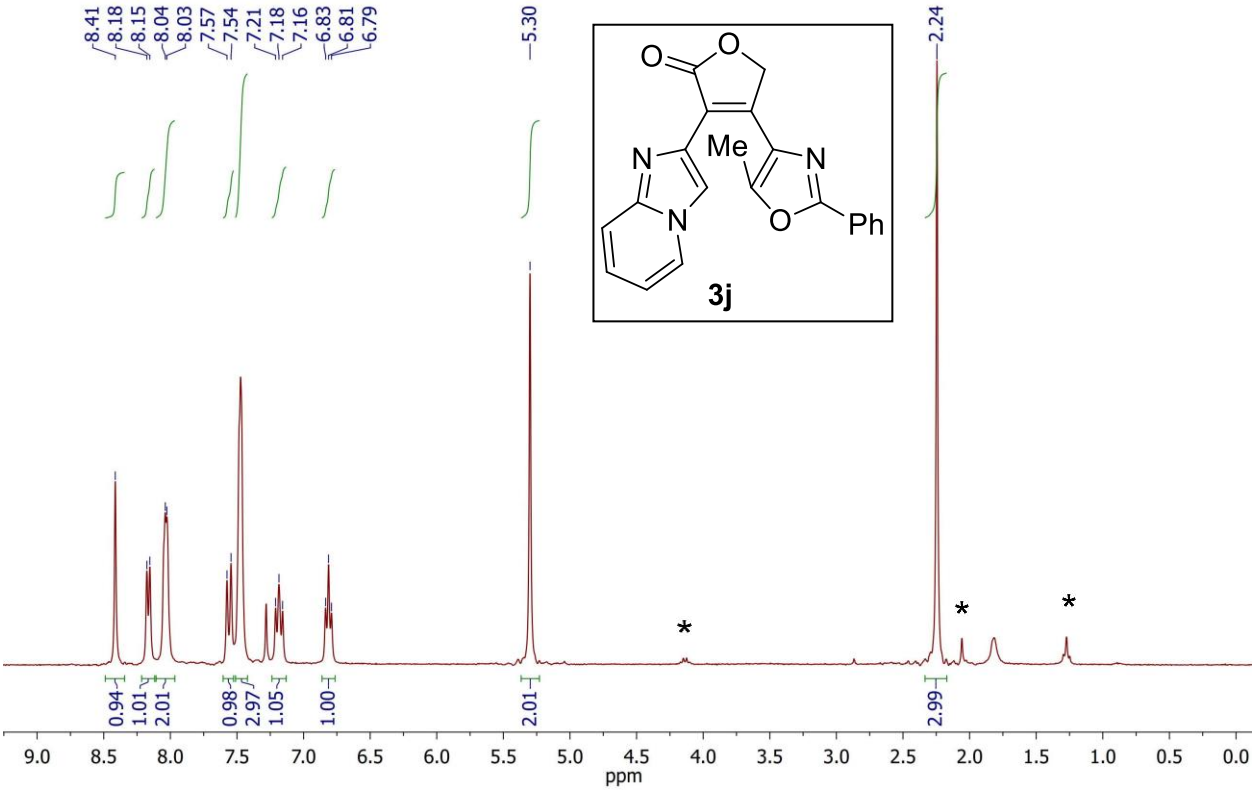


* Grease

^{13}C{^{1}H} NMR spectrum of compound 3i

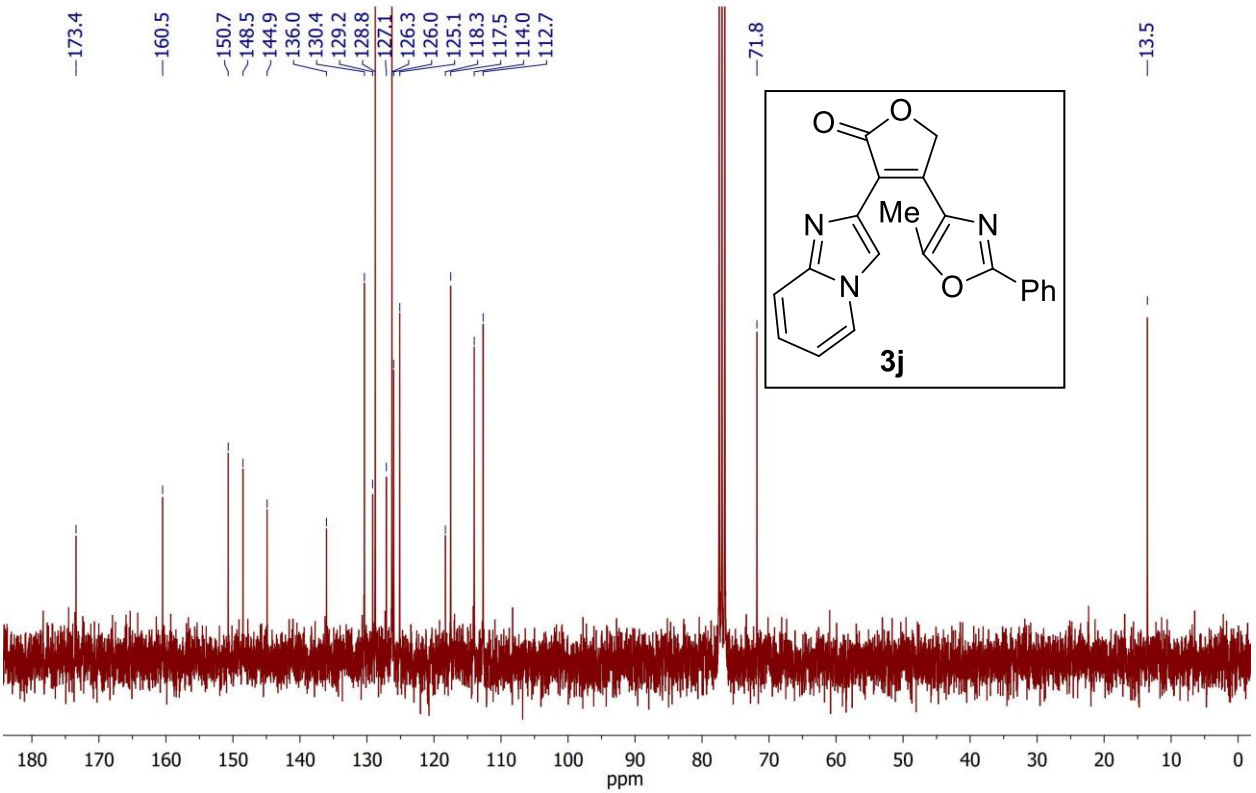


^{1}H NMR spectrum of compound 3j

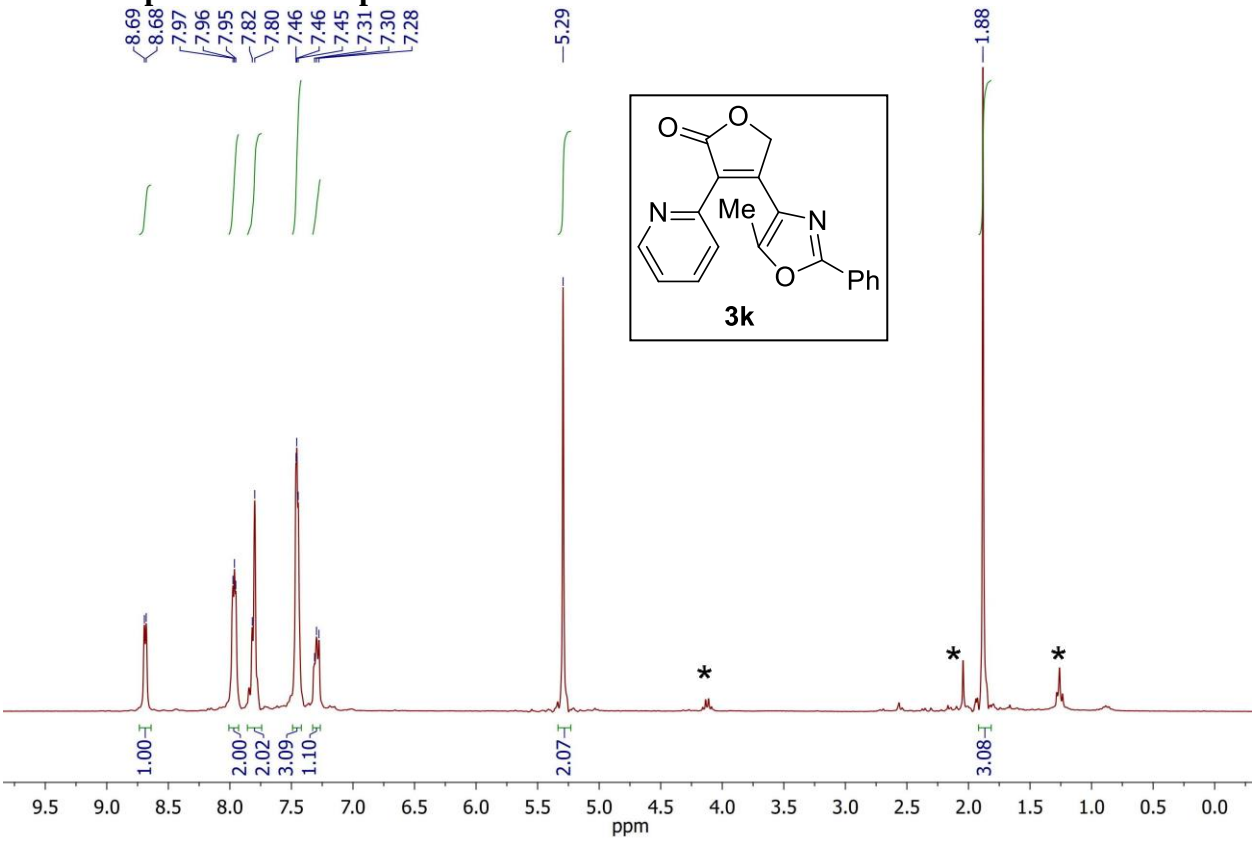


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 3j

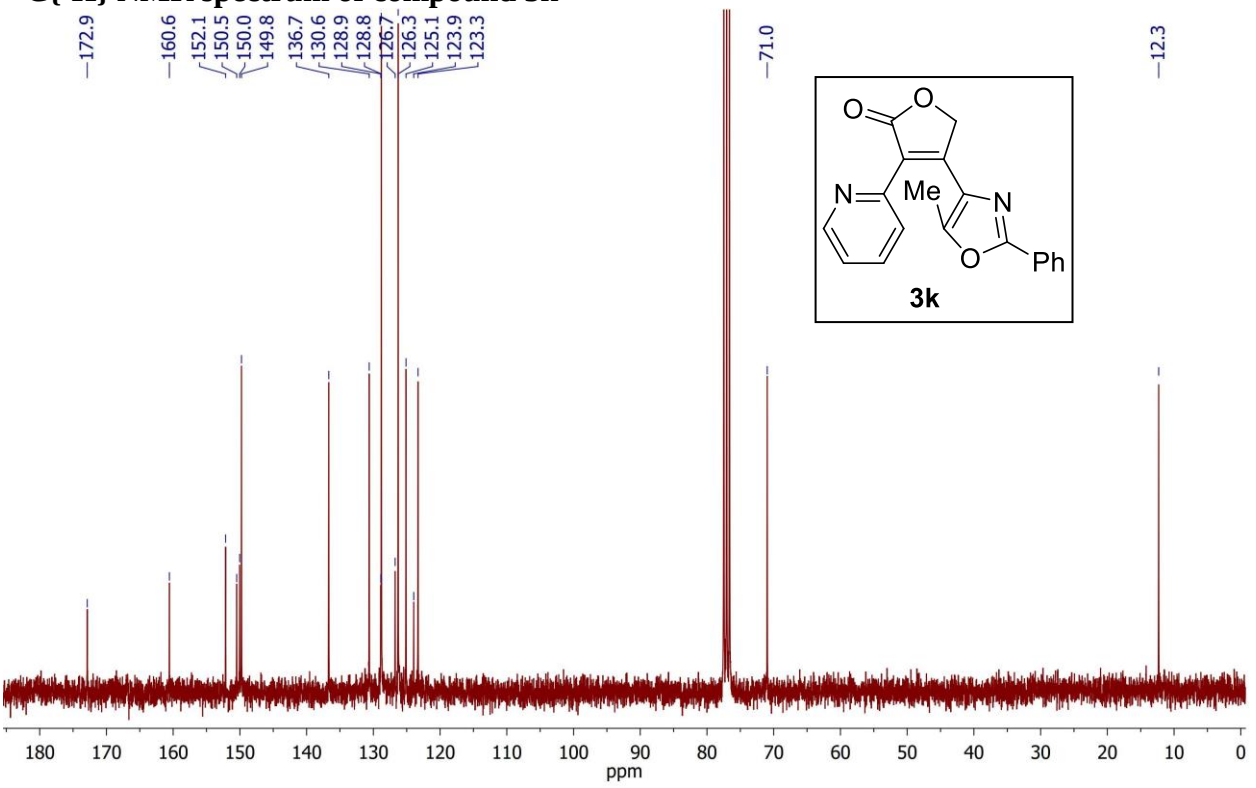


^{1}H NMR spectrum of compound 3k

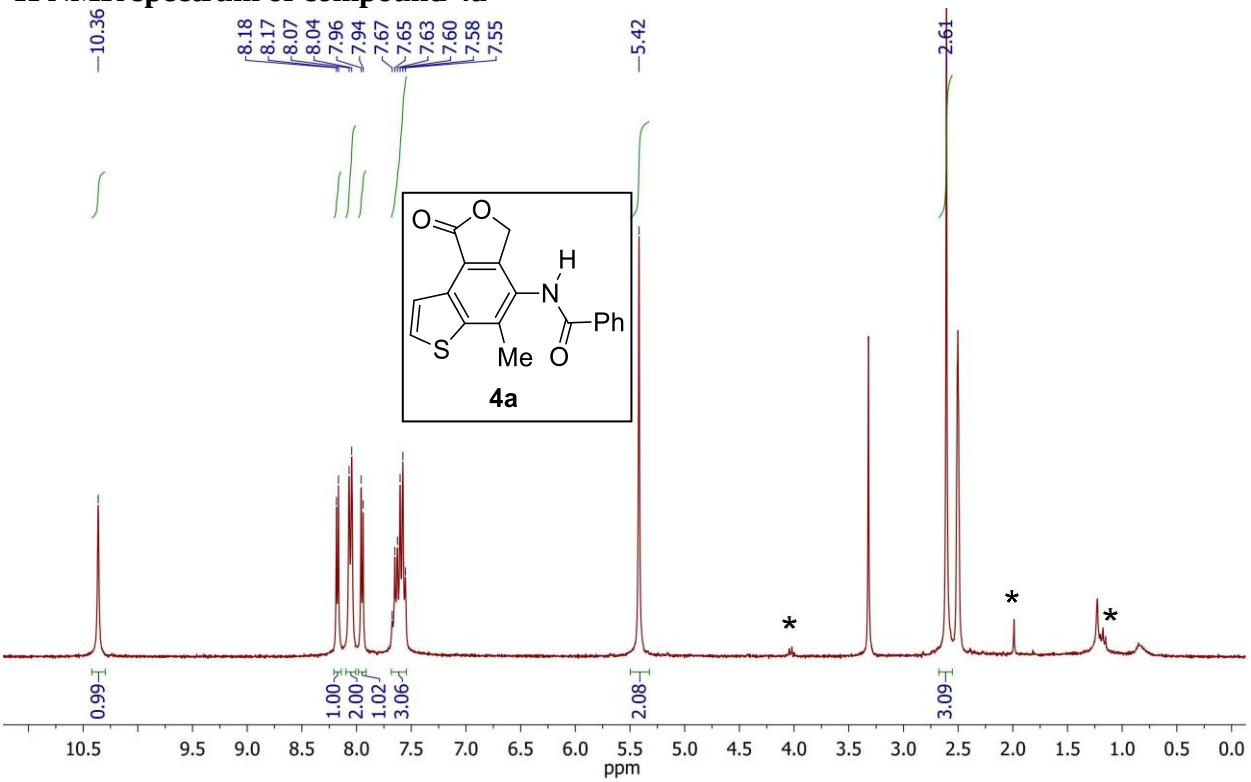


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 3k

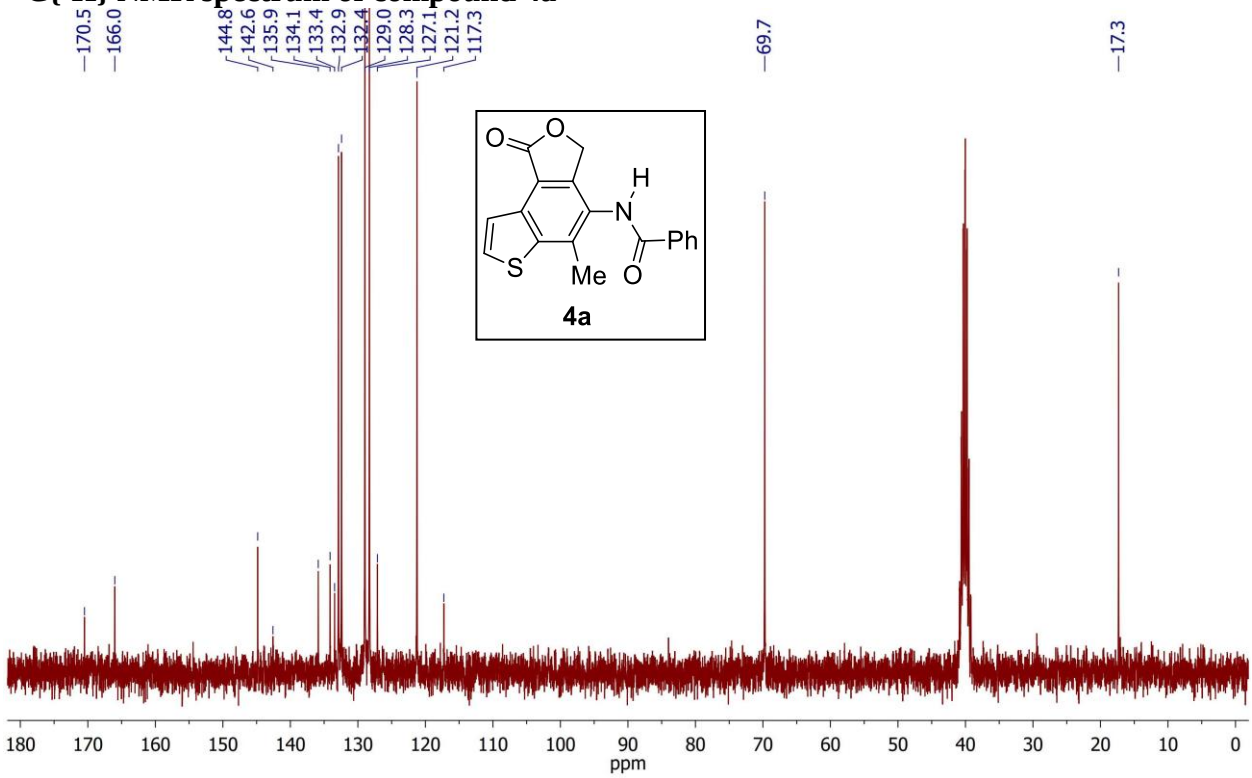


^{1}H NMR spectrum of compound 4a

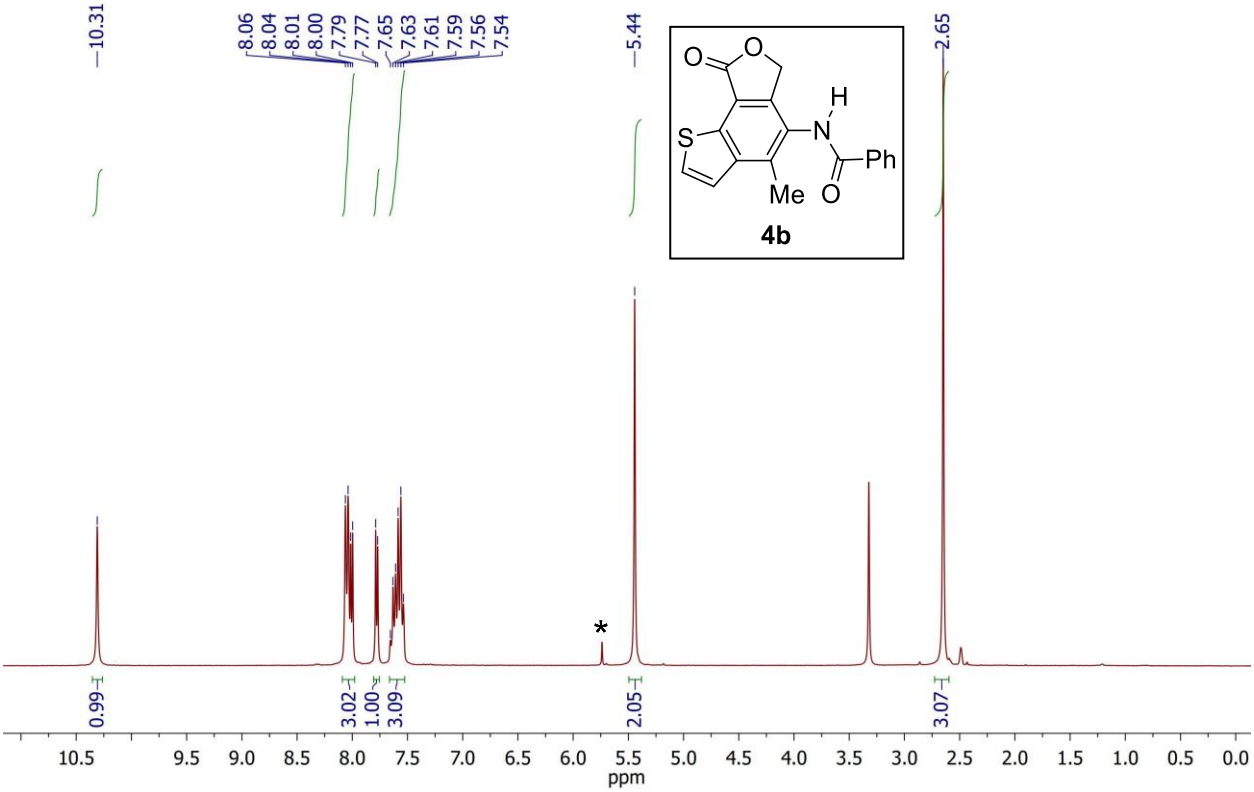


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 4a

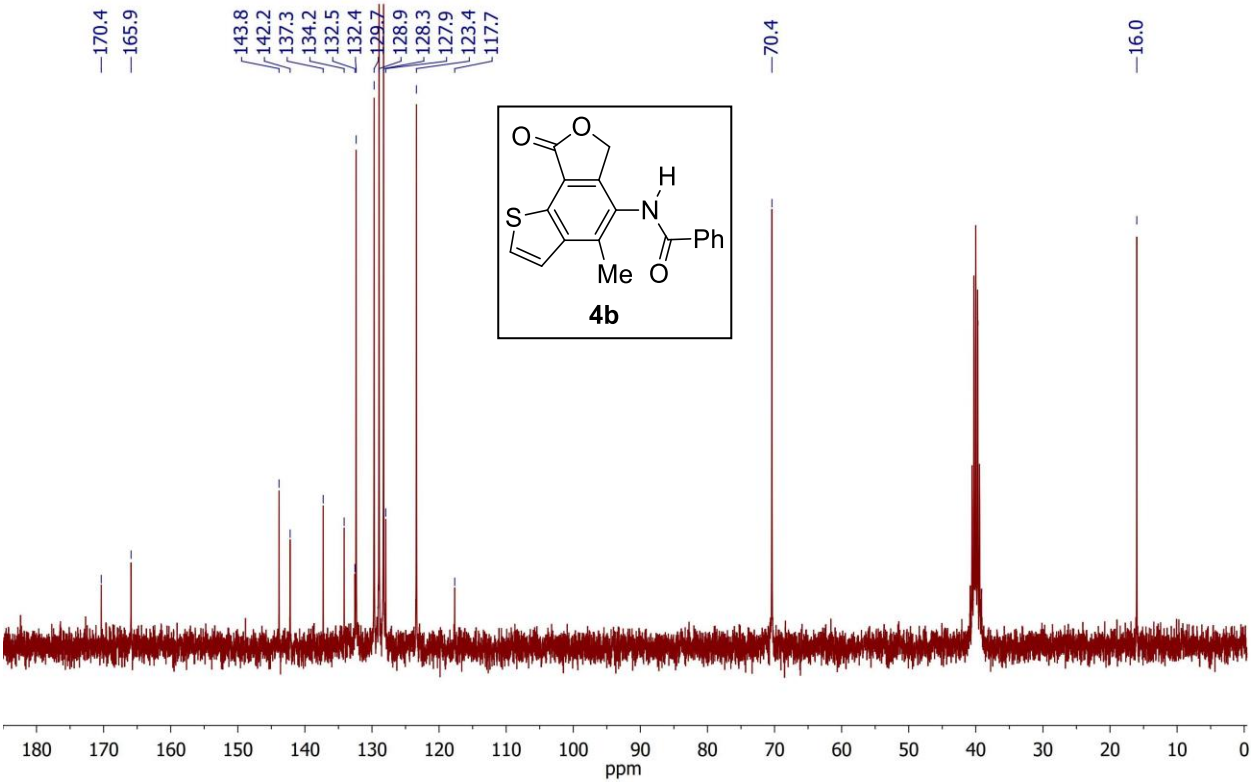


^{1}H NMR spectrum of compound 4b

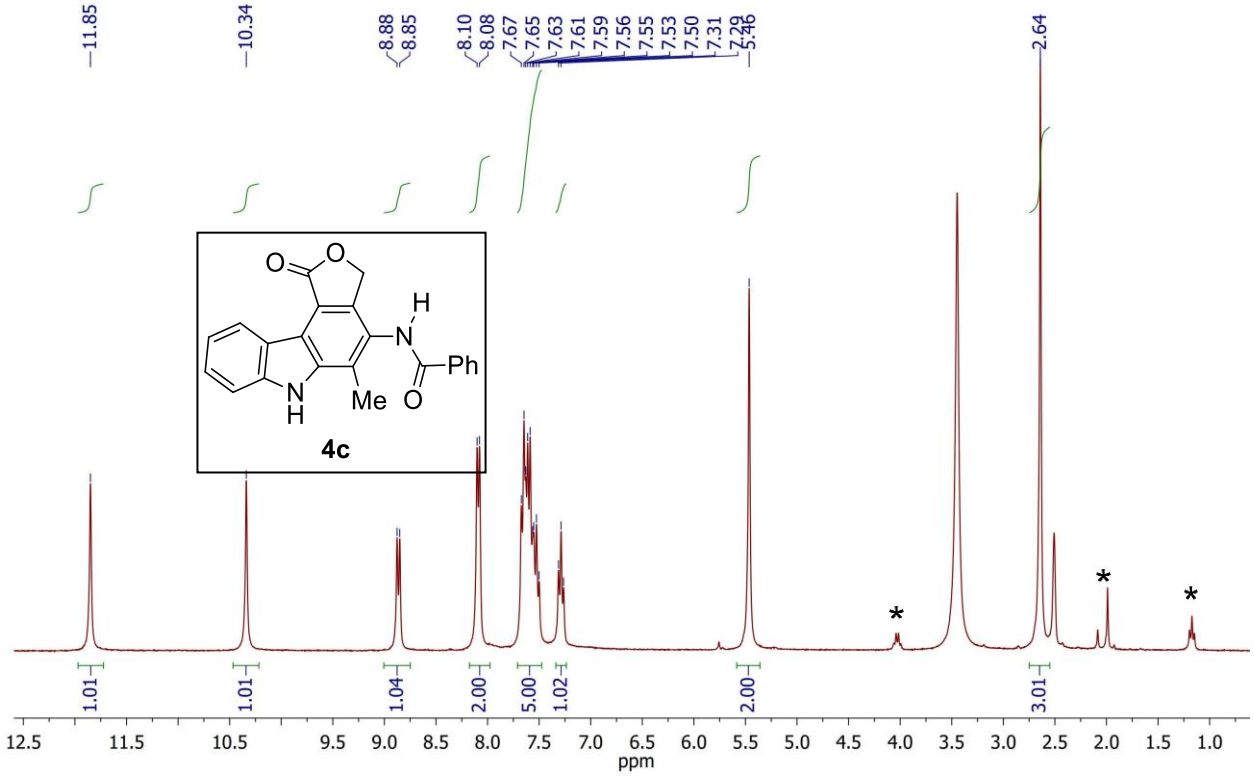


* Dichloromethane

^{13}C{^{1}H} NMR spectrum of compound 4b

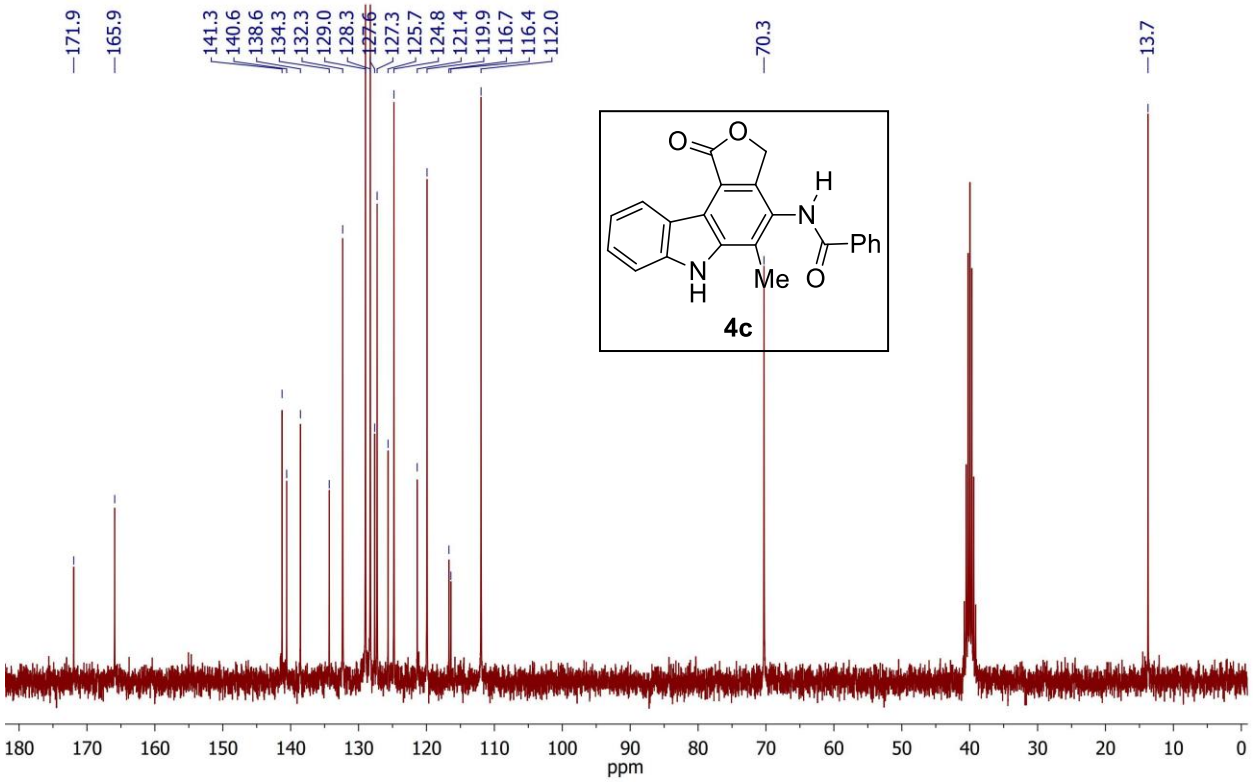


^{1}H NMR spectrum of compound 4c

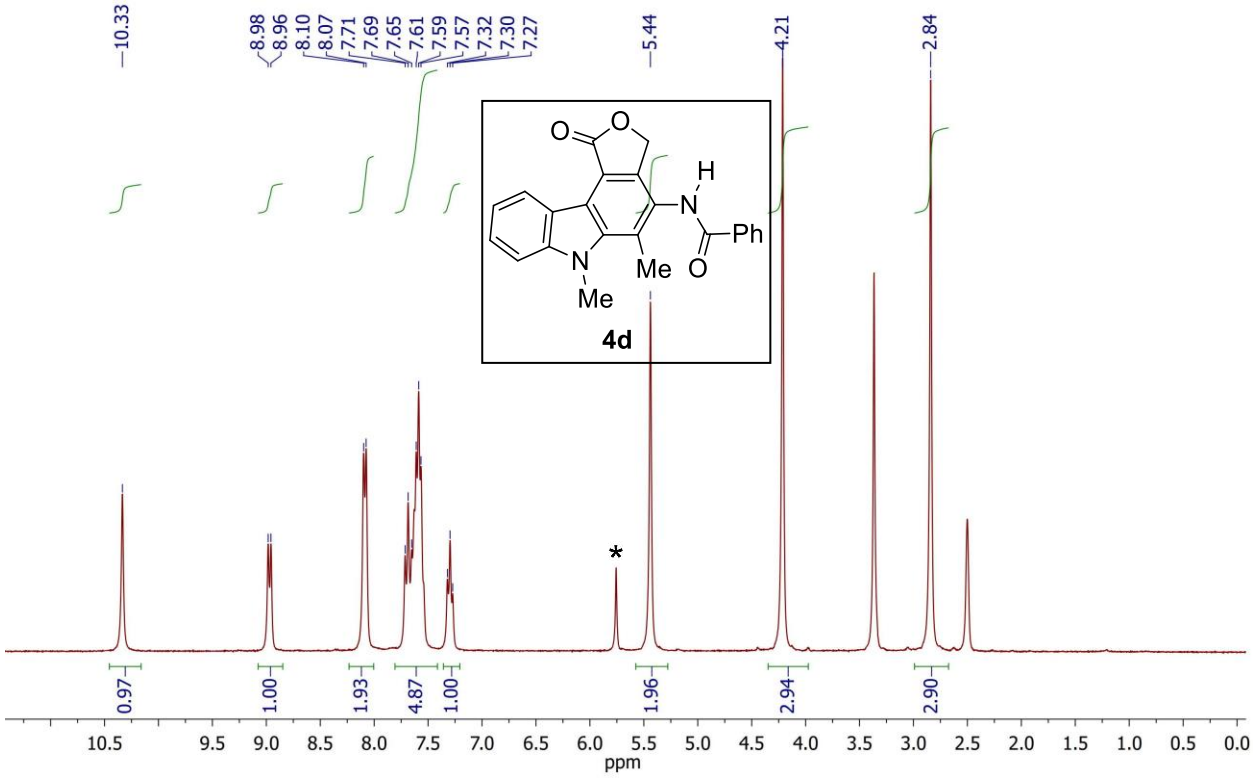


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 4c

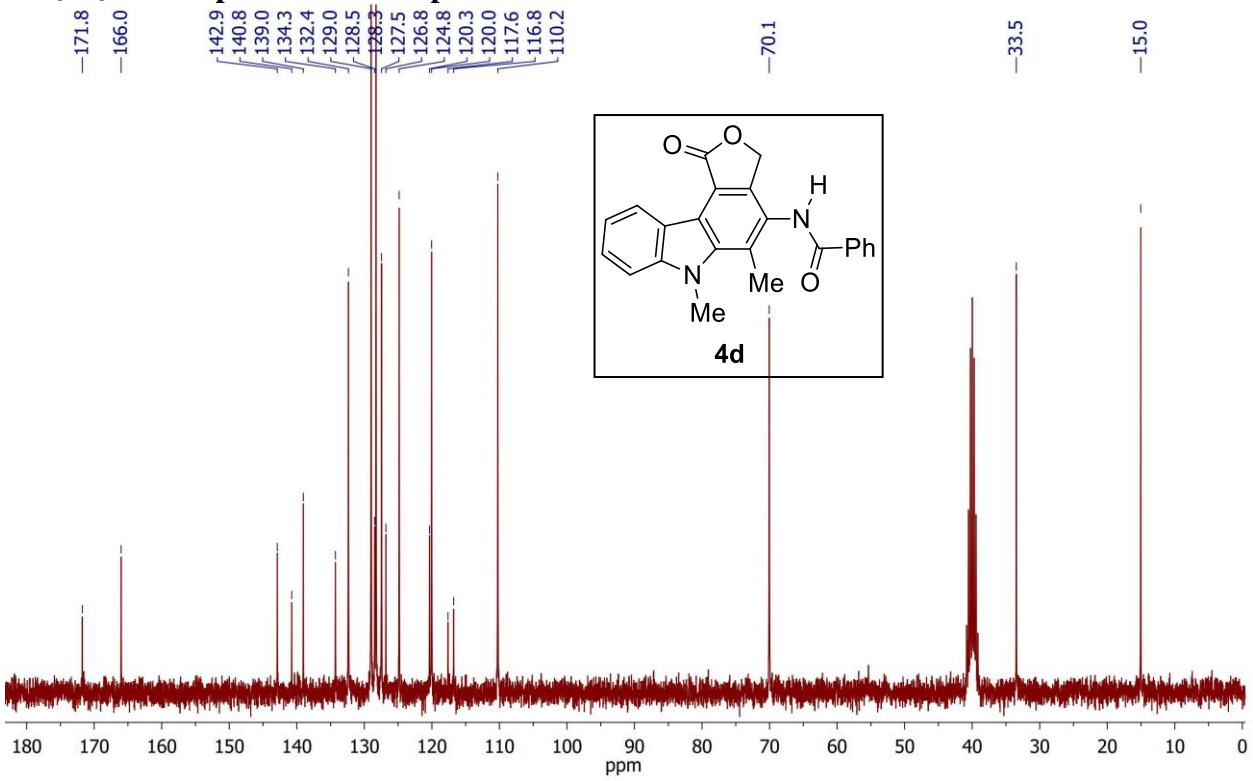


^{1}H NMR spectrum of compound 4d

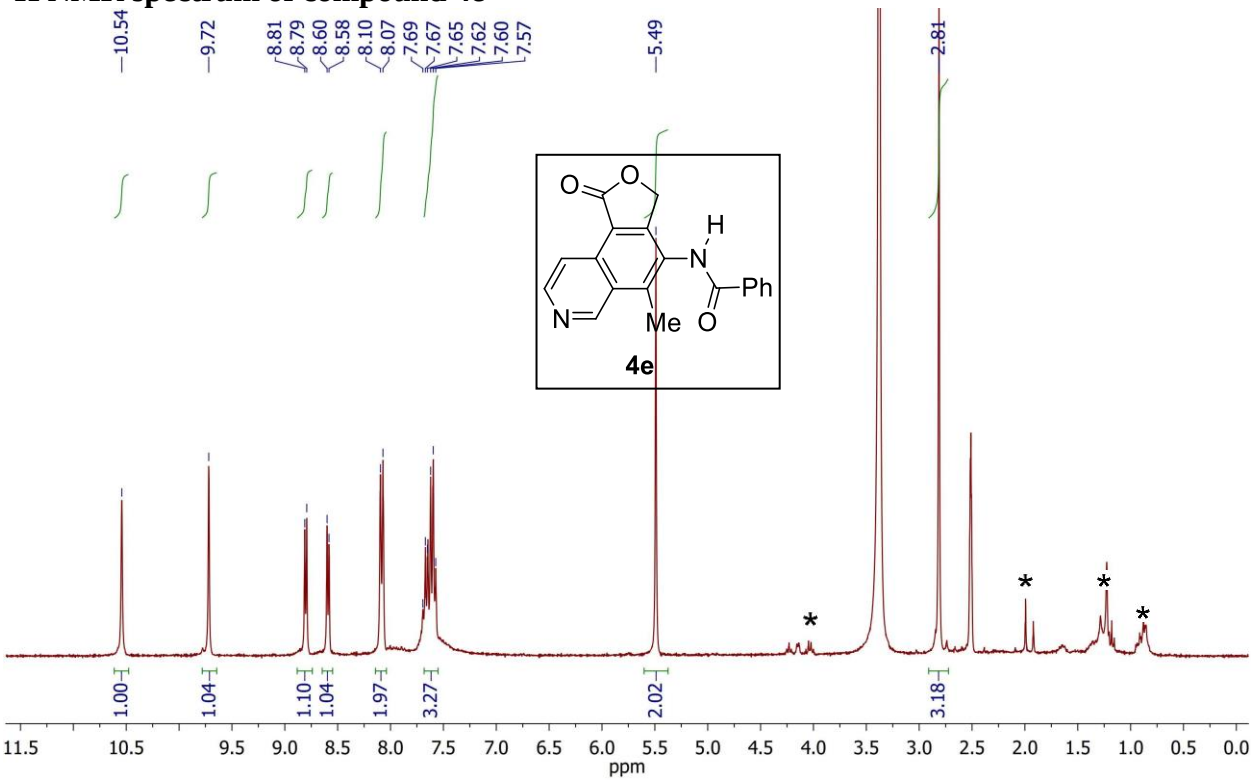


* Dichloromethane

^{13}C{^{1}H} NMR spectrum of compound 4d

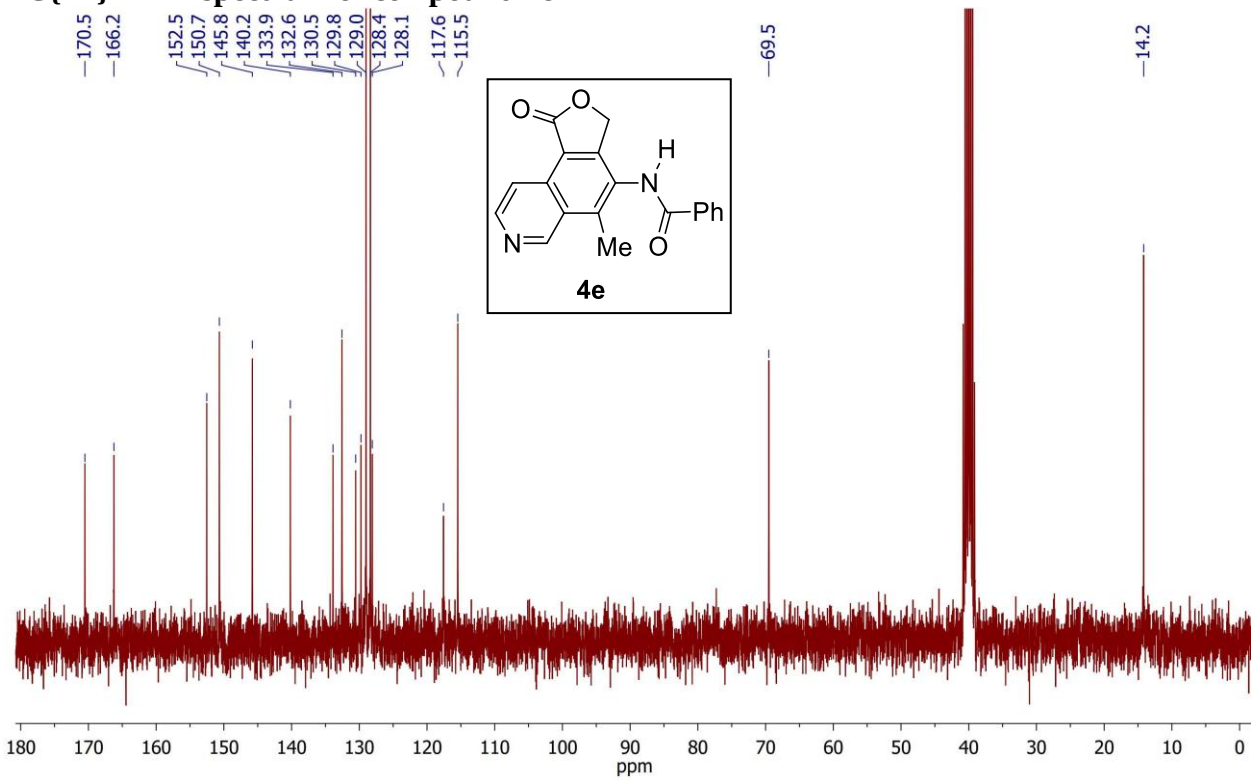


^{1}H NMR spectrum of compound 4e

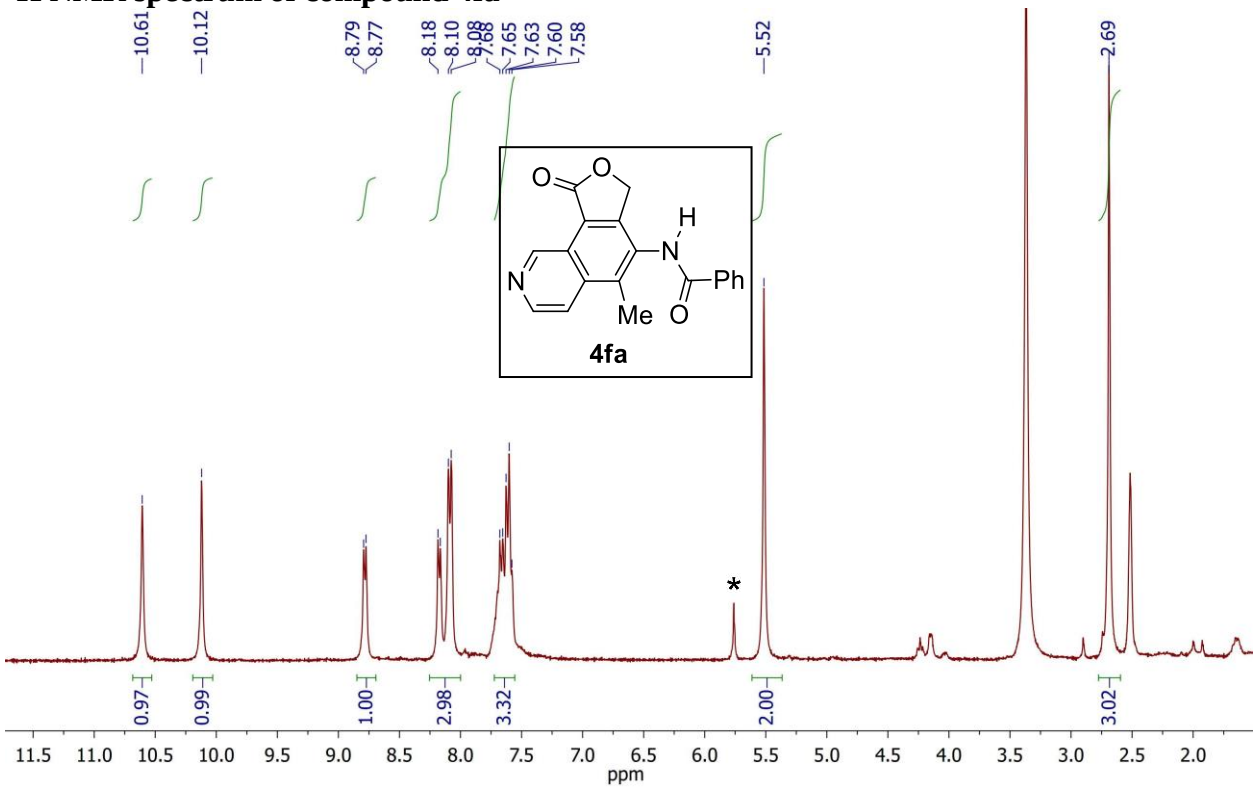


* Ethyl acetate and hexane

^{13}C{^{1}H} NMR spectrum of compound 4e

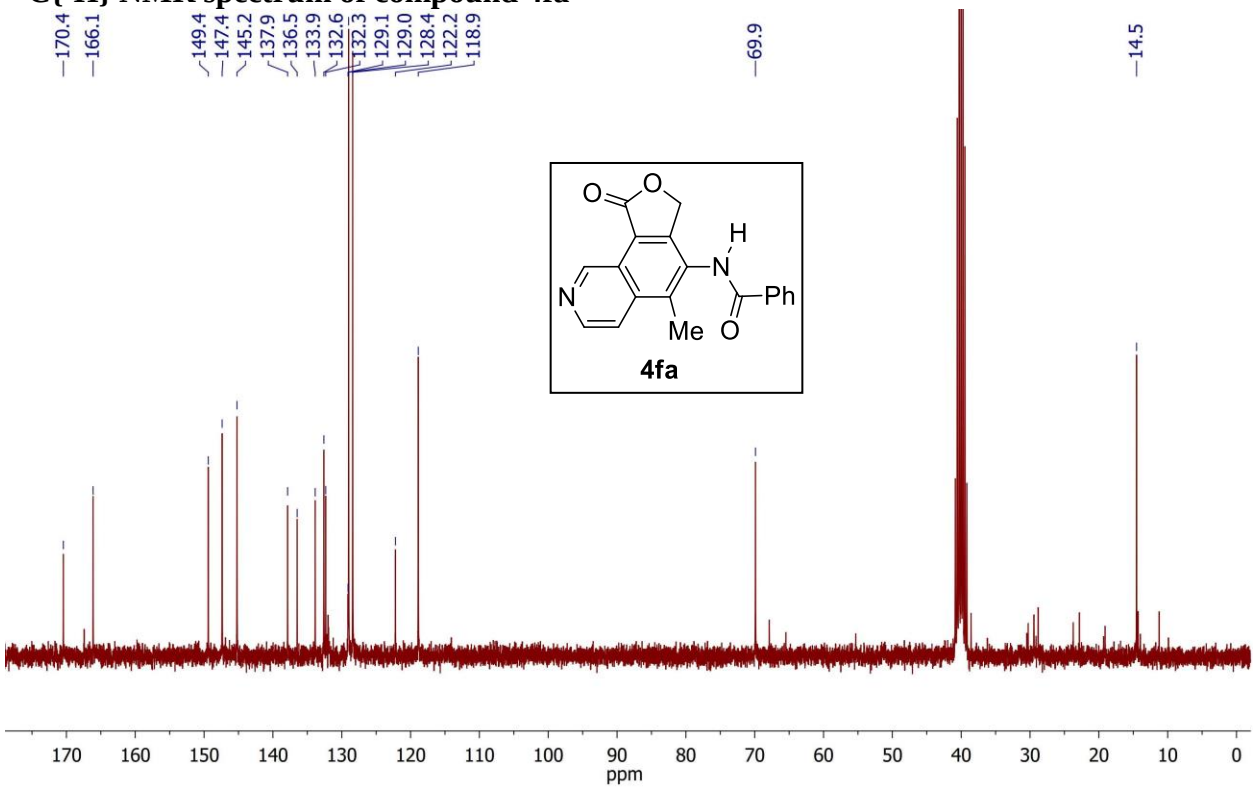


^{1}H NMR spectrum of compound 4fa

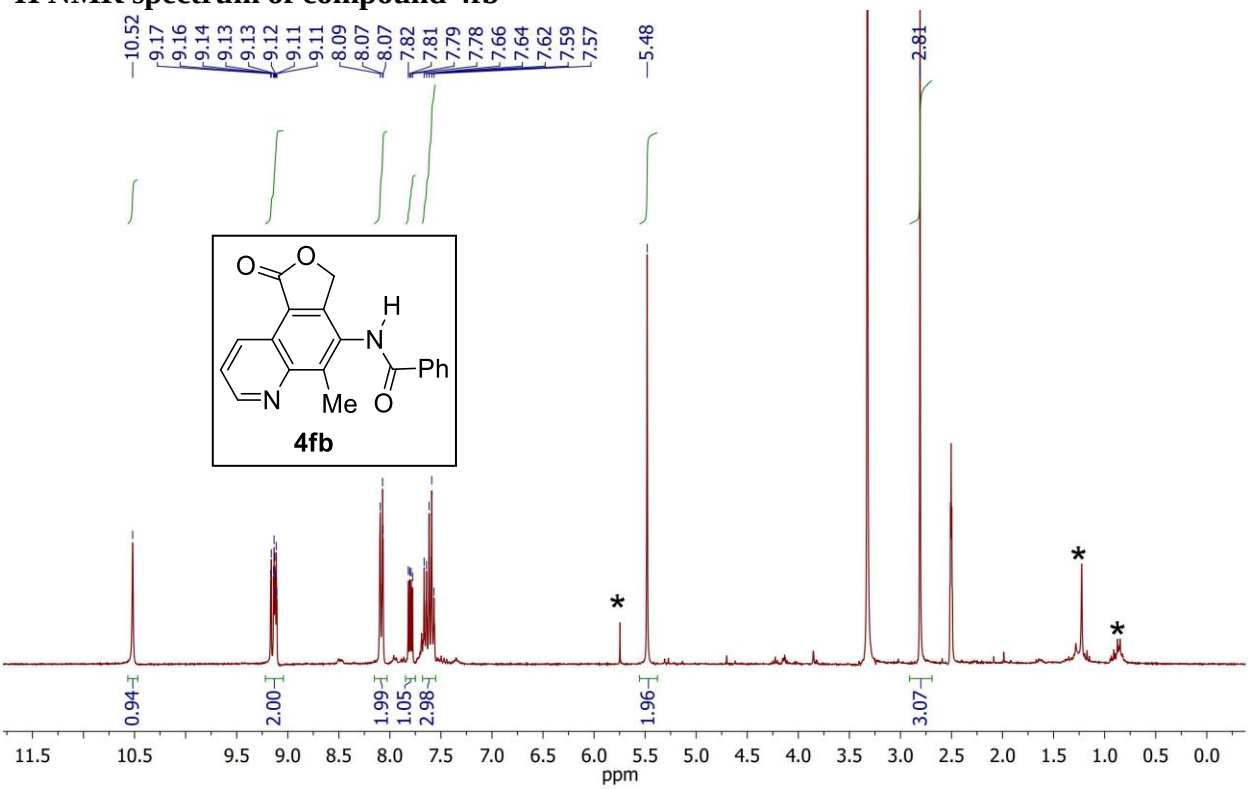


* Dichloromethane

^{13}C{^{1}H} NMR spectrum of compound 4fa

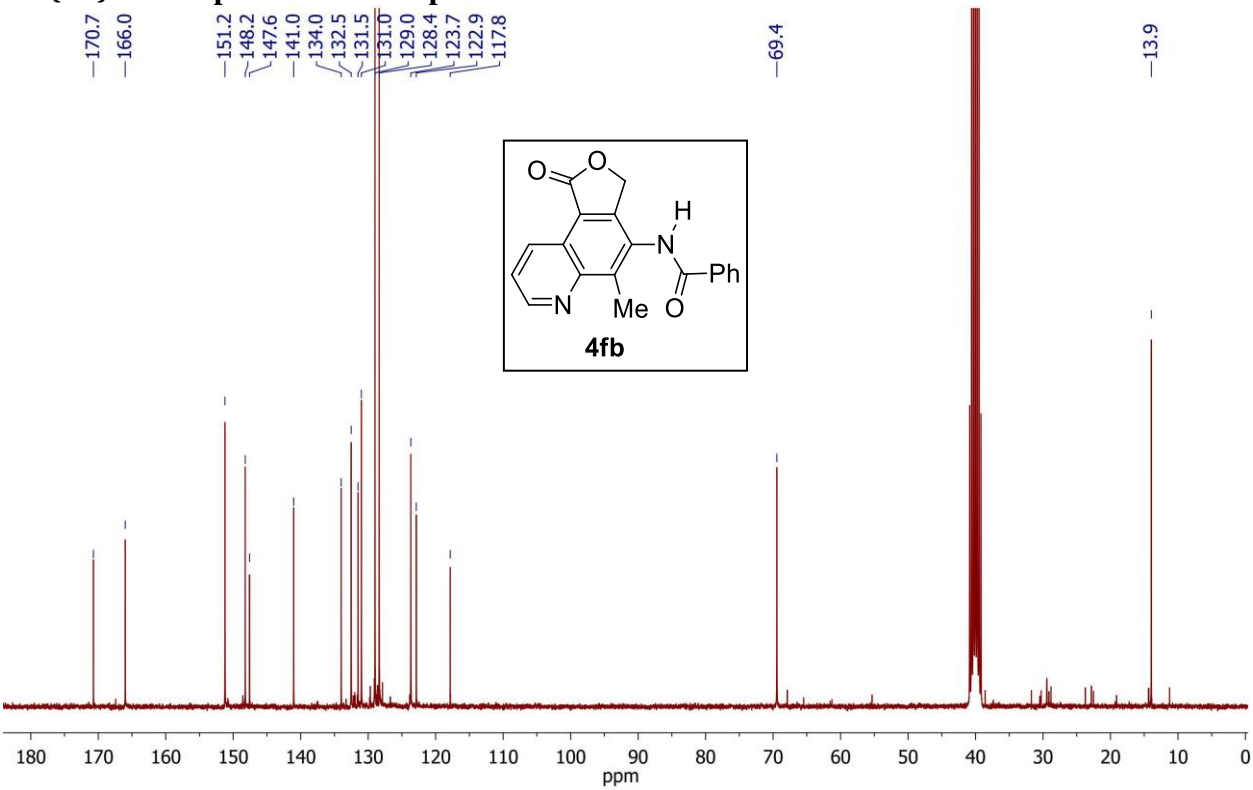


^{1}H NMR spectrum of compound 4fb

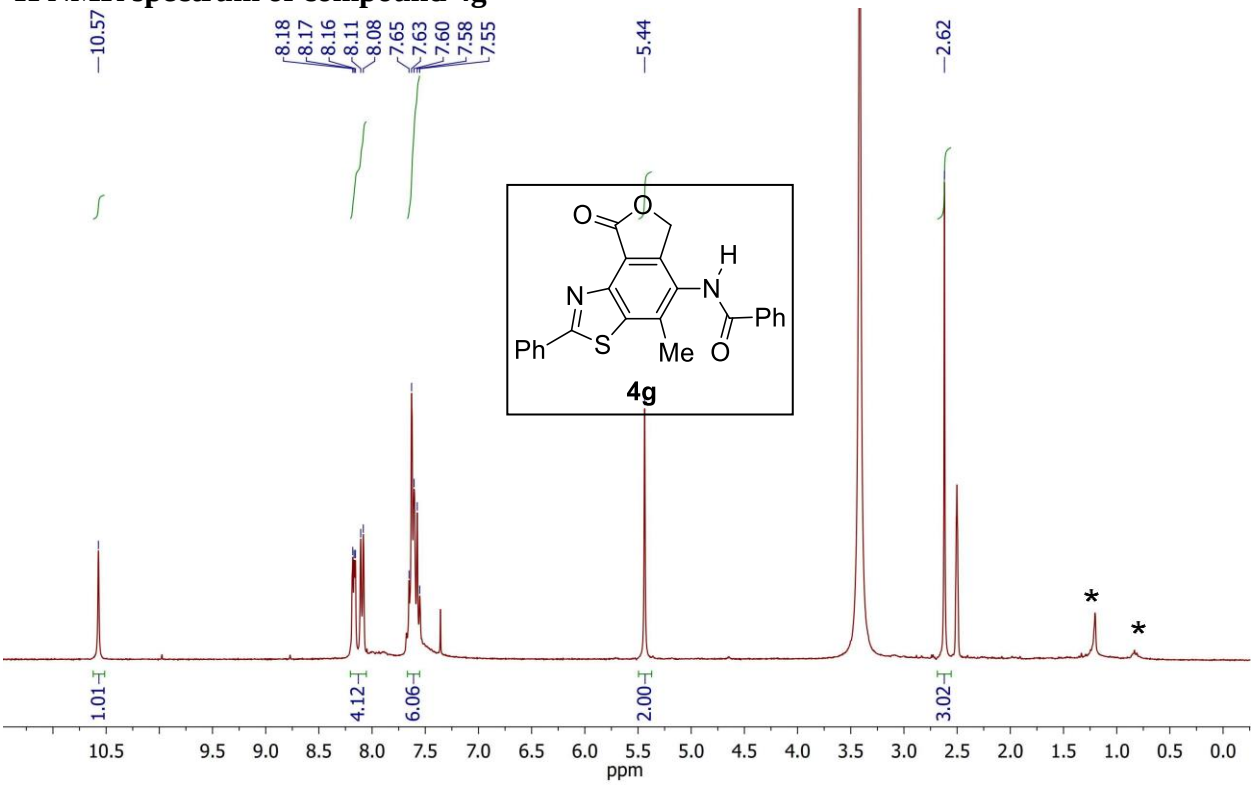


* Dichloromethane (5.76 ppm) and grease

^{13}C{^{1}H} NMR spectrum of compound 4fb

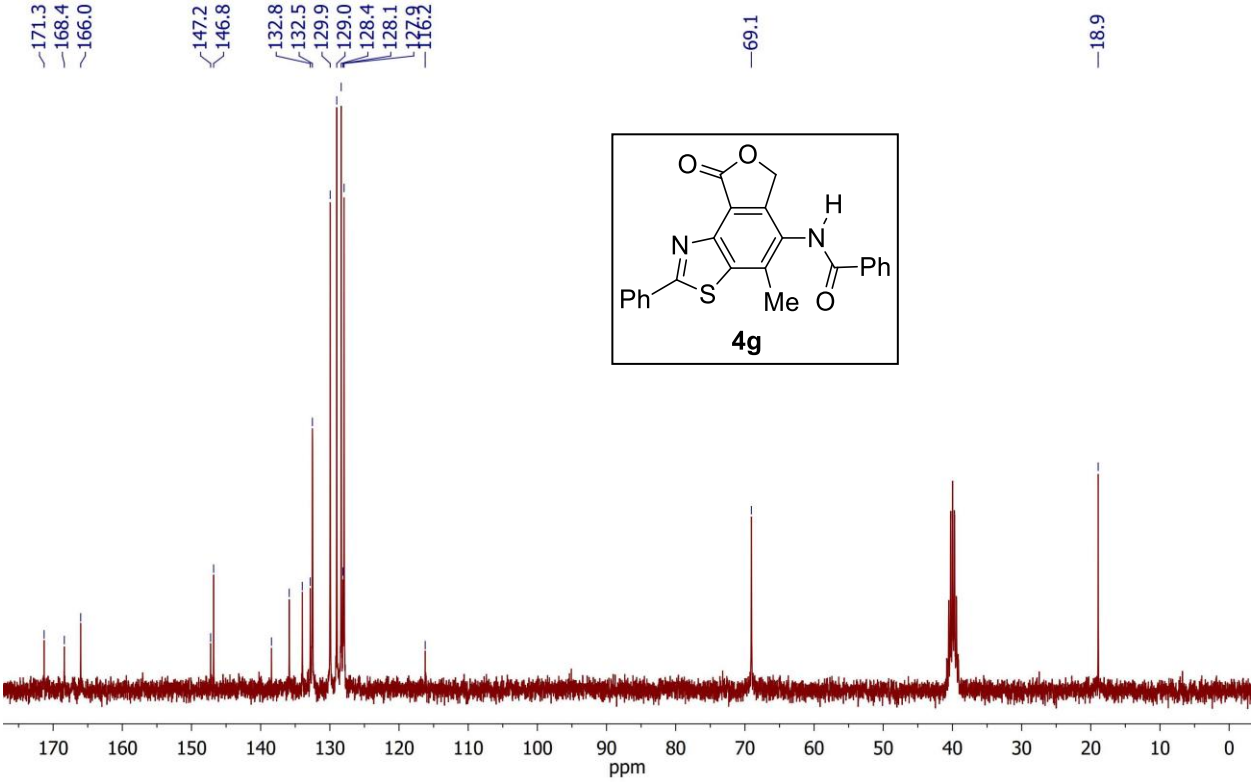


^{1}H NMR spectrum of compound 4g

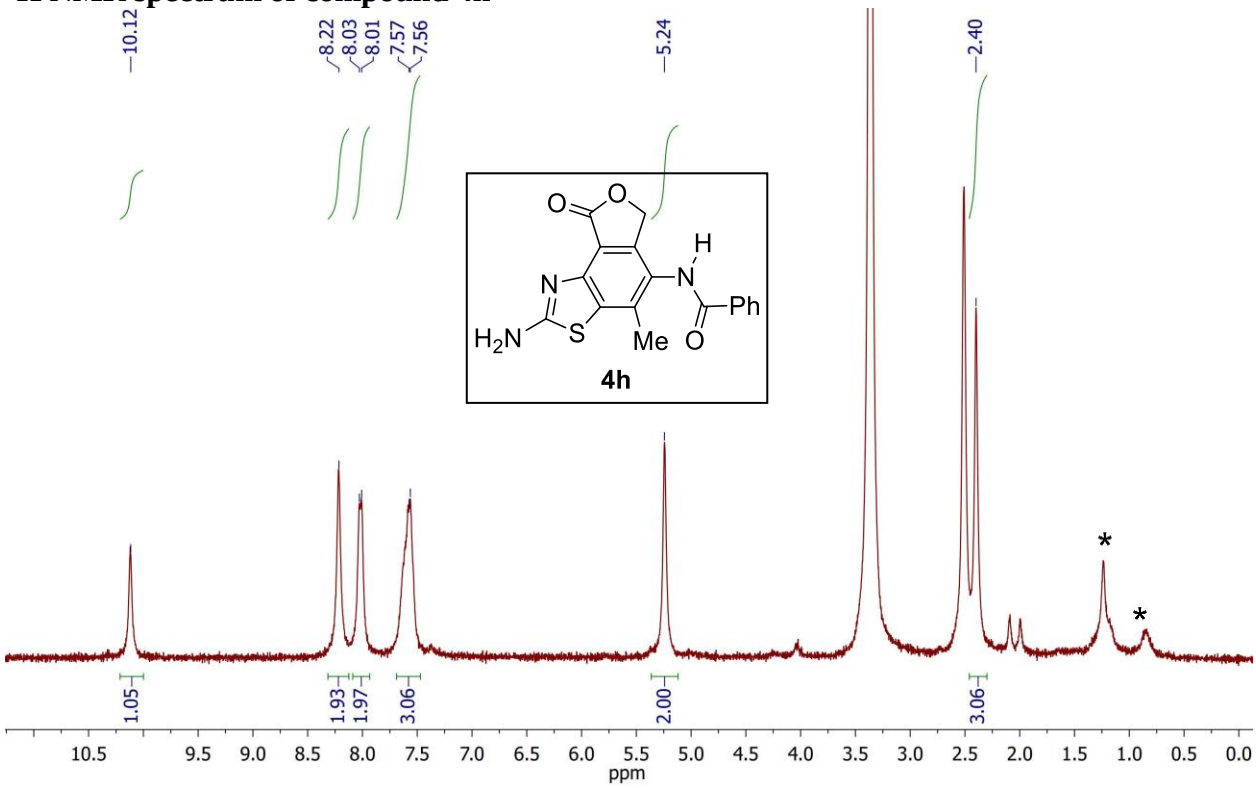


* Grease

^{13}C{^{1}H} NMR spectrum of compound 4g

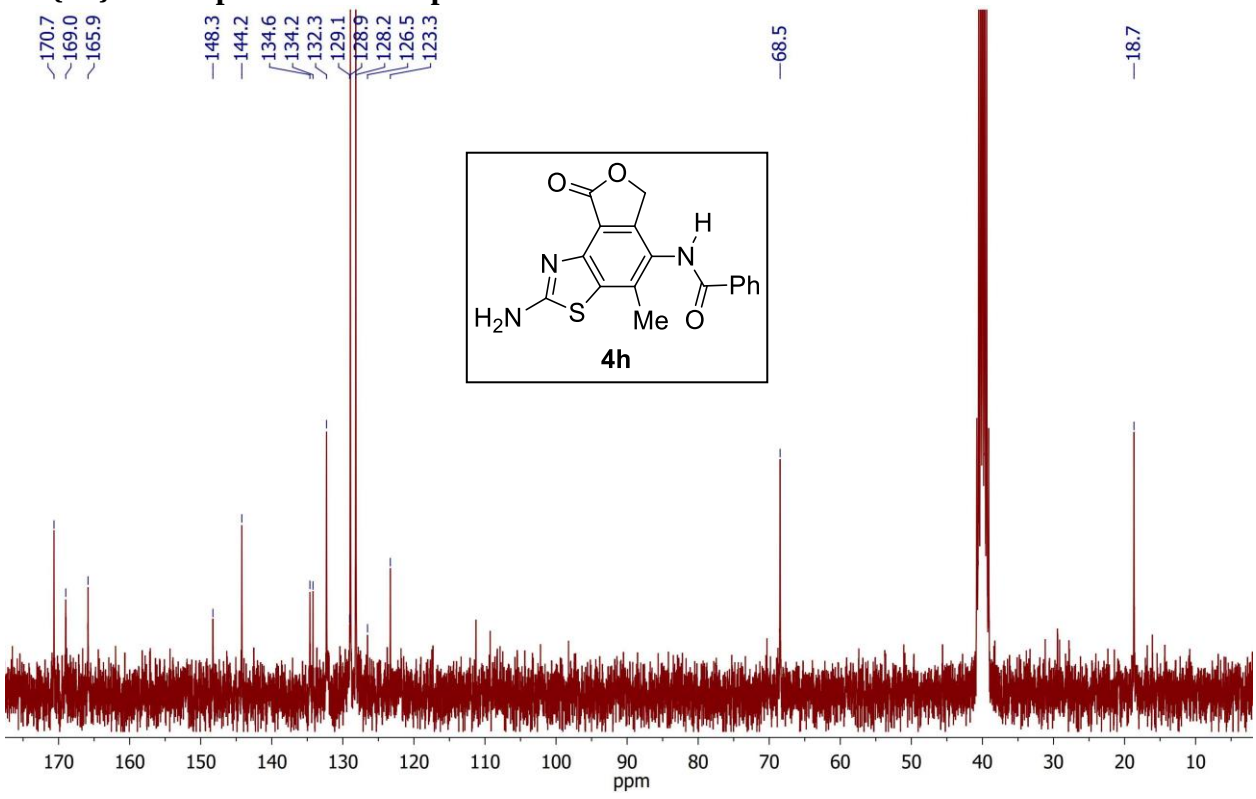


^{1}H NMR spectrum of compound 4h

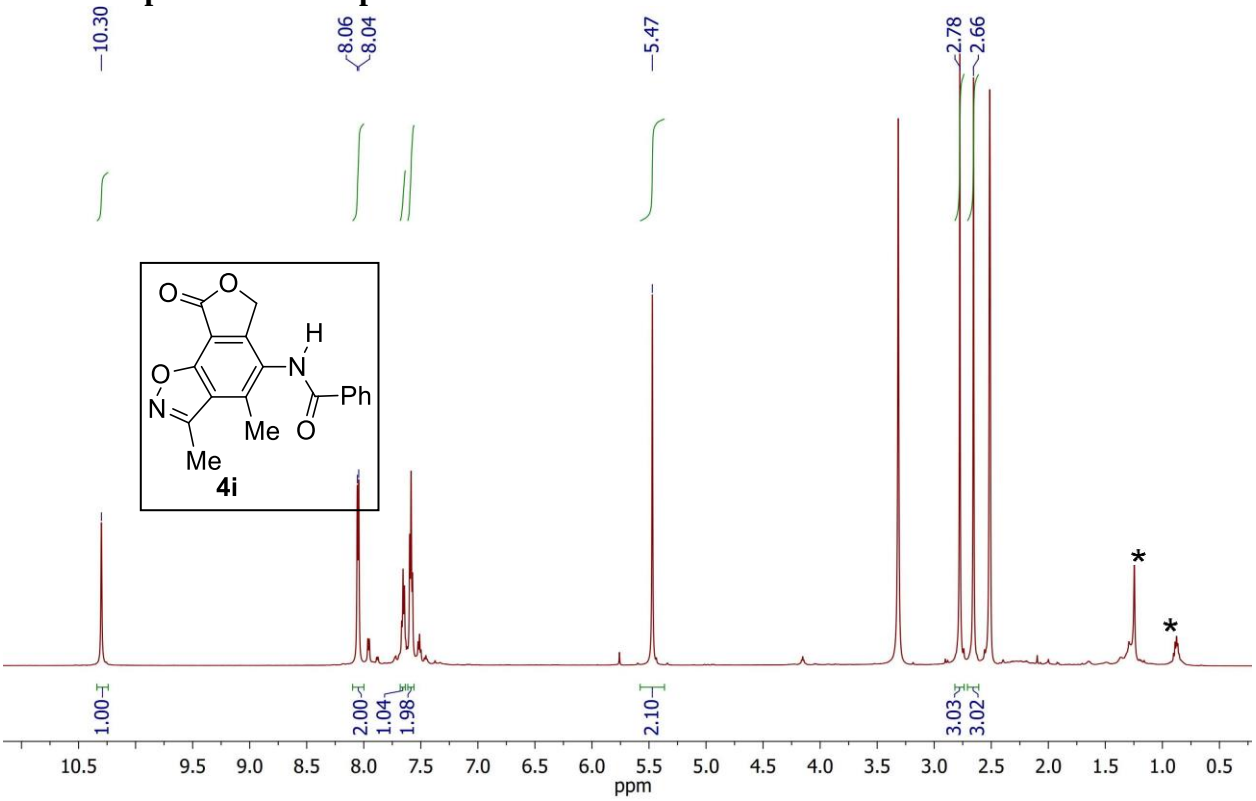


* Grease

^{13}C{^{1}H} NMR spectrum of compound 4h

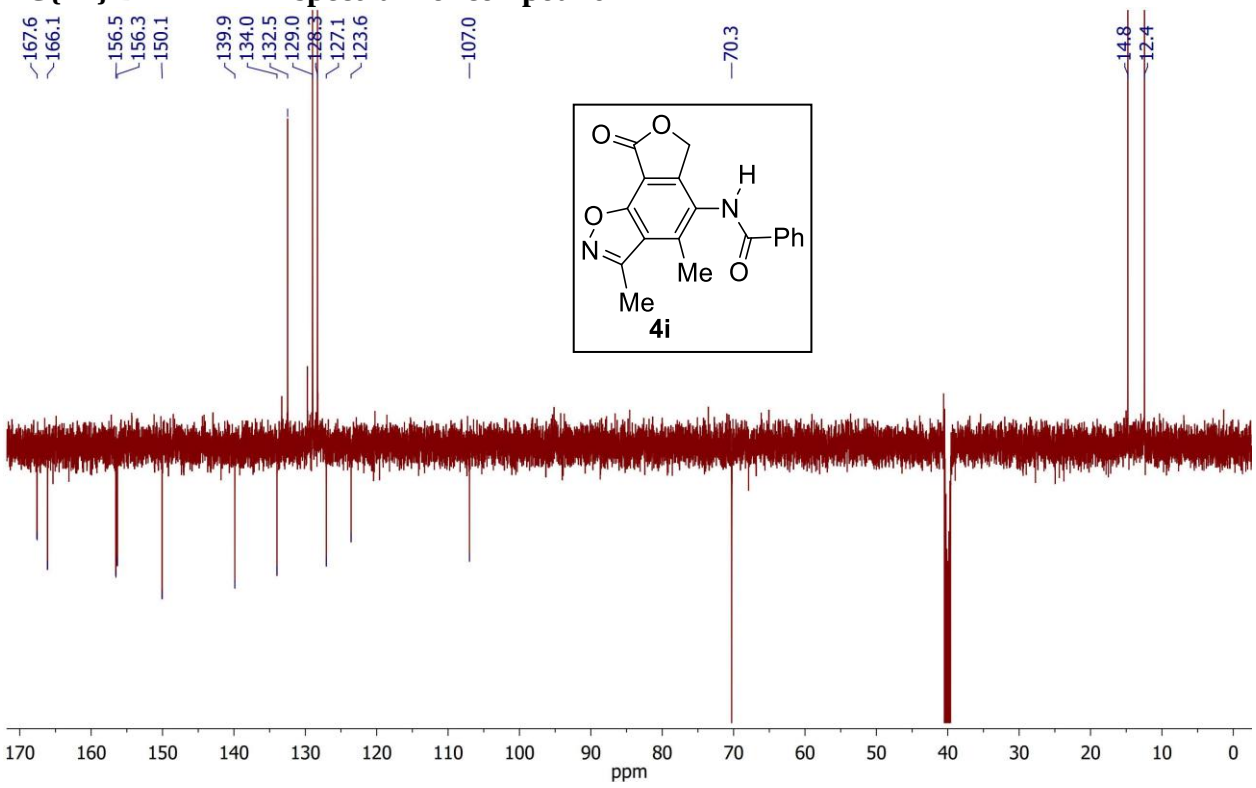


^{1}H NMR spectrum of compound 4i

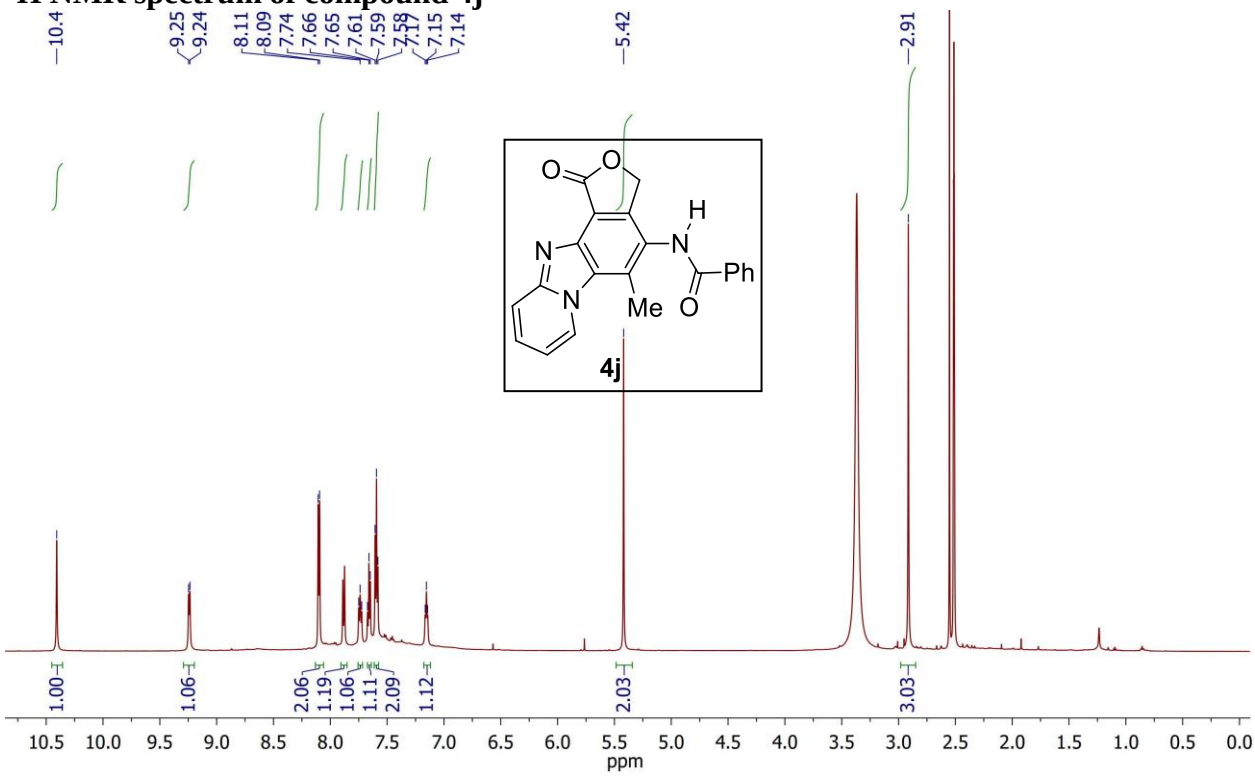


* Grease

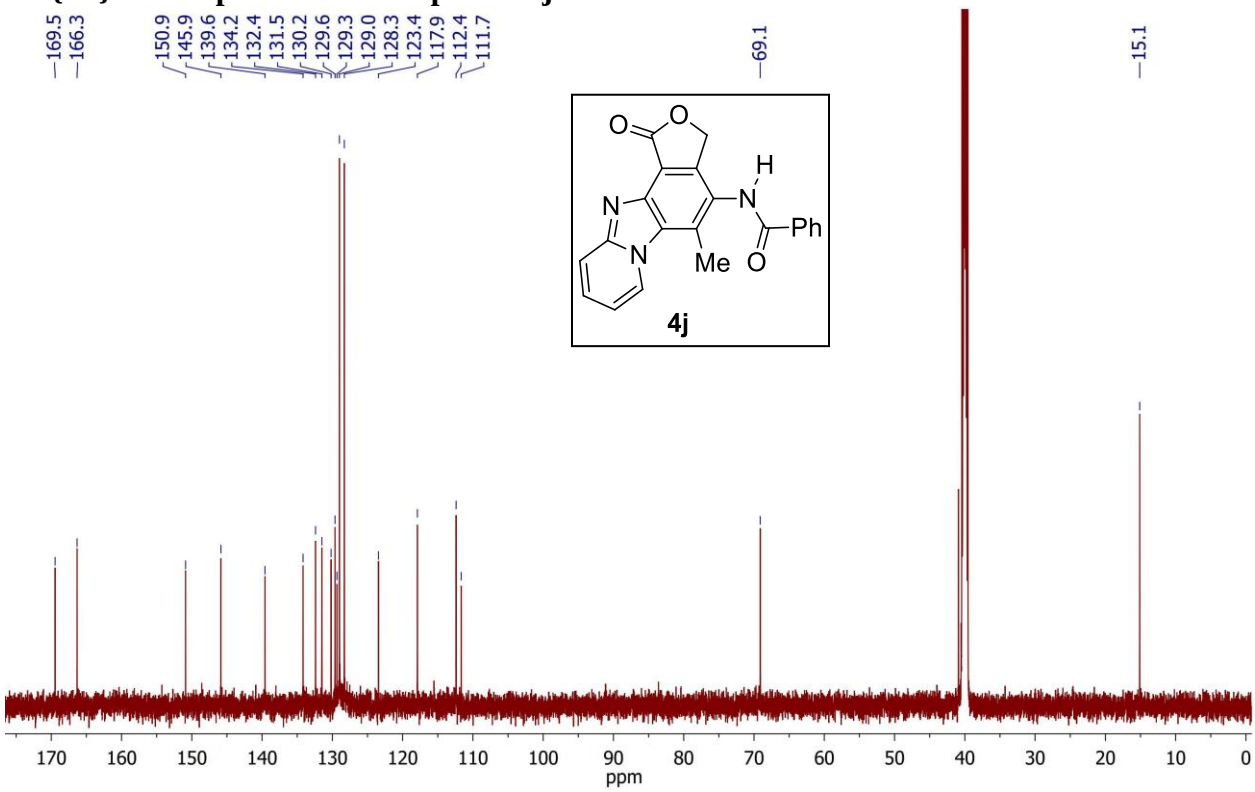
^{13}C{^{1}H} DEPT NMR spectrum of compound 4i



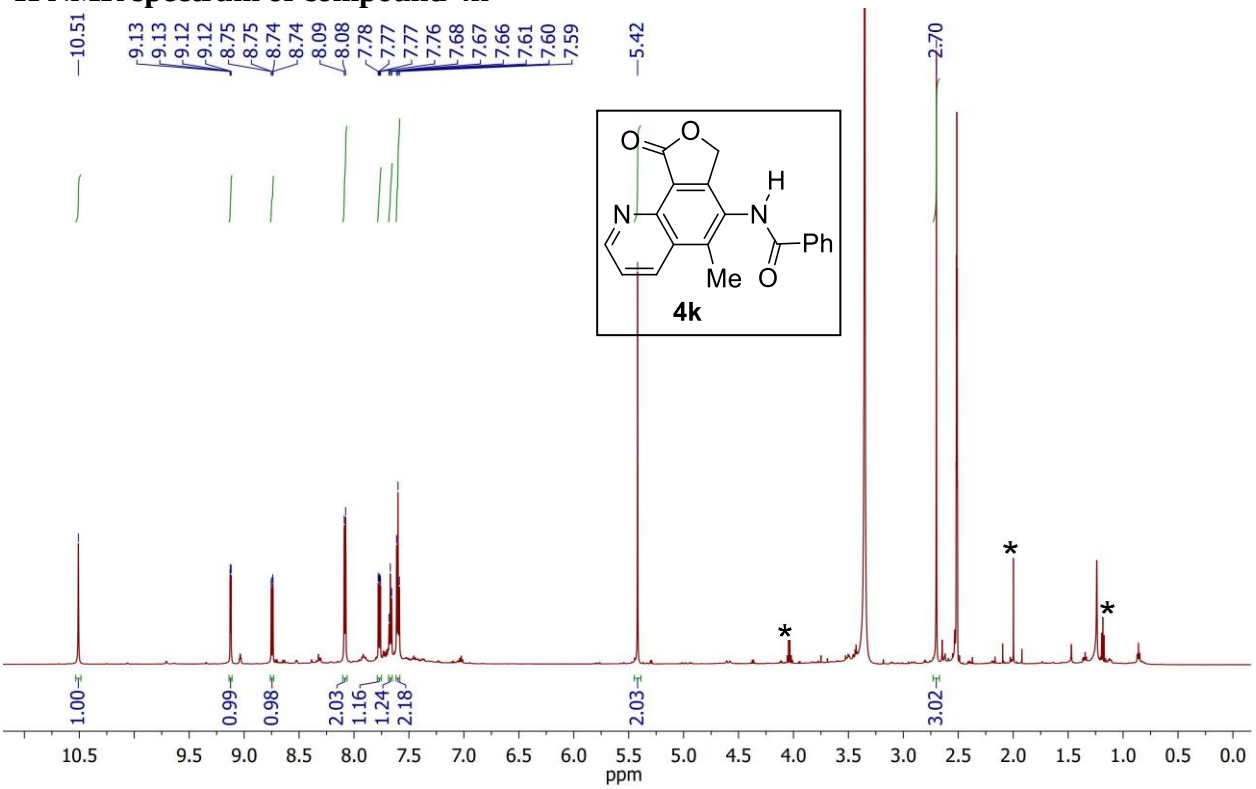
^{1}H NMR spectrum of compound 4j



^{13}C{^{1}H} NMR spectrum of compound 4j

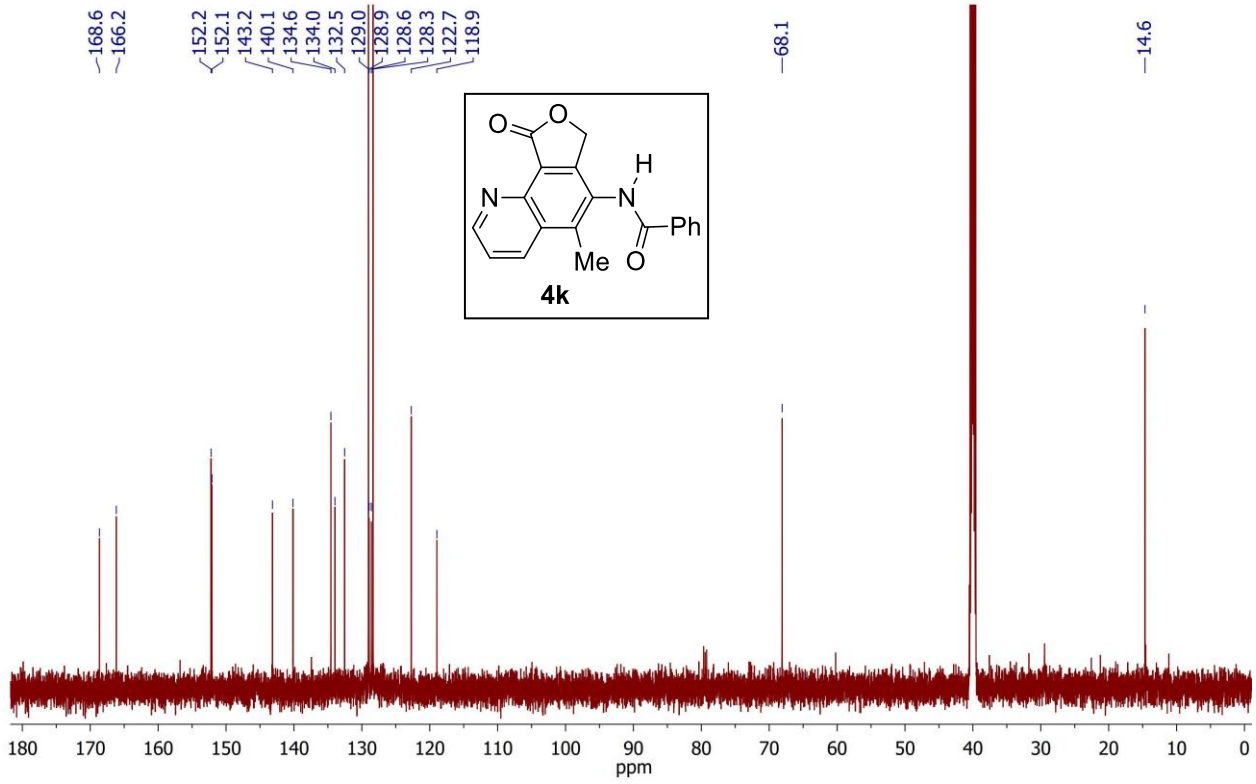


^{1}H NMR spectrum of compound 4k

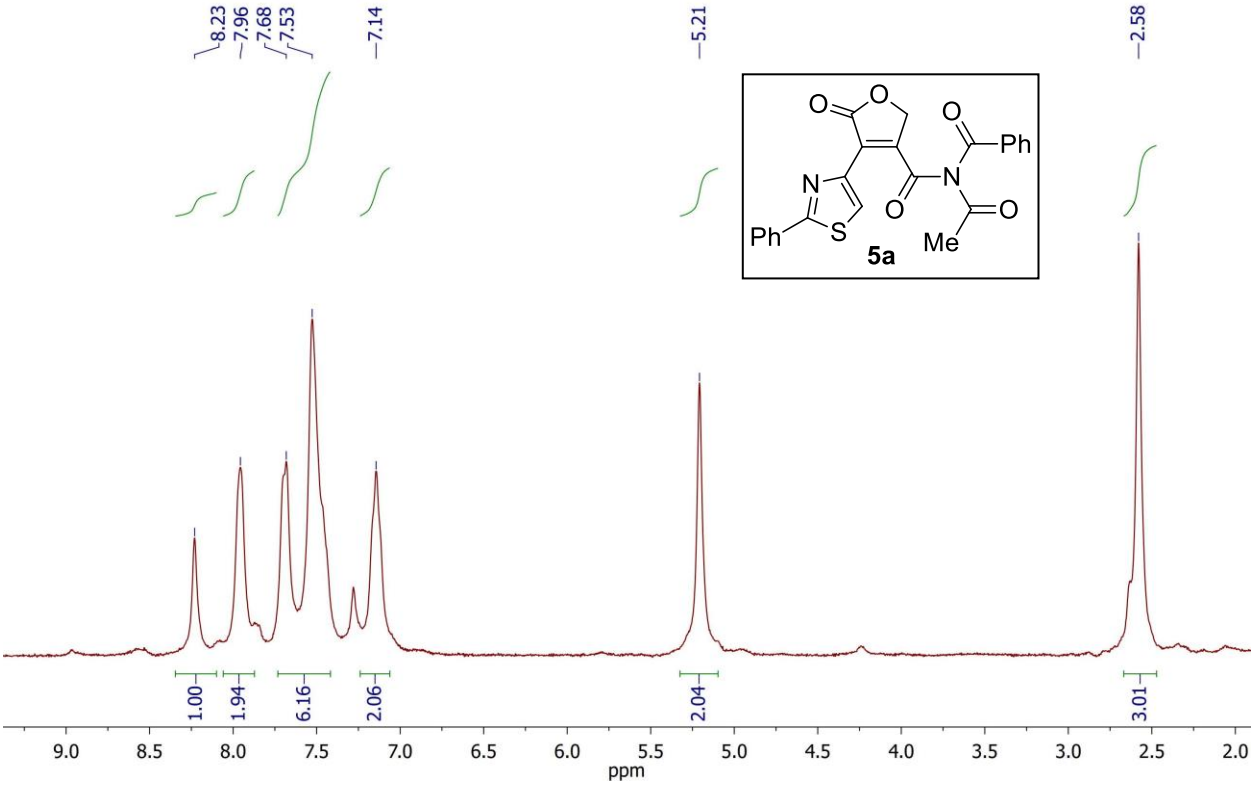


* Ethyl acetate

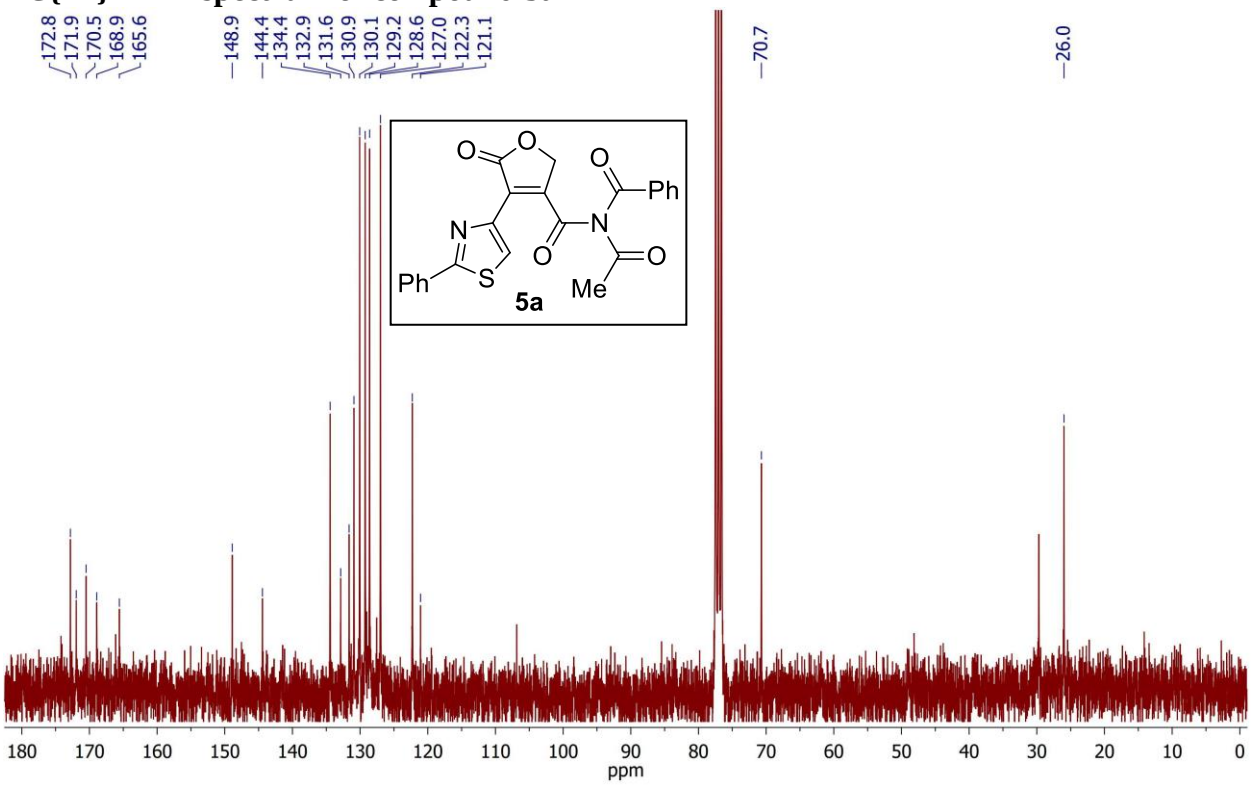
^{13}C{^{1}H} NMR spectrum of compound 4k



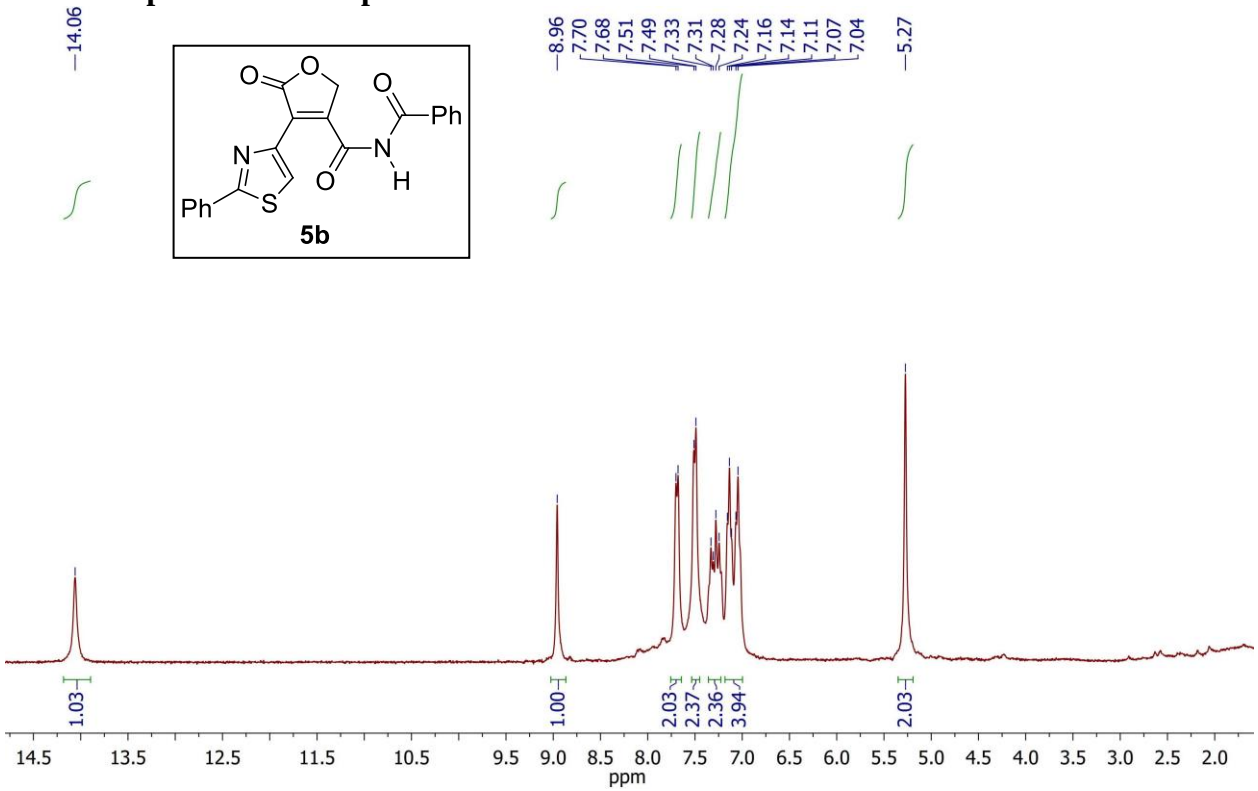
^{1}H NMR spectrum of compound 5a



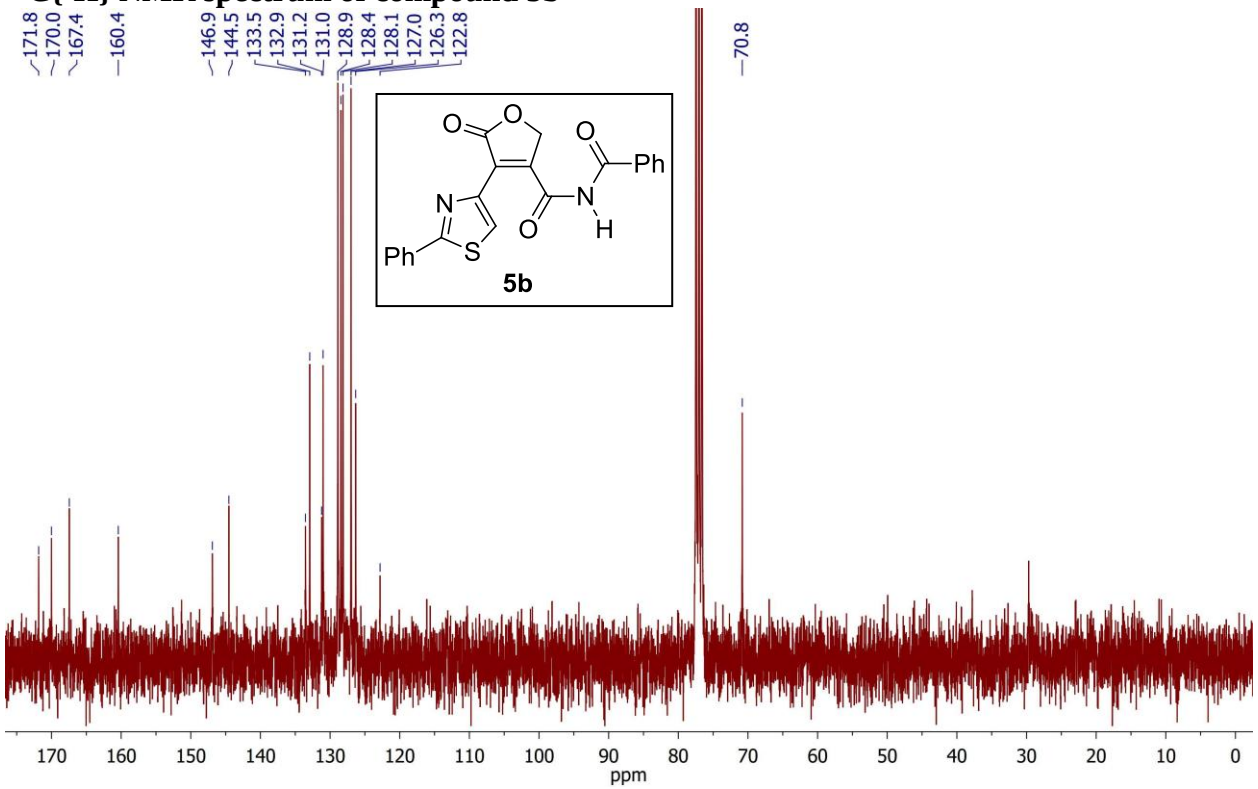
^{13}C{^{1}H} NMR spectrum of compound 5a



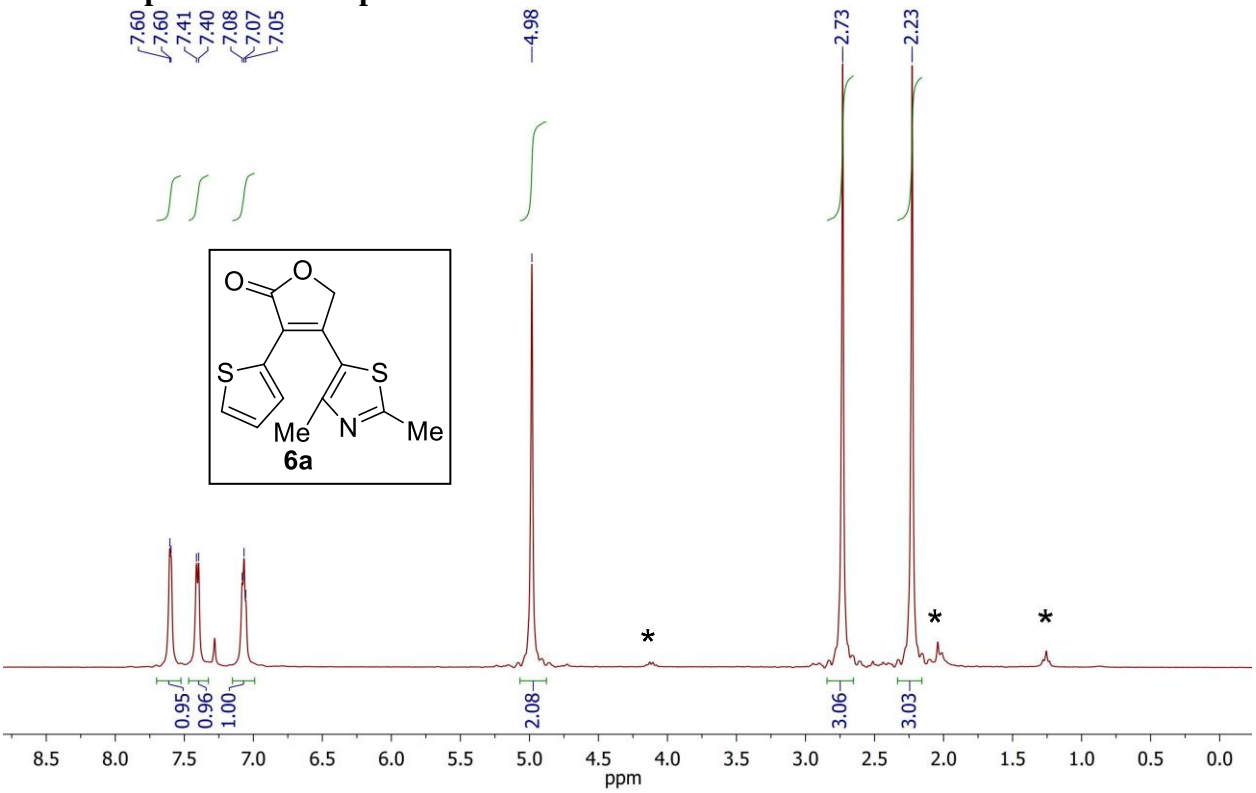
^{1}H NMR spectrum of compound 5b



^{13}C{^{1}H} NMR spectrum of compound 5b

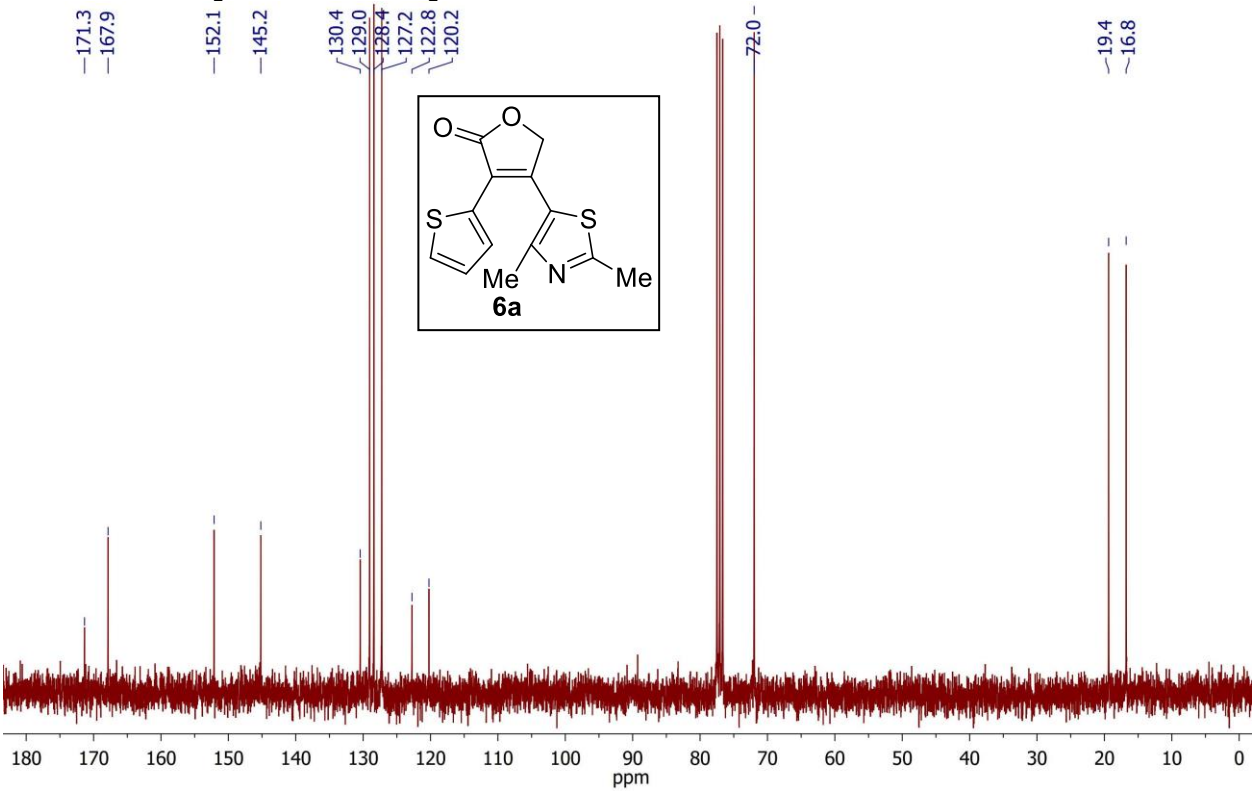


^{1}H NMR spectrum of compound 6a

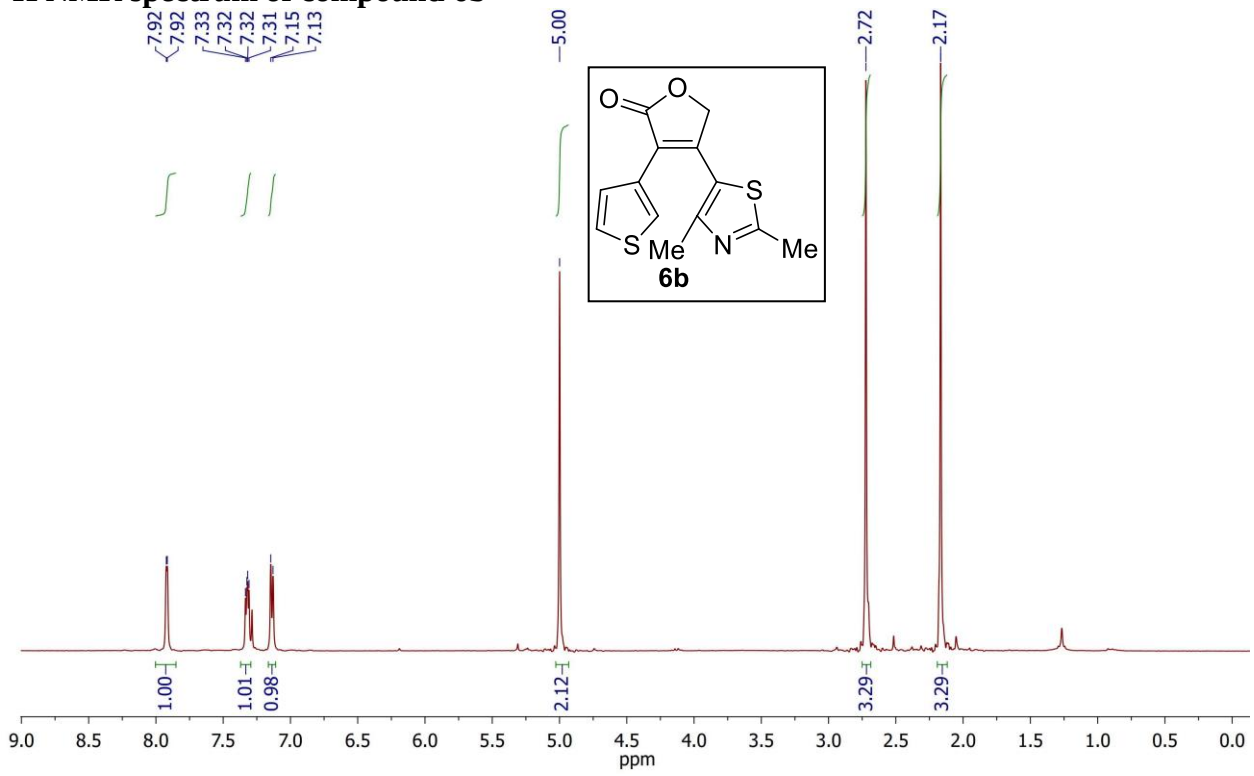


* Ethyl acetate

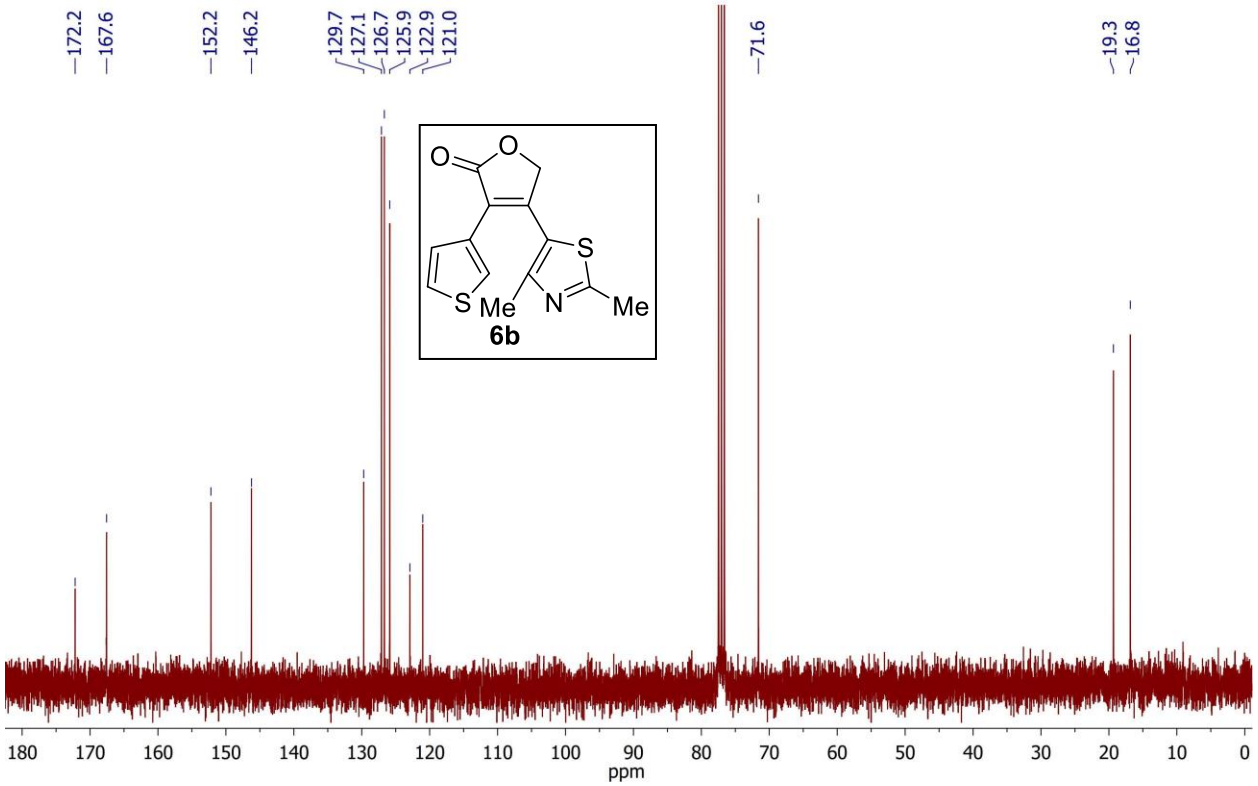
^{13}C{^{1}H} NMR spectrum of compound 6a



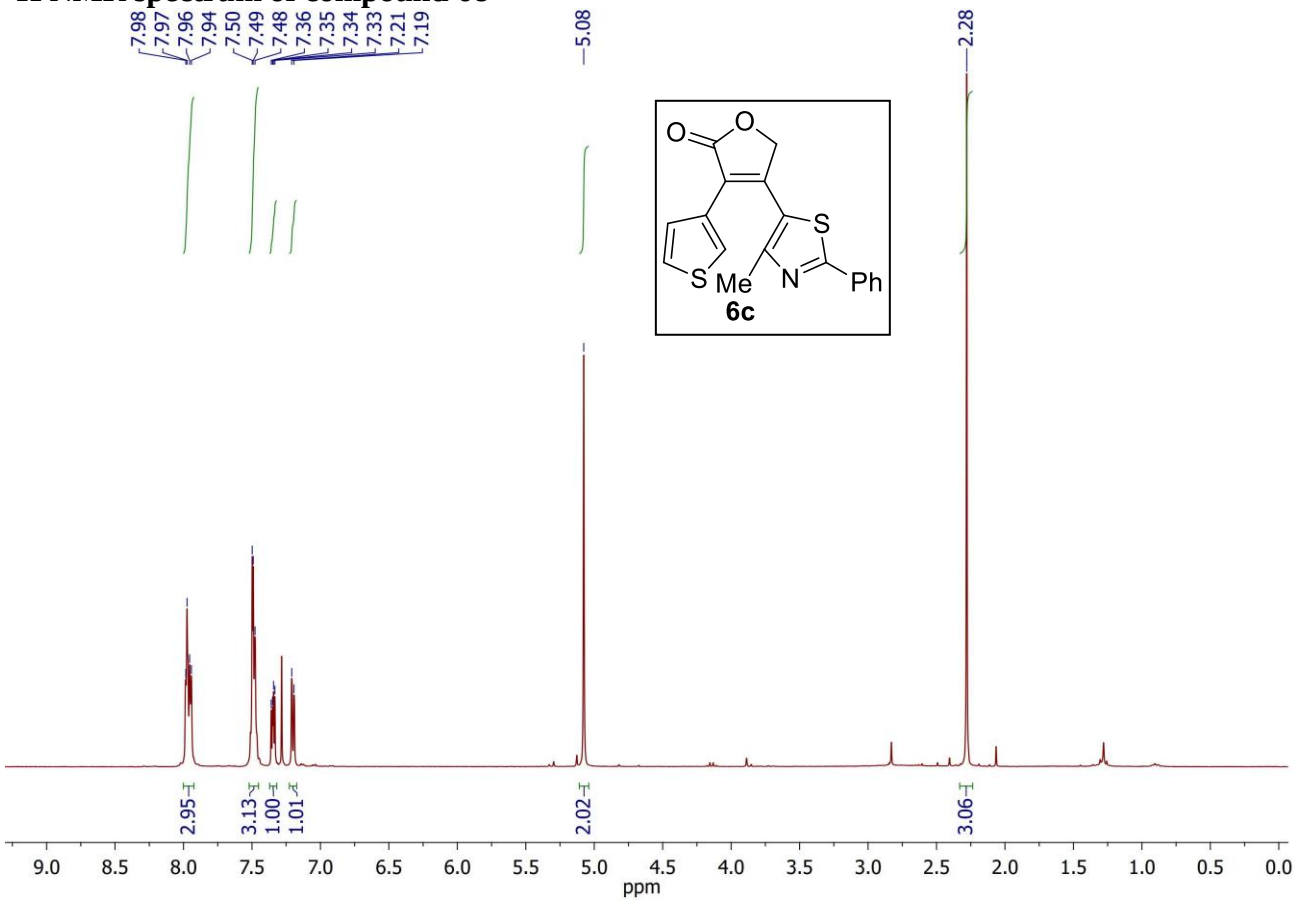
^{1}H NMR spectrum of compound 6b



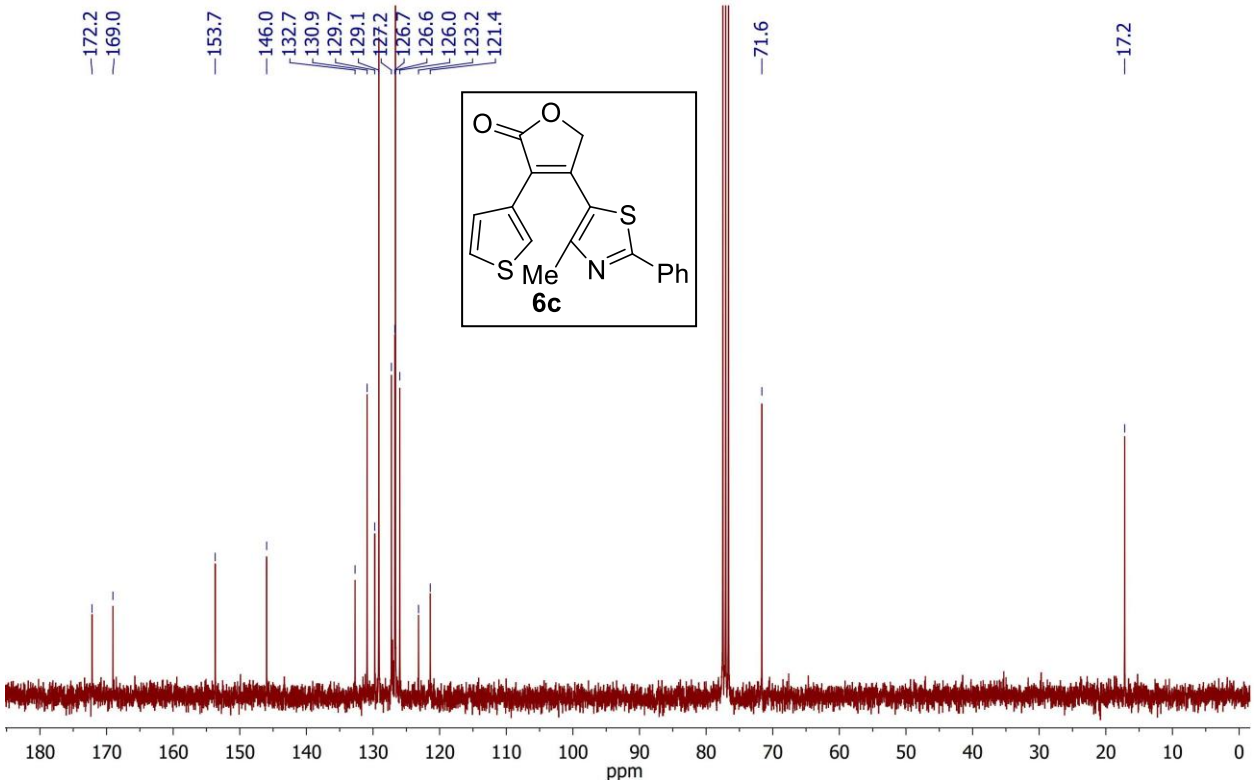
^{13}C{^{1}H} NMR spectrum of compound 6b



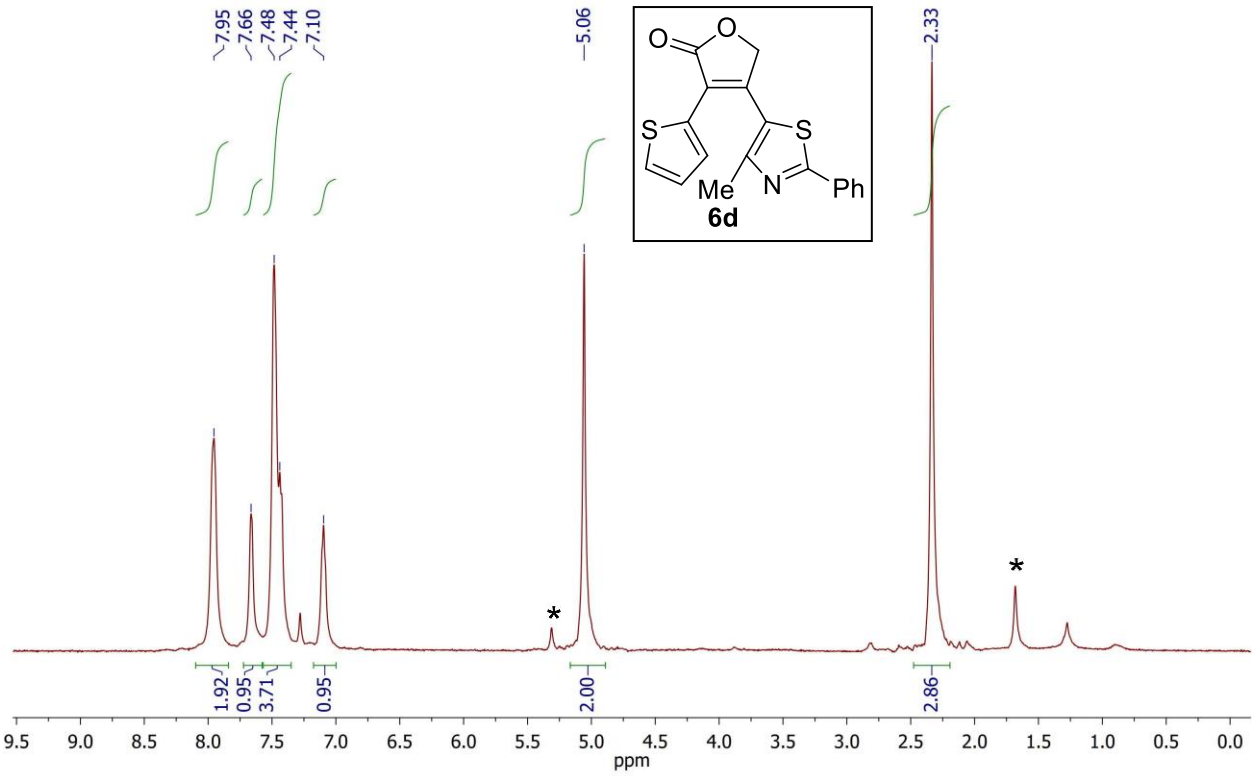
^{1}H NMR spectrum of compound 6c

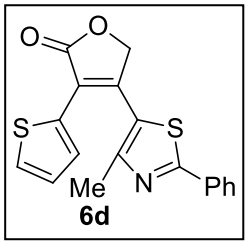


^{13}C{^{1}H} NMR spectrum of compound 6c



^{1}H NMR spectrum of compound 6d

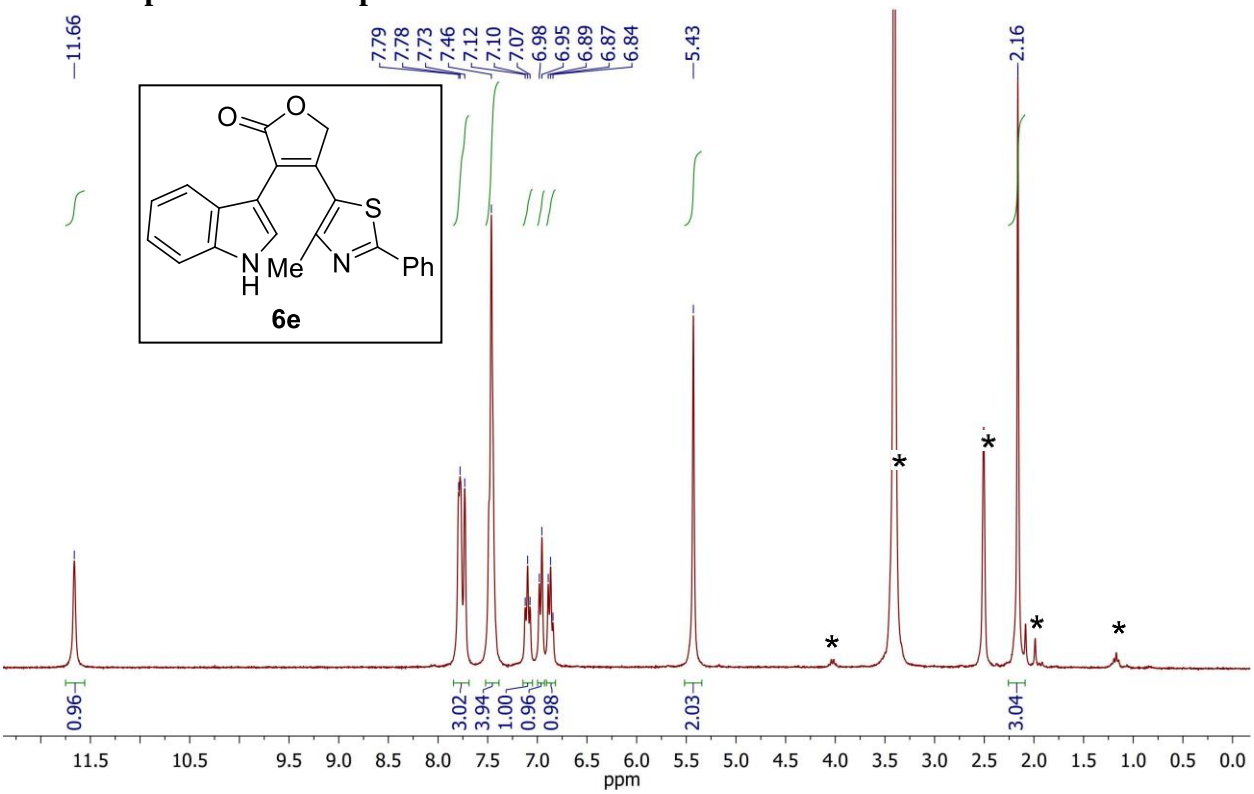




* Dichloromethane (5.30 ppm), H_2O (1.70 ppm)

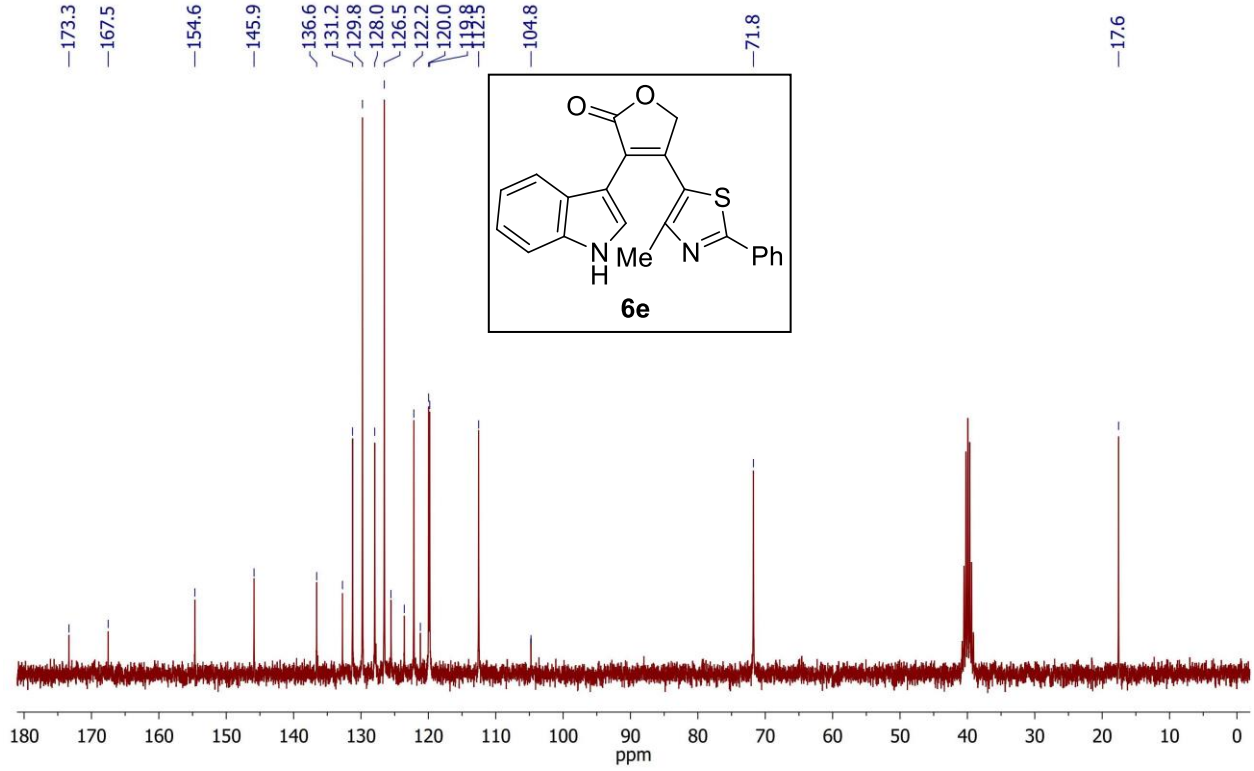
^{13}C{^{1}H} NMR spectrum of compound 6d

^{1}H NMR spectrum of compound 6e

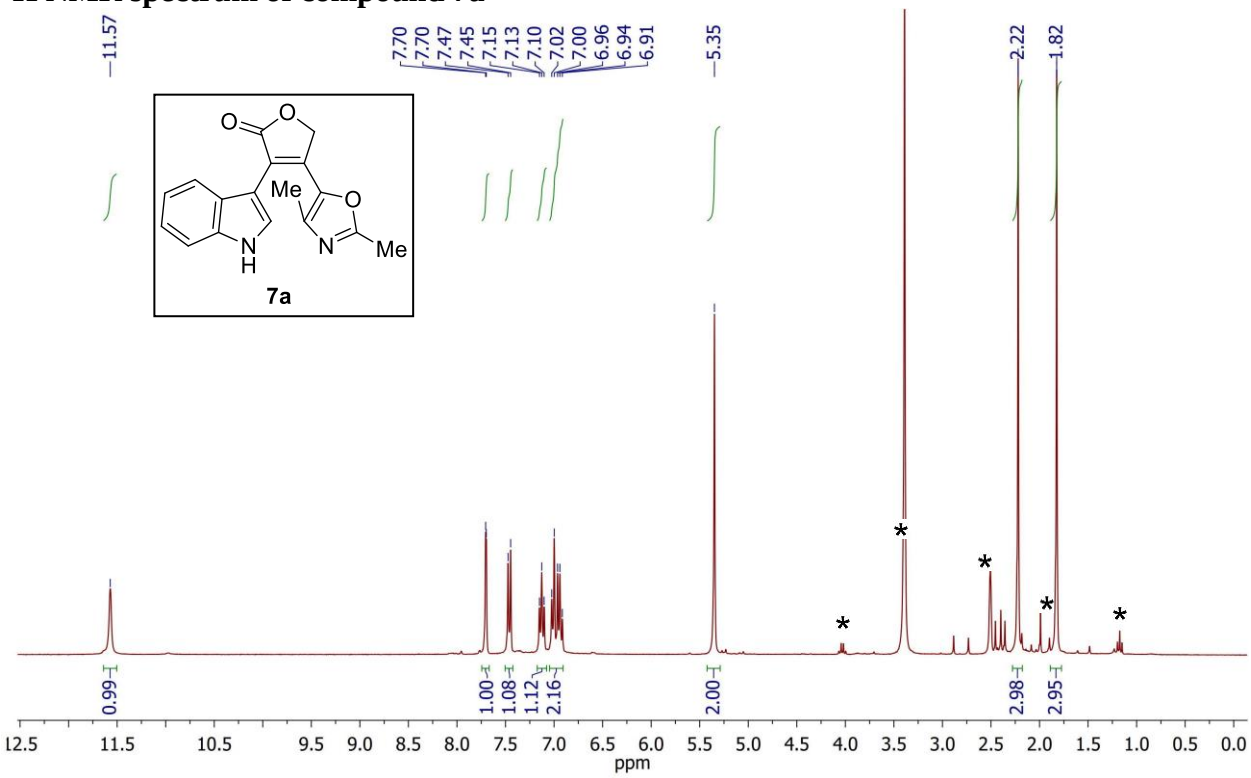


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 6e

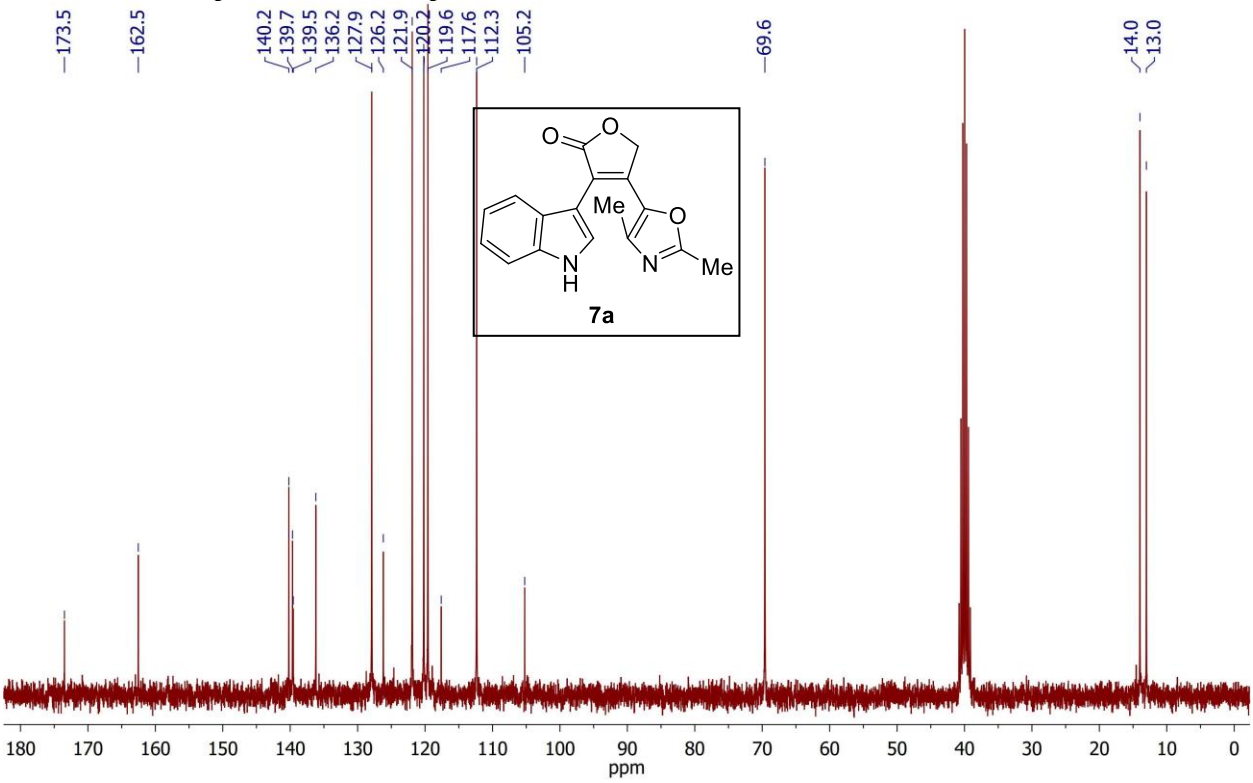


^{1}H NMR spectrum of compound 7a

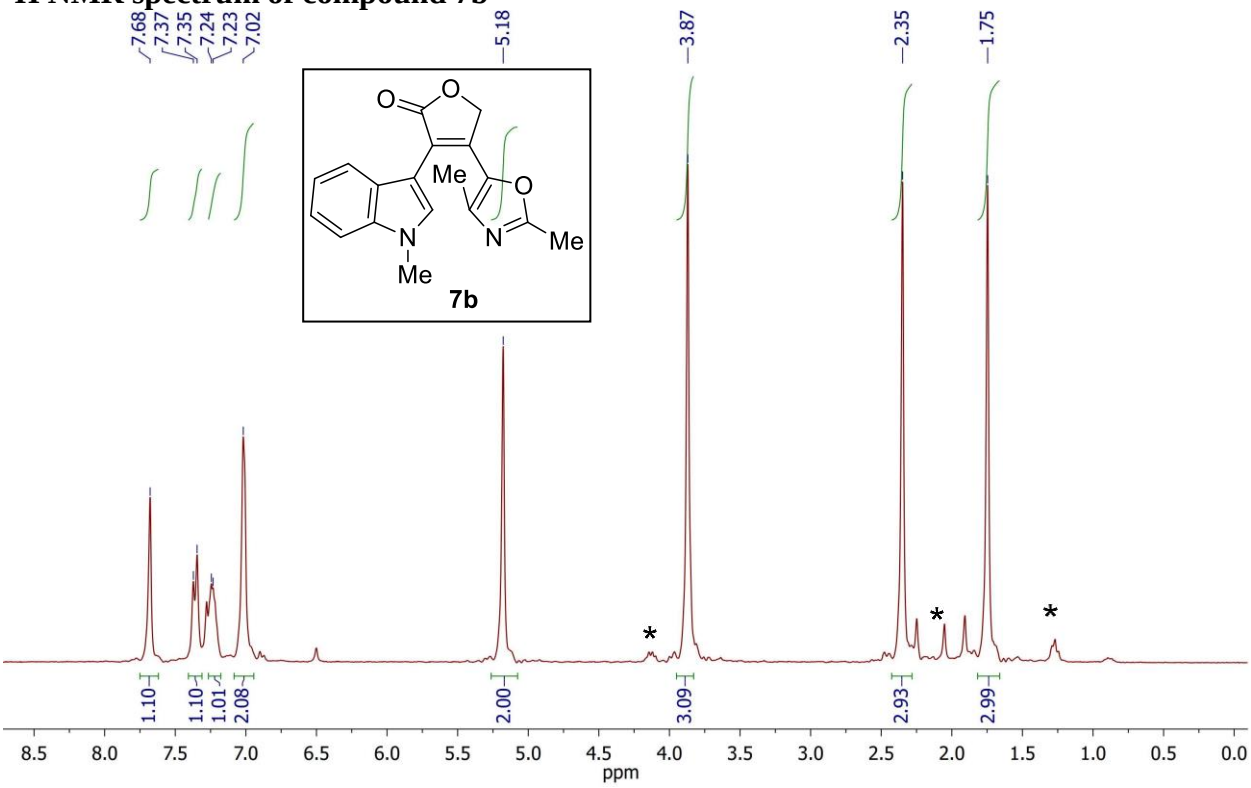


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 7a

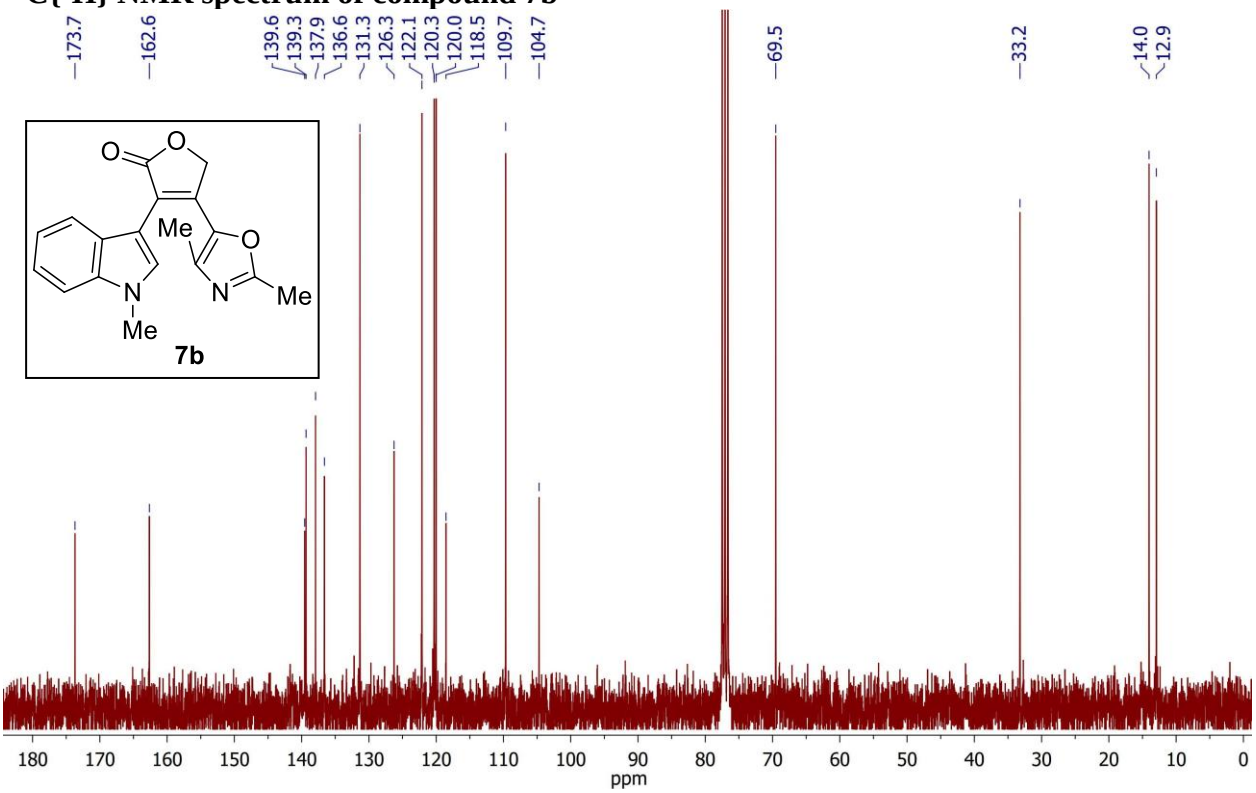


^{1}H NMR spectrum of compound 7b

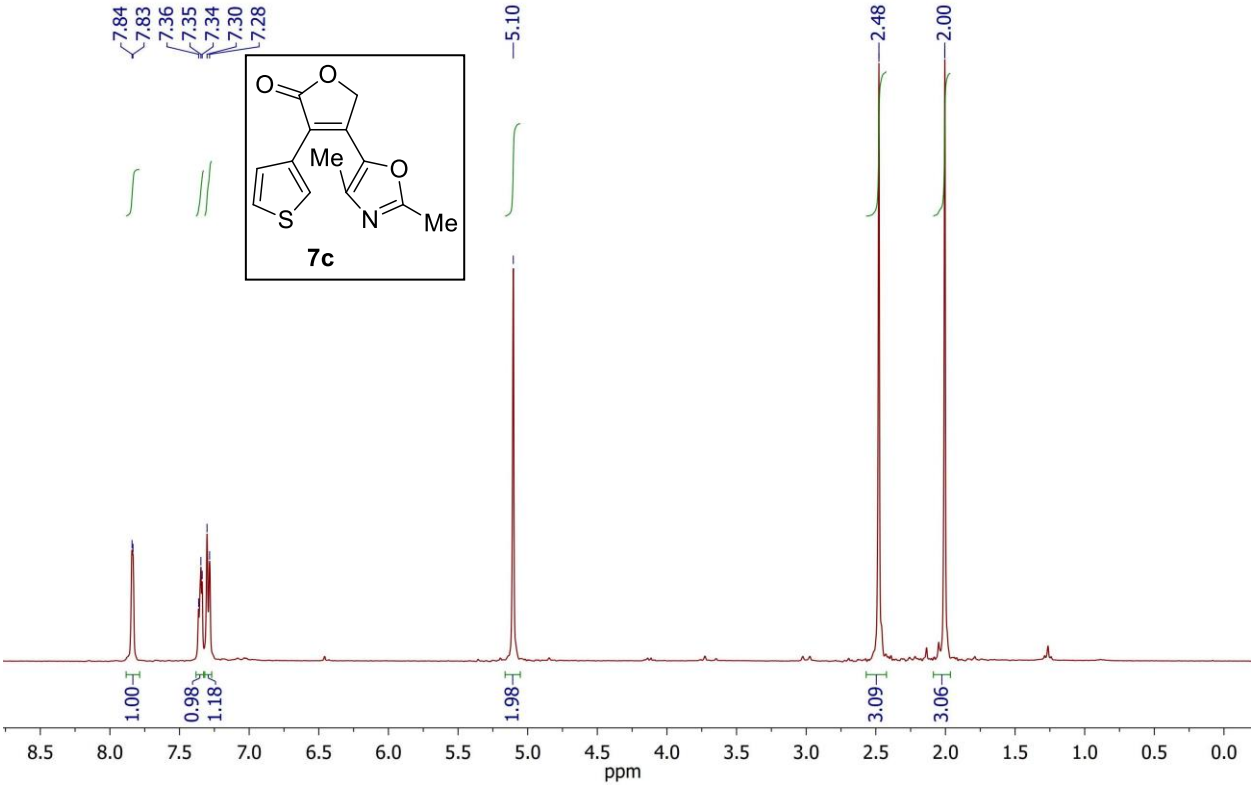


* Ethyl acetate

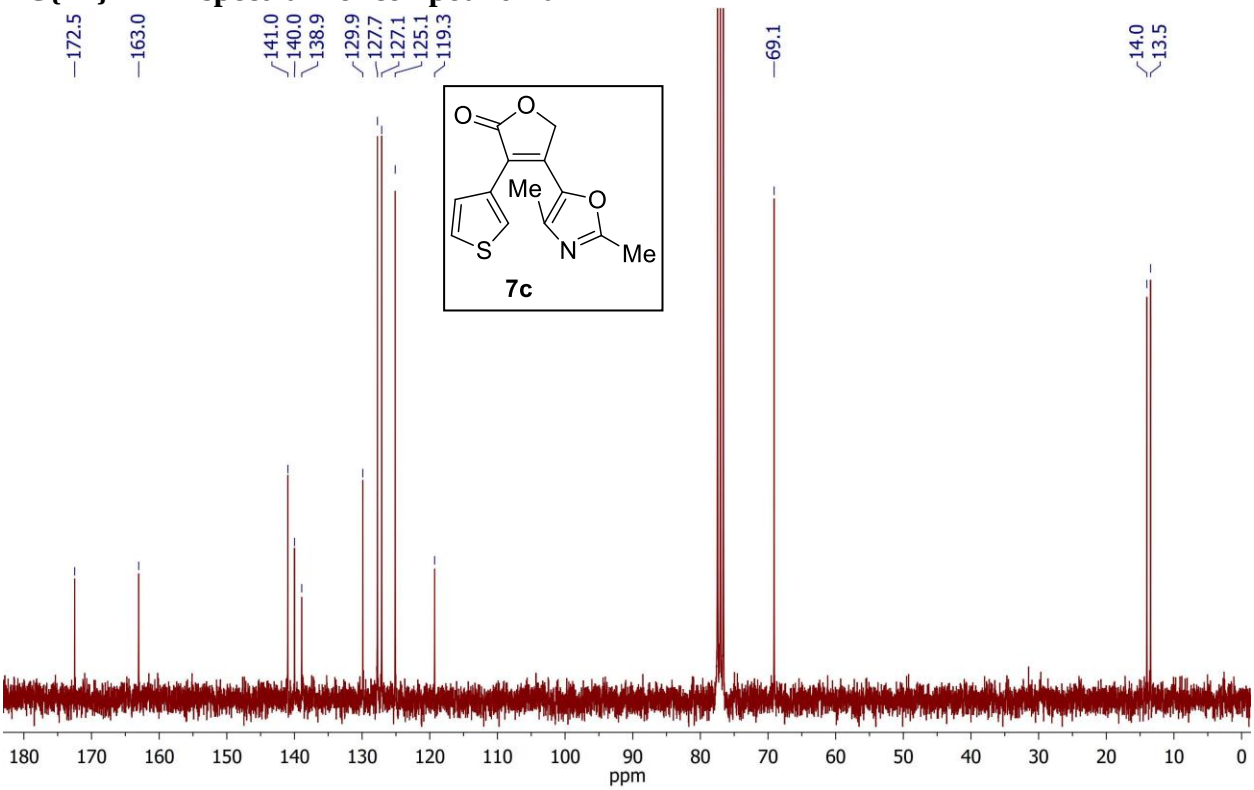
^{13}C{^{1}H} NMR spectrum of compound 7b



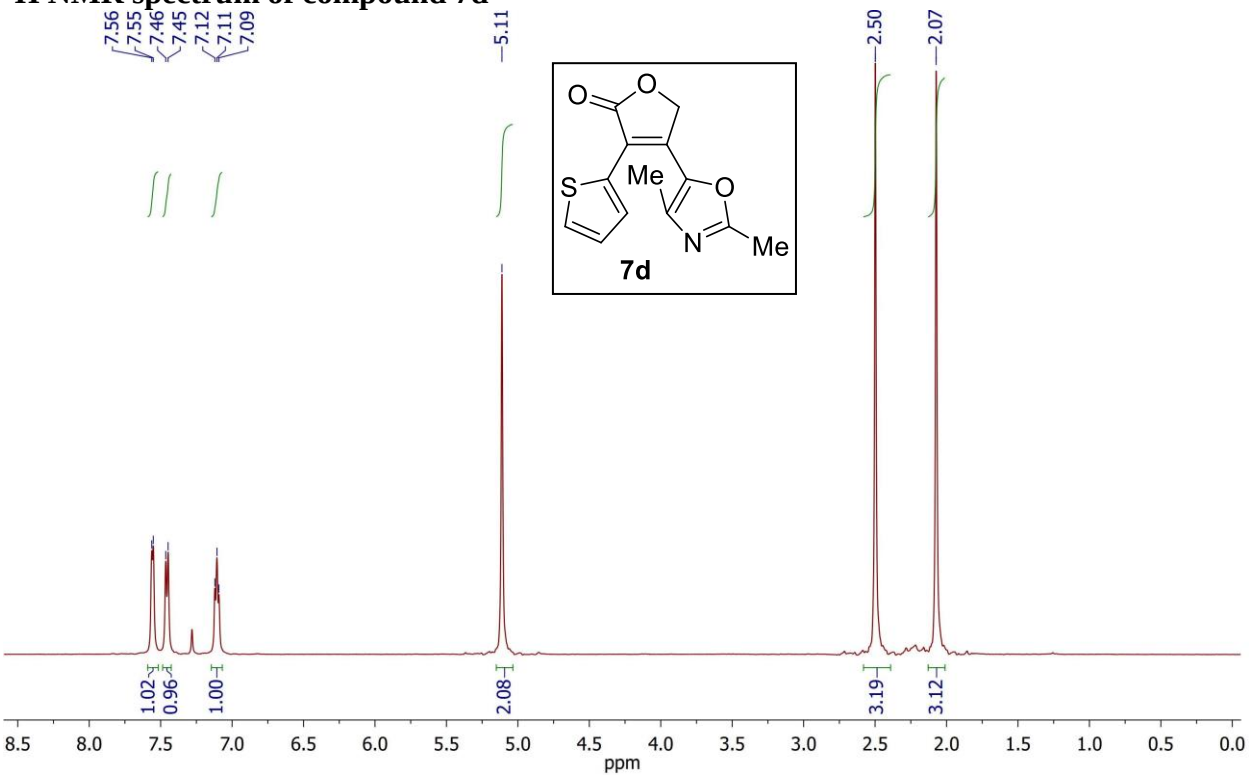
^{1}H NMR spectrum of compound 7c



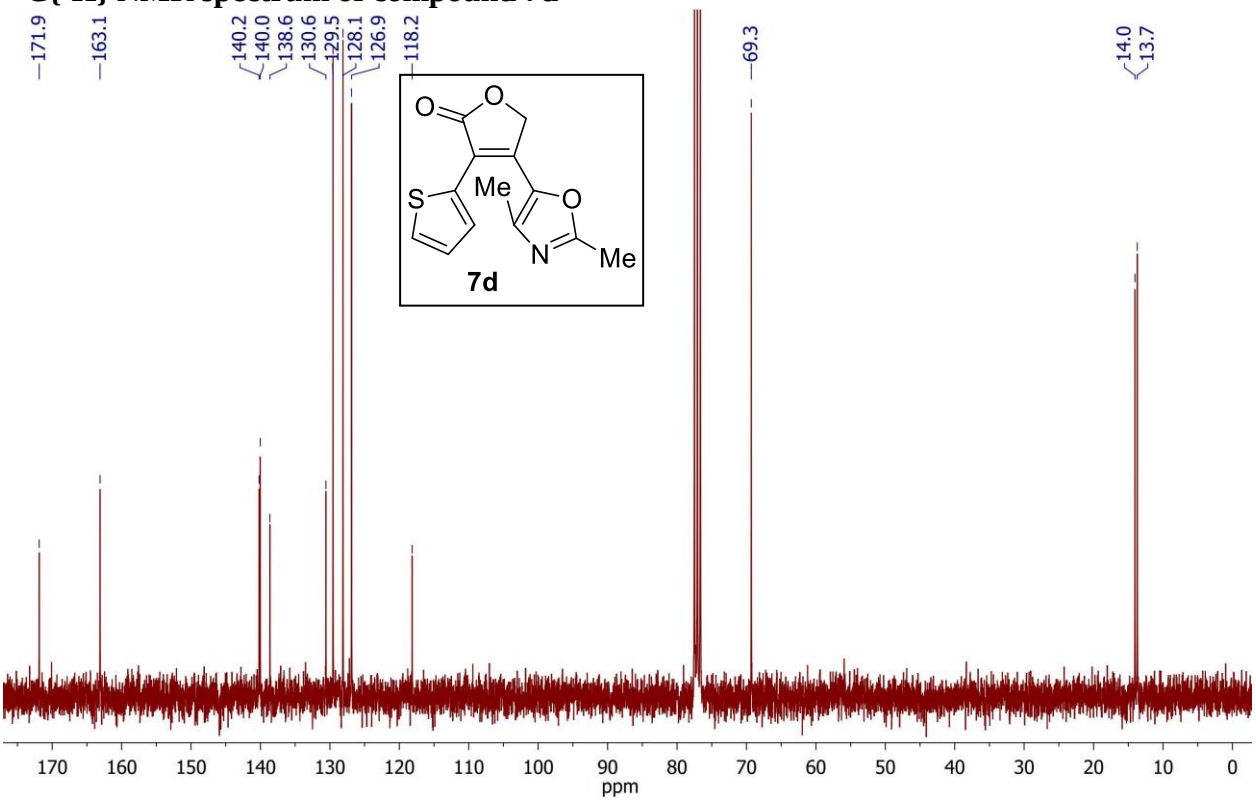
^{13}C{^{1}H} NMR spectrum of compound 7c



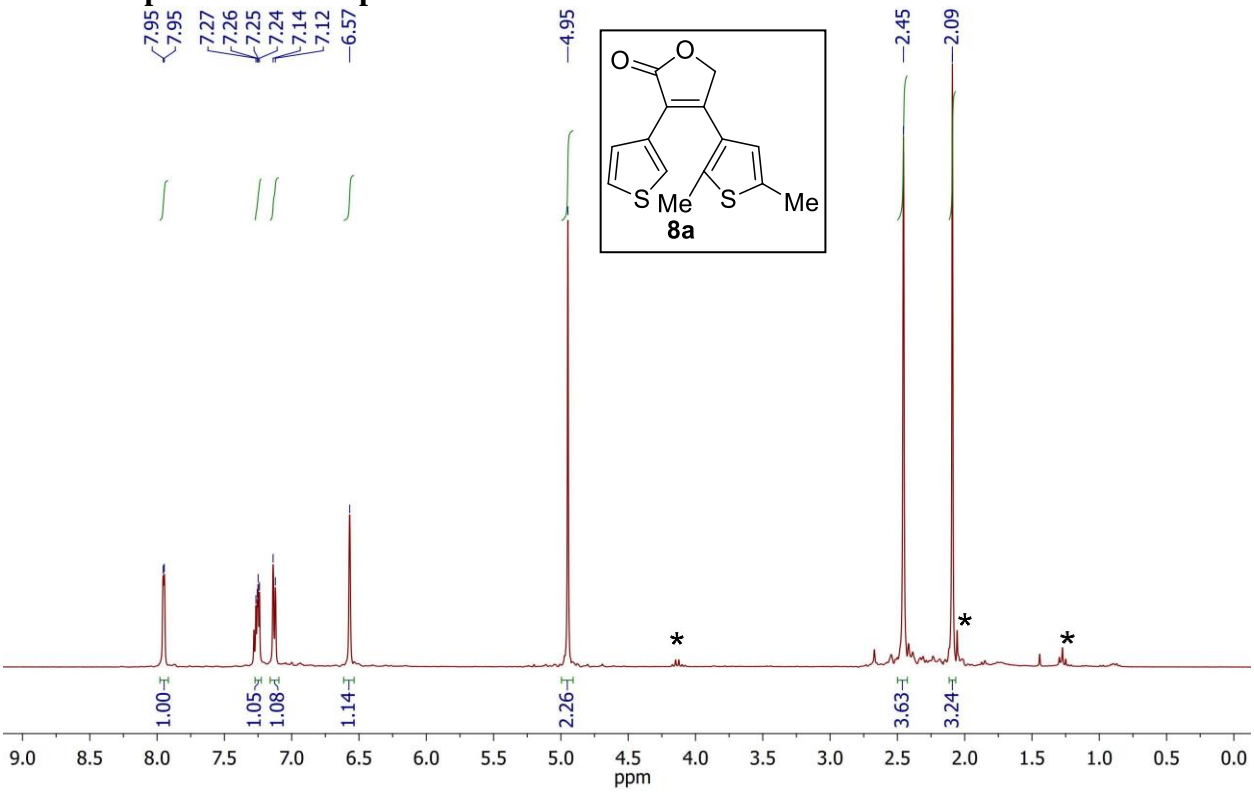
^{1}H NMR spectrum of compound 7d



^{13}C{^{1}H} NMR spectrum of compound 7d

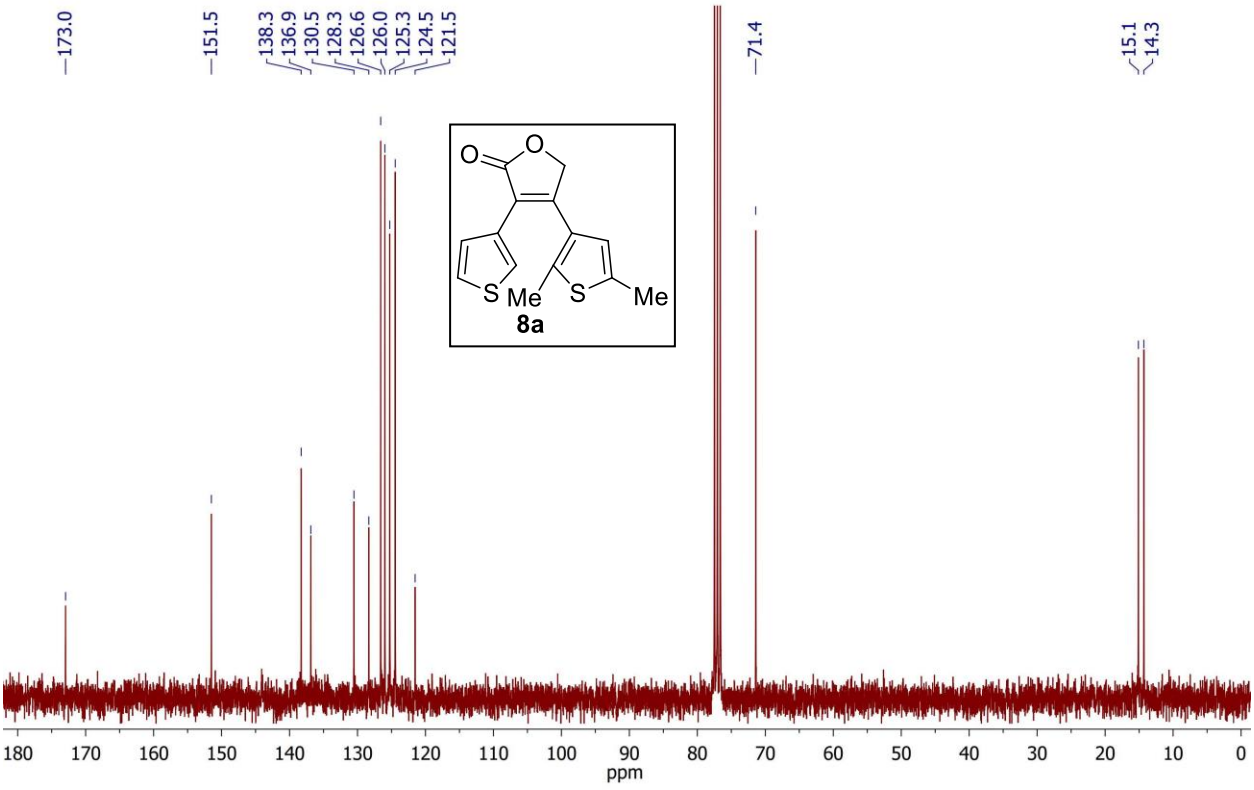


^{1}H NMR spectrum of compound 8a

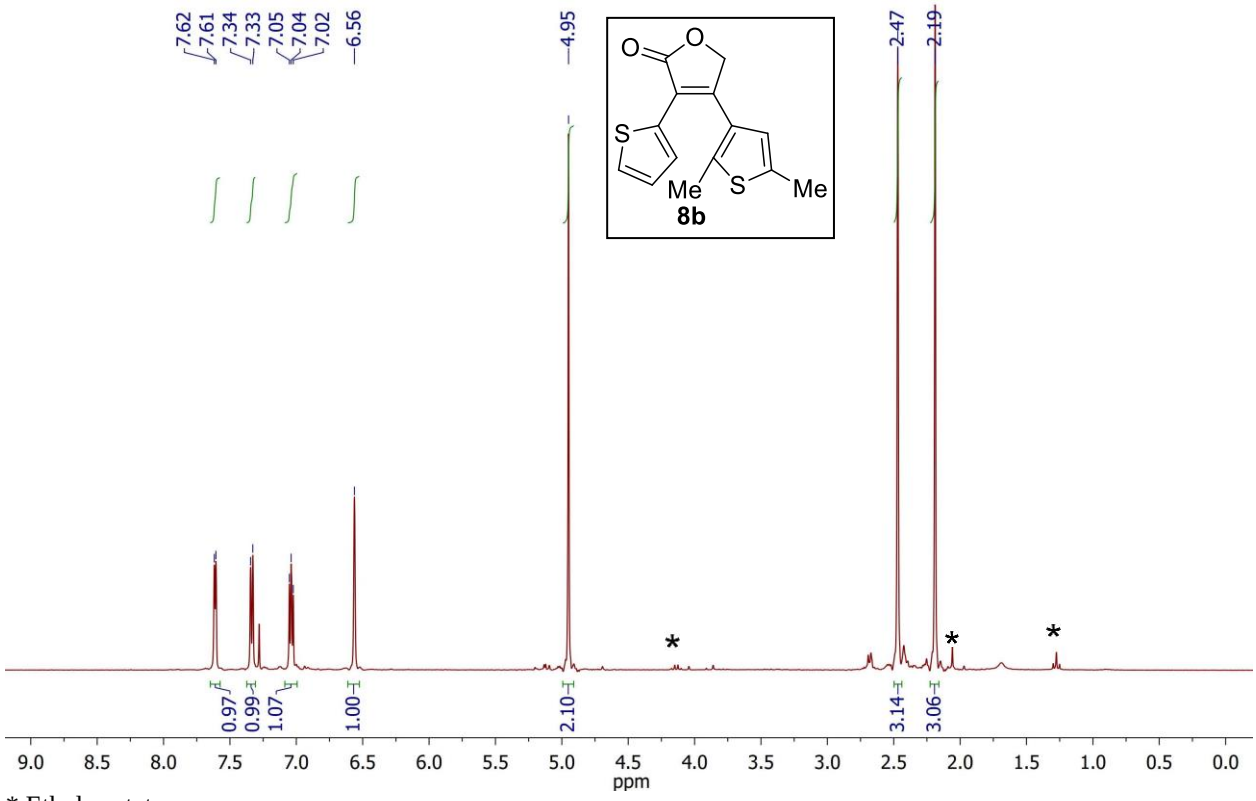


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 8a

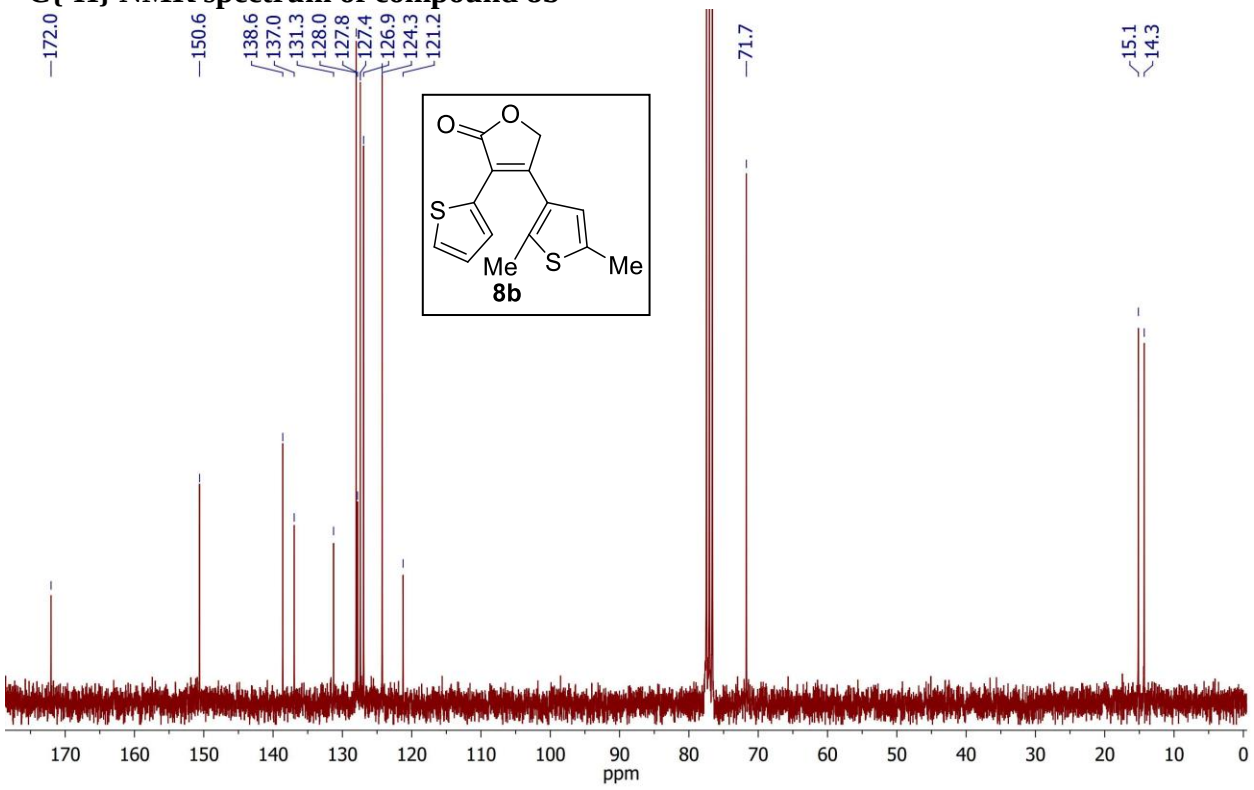


^{1}H NMR spectrum of compound 8b

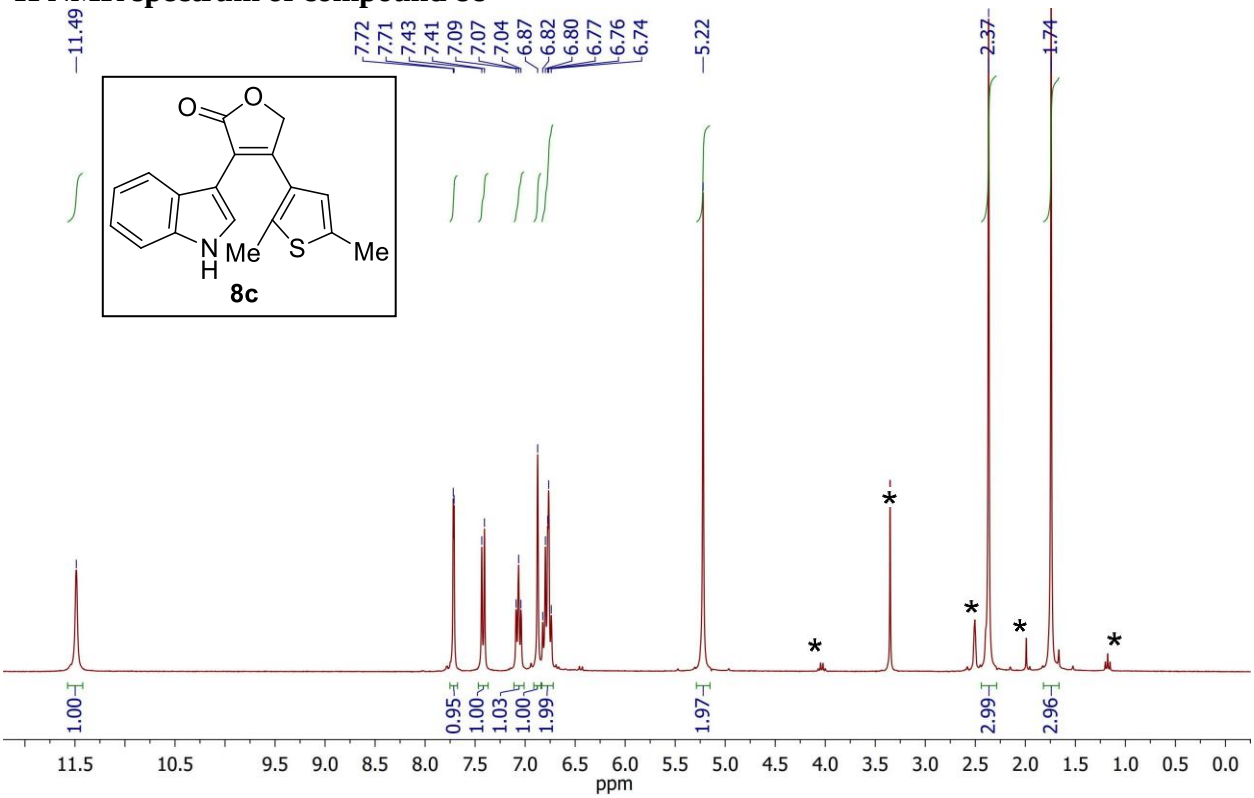


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 8b

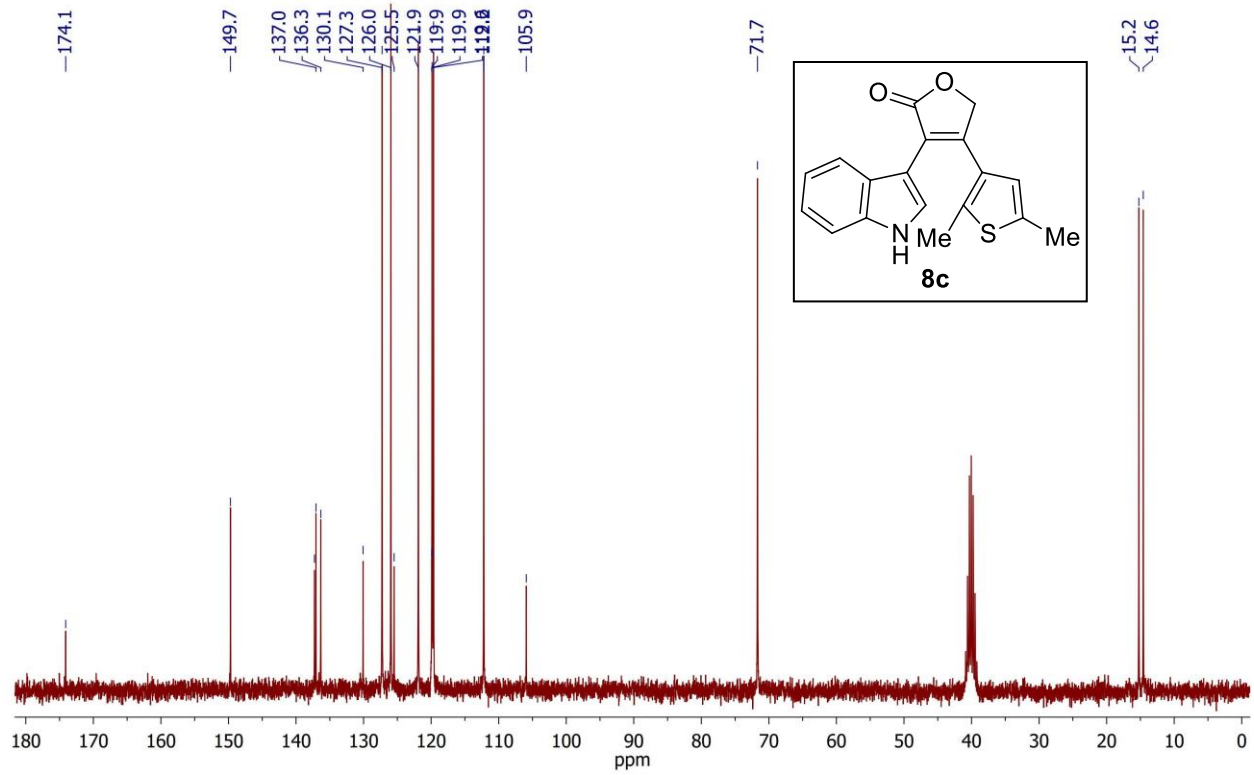


^{1}H NMR spectrum of compound 8c

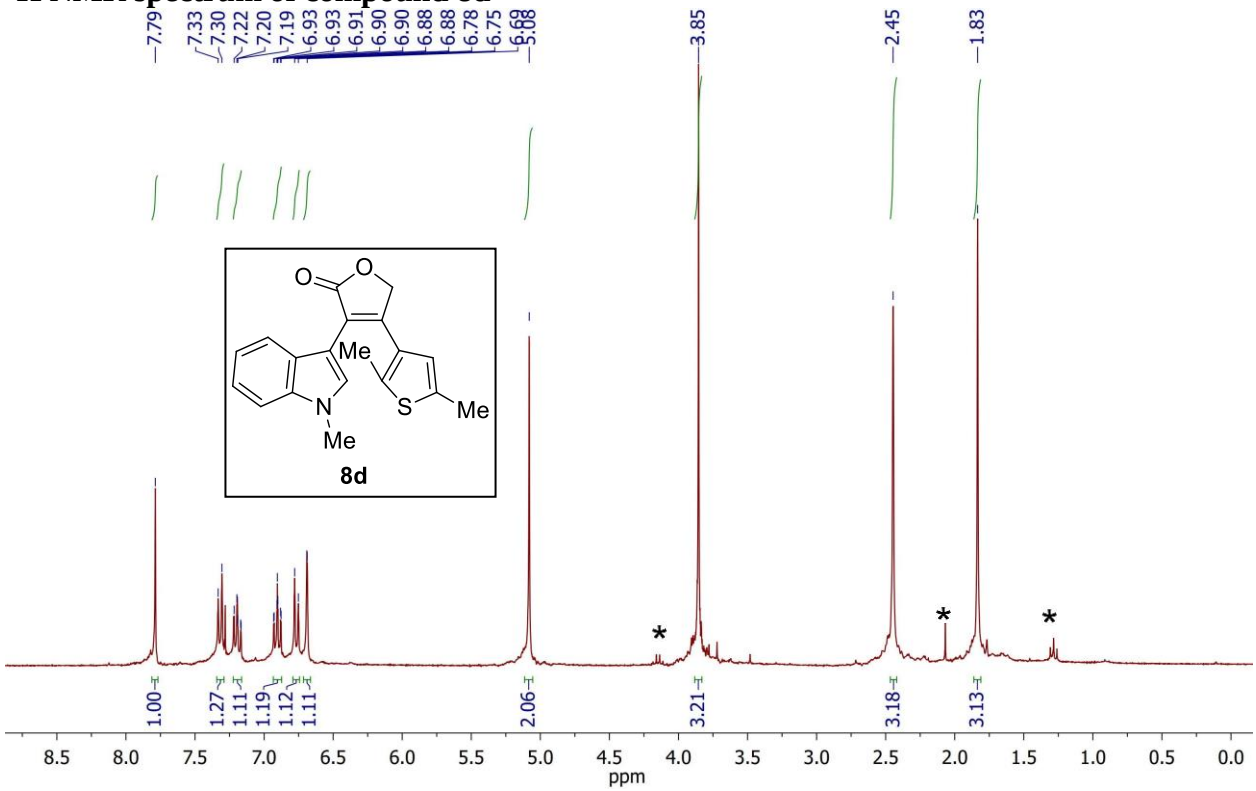


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 8c

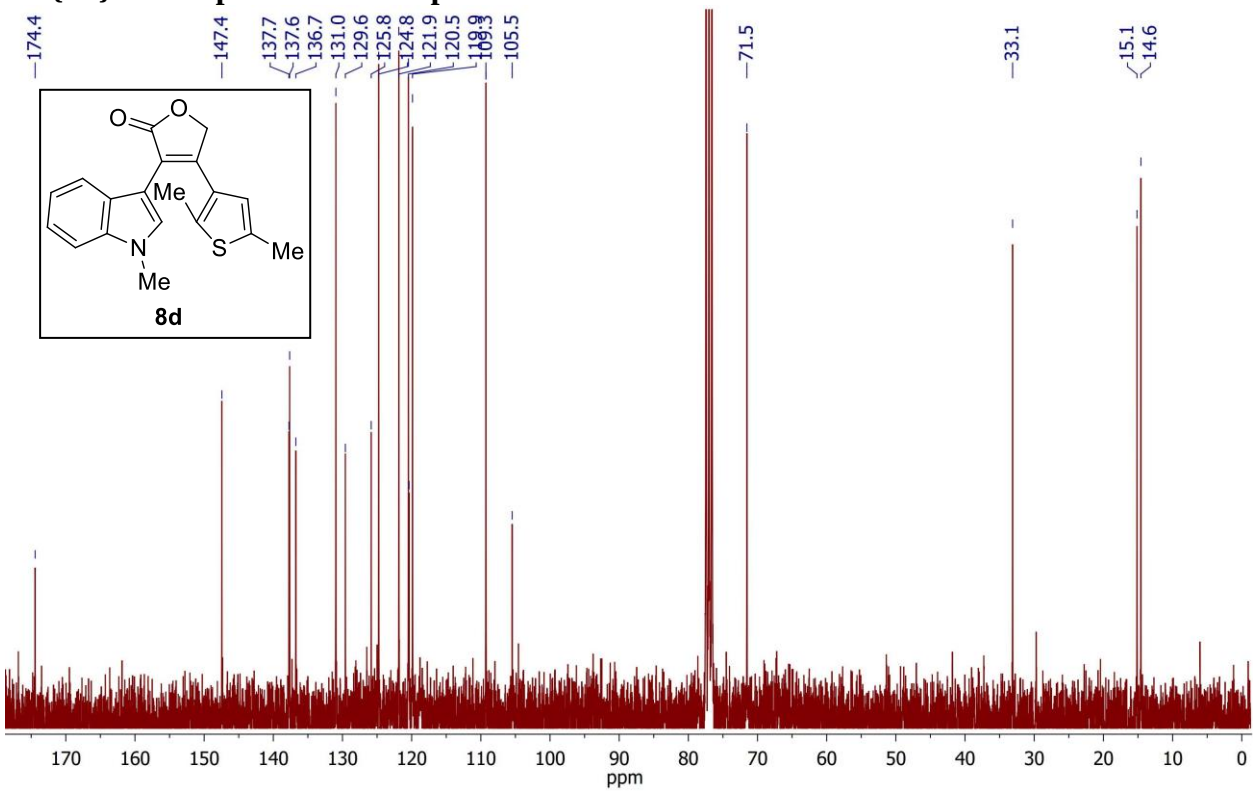


^{1}H NMR spectrum of compound 8d

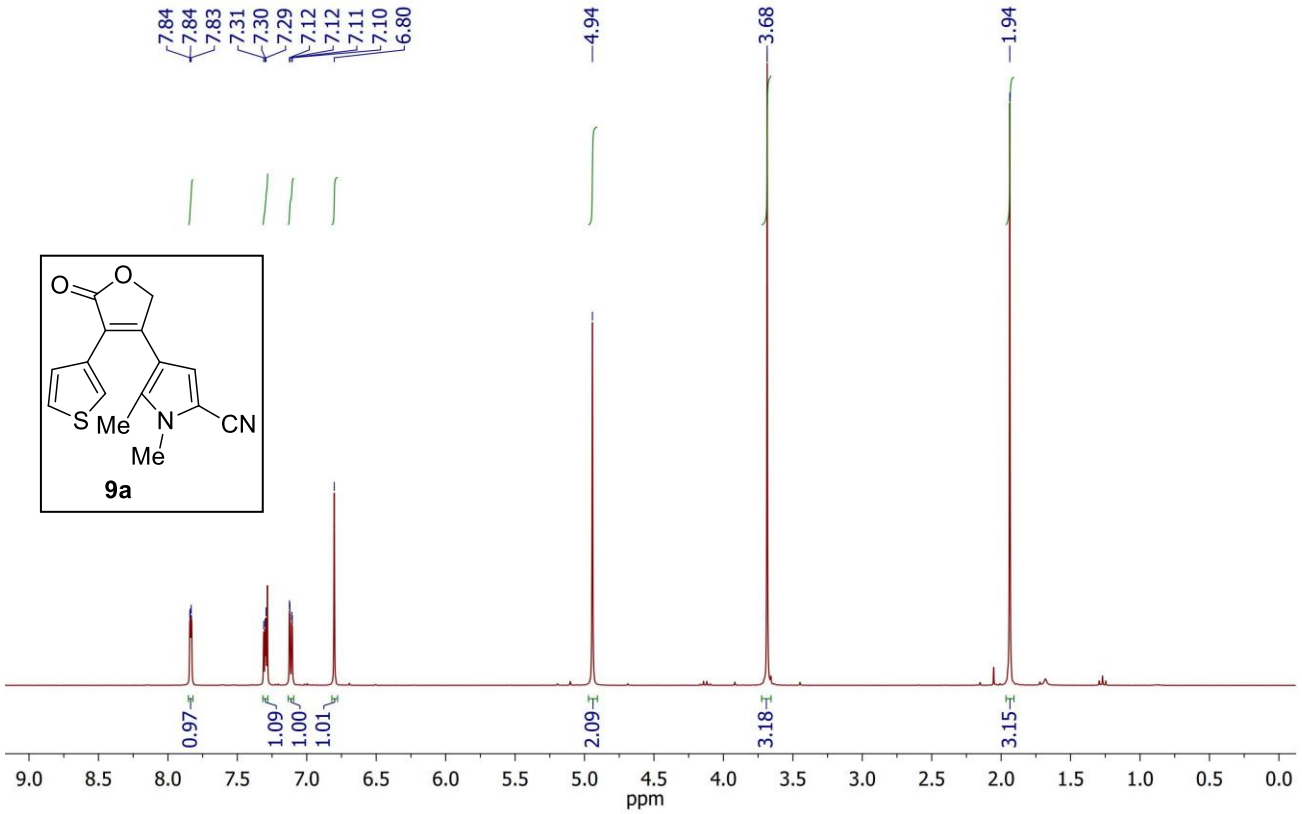


* Ethyl acetate

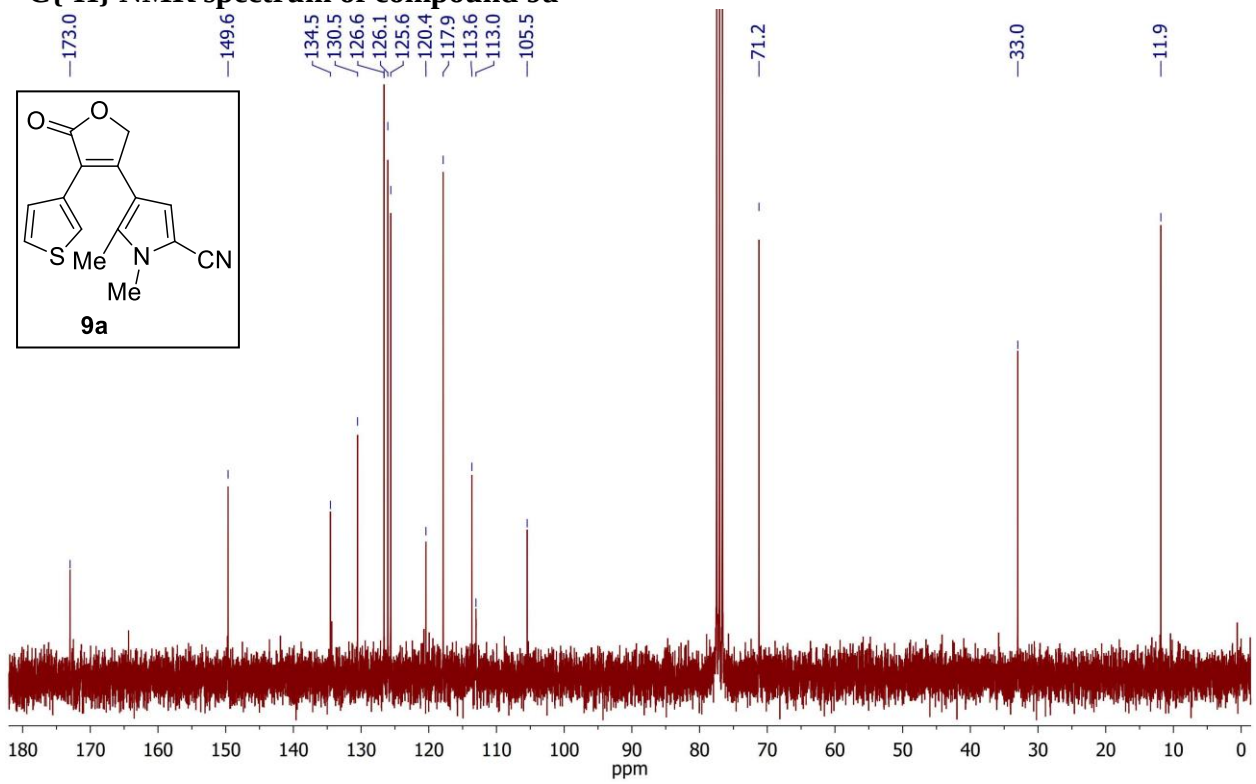
^{13}C{^{1}H} NMR spectrum of compound 8d



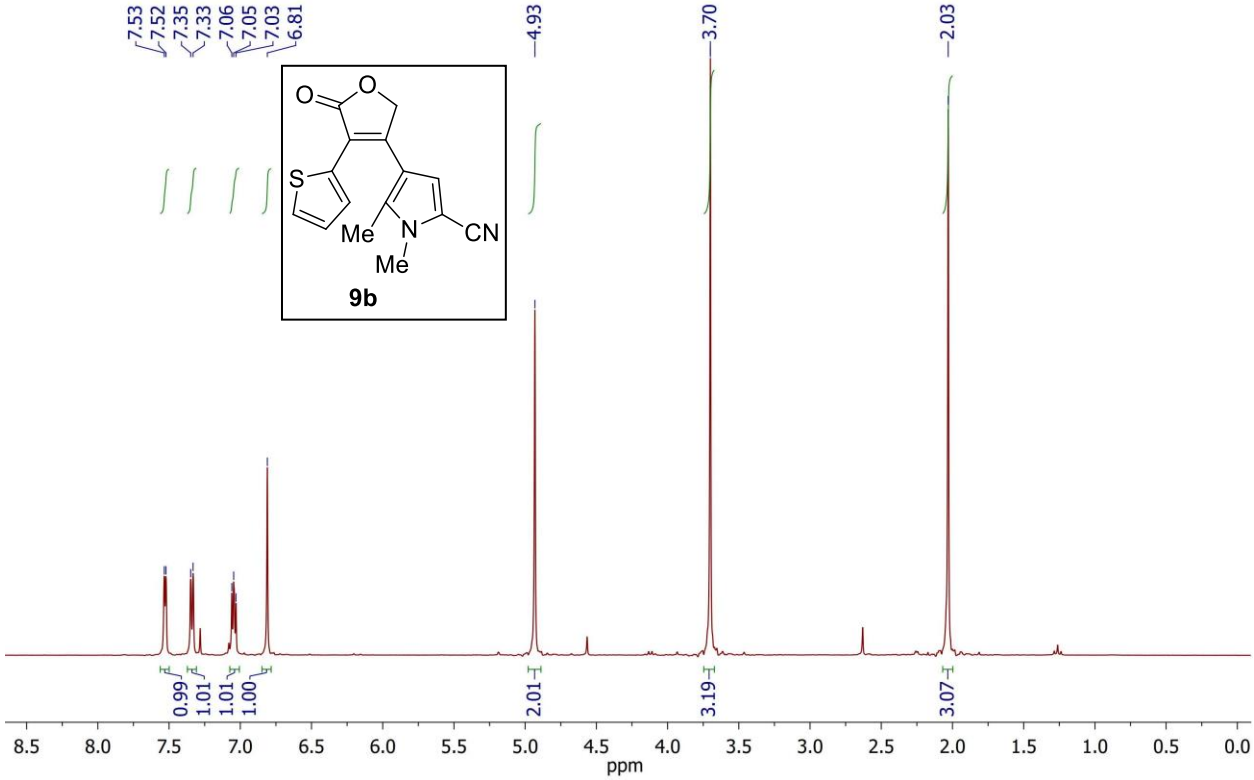
^{1}H NMR spectrum of compound 9a



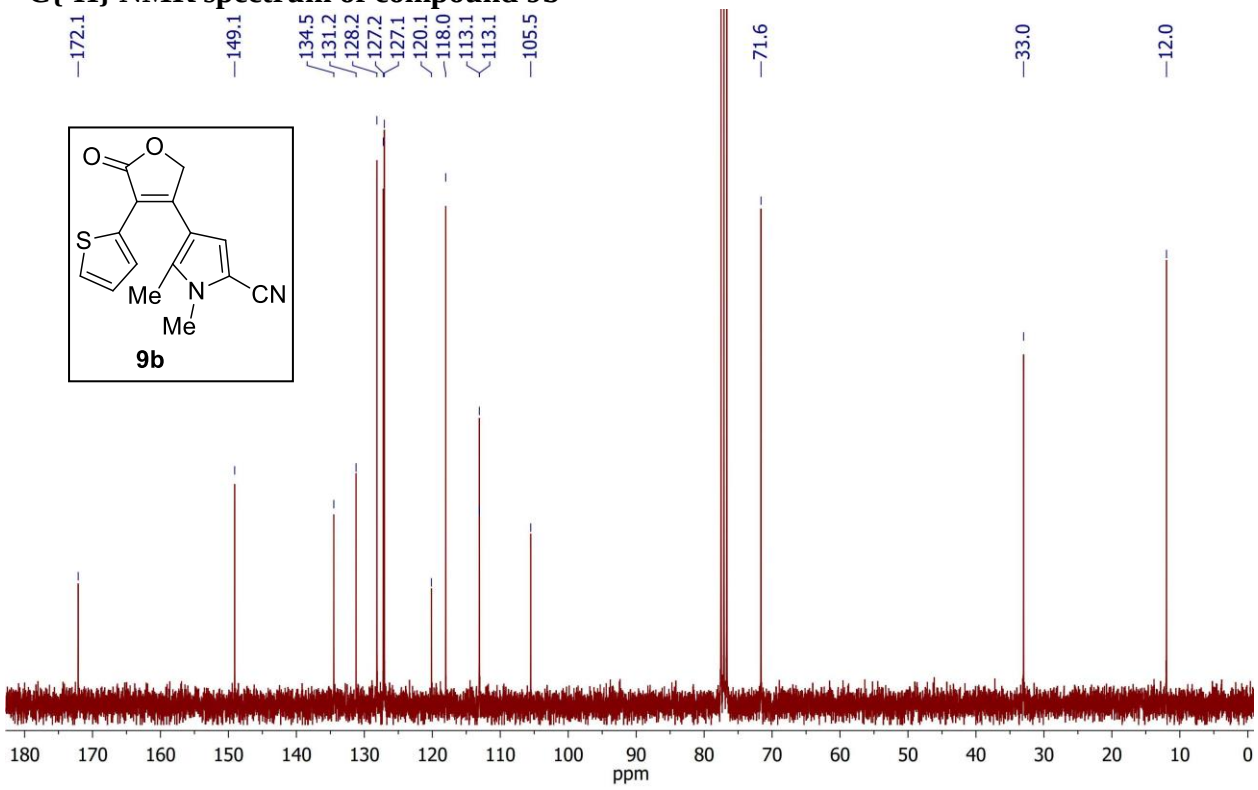
^{13}C{^{1}H} NMR spectrum of compound 9a



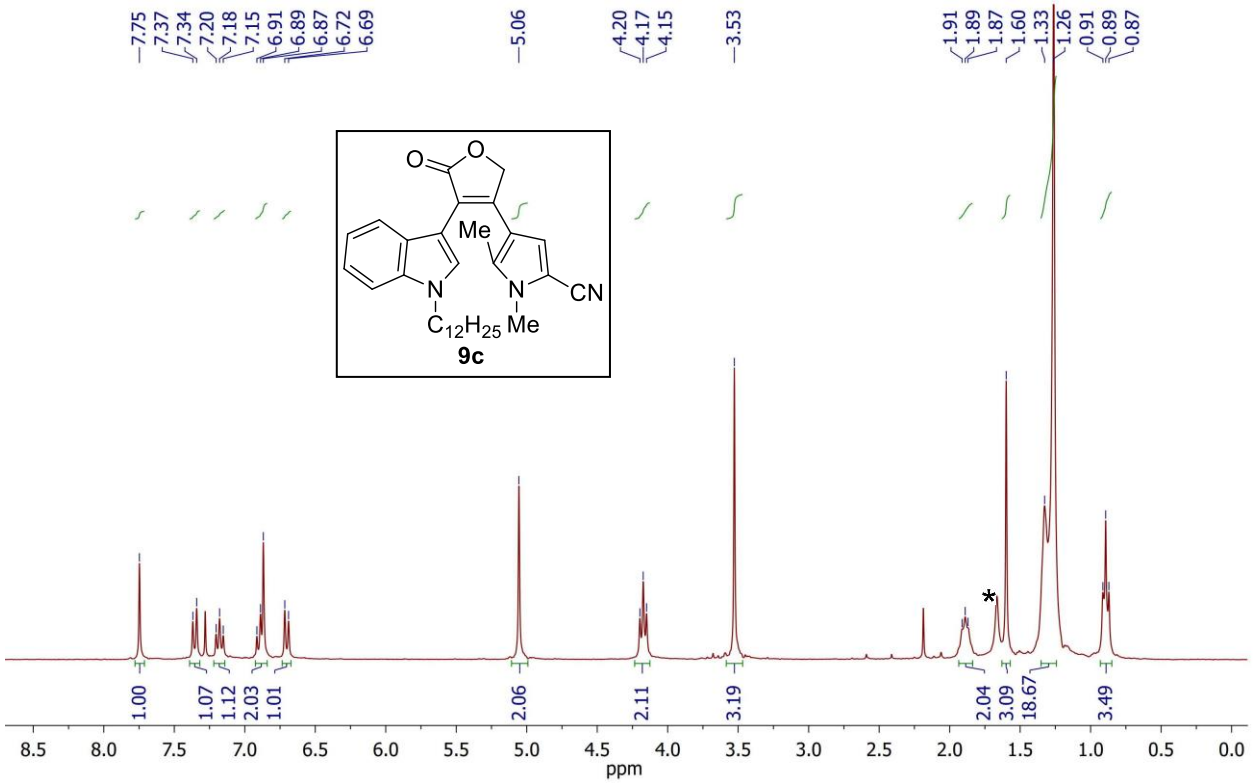
^{1}H NMR spectrum of compound 9b



^{13}C{^{1}H} NMR spectrum of compound 9b

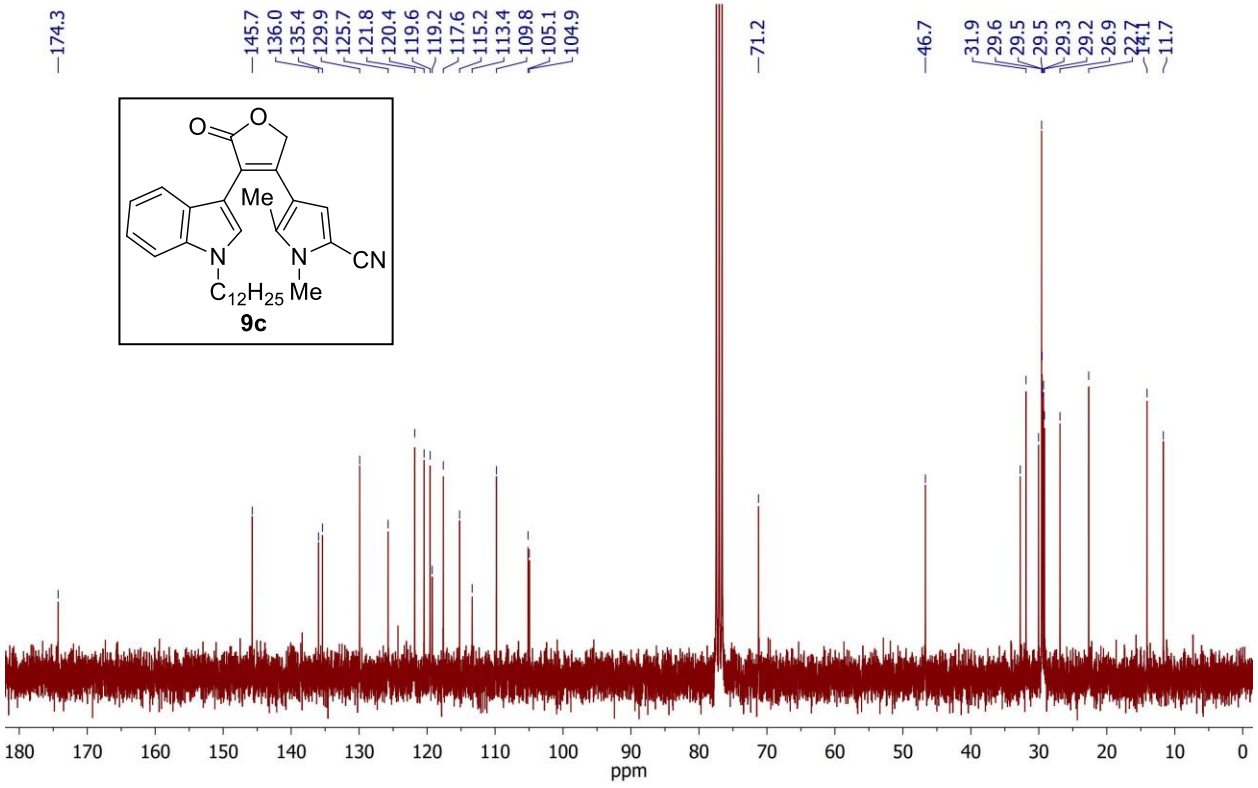


^{1}H NMR spectrum of compound 9c

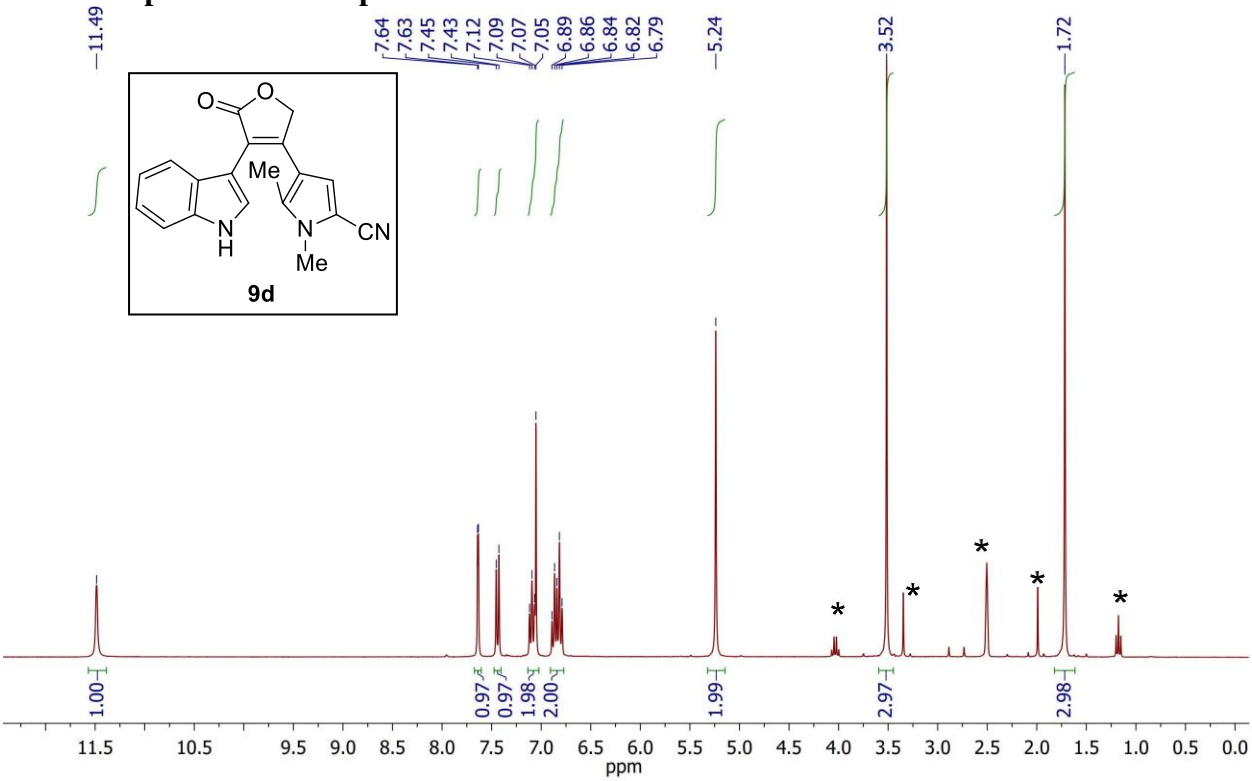


* H_2O

^{13}C{^{1}H} NMR spectrum of compound 9c

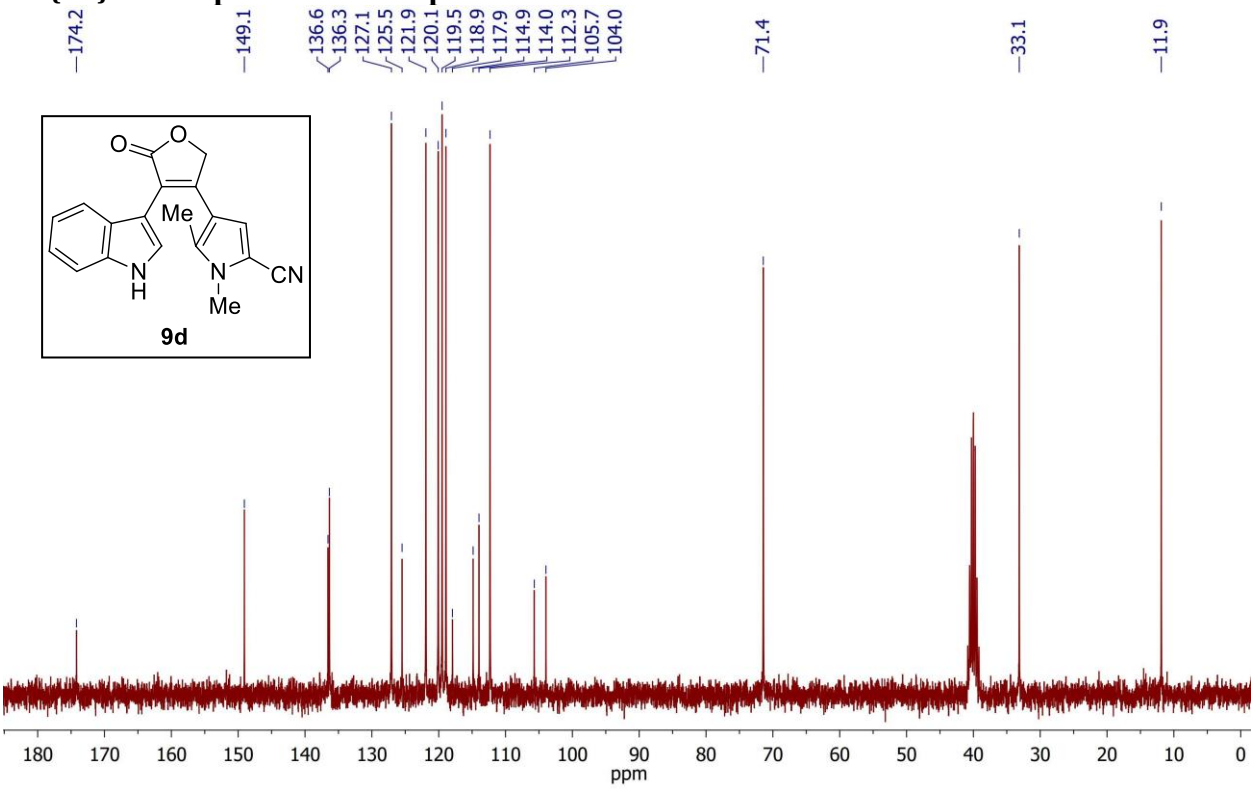


^{1}H NMR spectrum of compound 9d

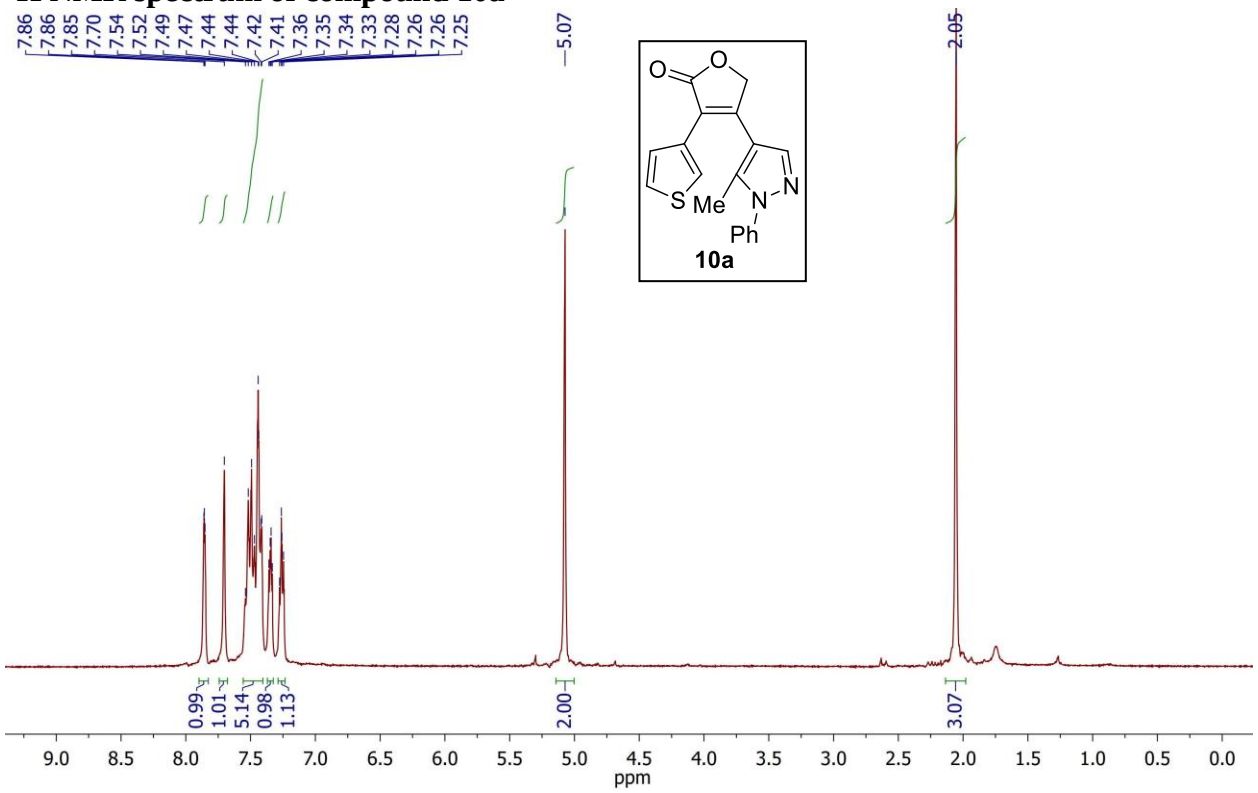


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

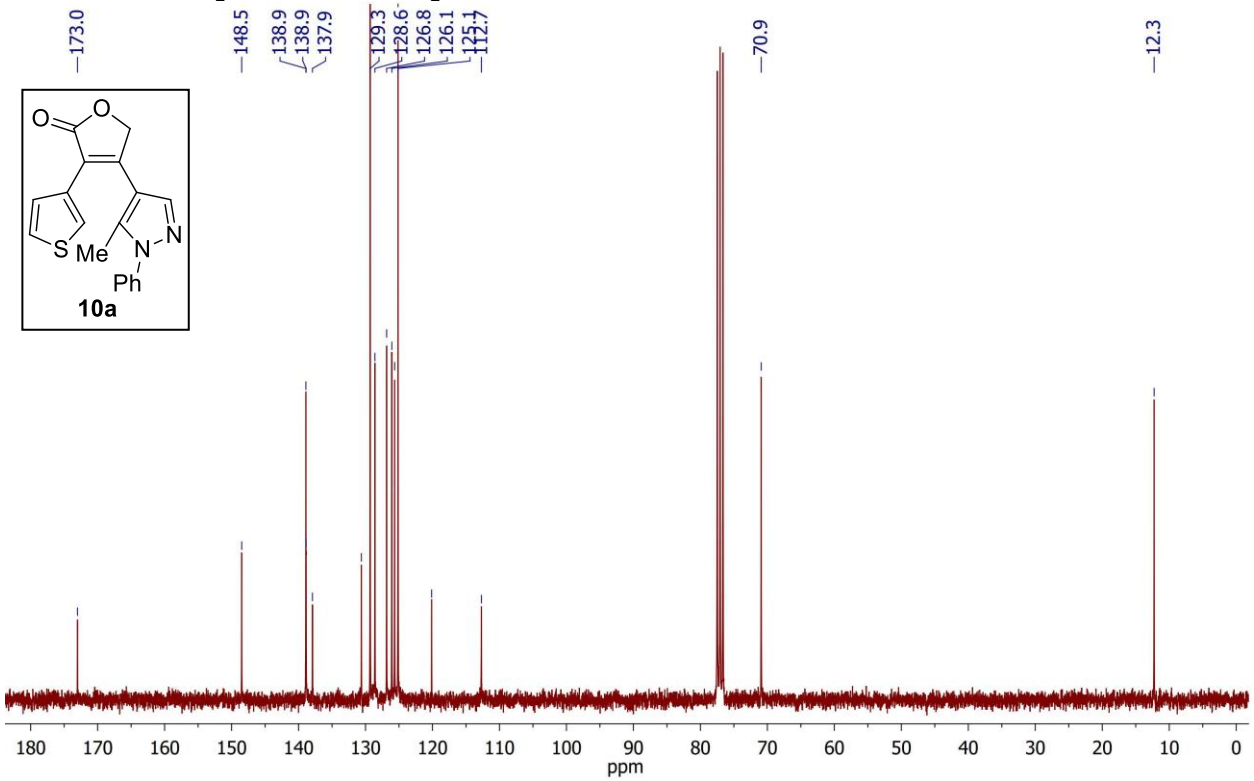
^{13}C{^{1}H} NMR spectrum of compound 9d



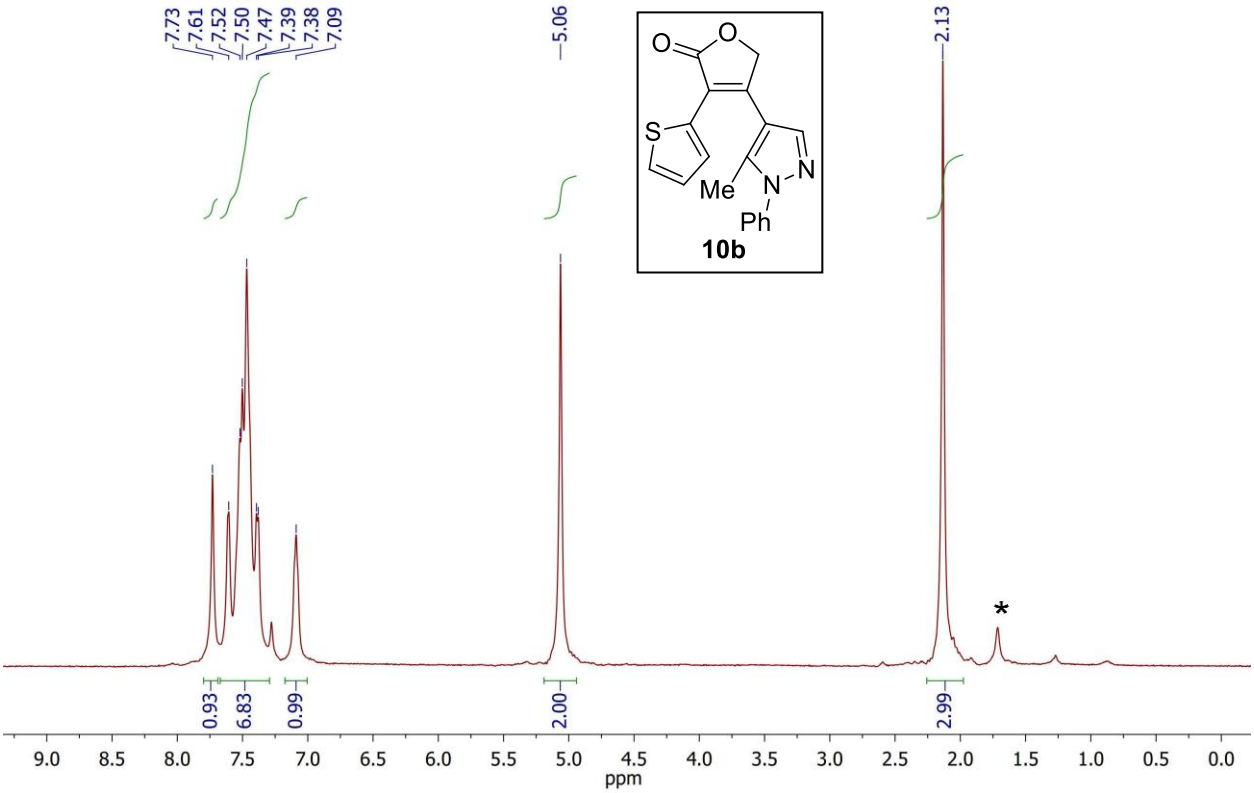
^{1}H NMR spectrum of compound 10a



^{13}C{^{1}H} NMR spectrum of compound 10a

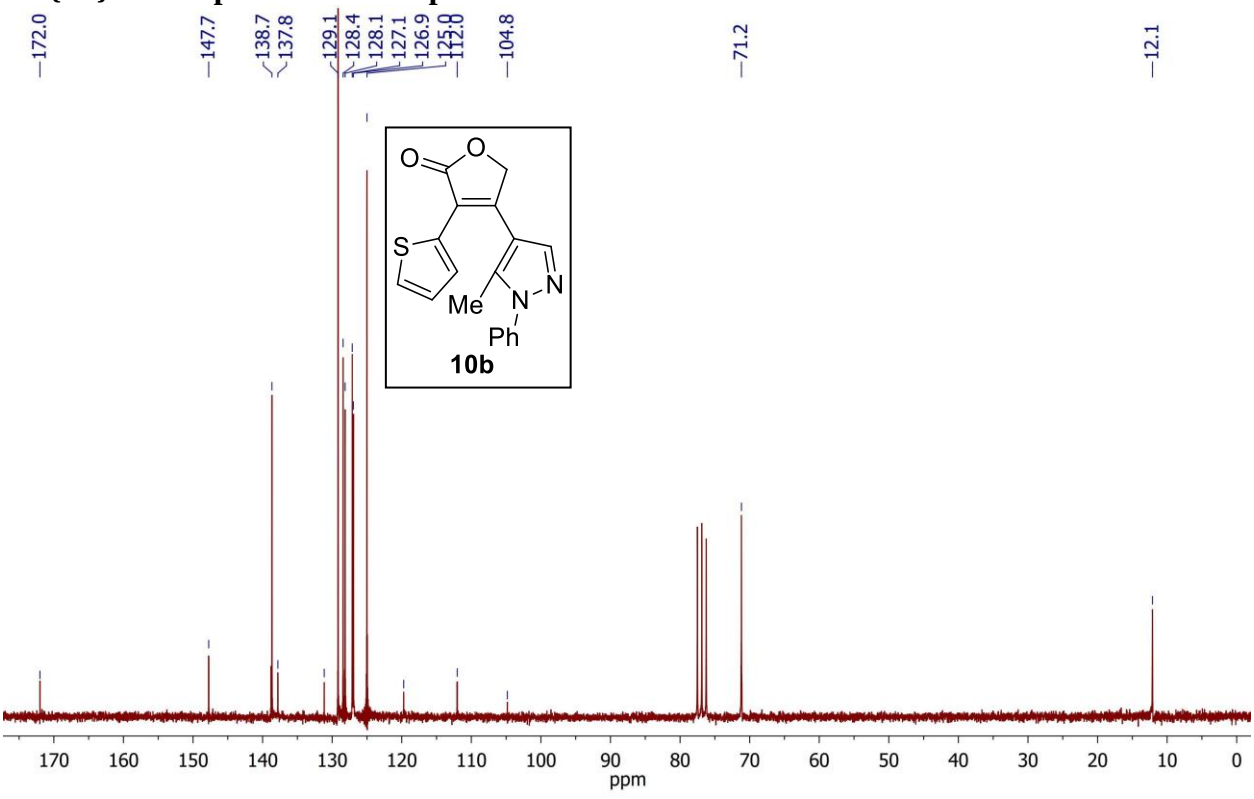


^{1}H NMR spectrum of compound 10b

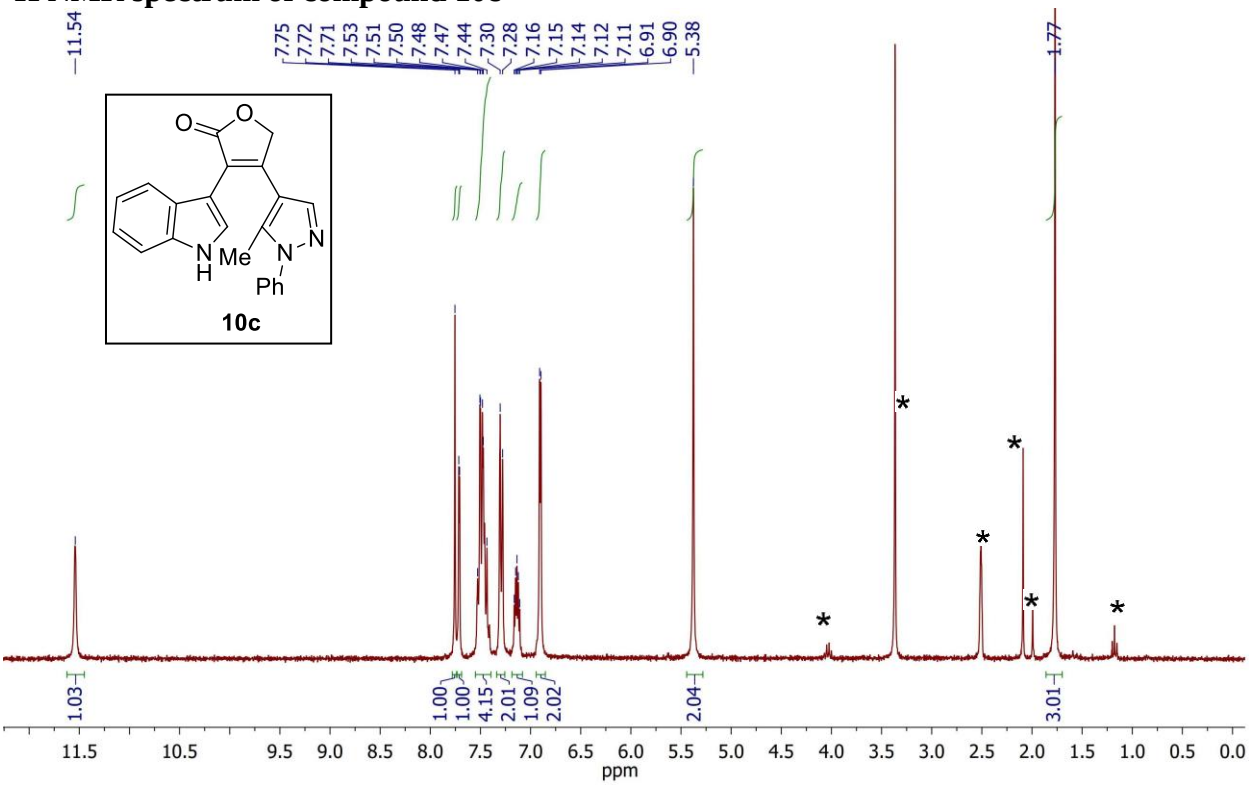


* H_2O

^{13}C{^{1}H} NMR spectrum of compound 10b

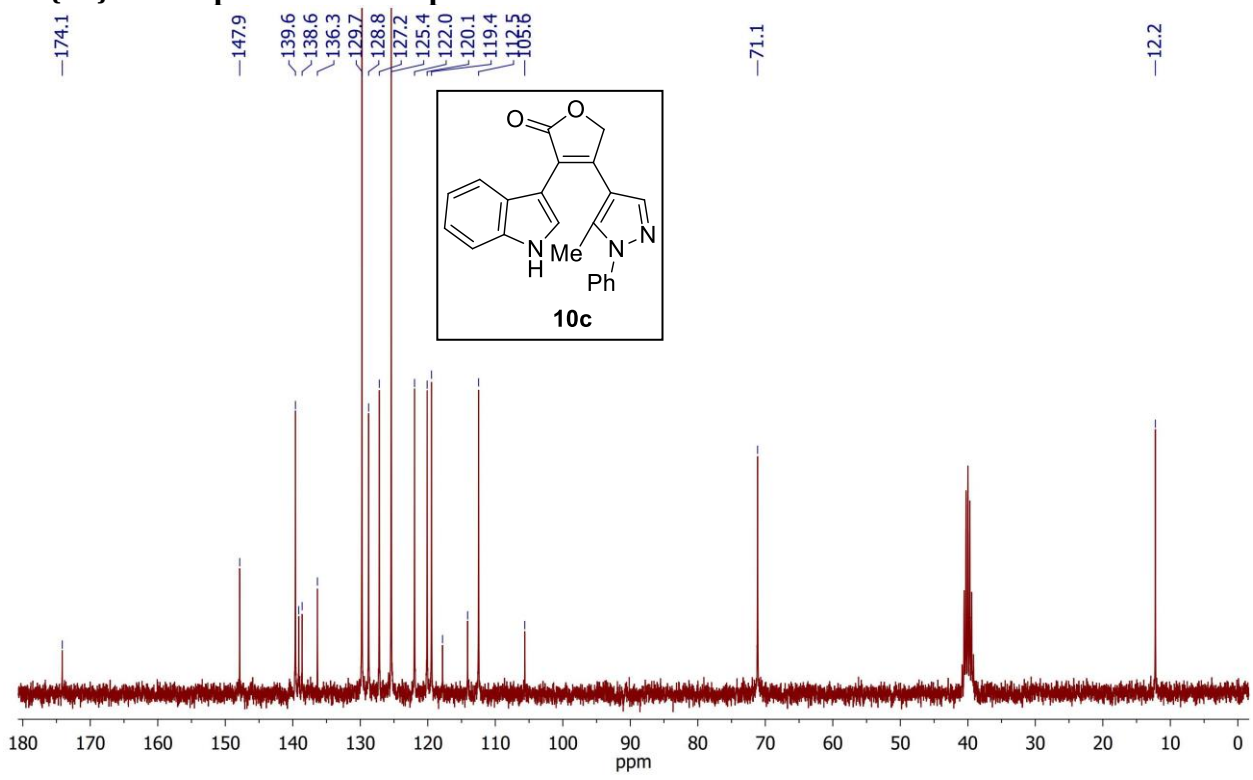


^{1}H NMR spectrum of compound 10c

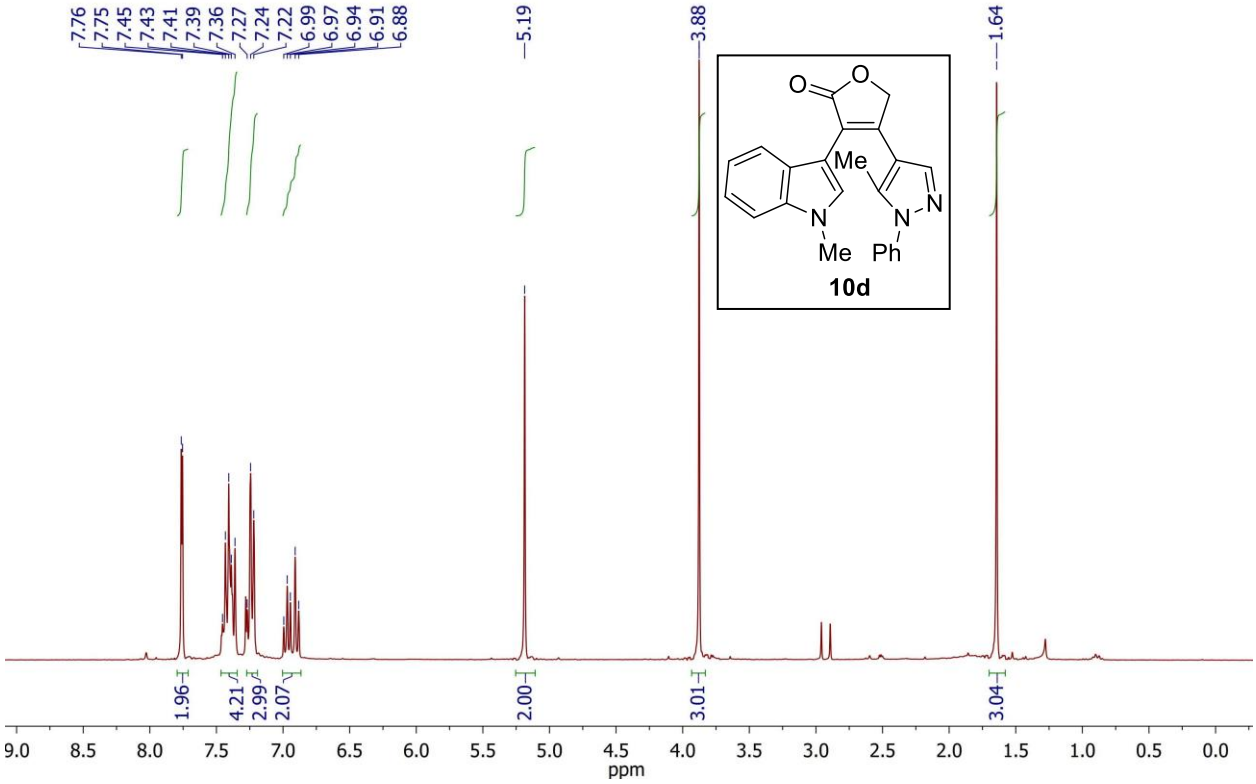


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

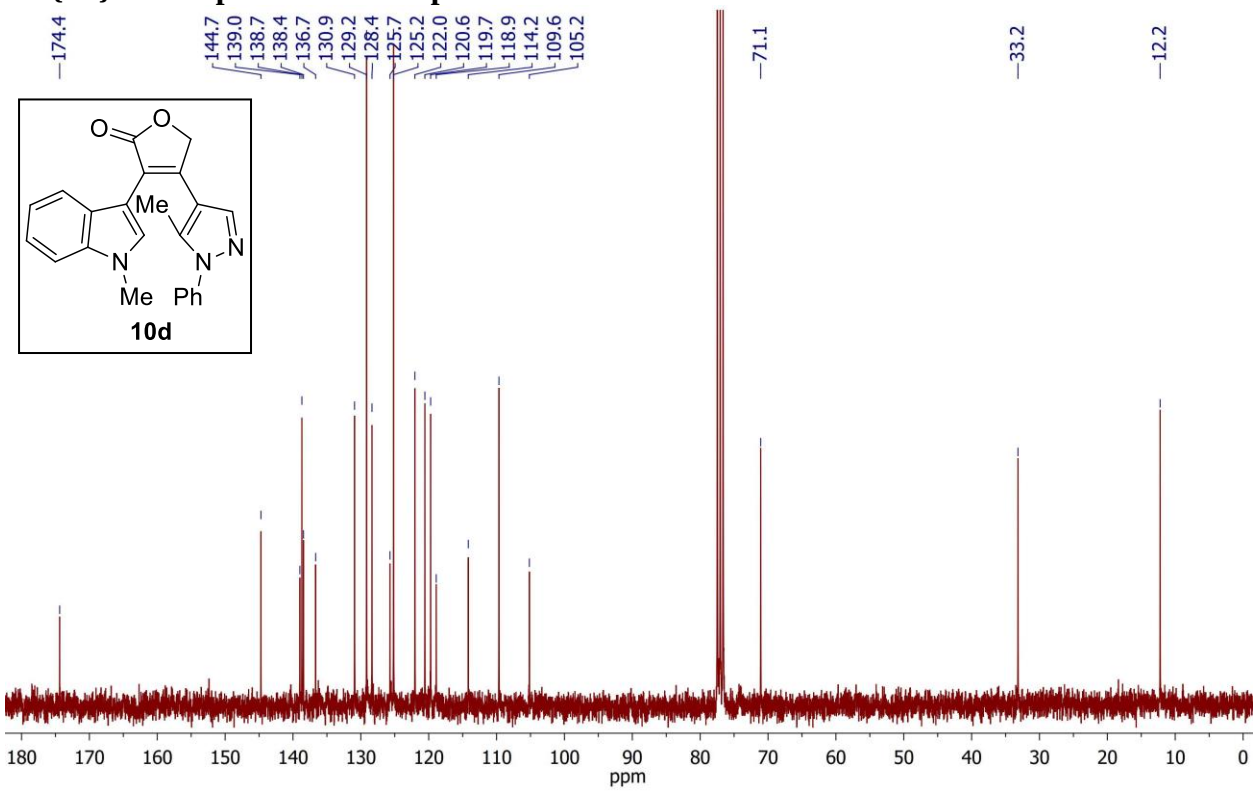
^{13}C{^{1}H} NMR spectrum of compound 10c



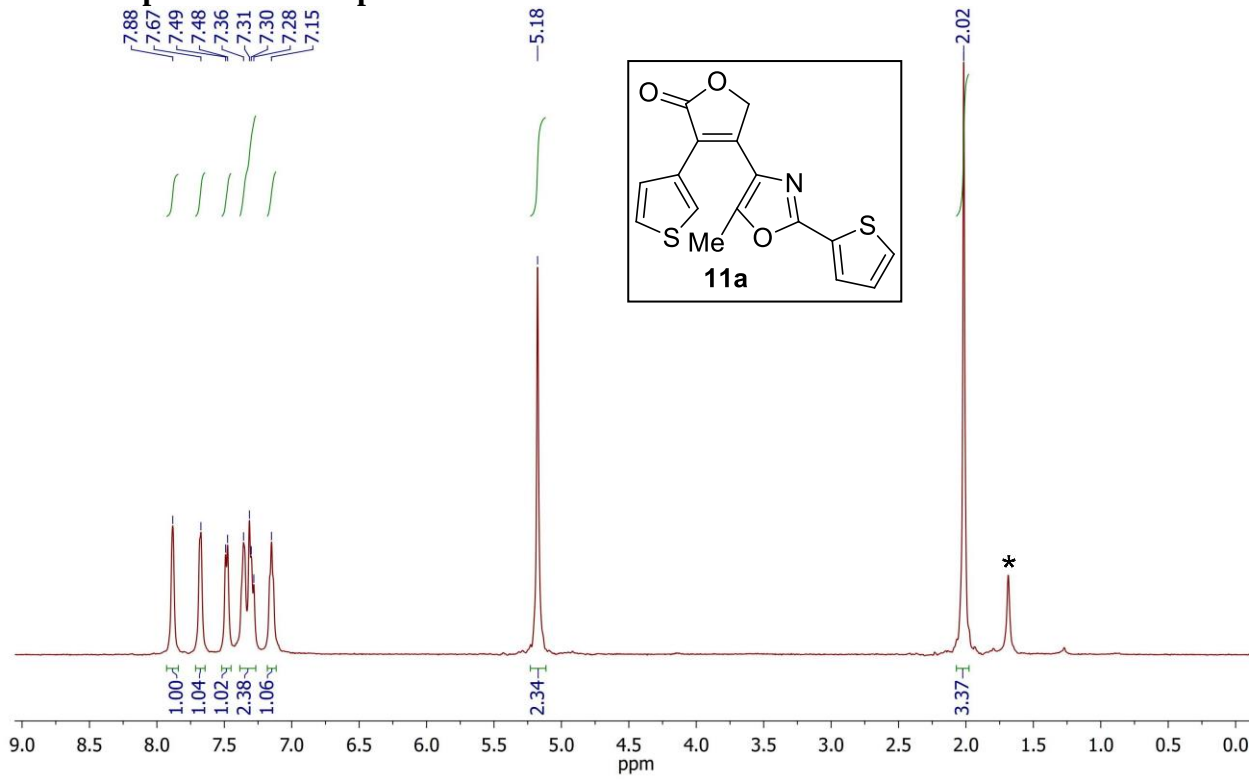
^{1}H NMR spectrum of compound 10d



^{13}C{^{1}H} NMR spectrum of compound 10d

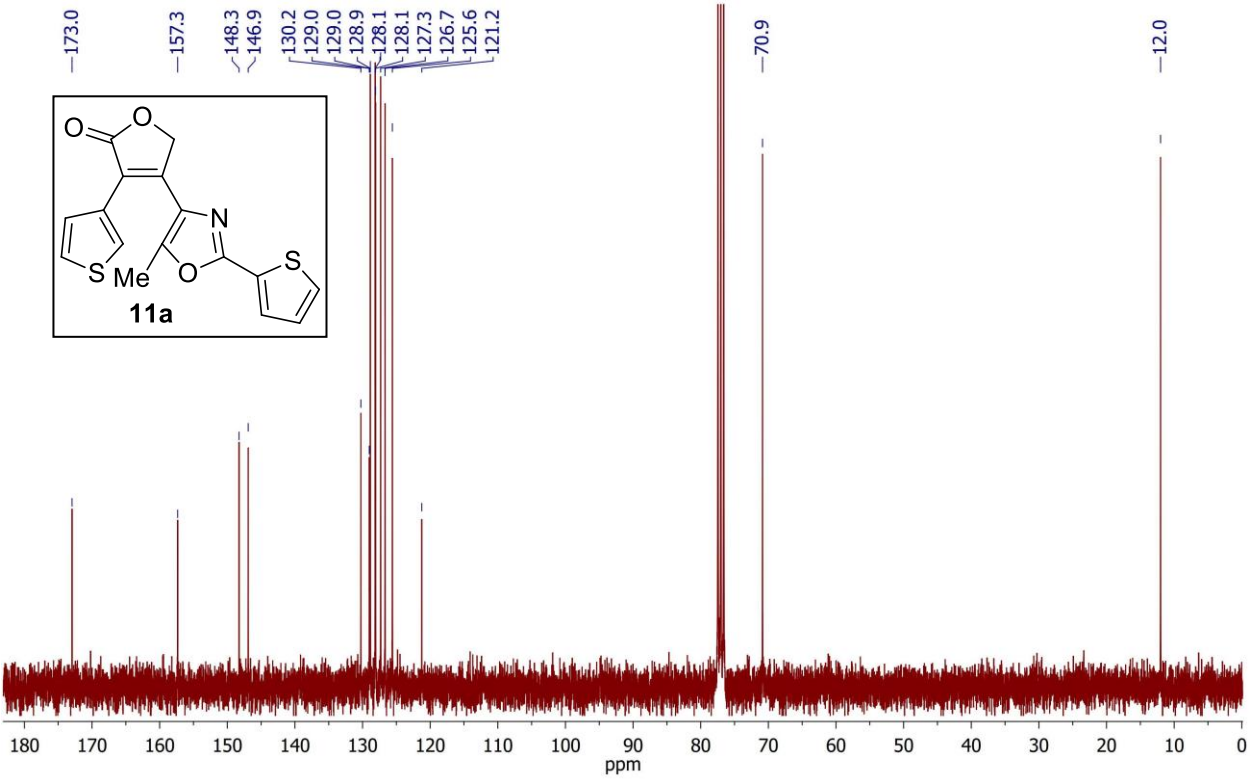


^{1}H NMR spectrum of compound 11a

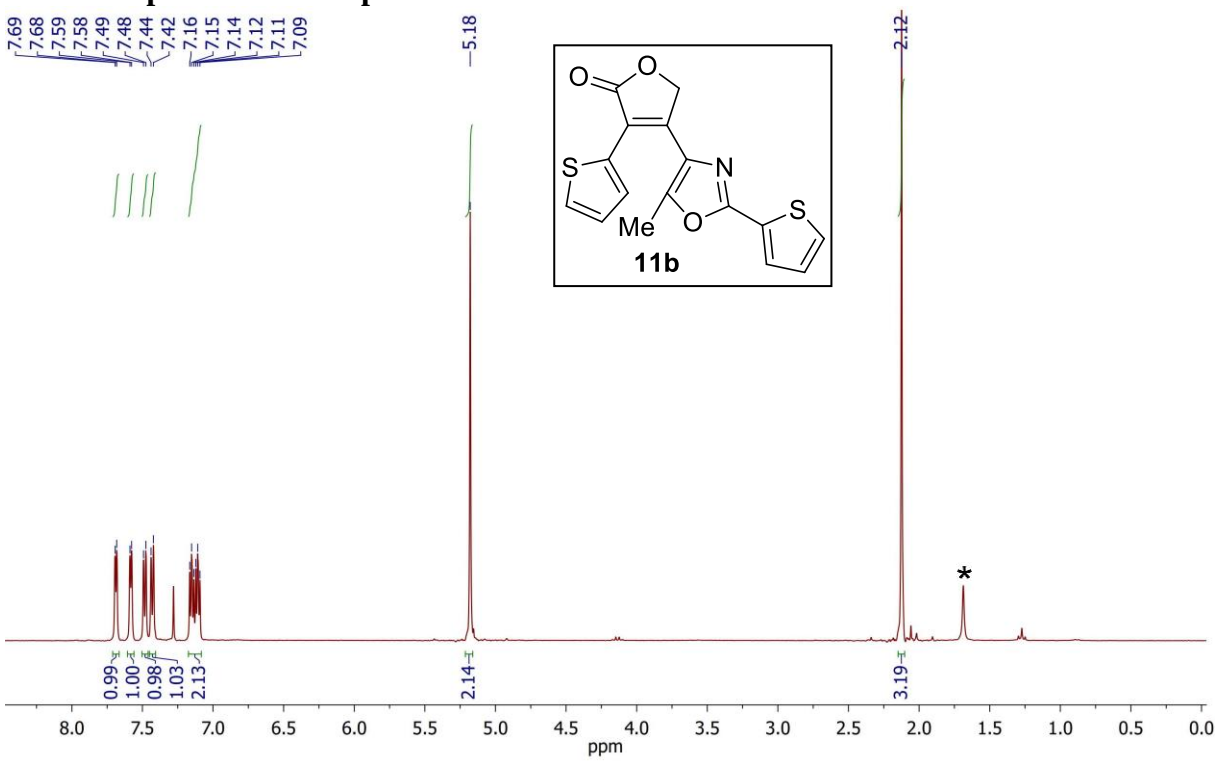


* H_2O

^{13}C{^{1}H} NMR spectrum of compound 11a

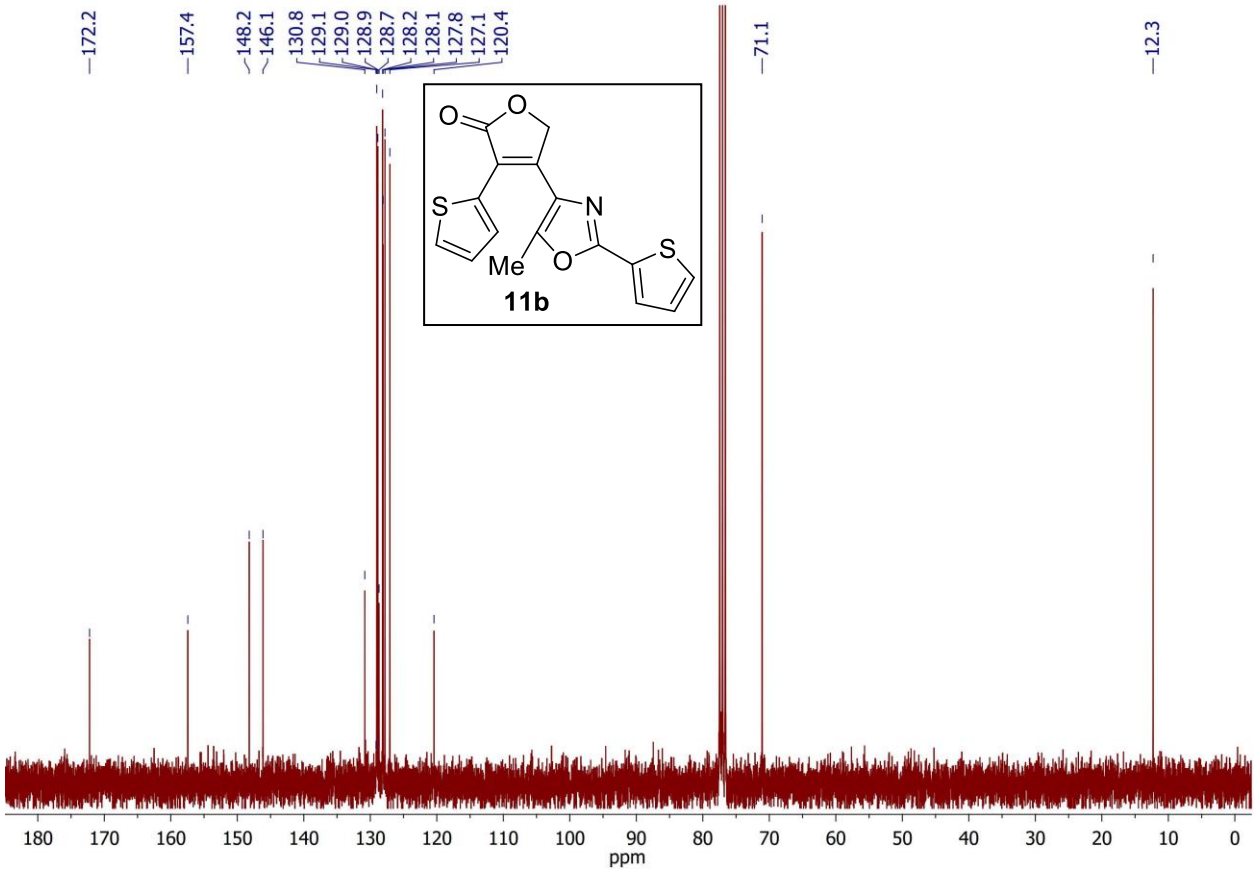


^{1}H NMR spectrum of compound 11b

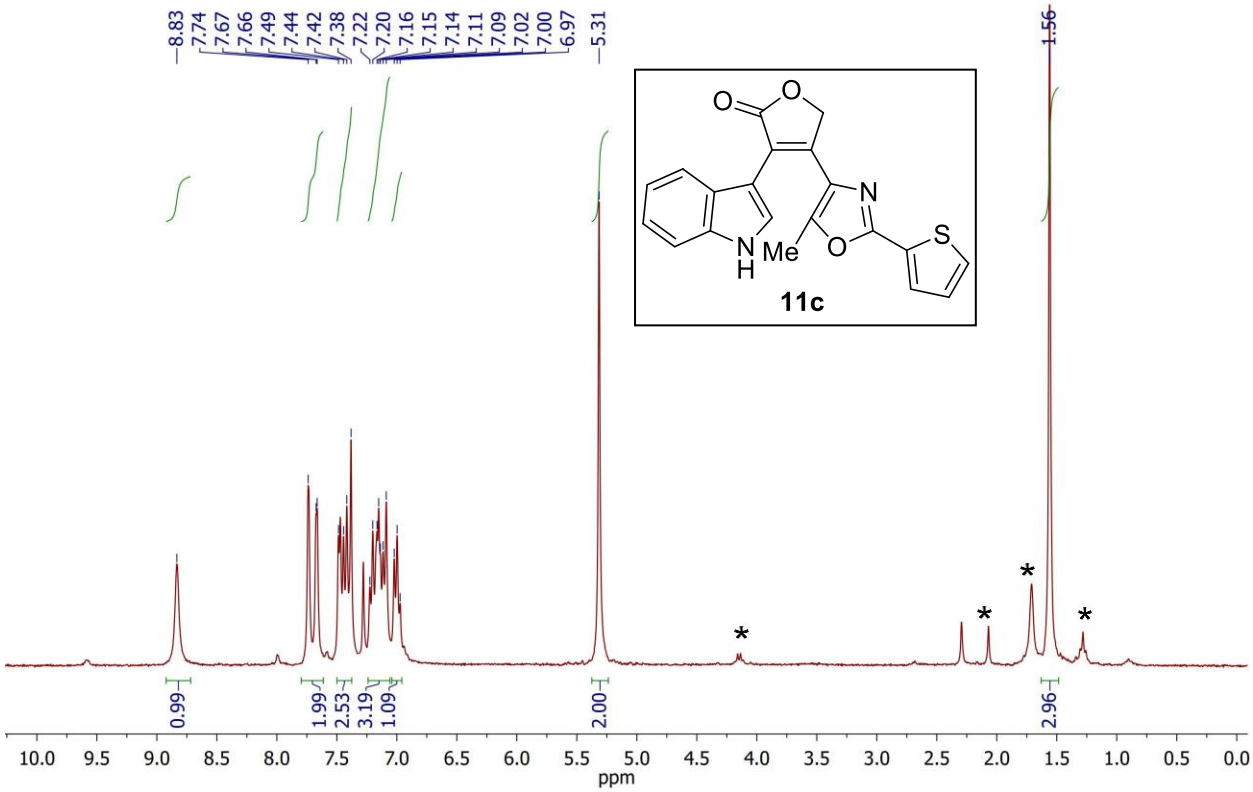


* H_2O

^{13}C{^{1}H} NMR spectrum of compound 11b

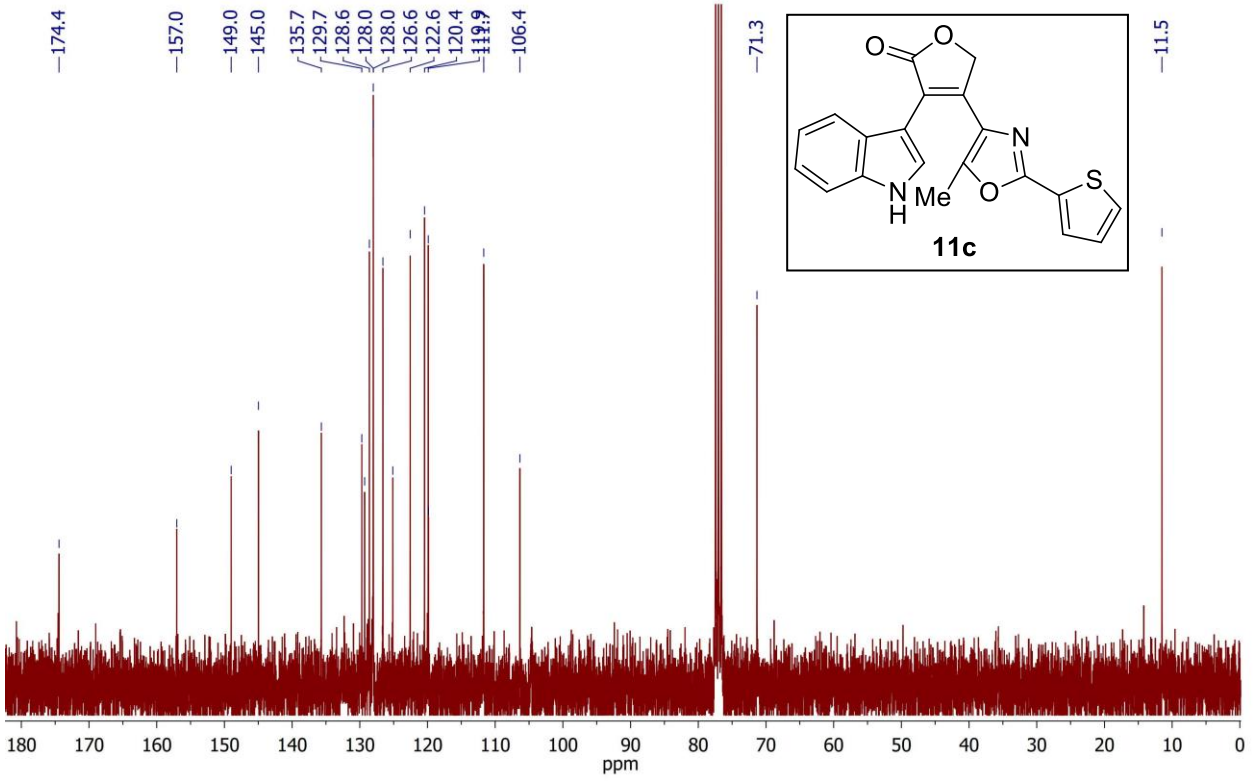


^{1}H NMR spectrum of compound 11c

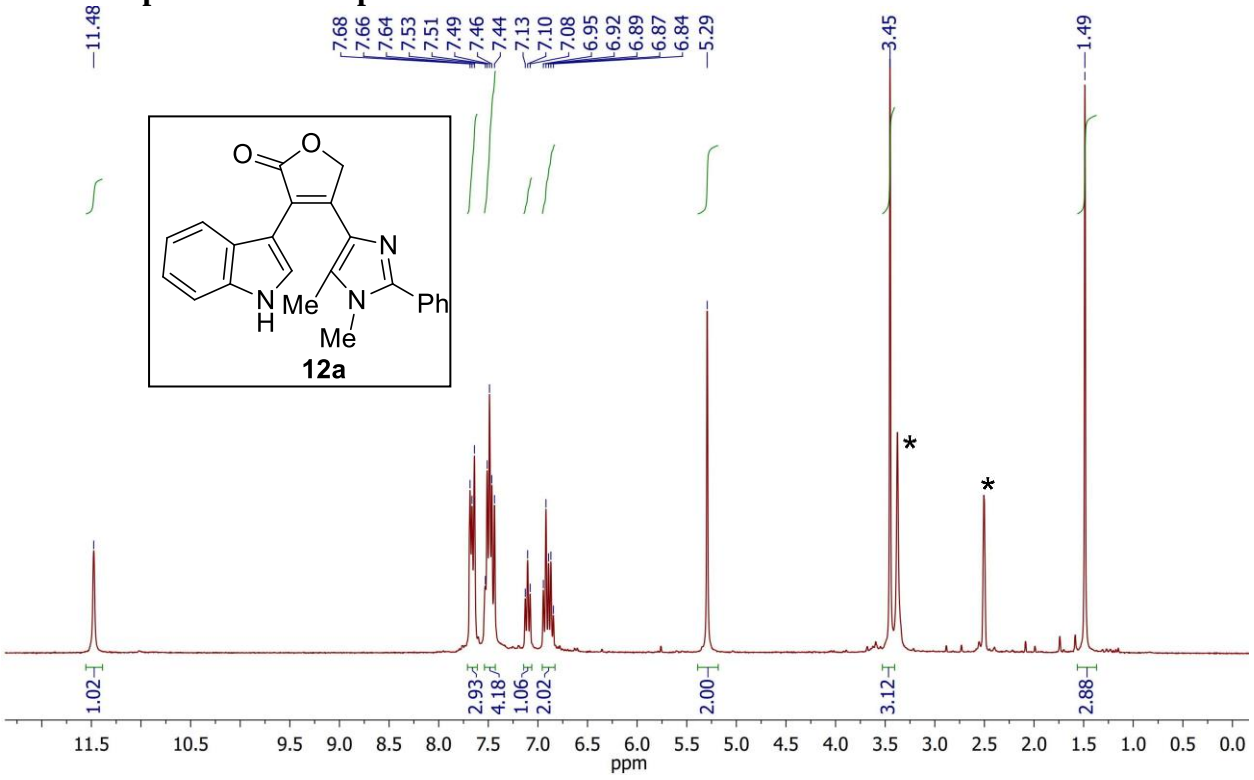


* Ethyl acetate and H_2O

^{13}C{^{1}H} NMR spectrum of compound 11c

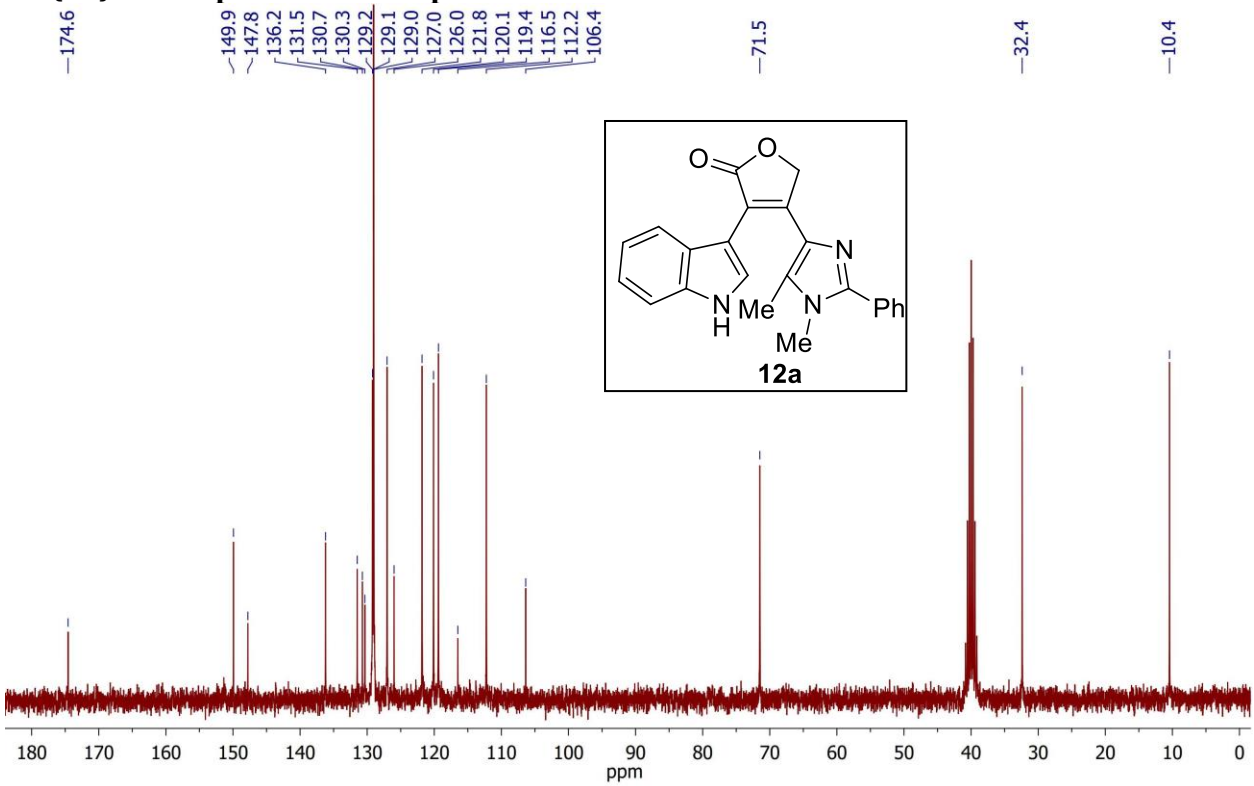


^{1}H NMR spectrum of compound 12a

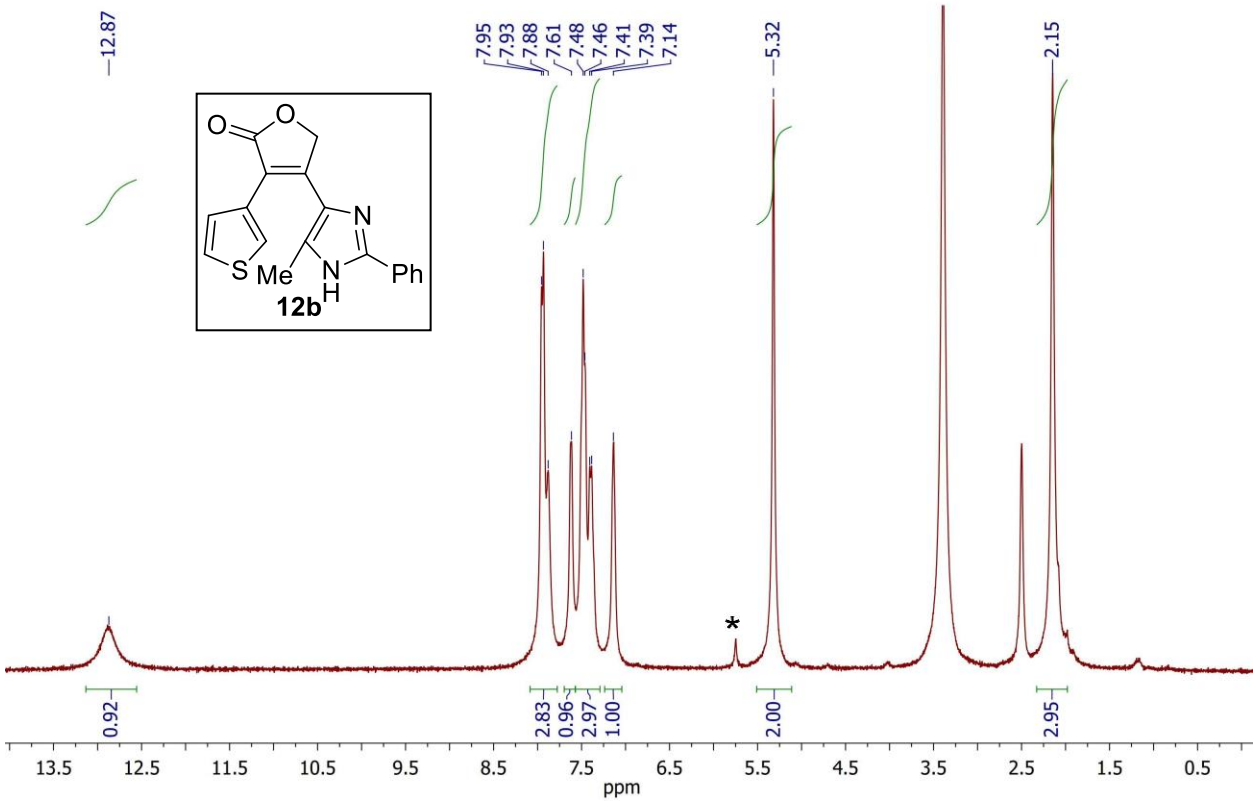


* H_2O and DMSO

^{13}C{^{1}H} NMR spectrum of compound 12a

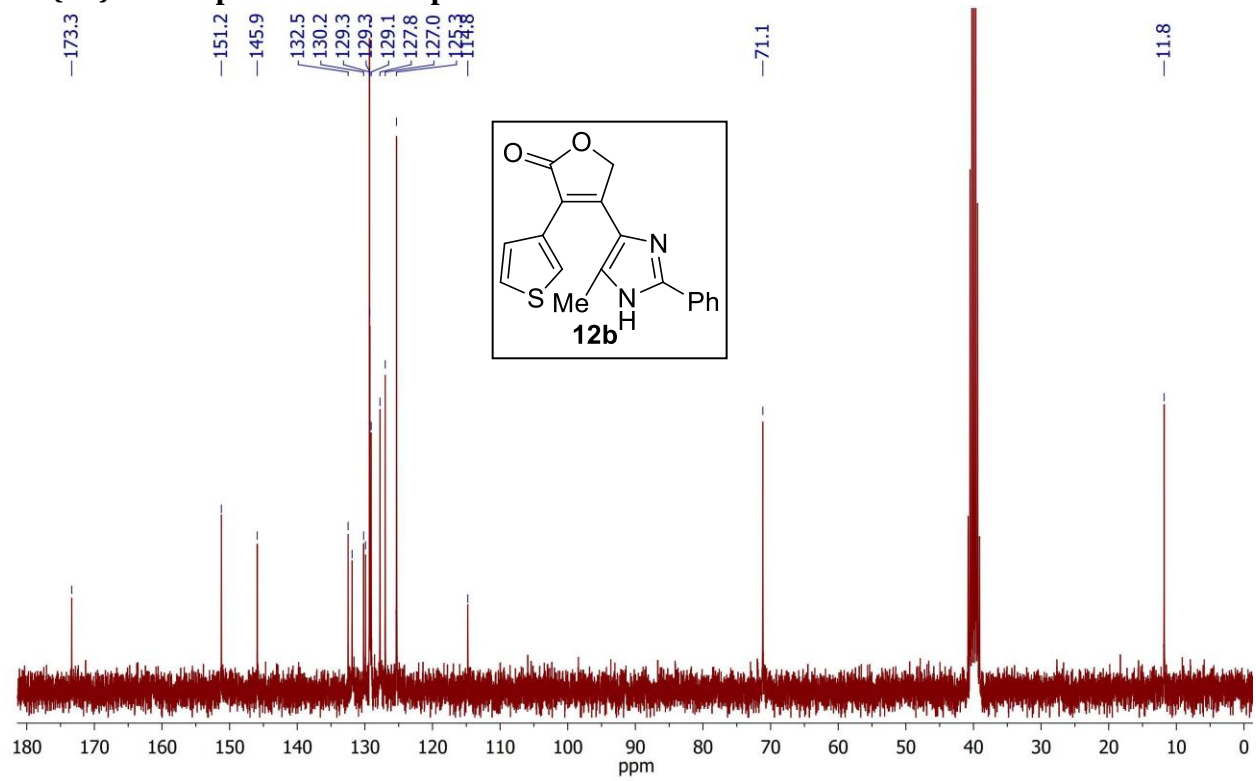


^{1}H NMR spectrum of compound 12b

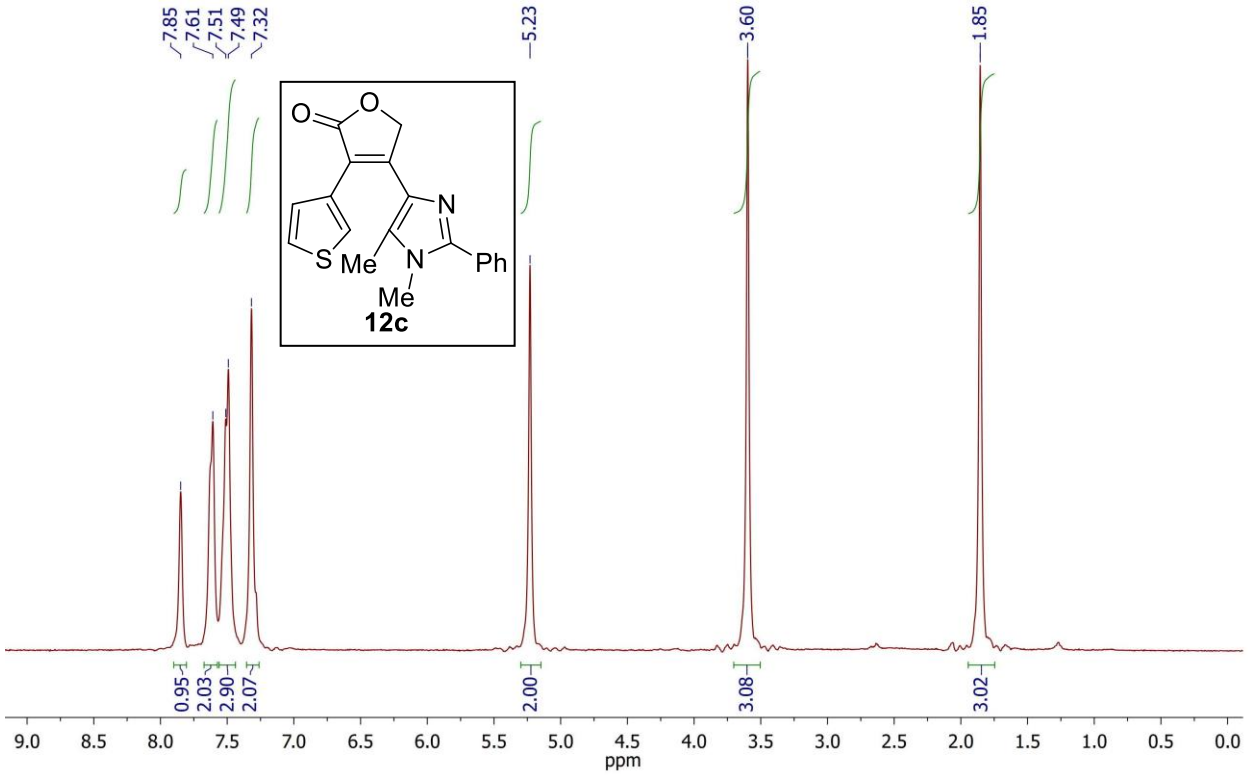


* Dichloromethane

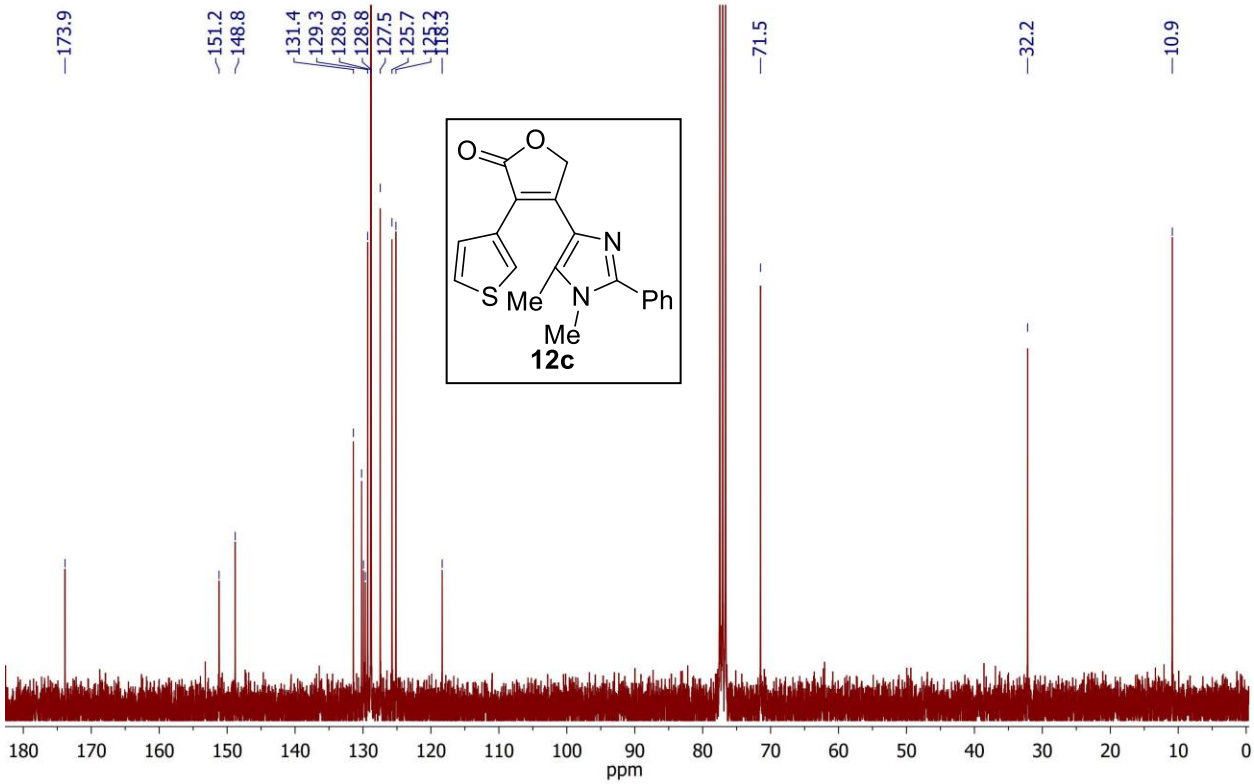
^{13}C{^{1}H} NMR spectrum of compound 12b



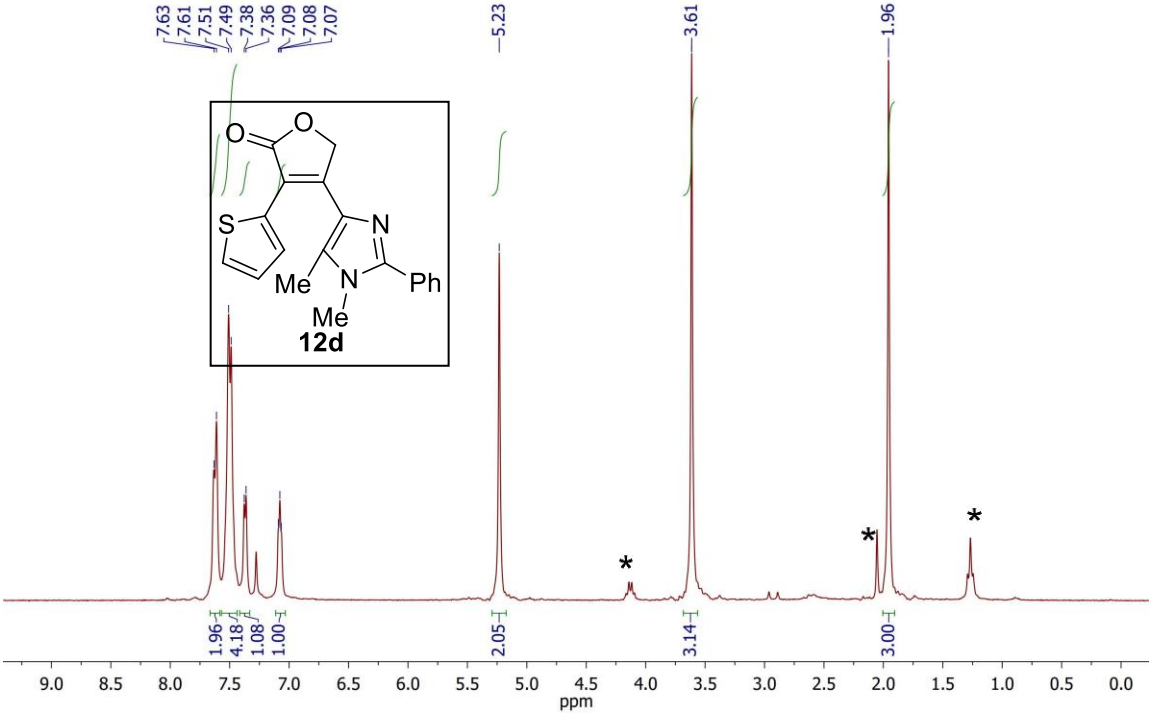
^{1}H NMR spectrum of compound 12c



^{13}C{^{1}H} NMR spectrum of compound 12c

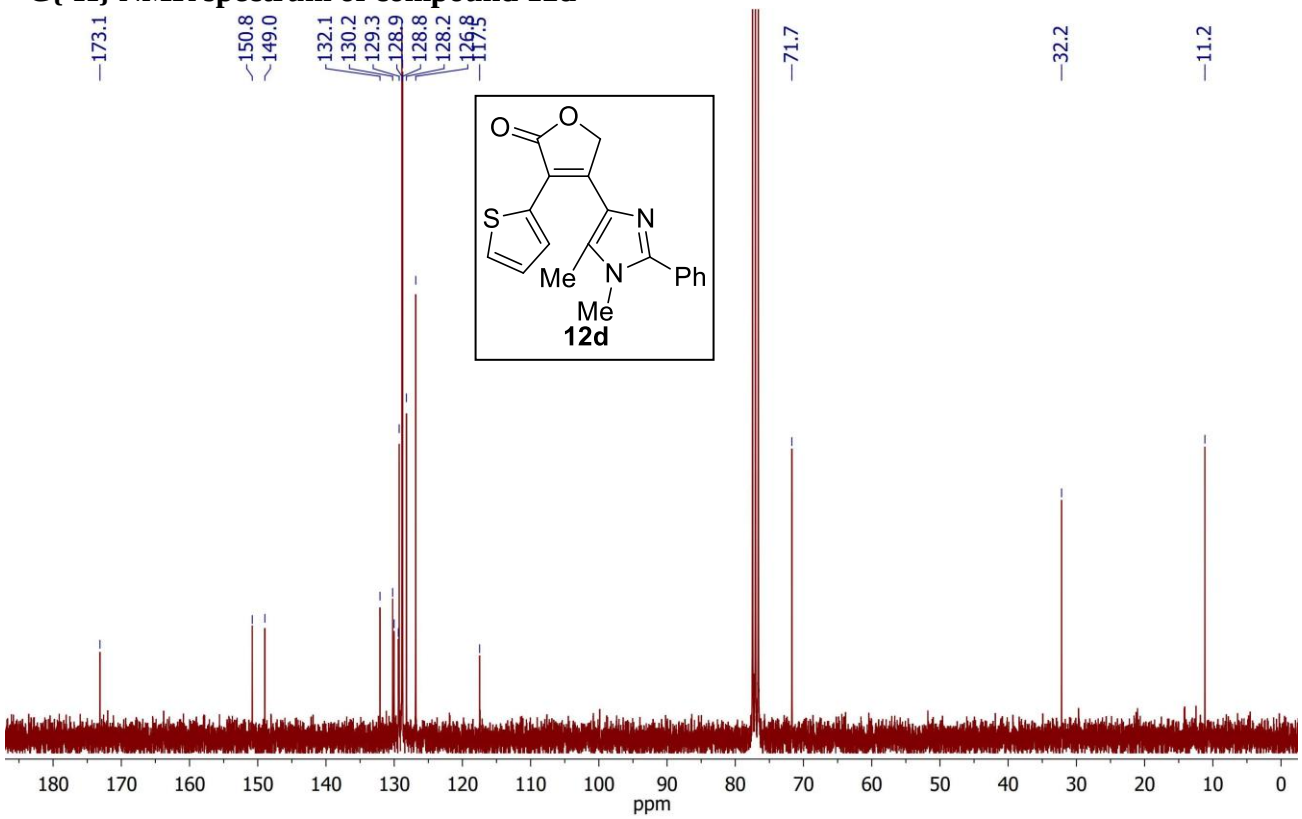


^{1}H NMR spectrum of compound 12d

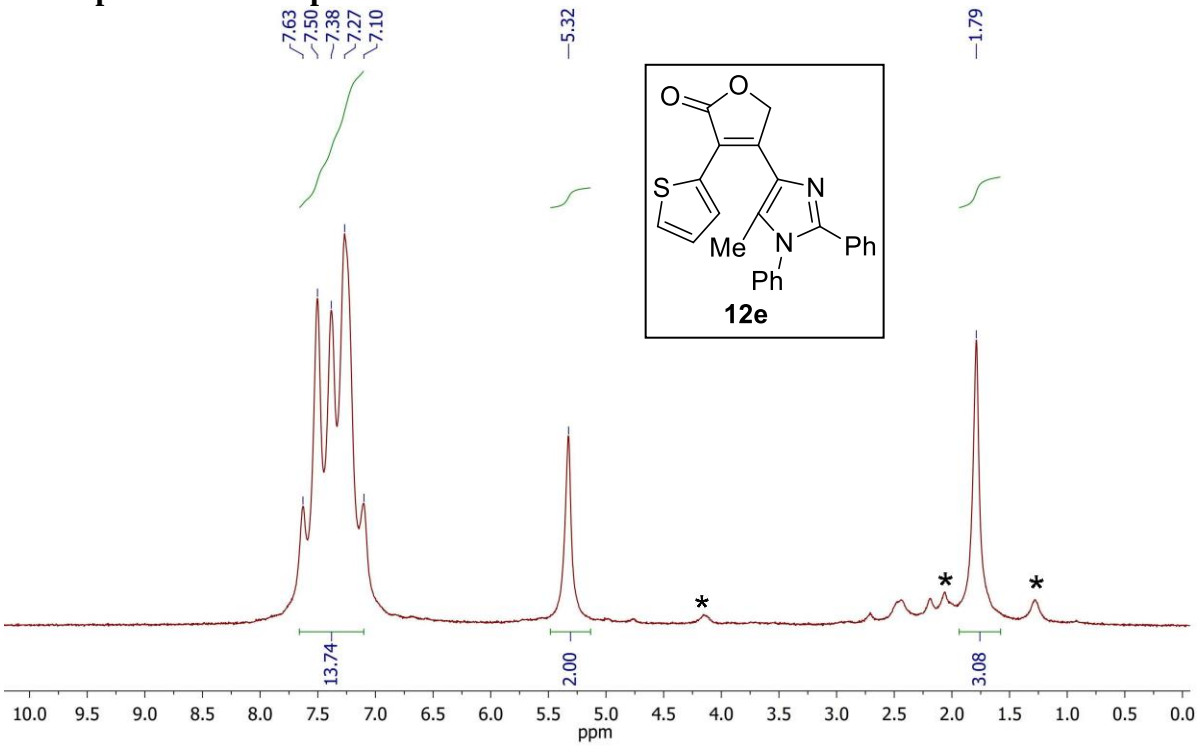


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 12d

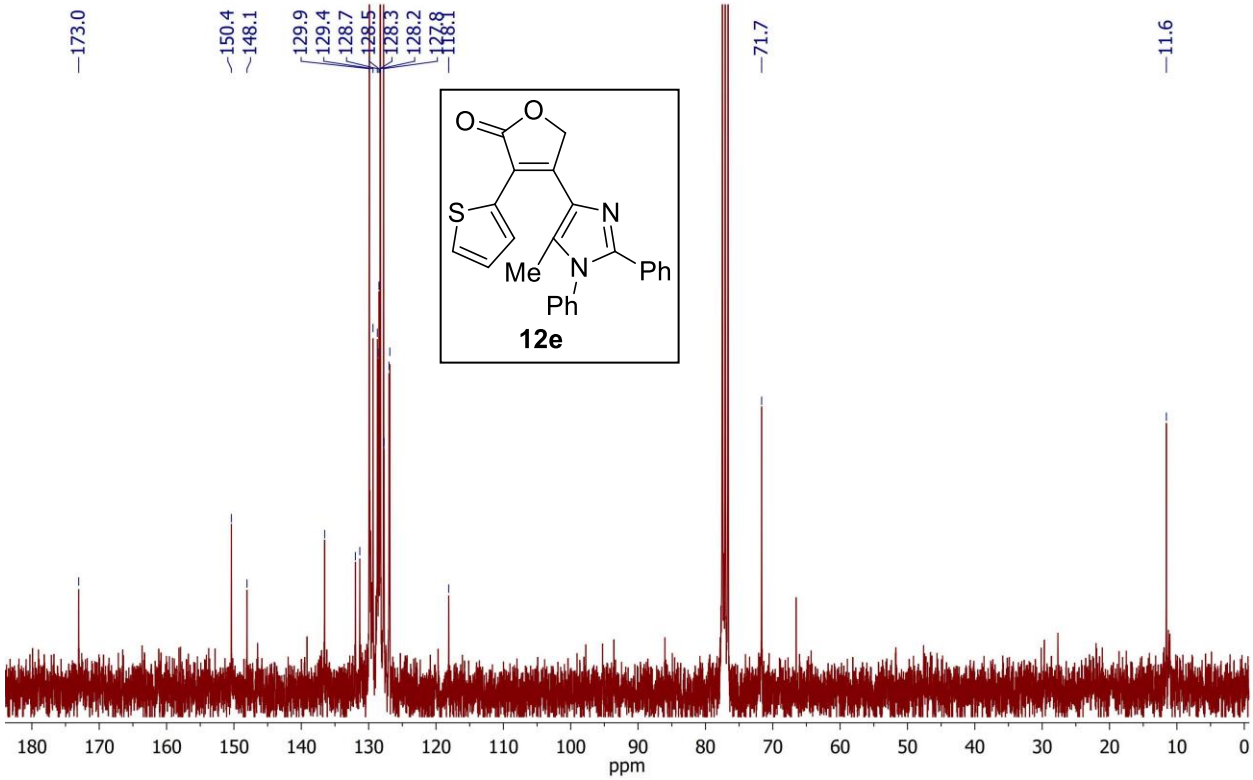


^{1}H NMR spectrum of compound 12e

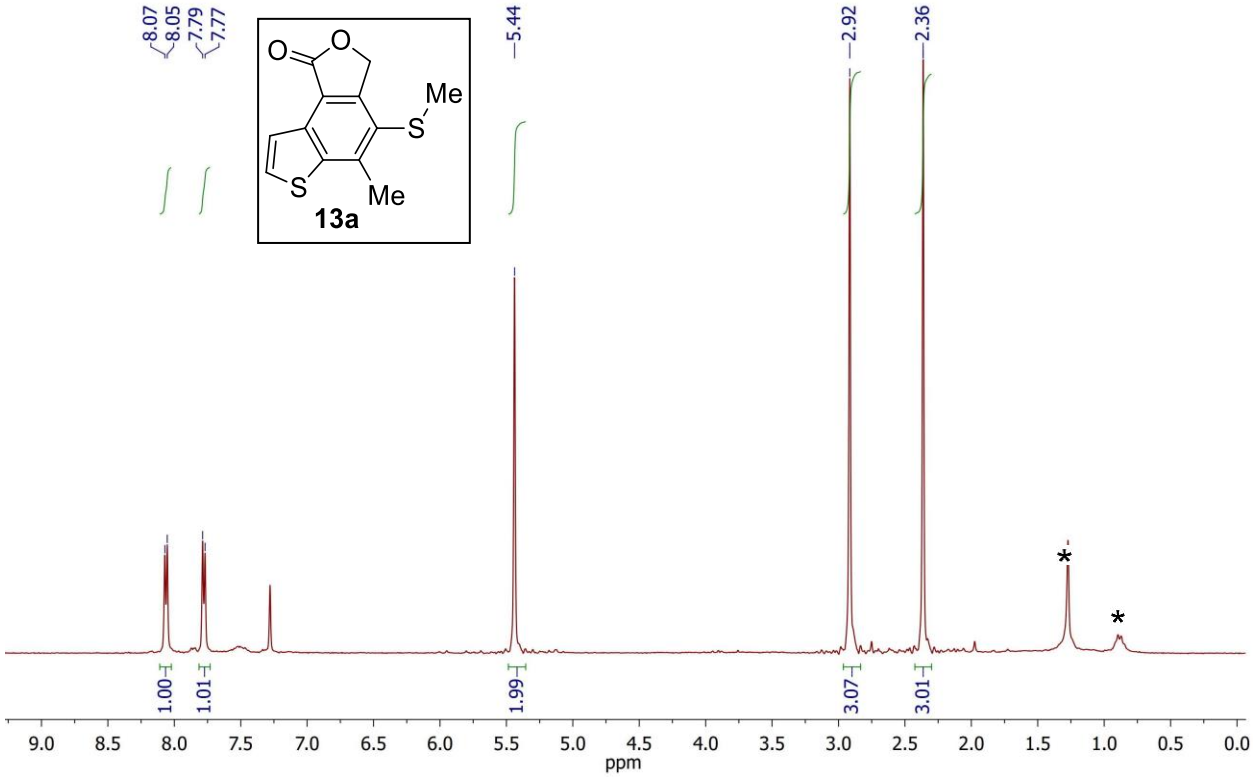


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 12e

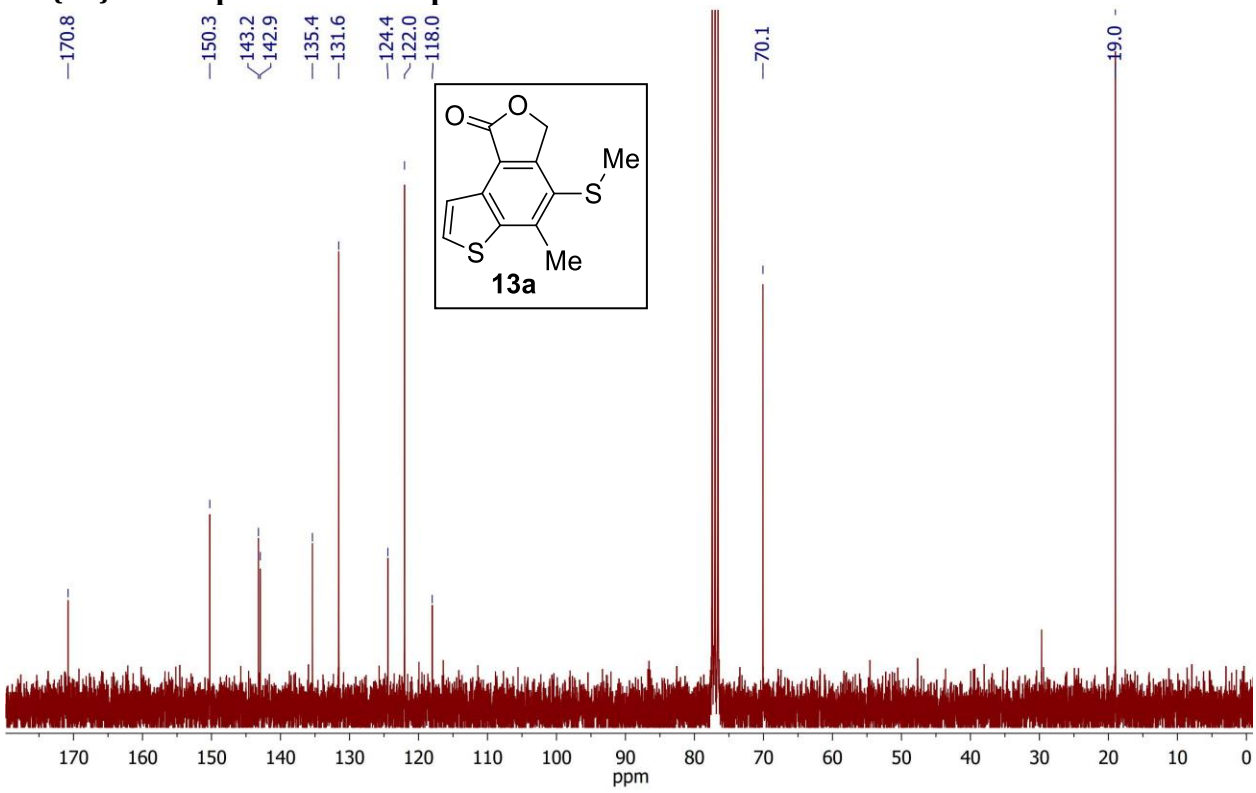


^{1}H NMR spectrum of compound 13a

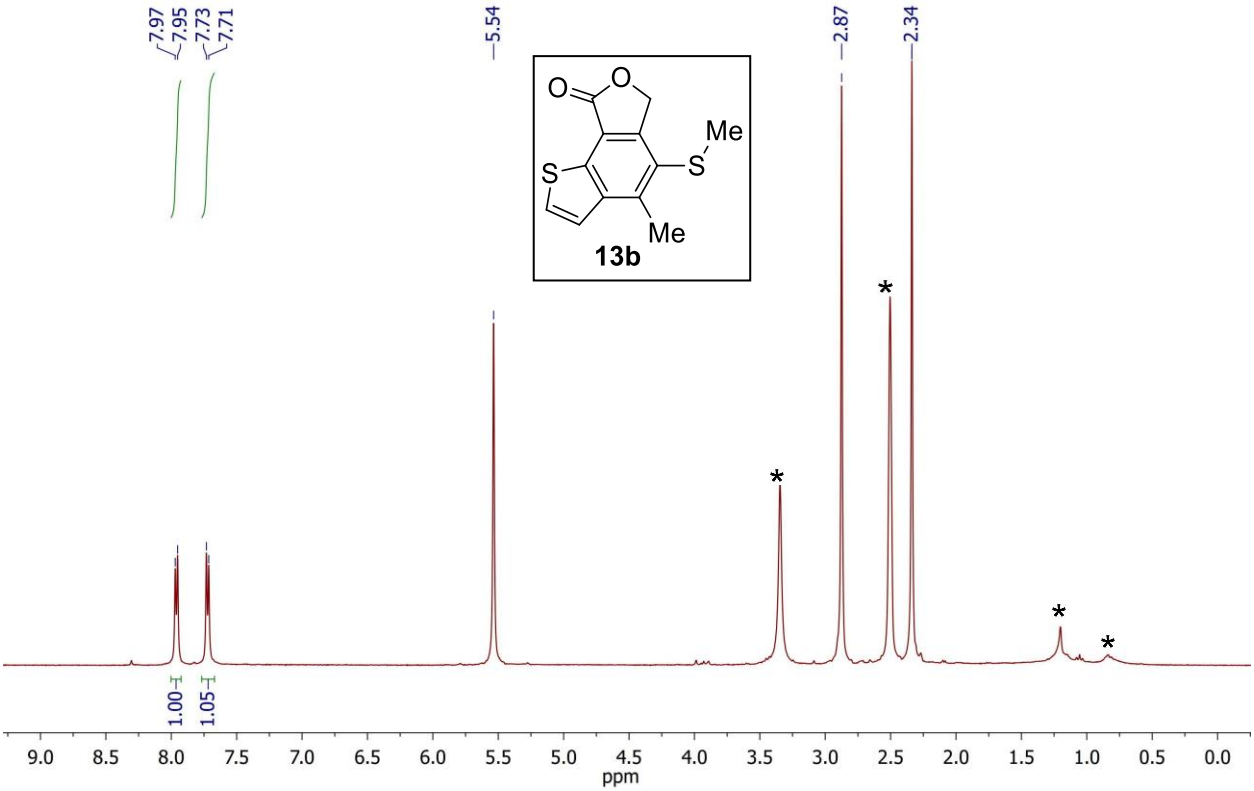


* Grease

^{13}C{^{1}H} NMR spectrum of compound 13a

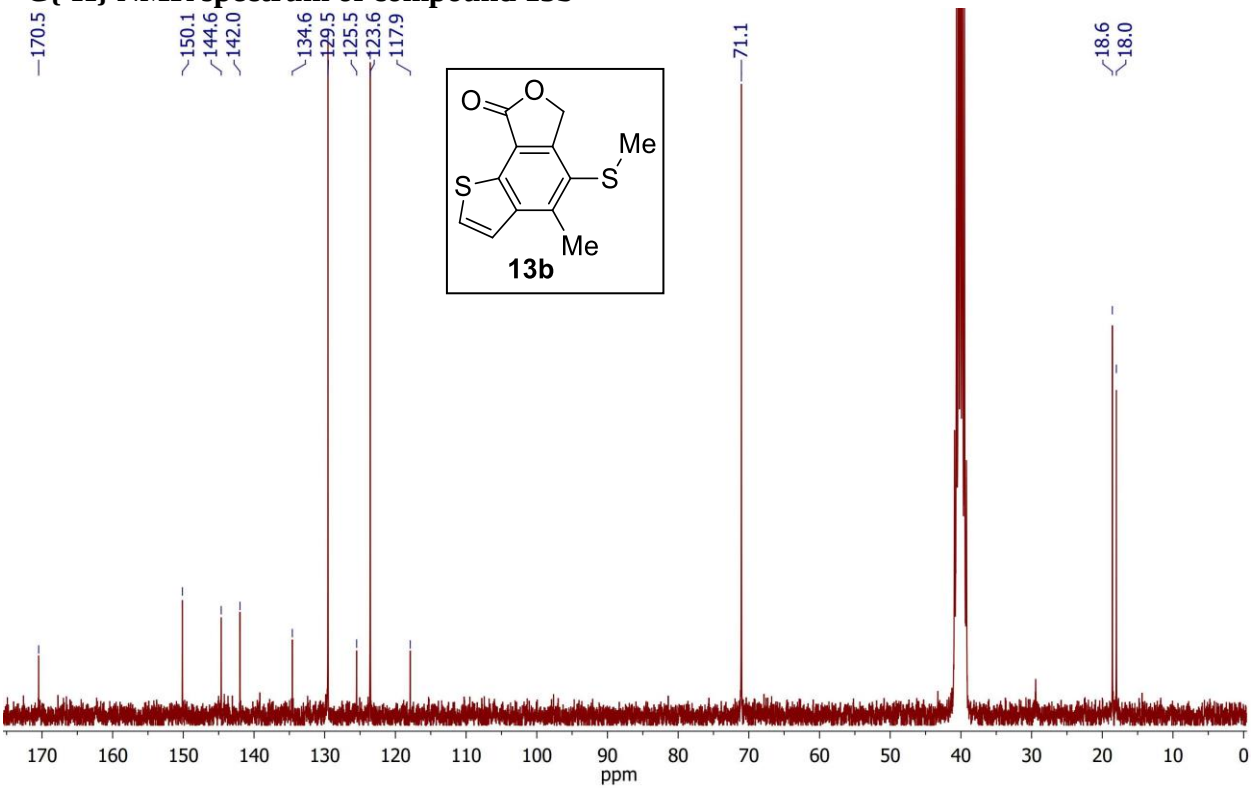


^{1}H NMR spectrum of compound 13b

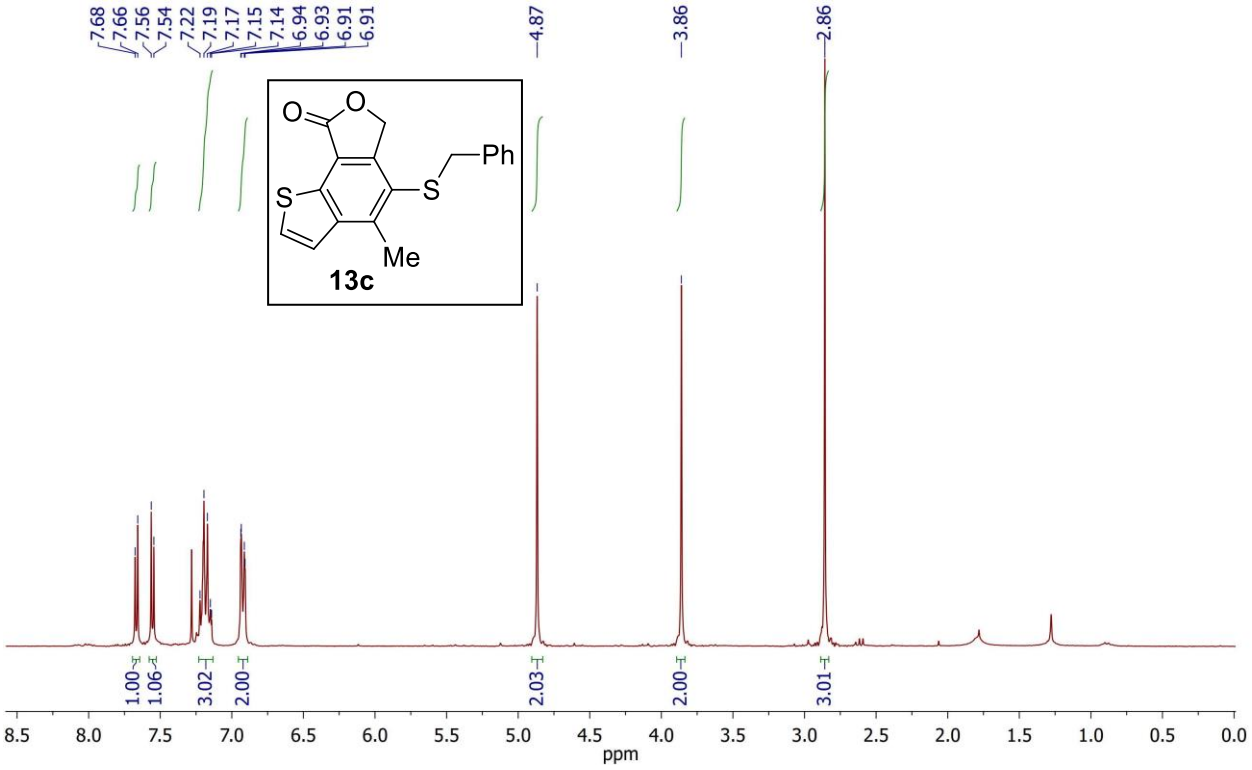


* H_2O (3.33 ppm), DMSO (2.50 ppm), grease

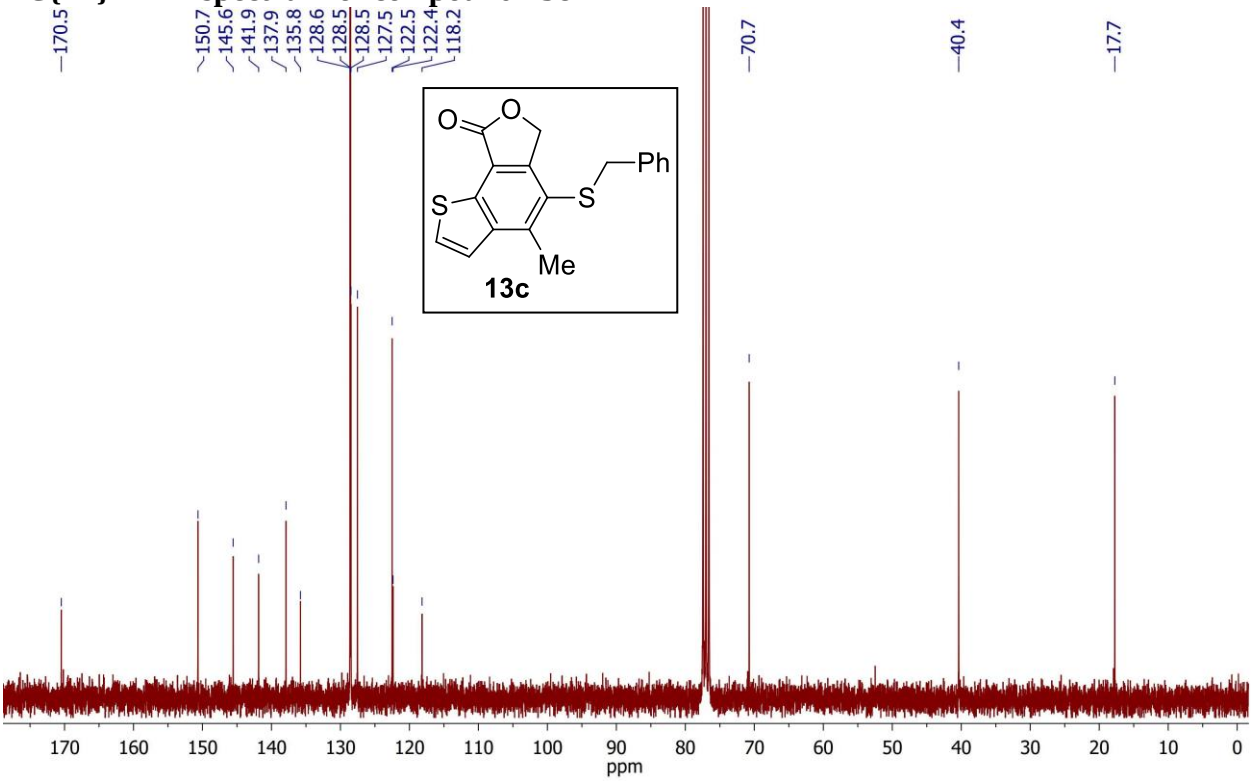
^{13}C{^{1}H} NMR spectrum of compound 13b



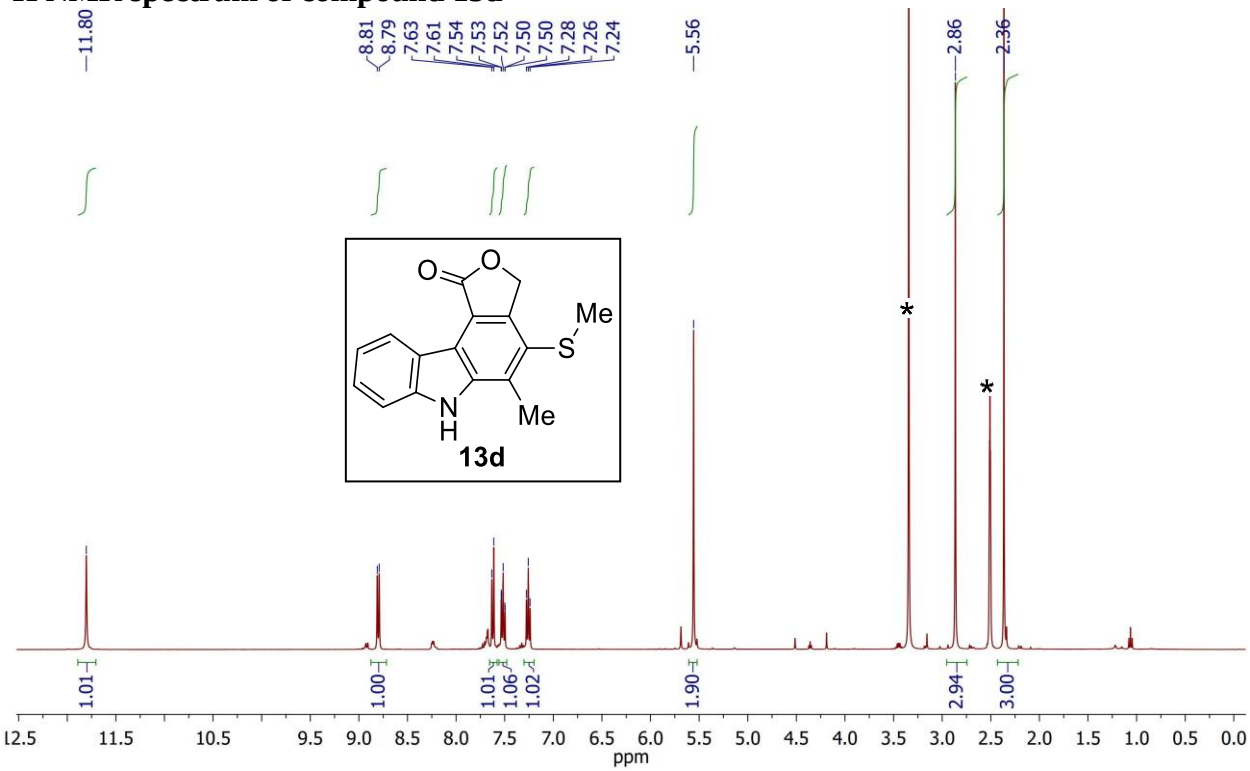
^{1}H NMR spectrum of compound 13c



^{13}C{^{1}H} NMR spectrum of compound 13c

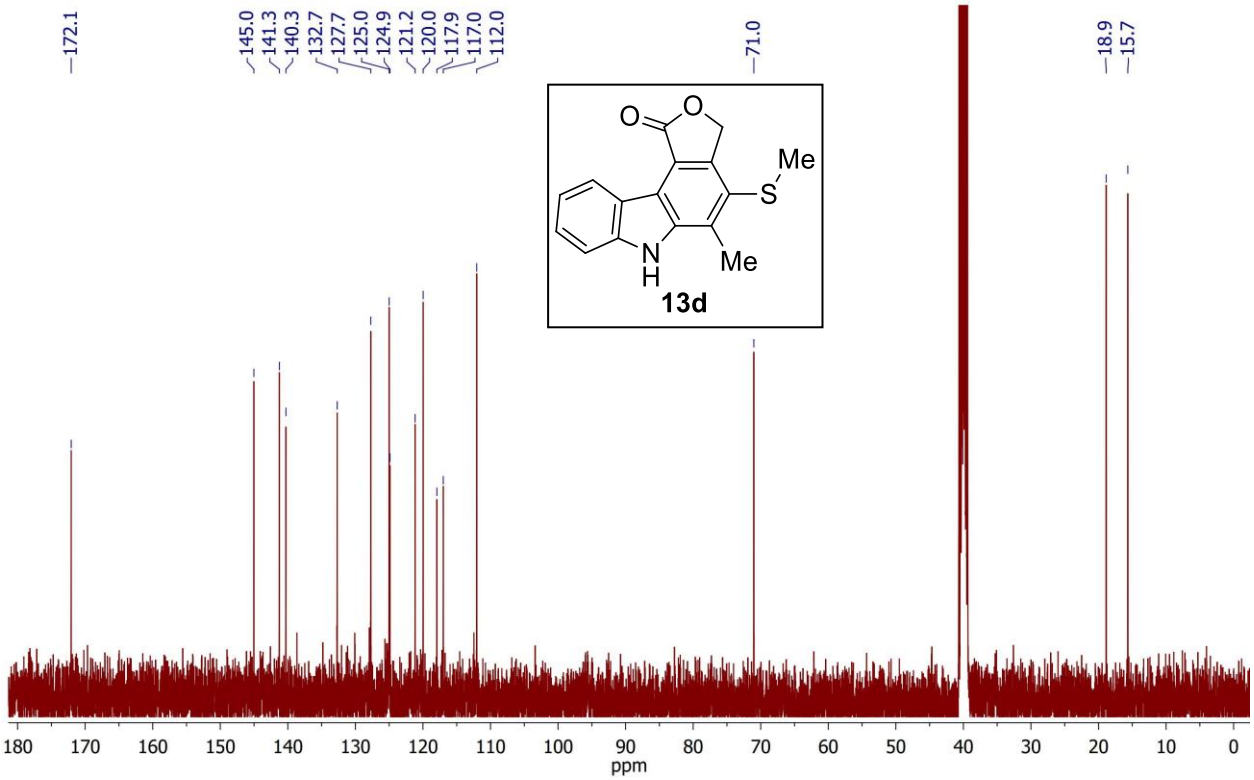


^{1}H NMR spectrum of compound 13d

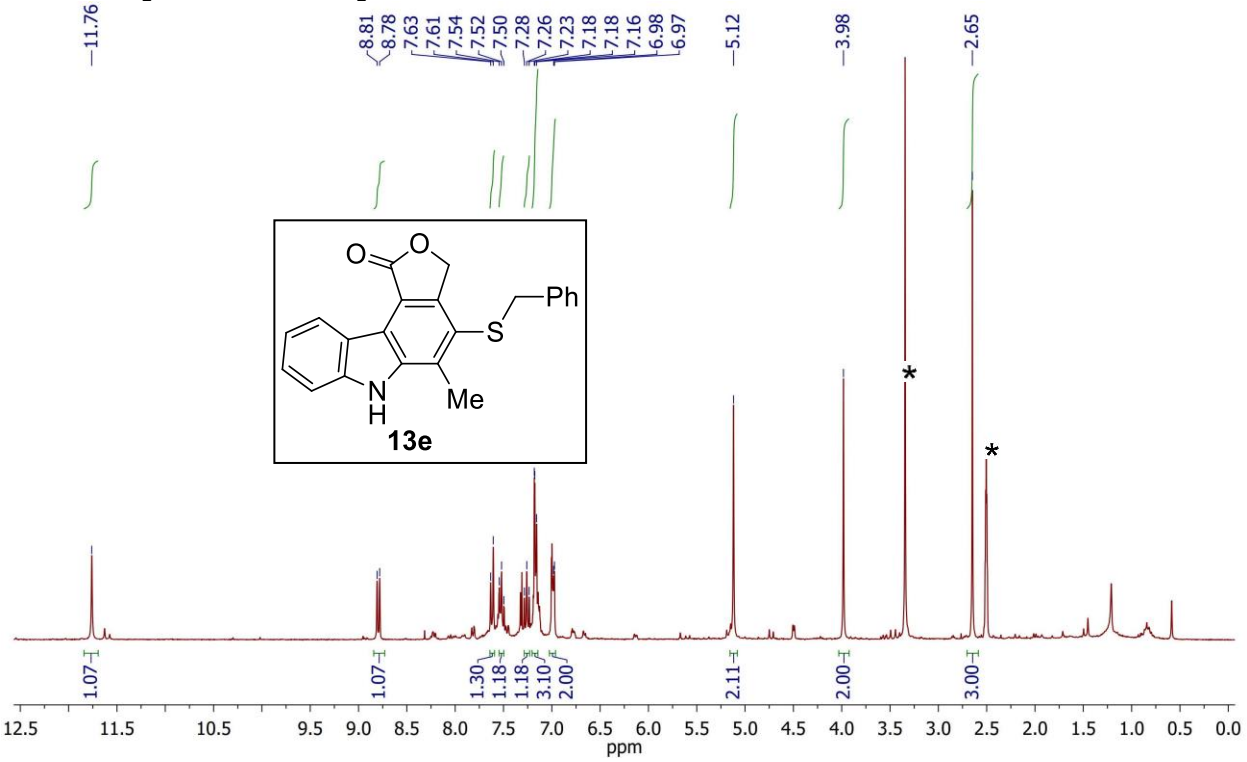


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 13d

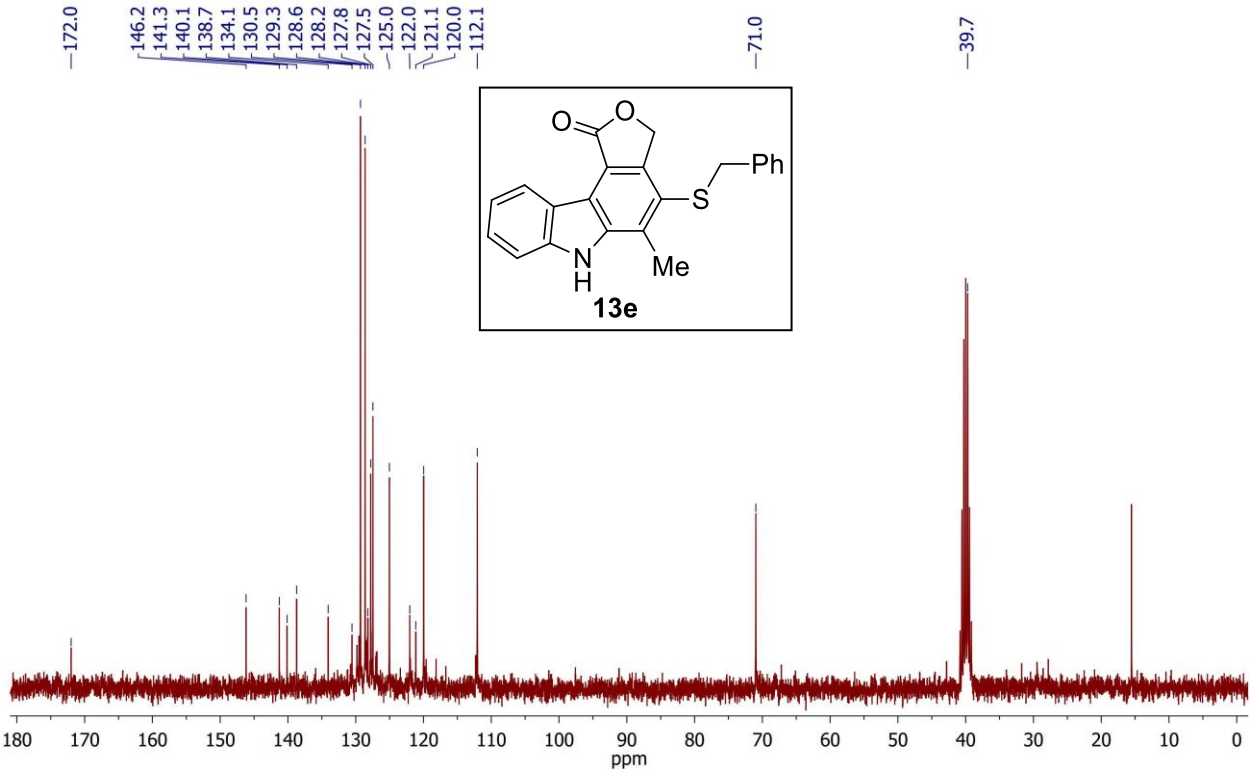


^{1}H NMR spectrum of compound 13e

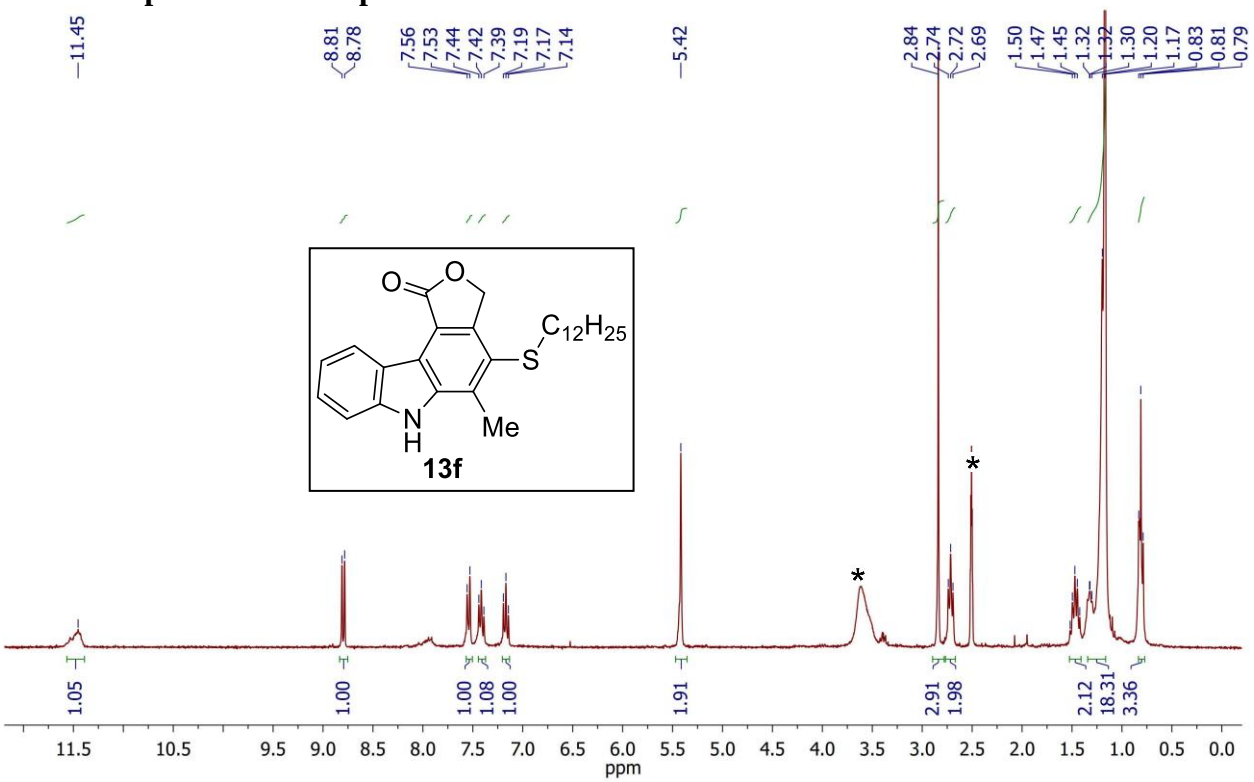


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 13e

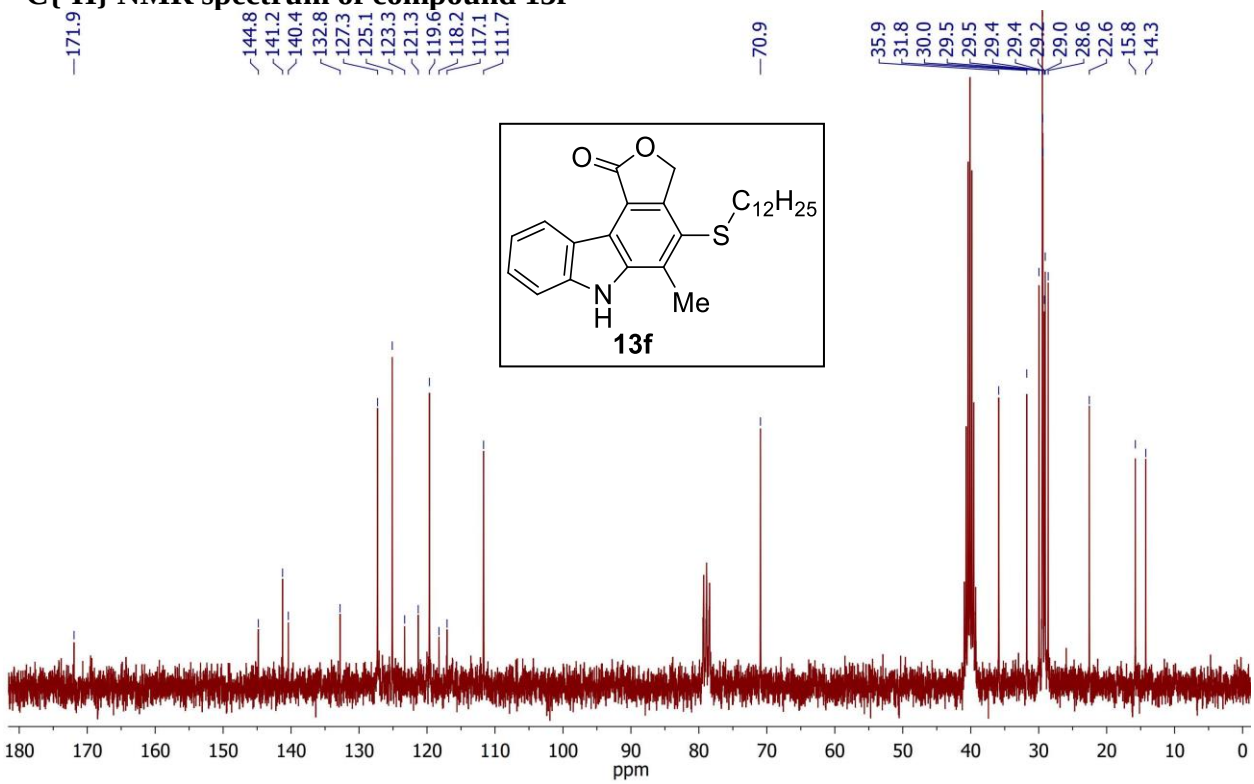


^{1}H NMR spectrum of compound 13f

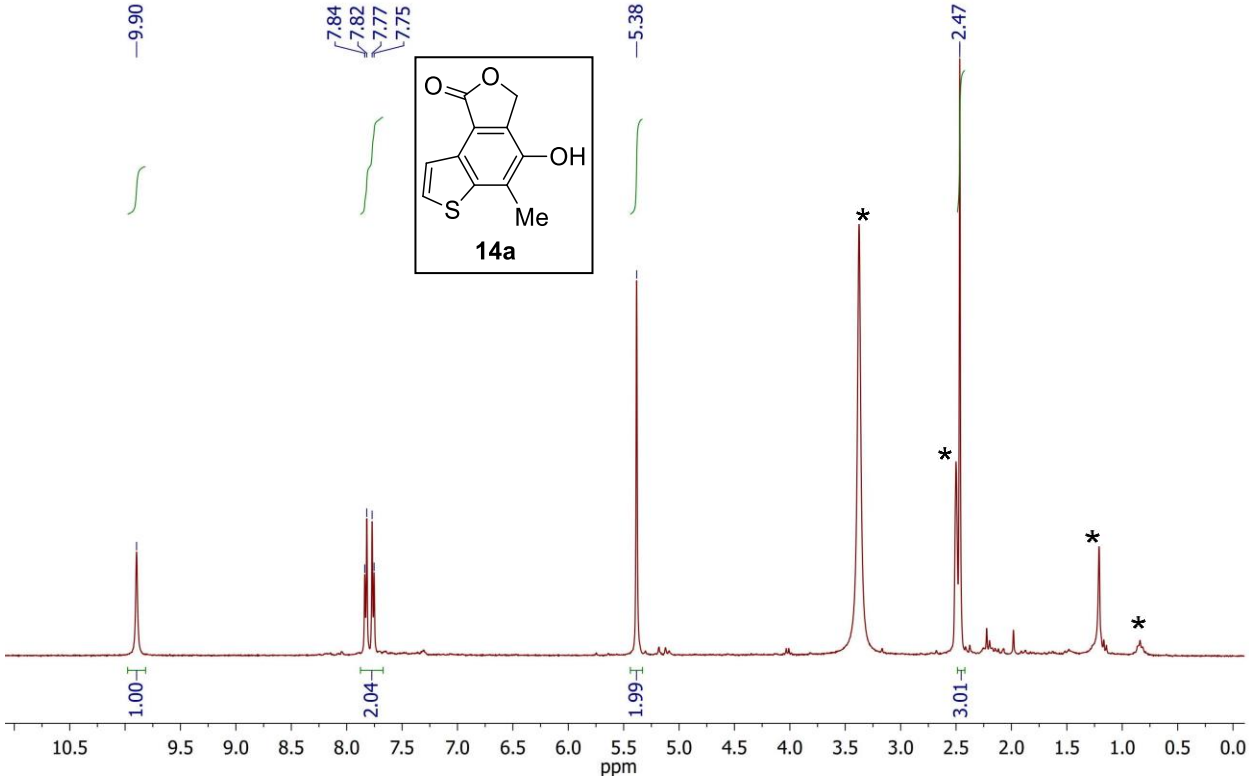


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 13f

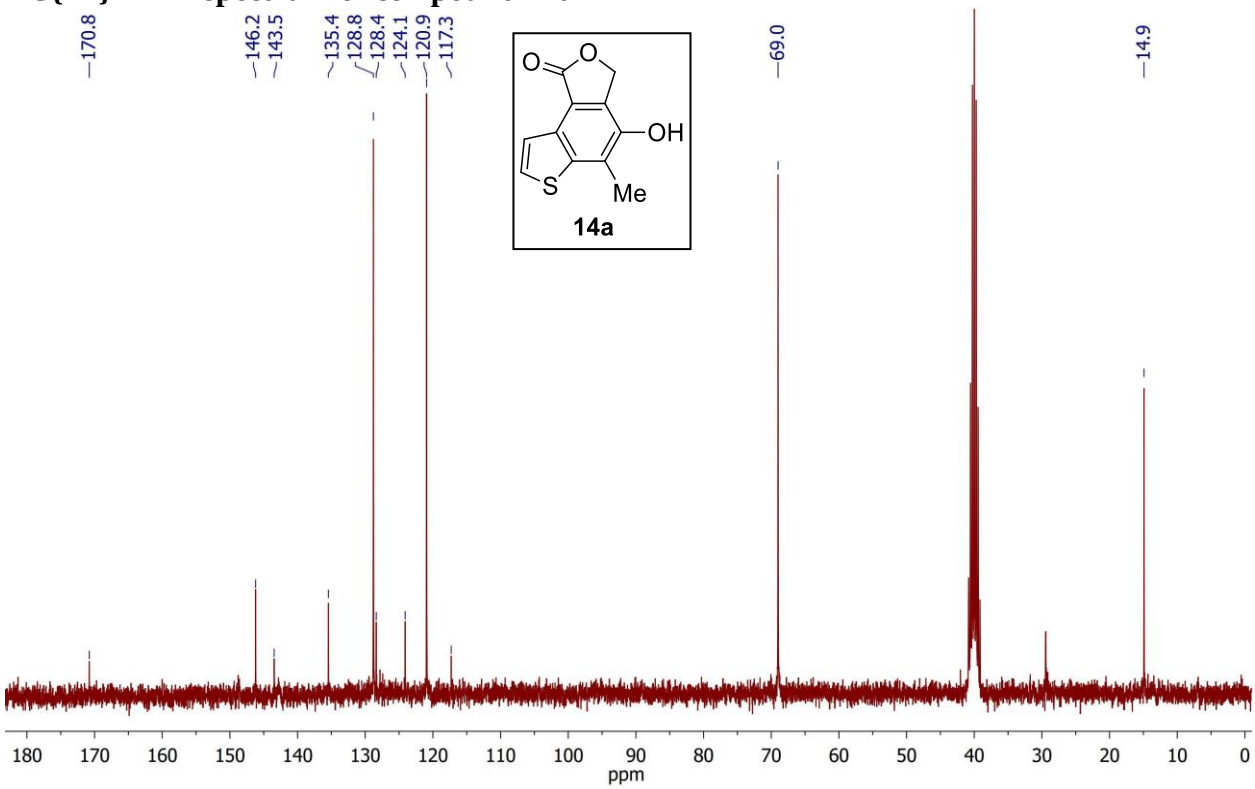


^{1}H NMR spectrum of compound 14a

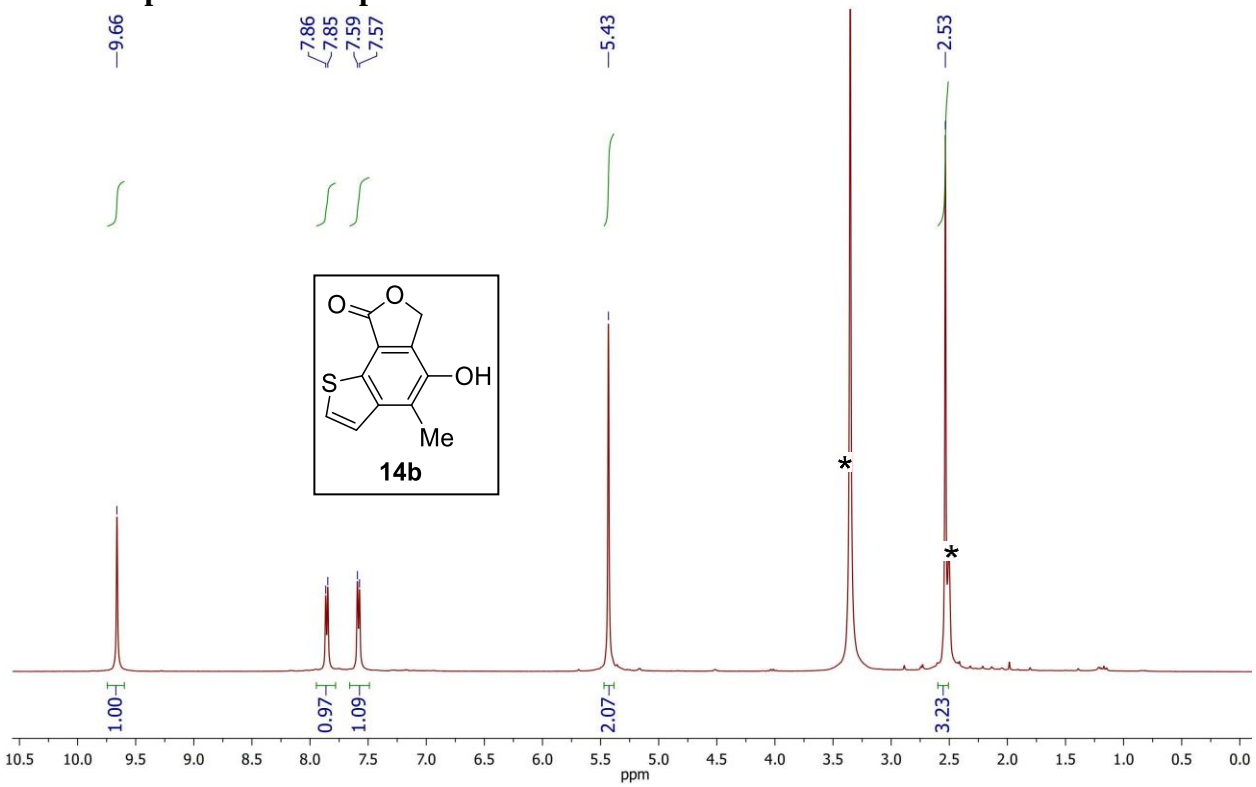


* H_2O (3.33 ppm), DMSO (2.50 ppm) and grease (1.26, 0.88 ppm)

^{13}C{^{1}H} NMR spectrum of compound 14a

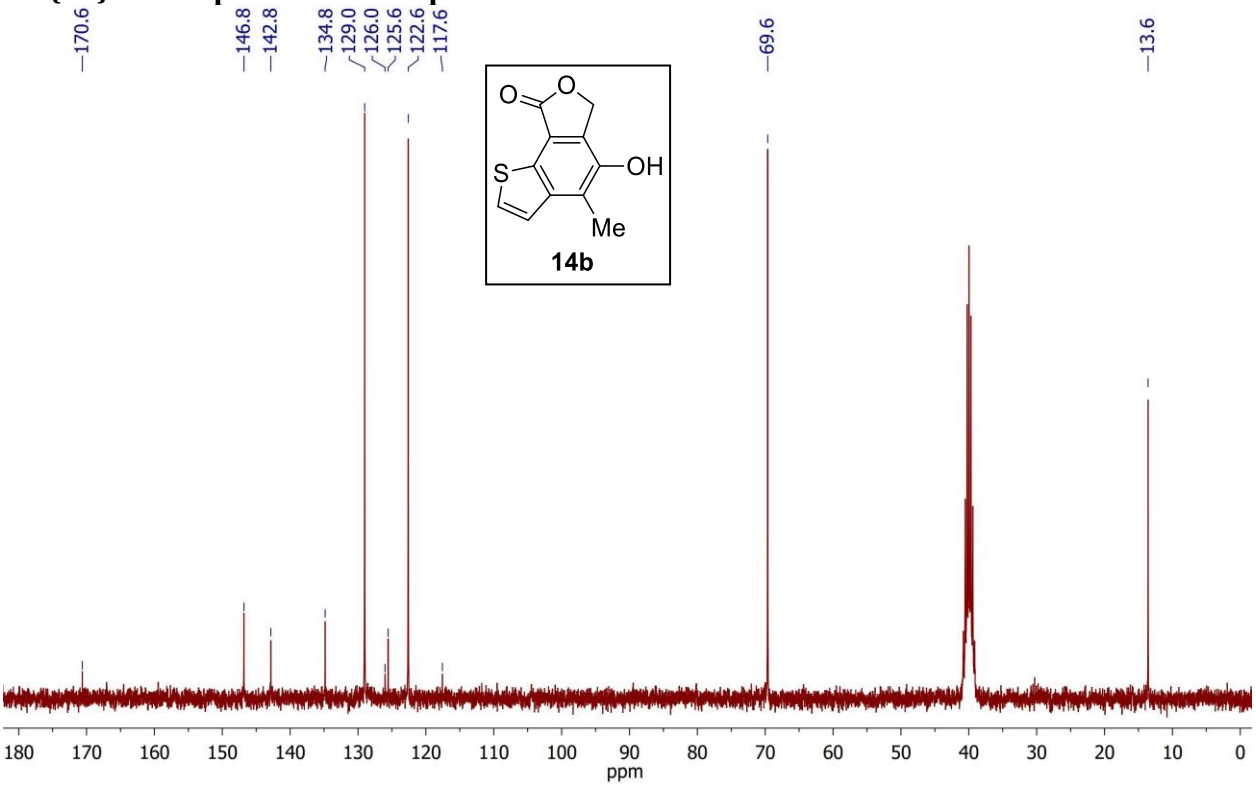


^{1}H NMR spectrum of compound 14b

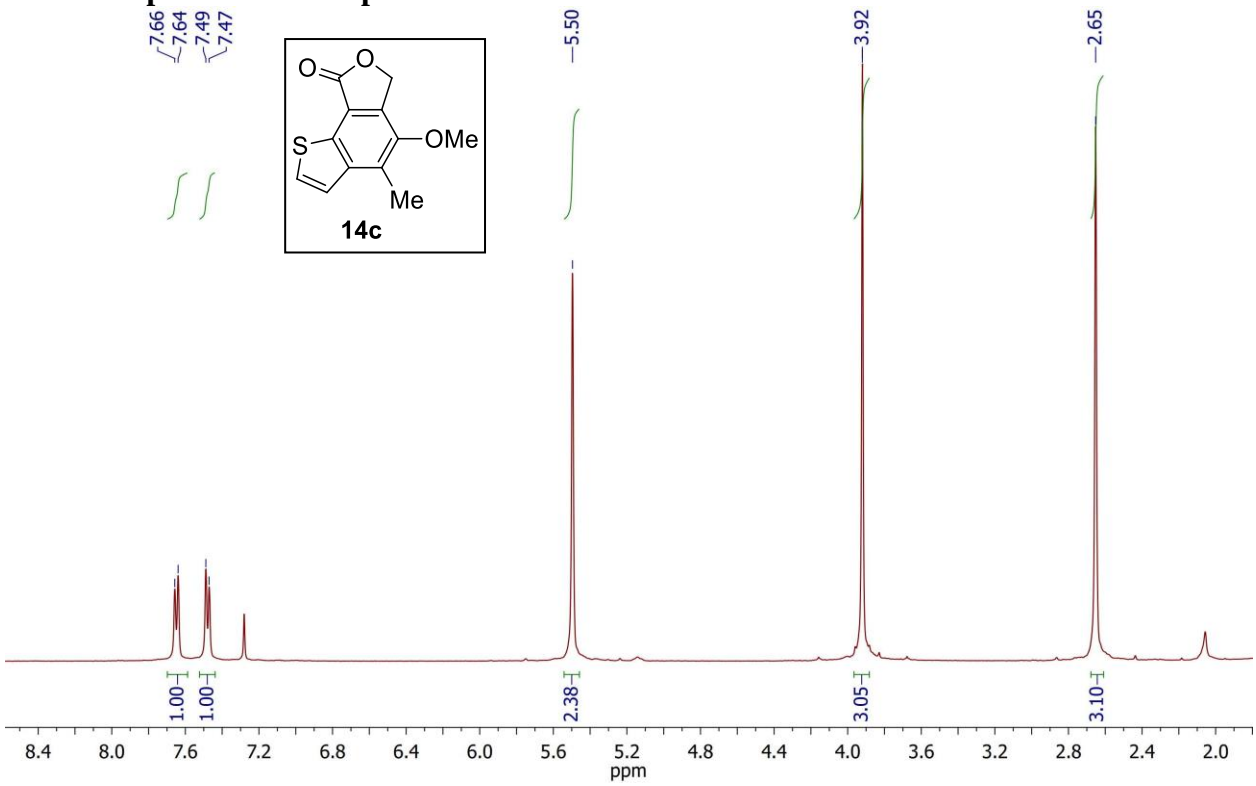


* H_2O (3.33 ppm), DMSO (2.50 ppm)

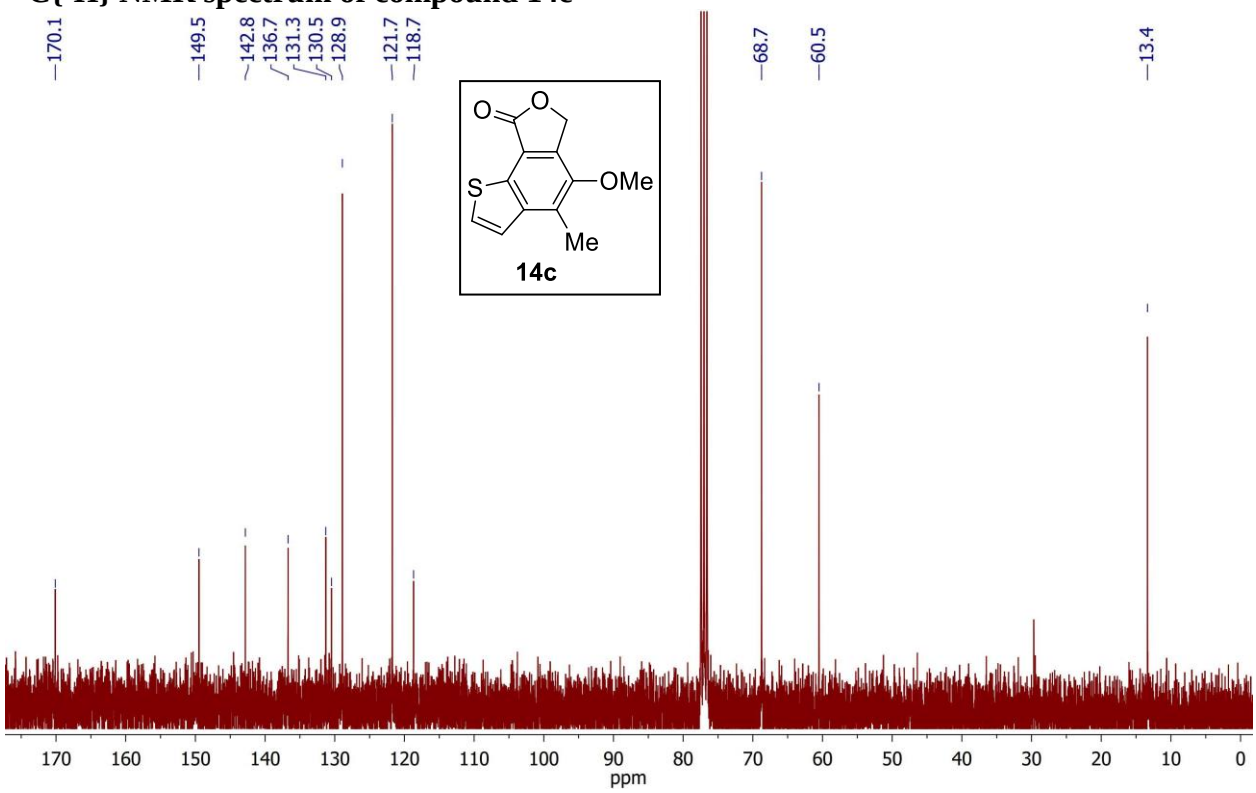
^{13}C{^{1}H} NMR spectrum of compound 14b



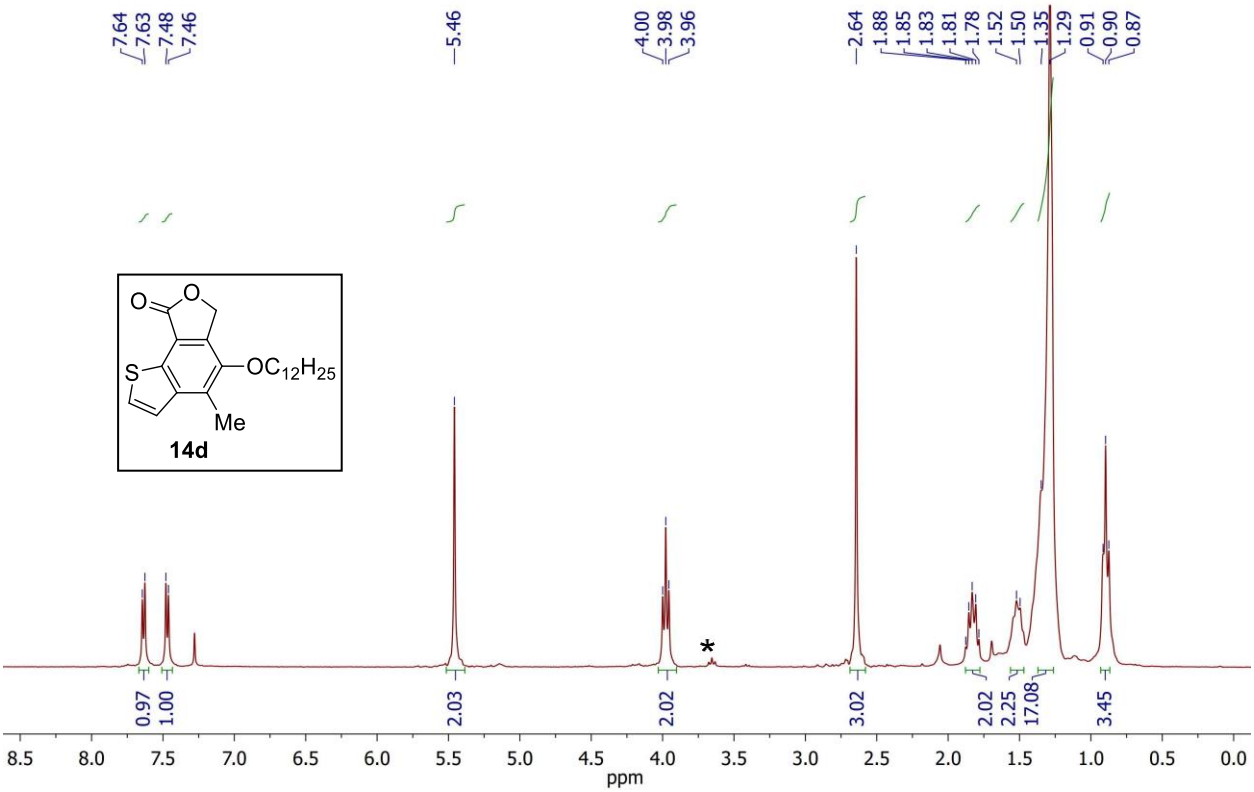
^{1}H NMR spectrum of compound 14c



^{13}C{^{1}H} NMR spectrum of compound 14c

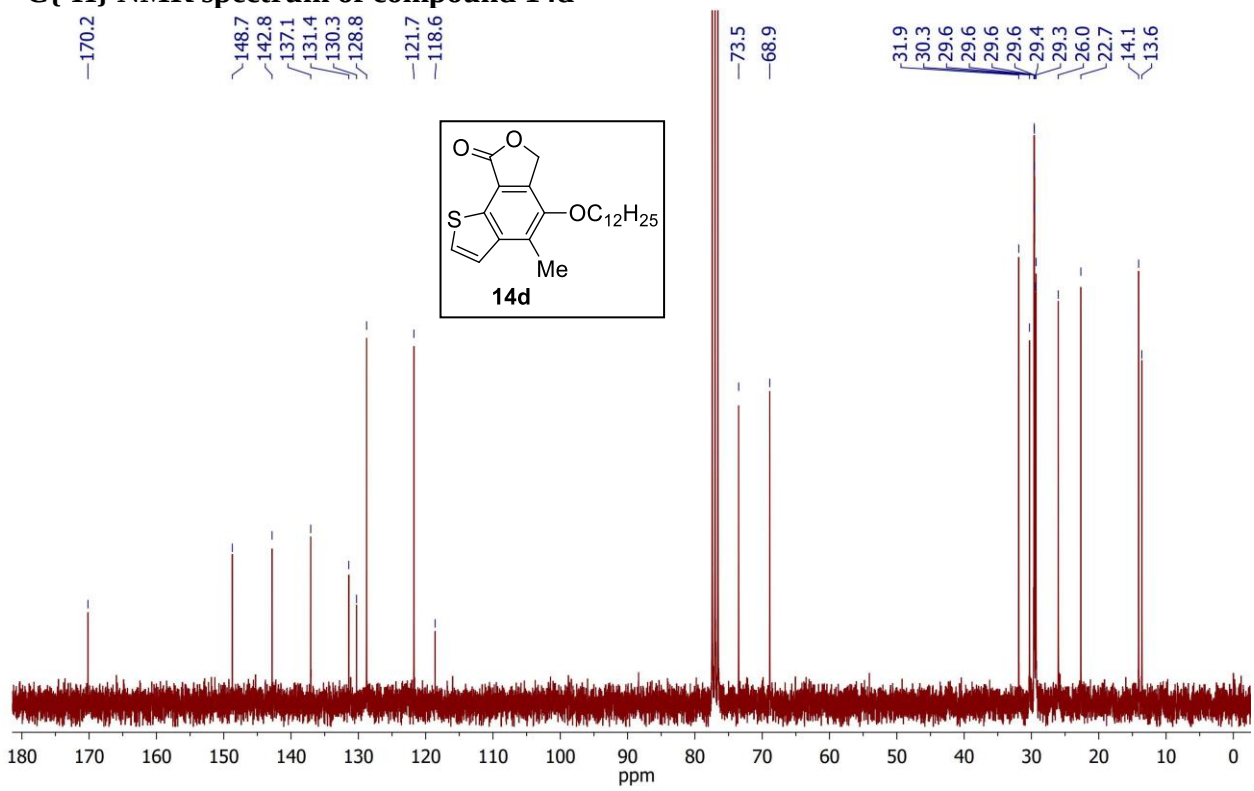


^{1}H NMR spectrum of compound 14d

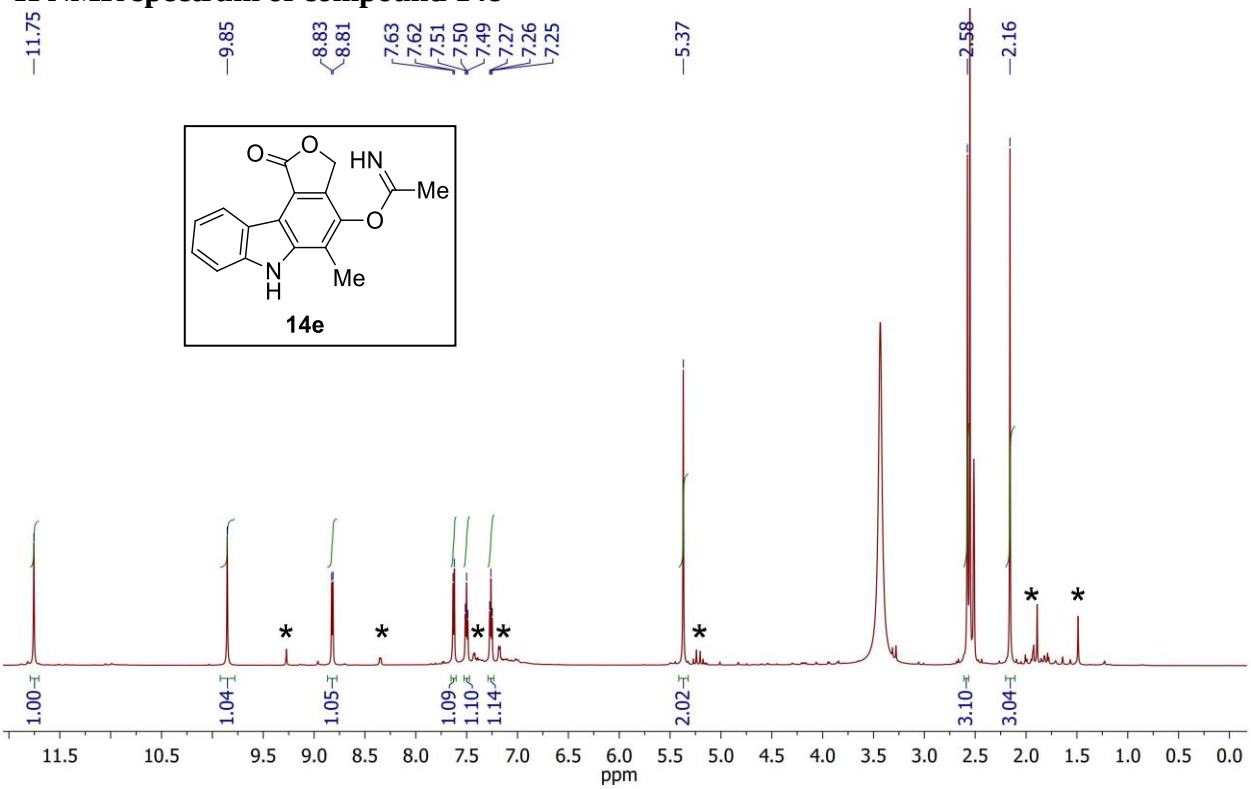


* Ethanol

^{13}C{^{1}H} NMR spectrum of compound 14d

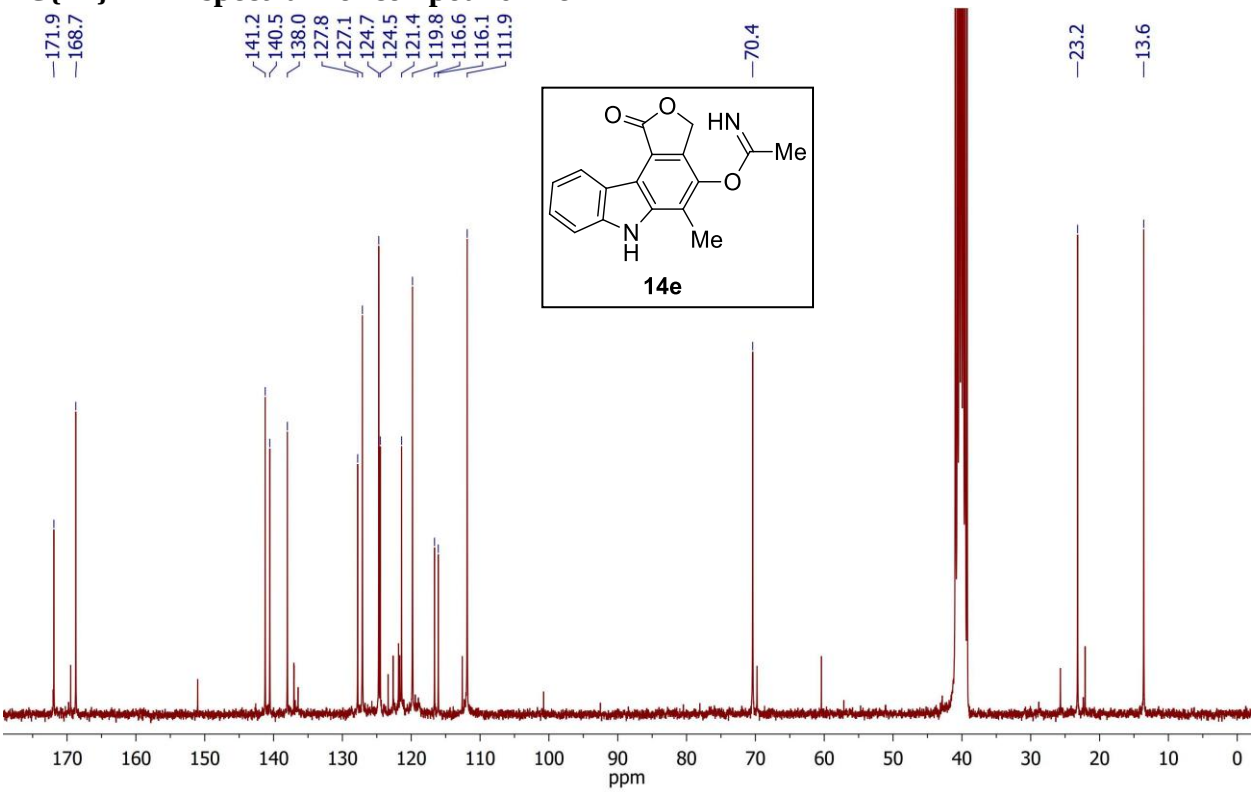


^{1}H NMR spectrum of compound 14e

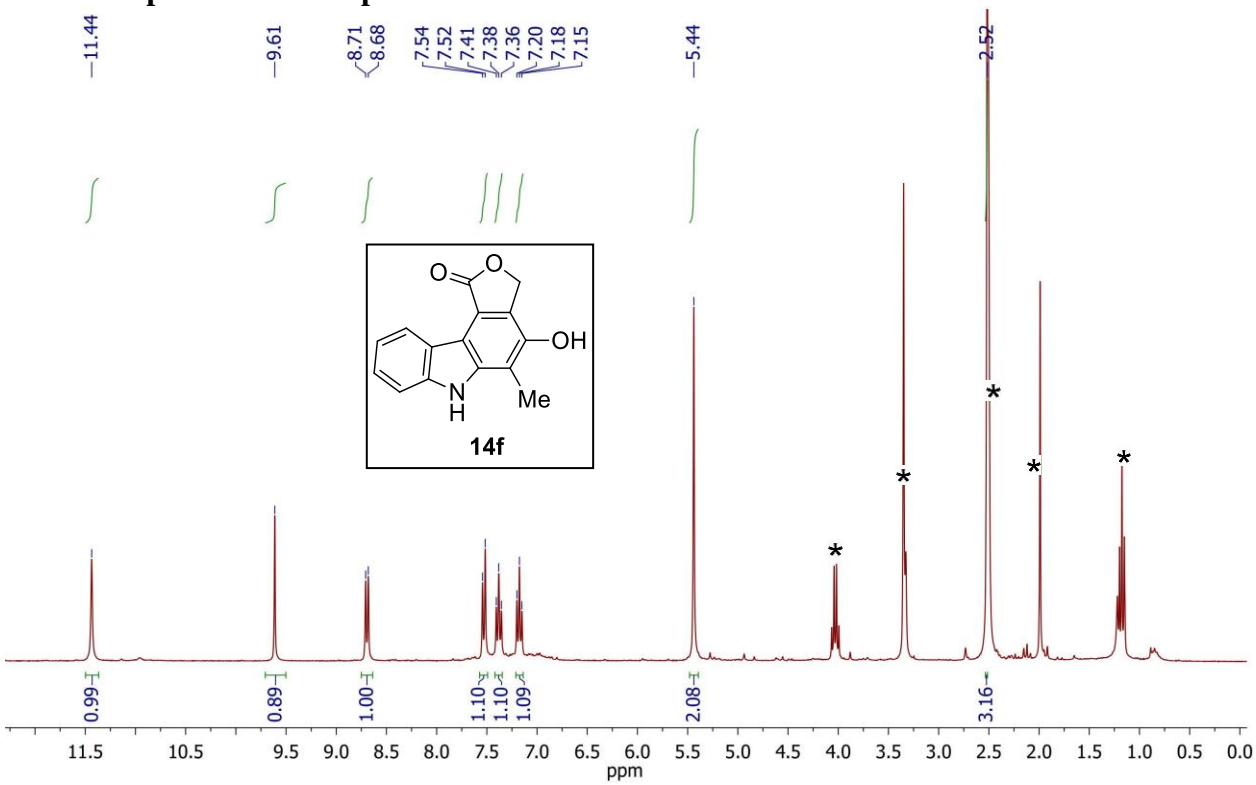


* Trace amounts of compound **23** (both photoproducts possess very similar R_f values)

^{13}C{^{1}H} NMR spectrum of compound 14e

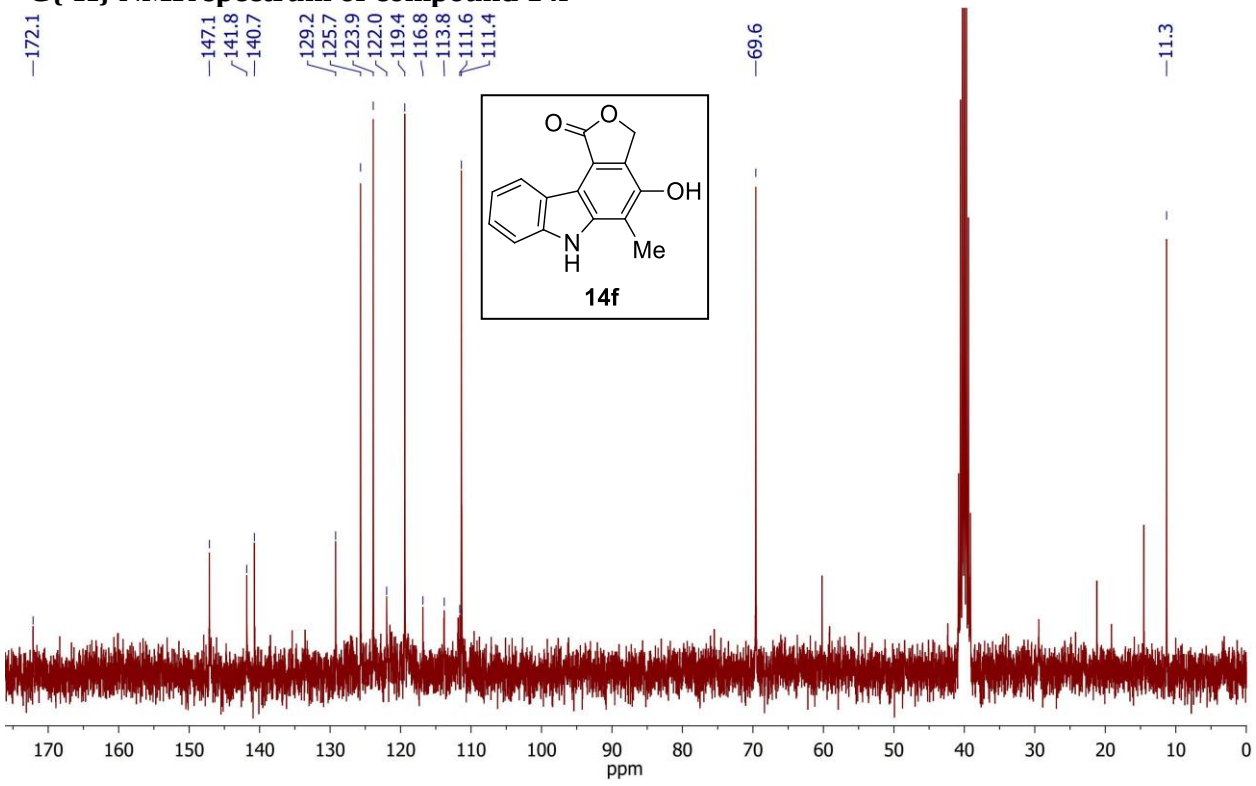


^{1}H NMR spectrum of compound 14f

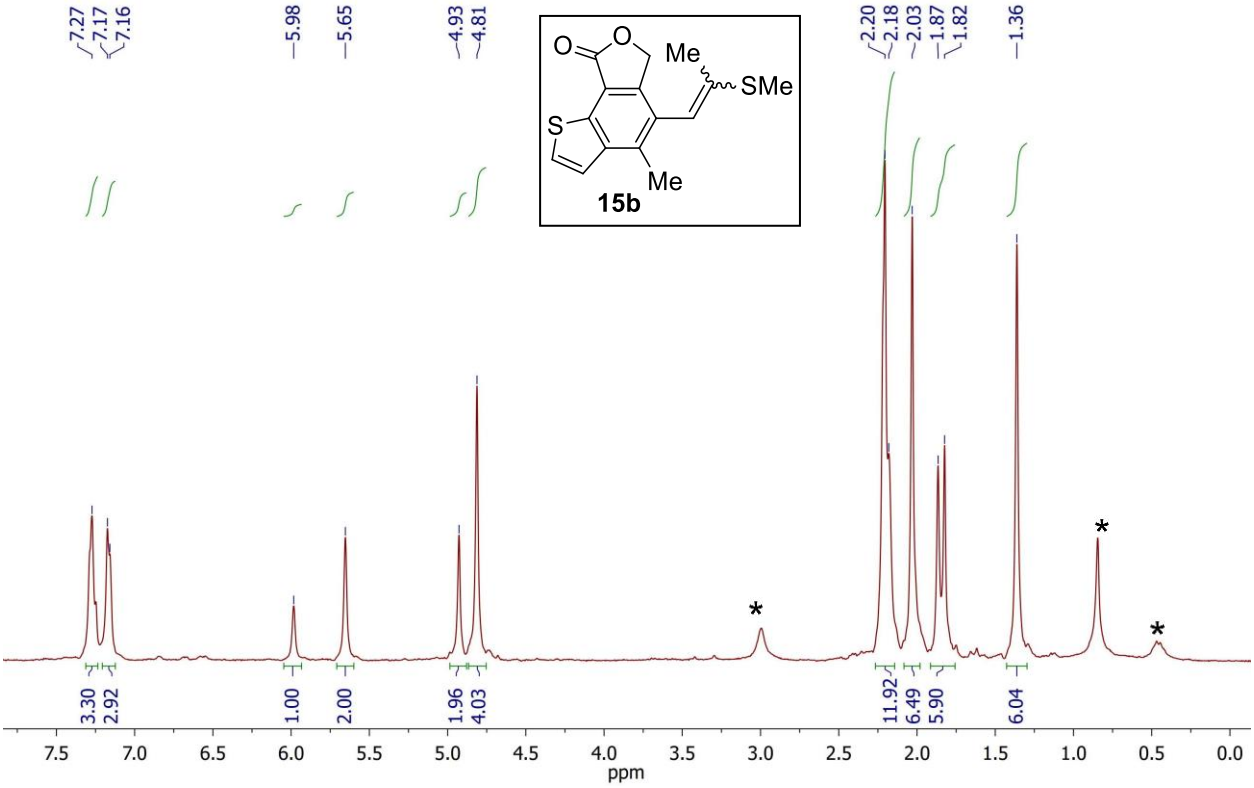


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 14f

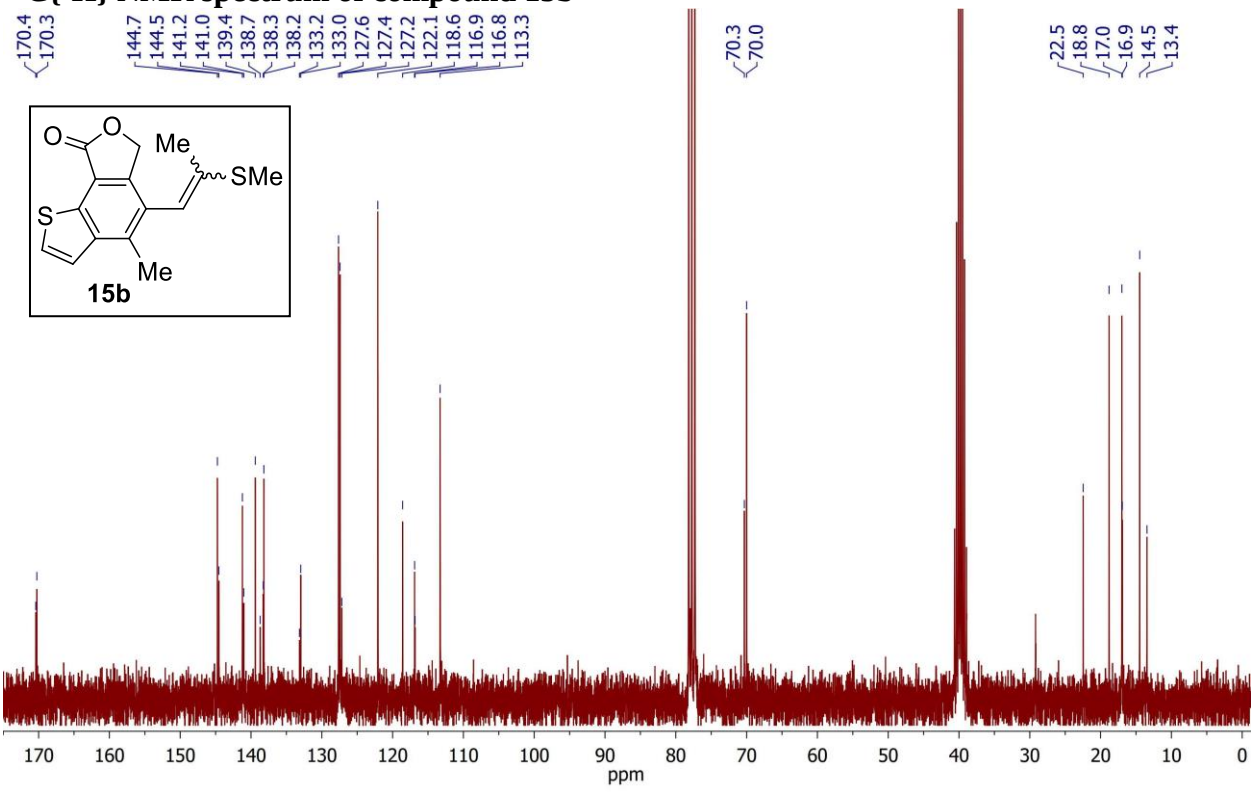


^{1}H NMR spectrum of compound 15b

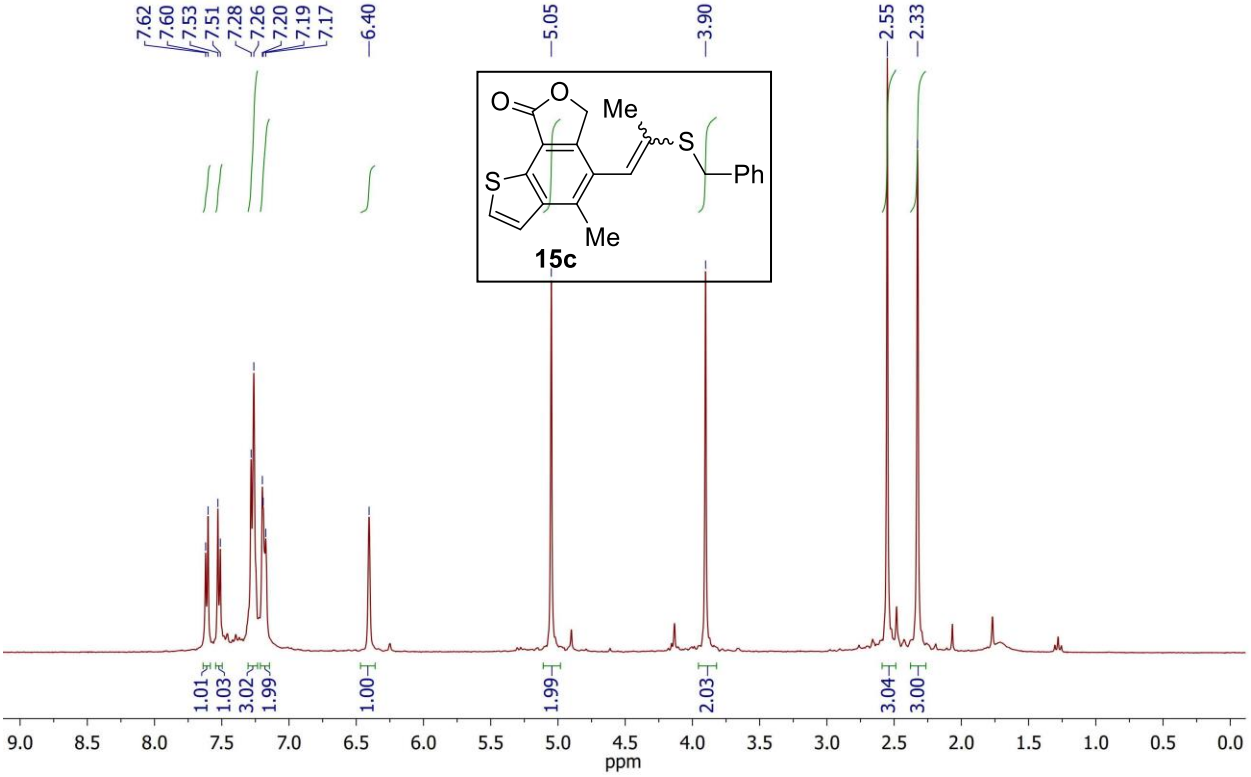


* H_2O and grease

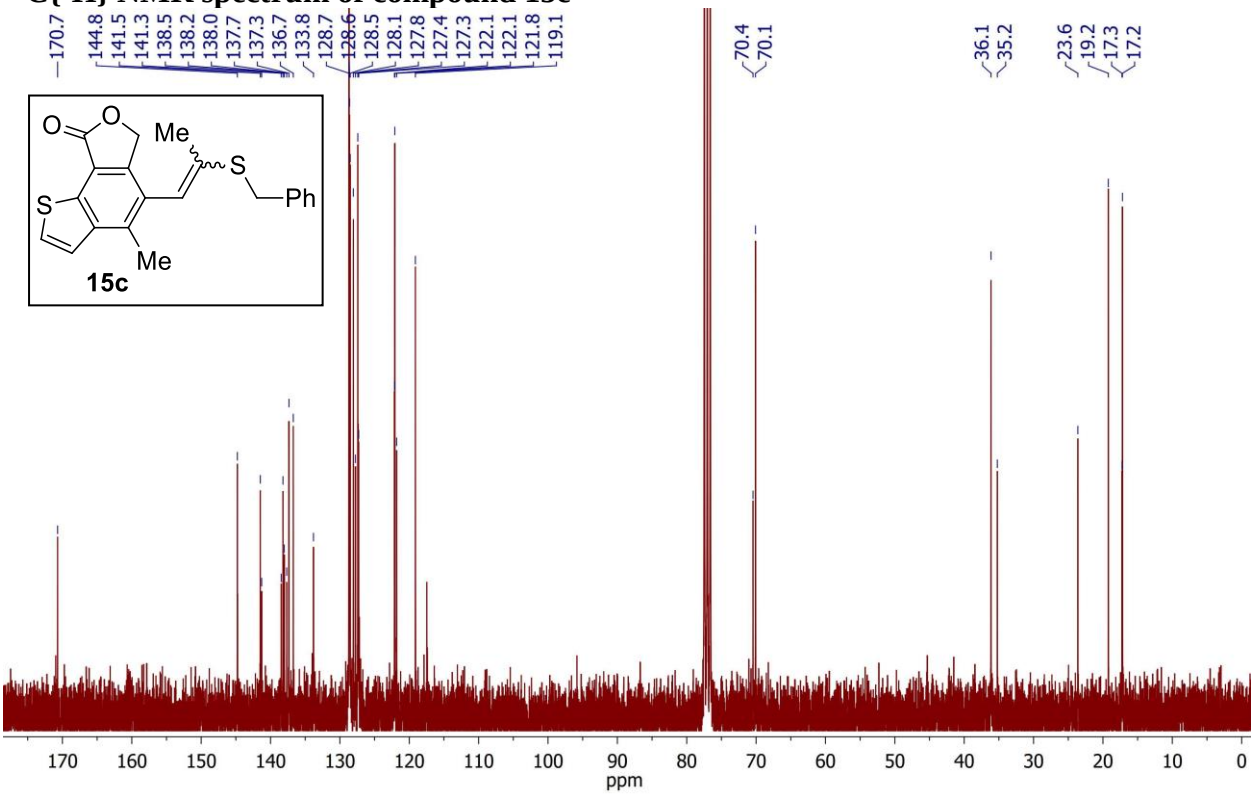
^{13}C{^{1}H} NMR spectrum of compound 15b



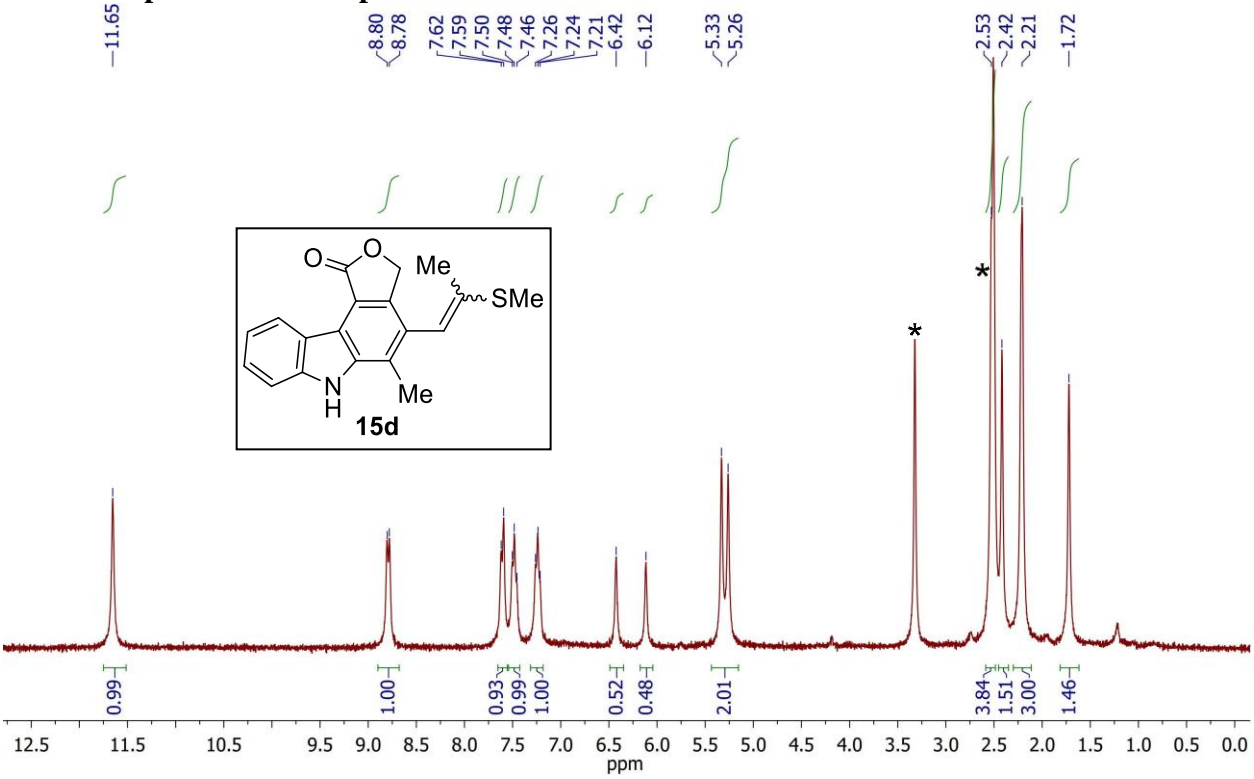
^{1}H NMR spectrum of compound 15c



^{13}C{^{1}H} NMR spectrum of compound 15c

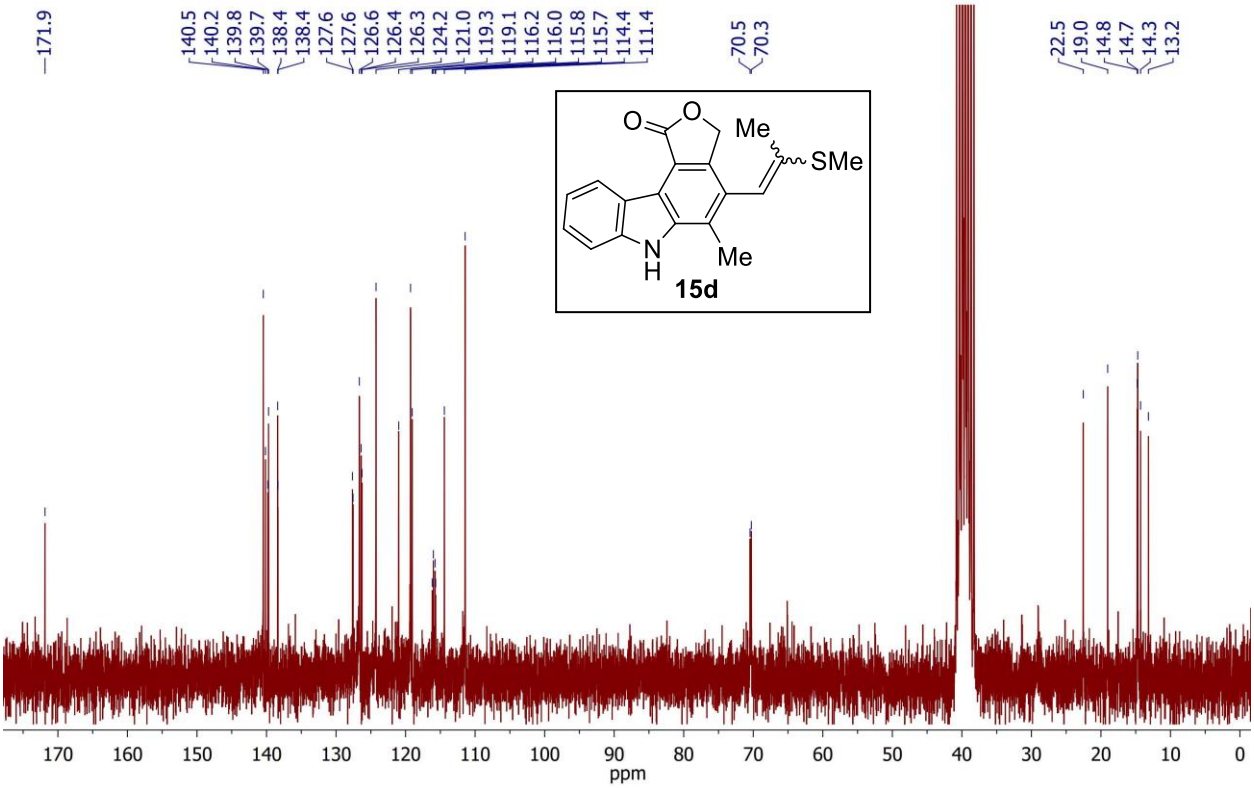


^{1}H NMR spectrum of compound 15d

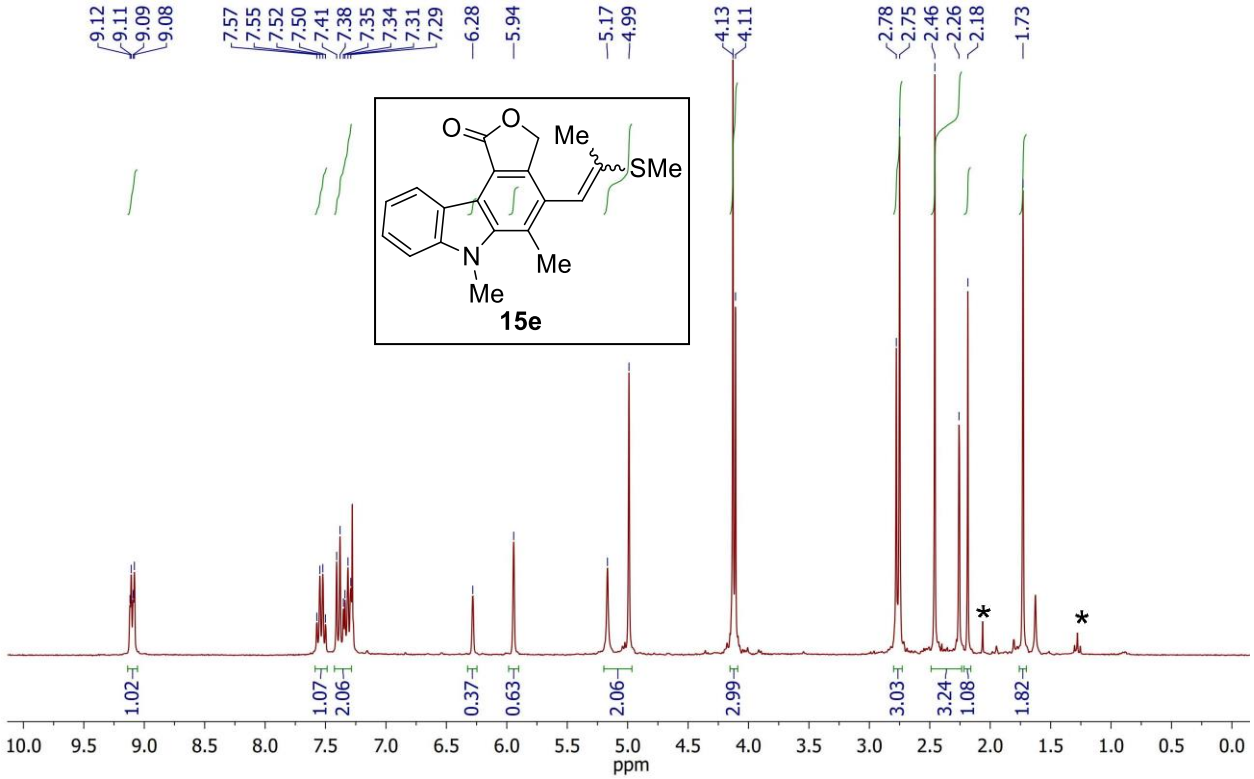


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 15d

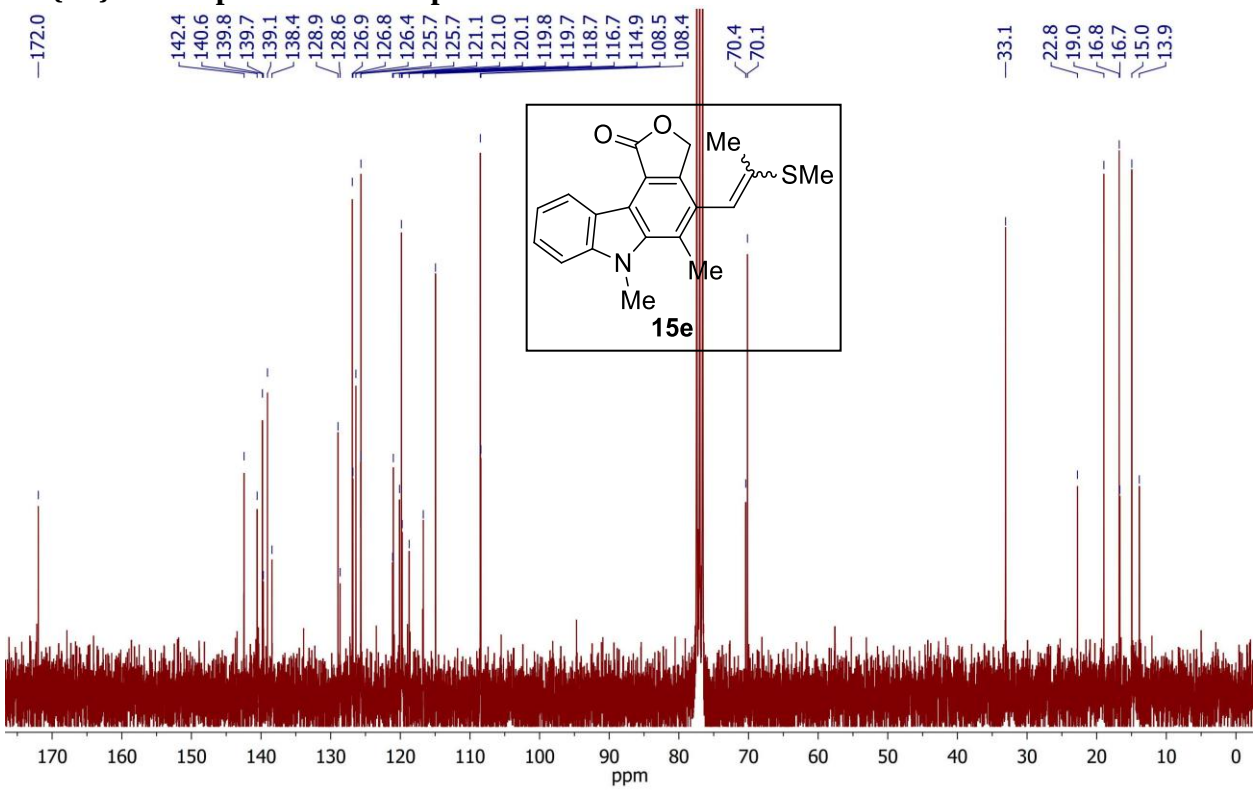


^{1}H NMR spectrum of compound 15e

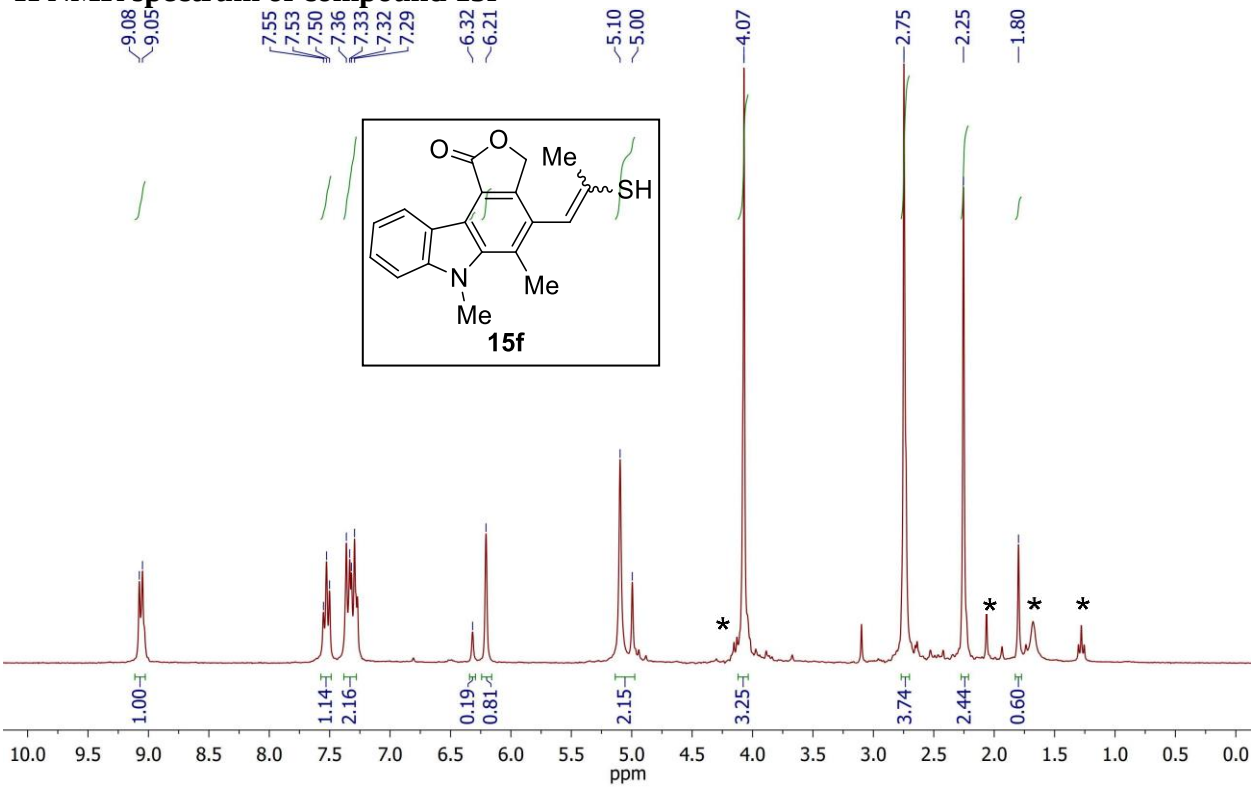


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 15e

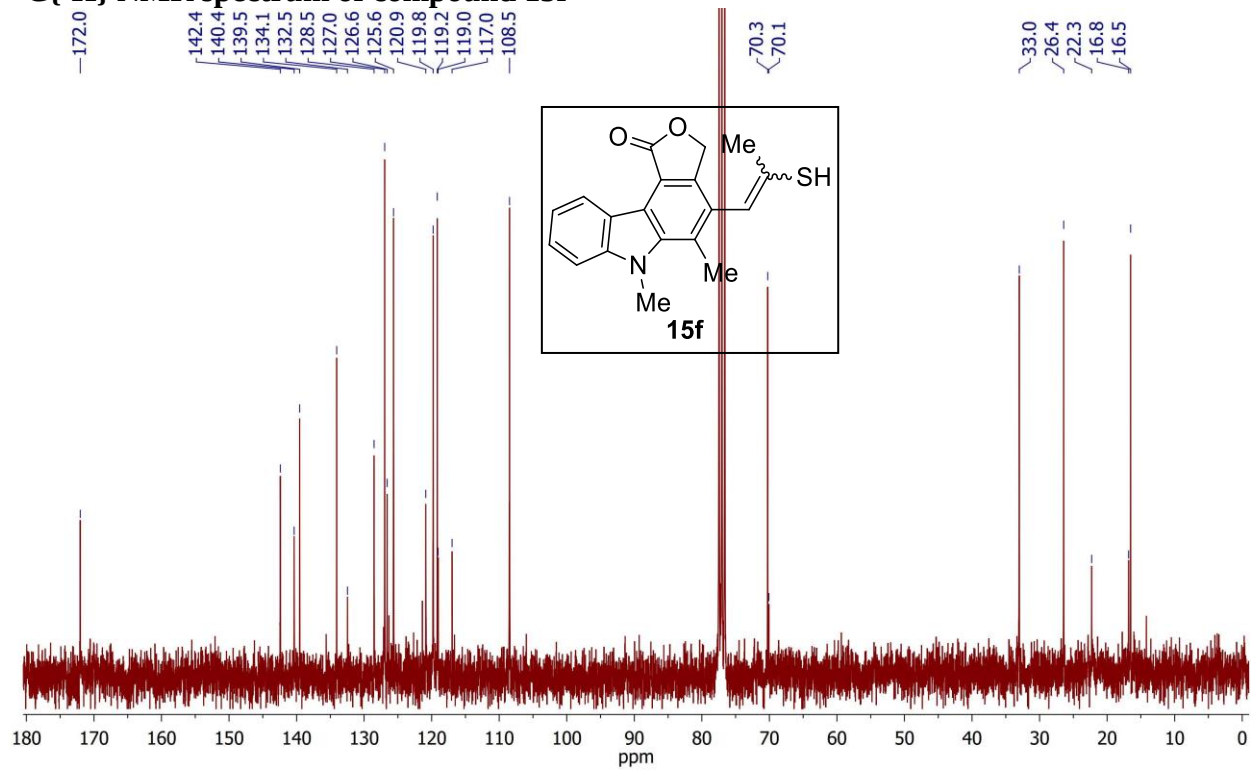


^{1}H NMR spectrum of compound 15f

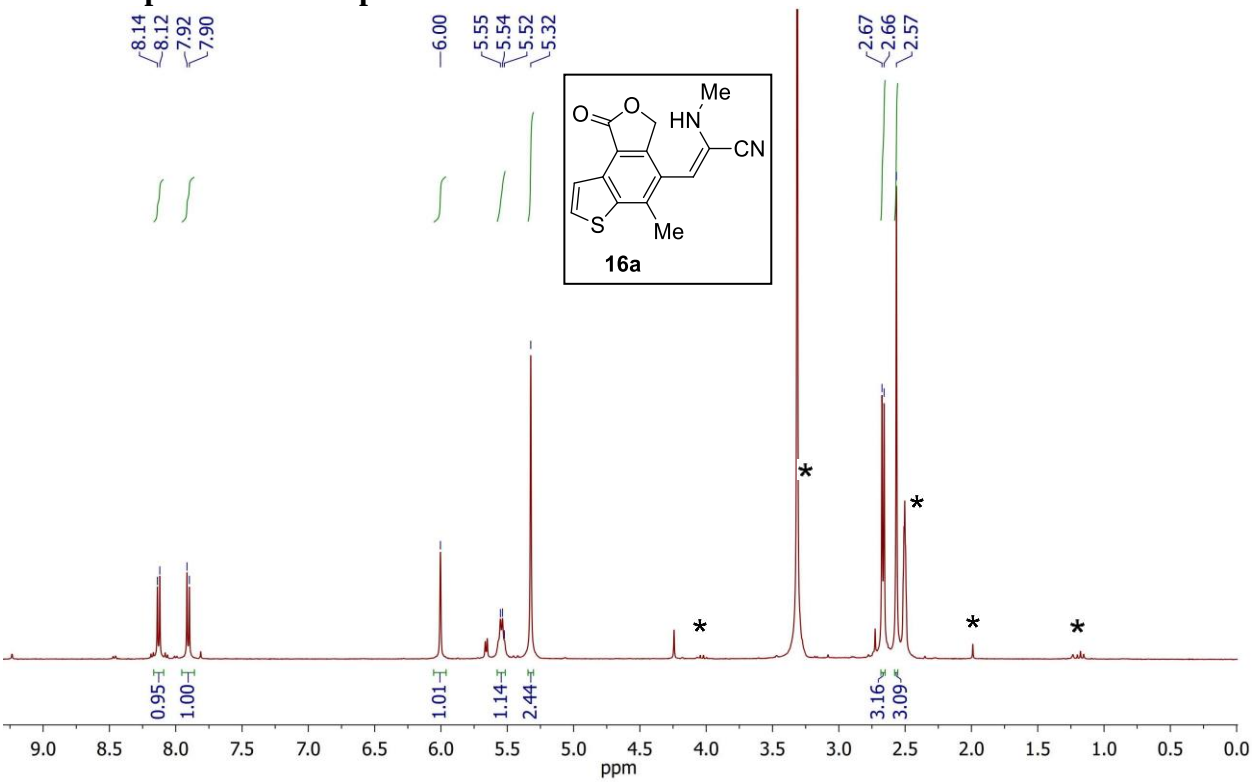


* Ethyl acetate and H_2O

^{13}C{^{1}H} NMR spectrum of compound 15f

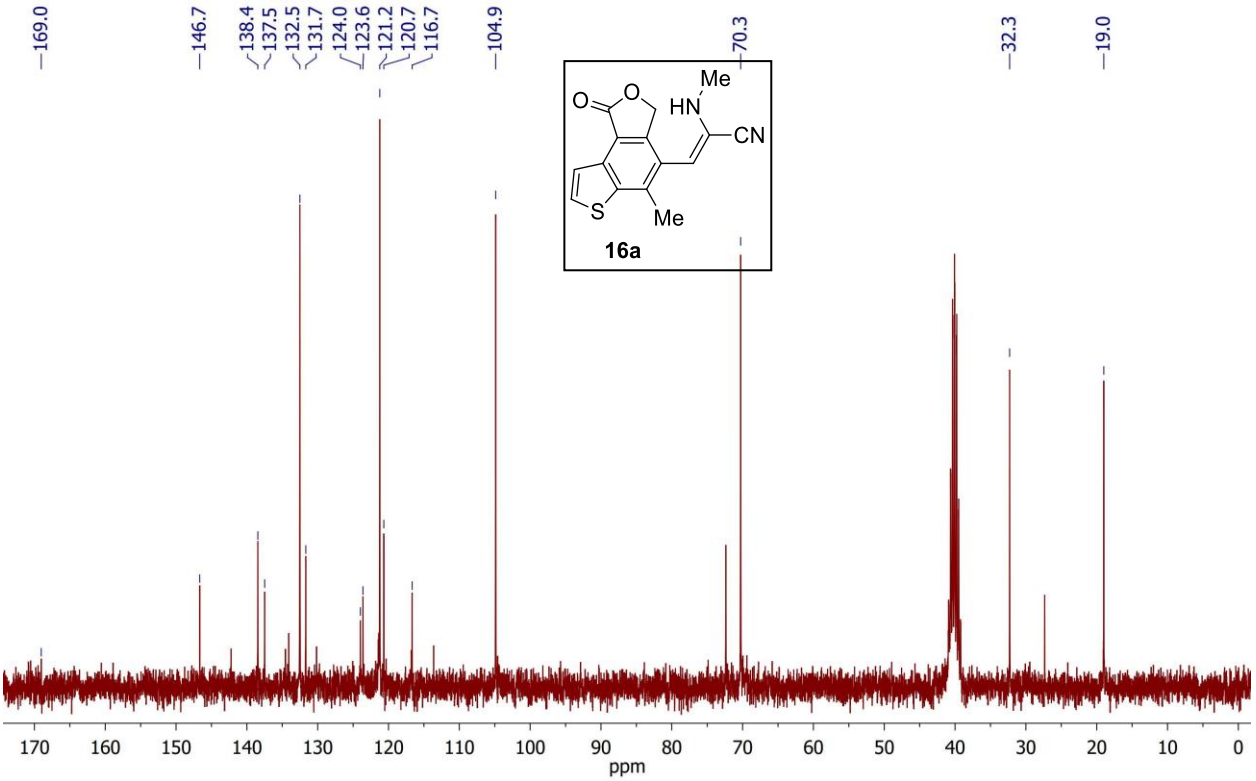


^{1}H NMR spectrum of compound 16a

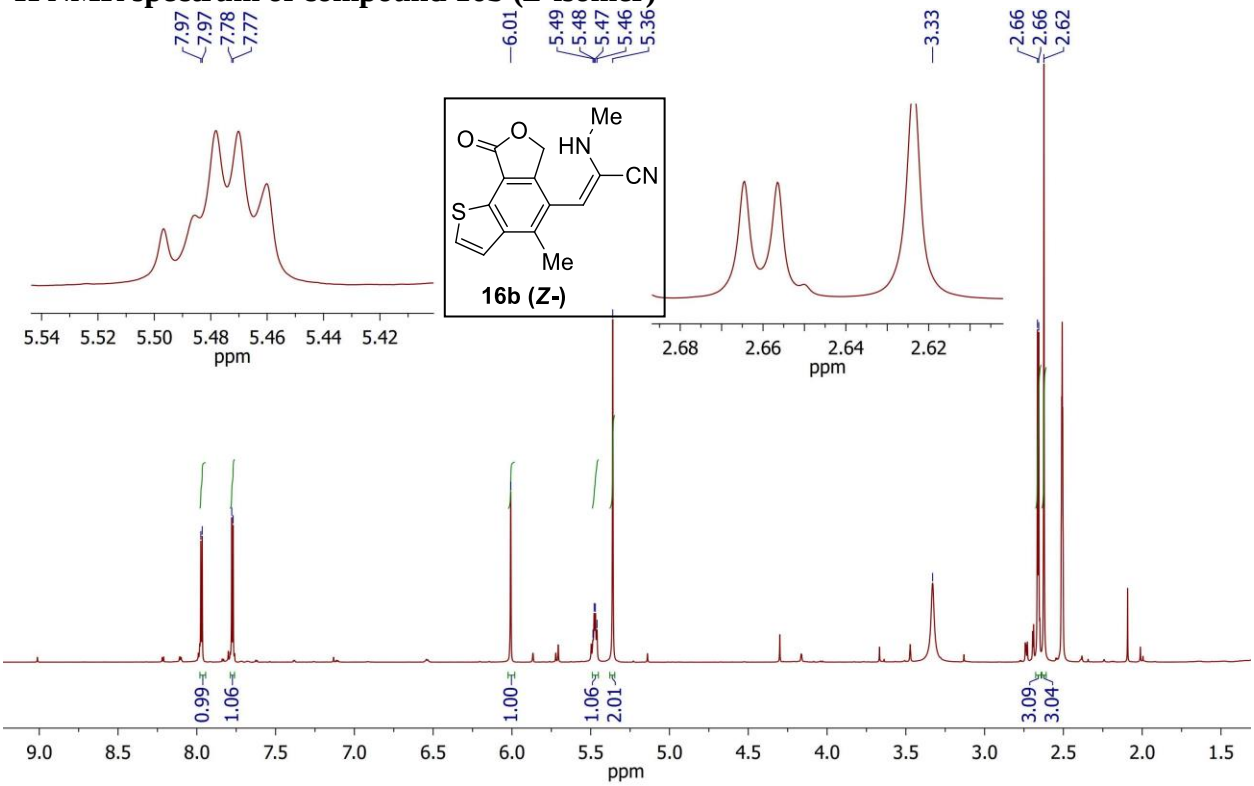


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

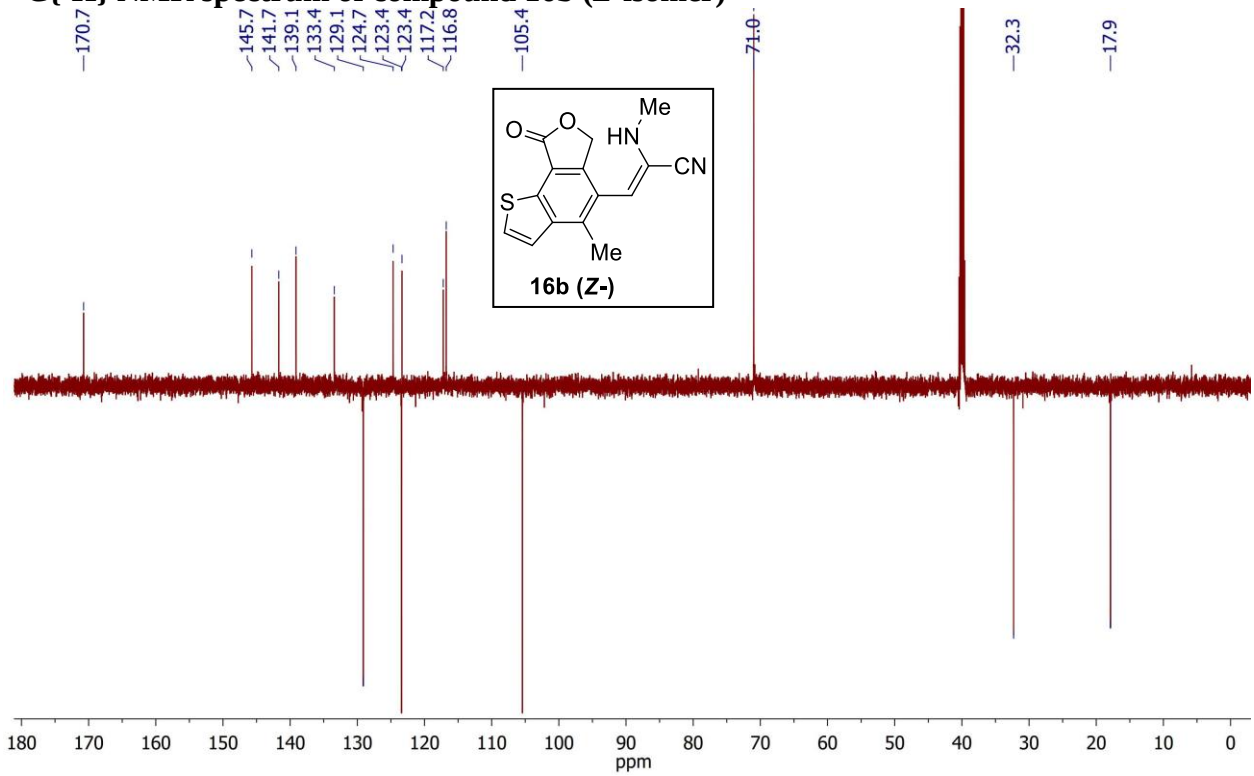
^{13}C{^{1}H} NMR spectrum of compound 16a



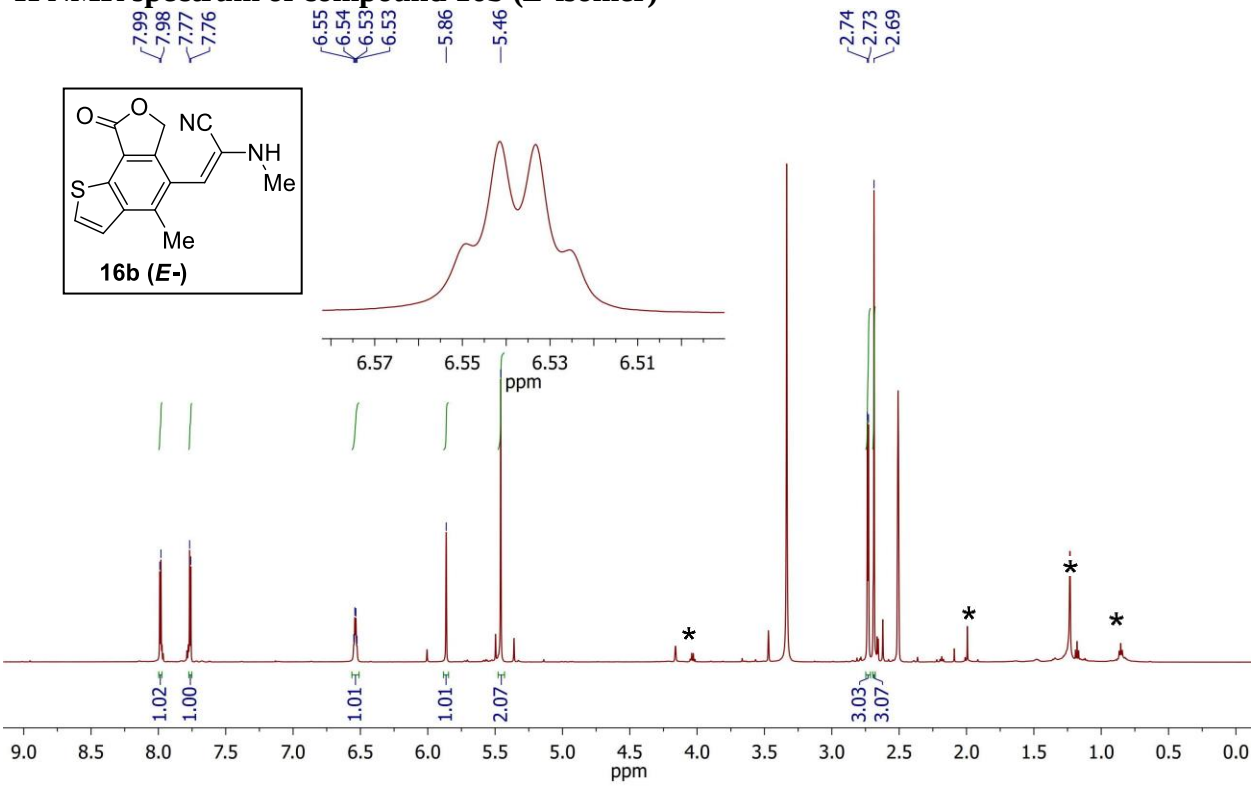
^{1}H NMR spectrum of compound 16b (*Z*-isomer)



^{13}C{^{1}H} NMR spectrum of compound 16b (*Z*-isomer)

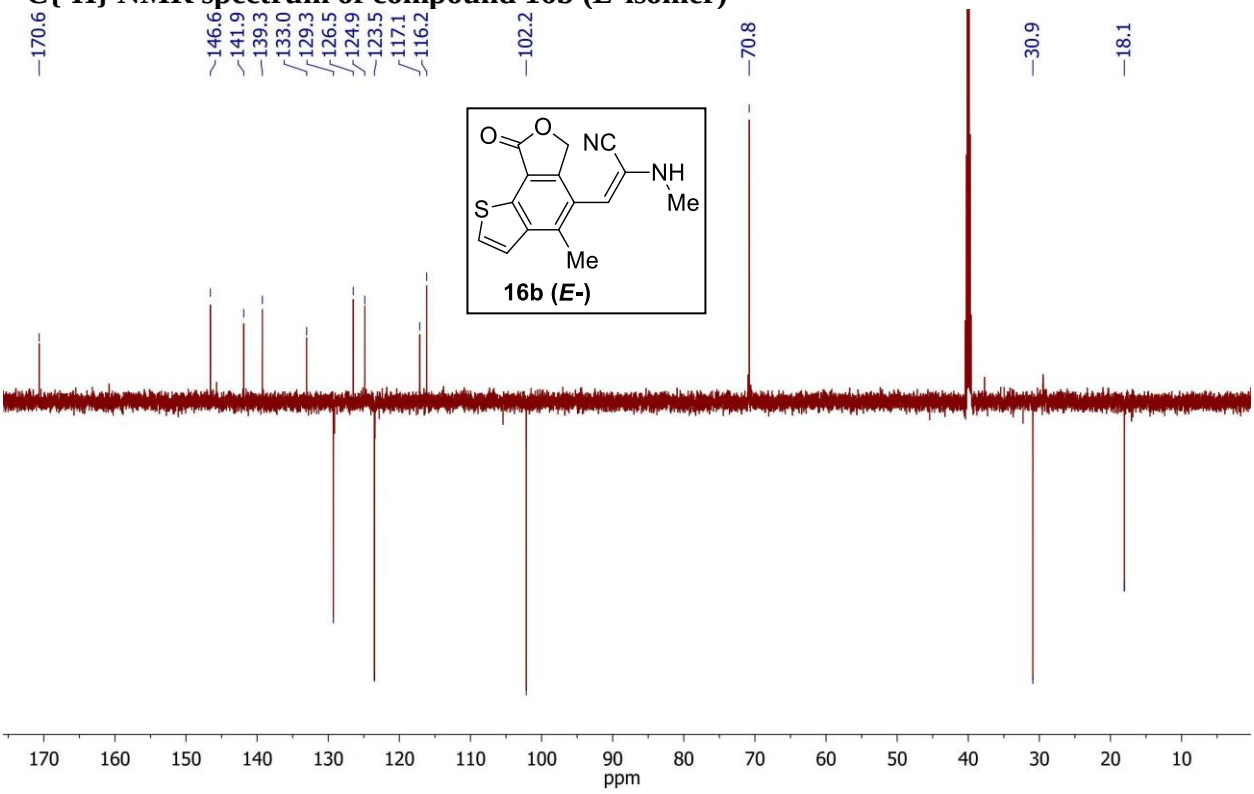


^{1}H NMR spectrum of compound 16b (*E*-isomer)

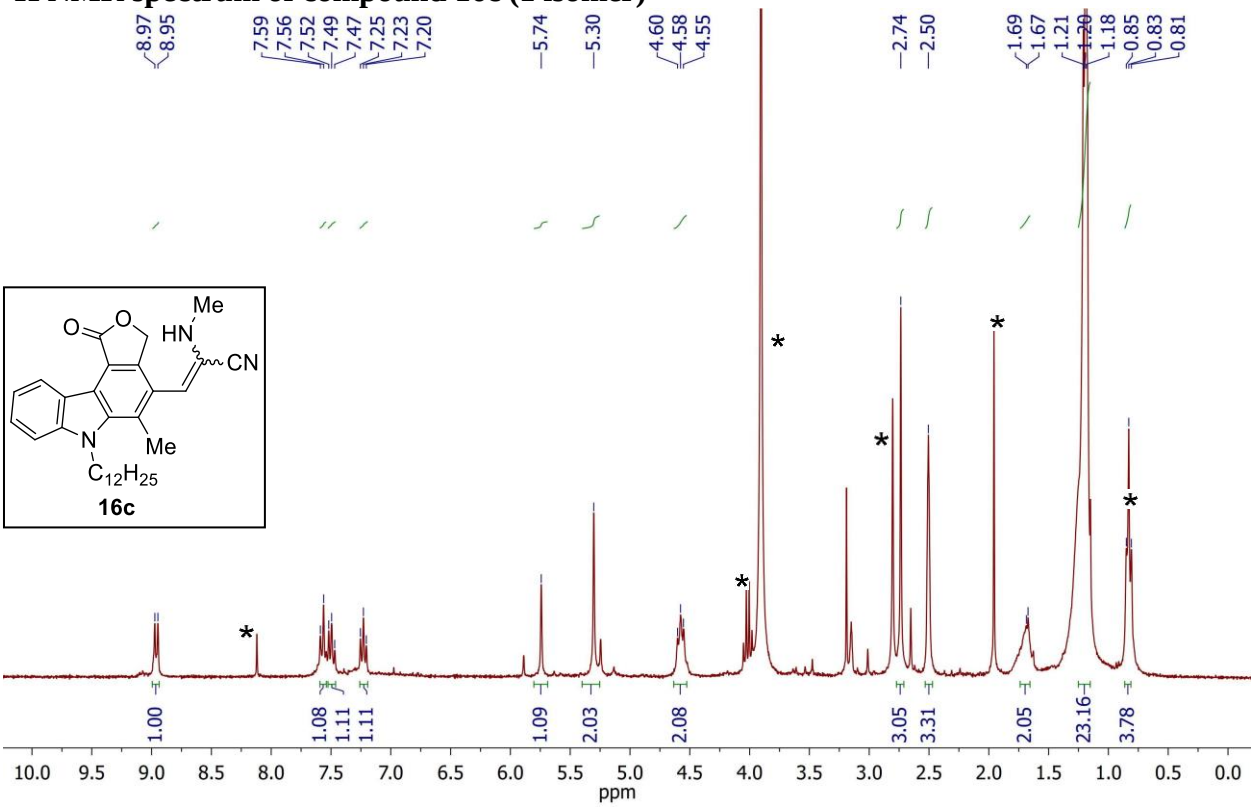


* Ethyl acetate and H_2O

^{13}C{^{1}H} NMR spectrum of compound 16b (*E*-isomer)

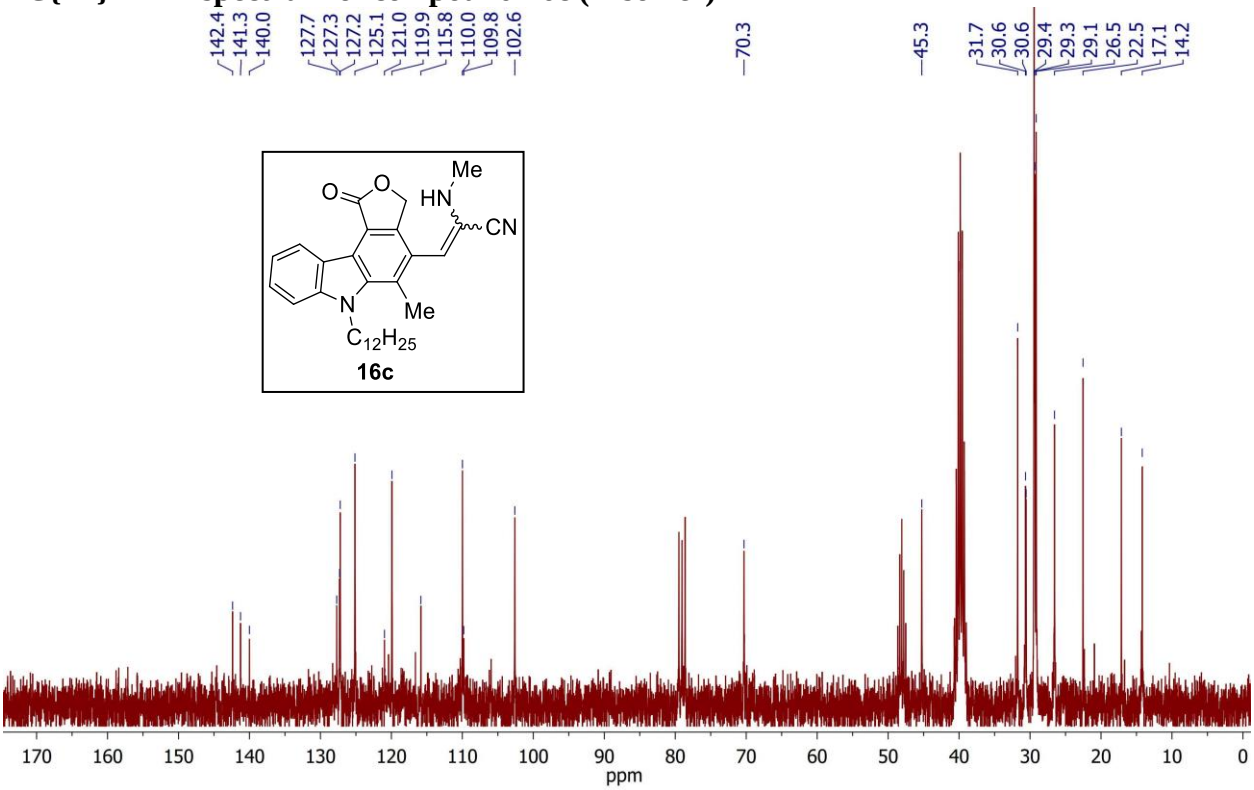


^{1}H NMR spectrum of compound 16c (1 isomer)

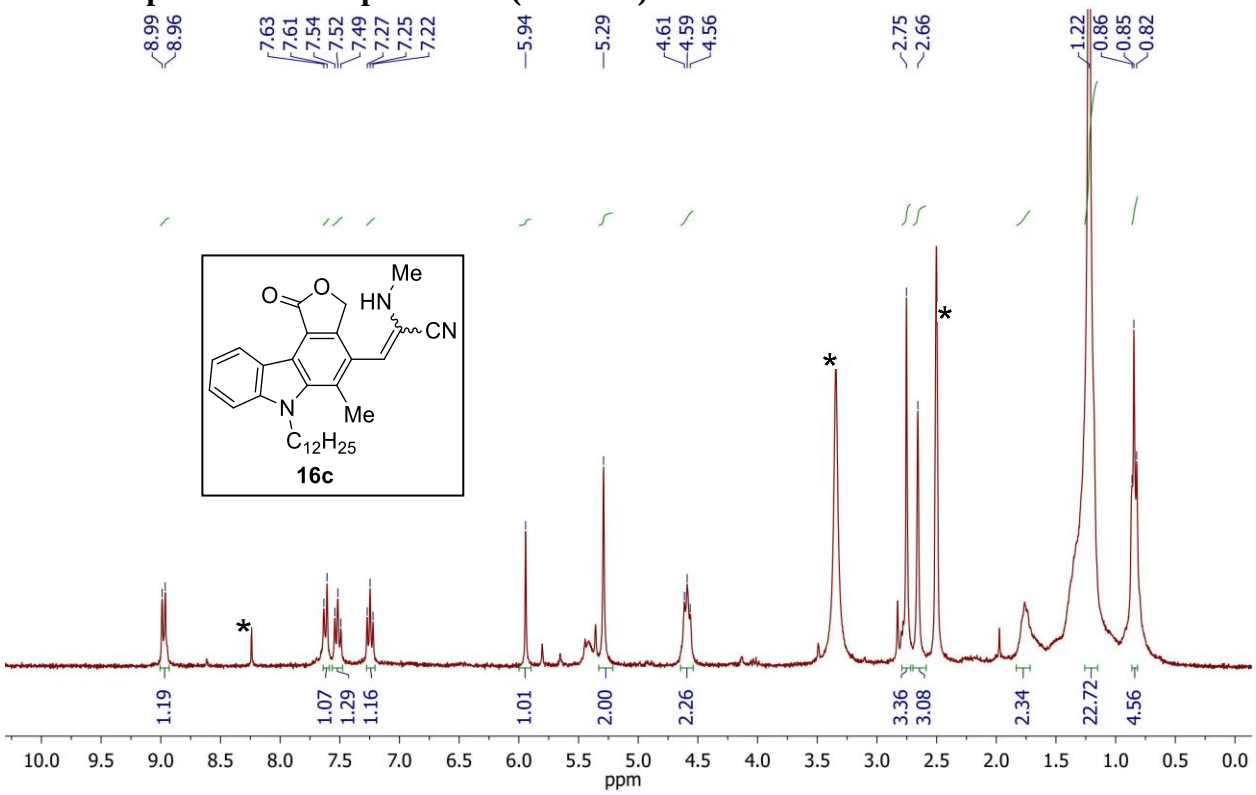


* Chloroform, Ethyl acetate, H_2O and DMSO [spectrum was obtained in the mixture $CDCl_3$/DMSO as solvent]

^{13}C{^{1}H} NMR spectrum of compound 16c (1 isomer)

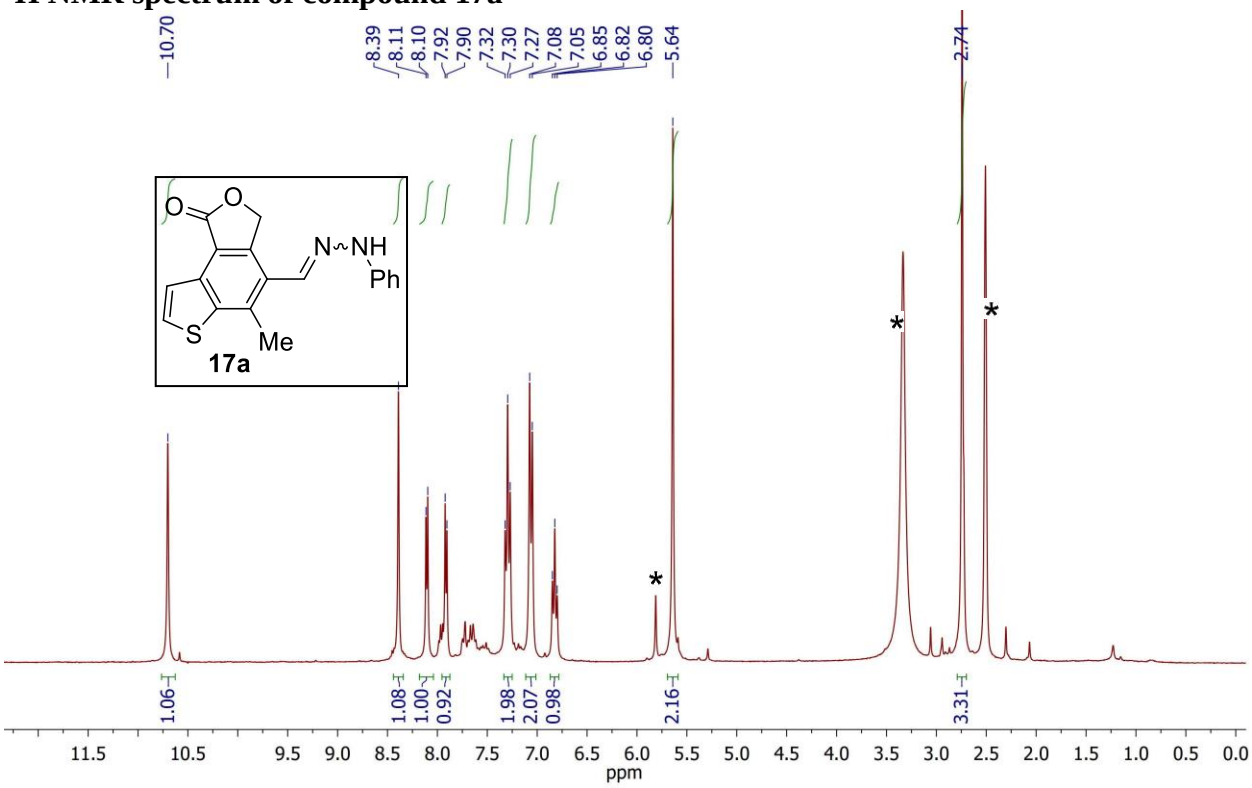


^{1}H NMR spectrum of compound 16c (2 isomer)



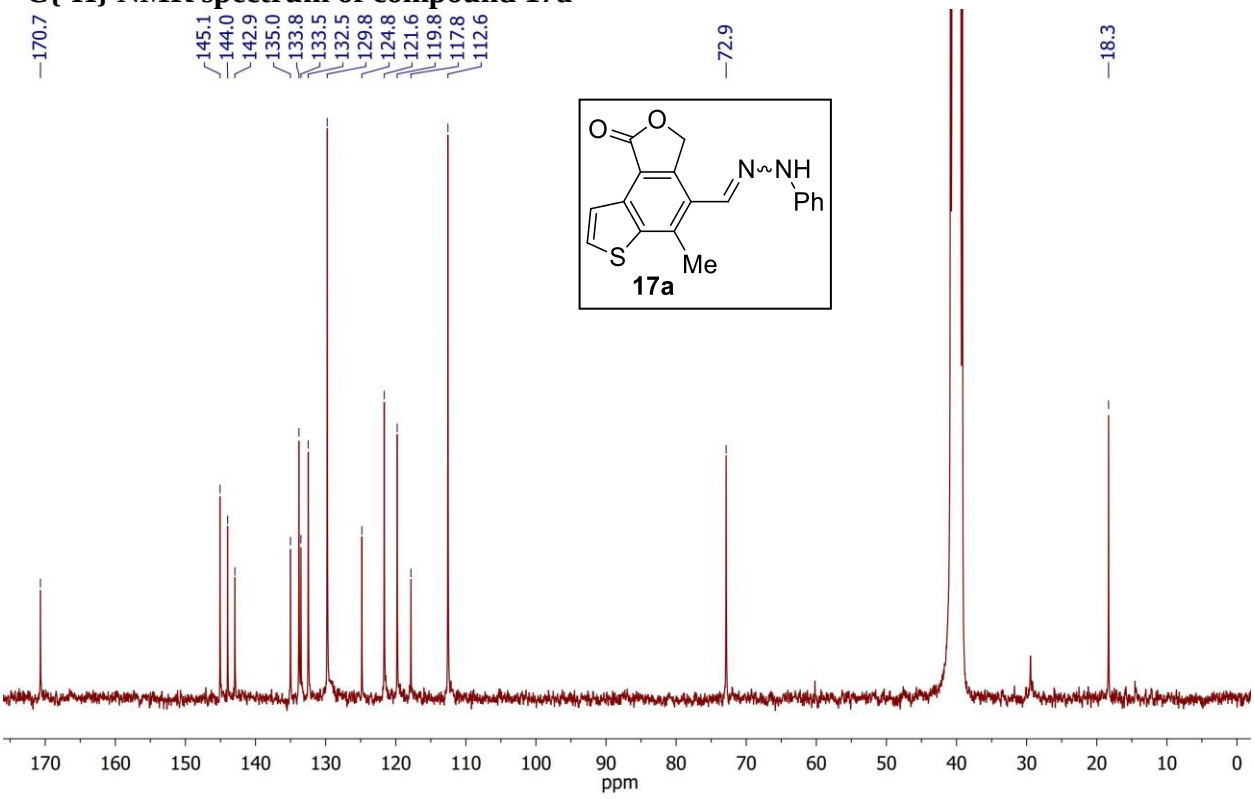
* Chloroform, H_2O and DMSO [spectrum was obtained in the mixture $CDCl_3$/DMSO as solvent]

^{1}H NMR spectrum of compound 17a

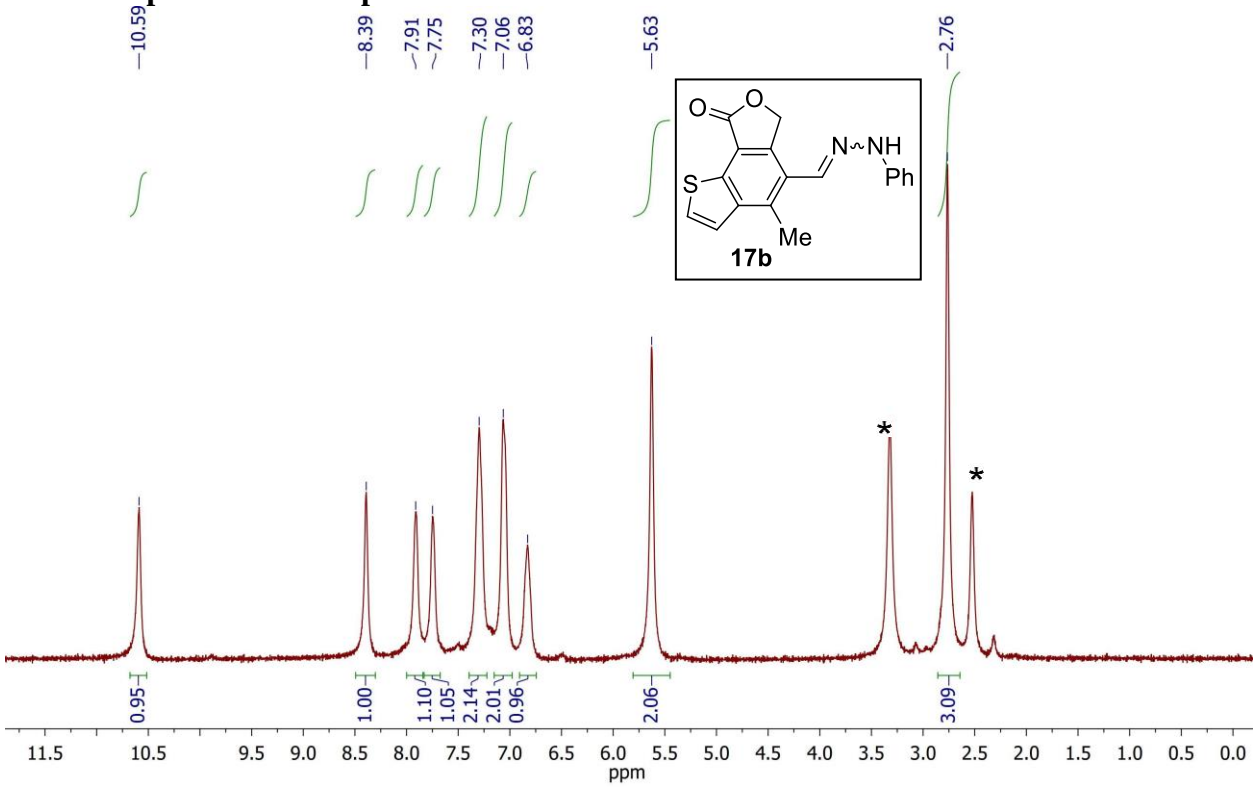


* Dichloromethane (5.76 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 17a

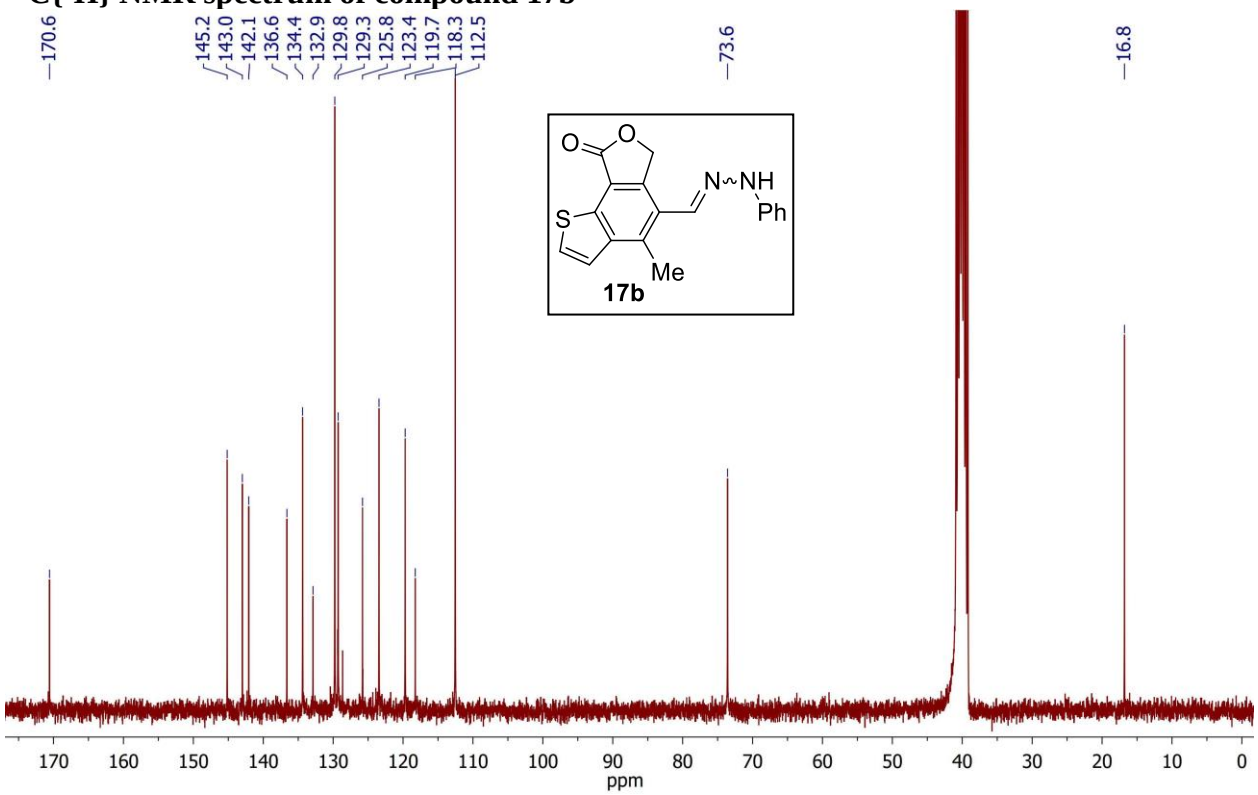


^{1}H NMR spectrum of compound 17b

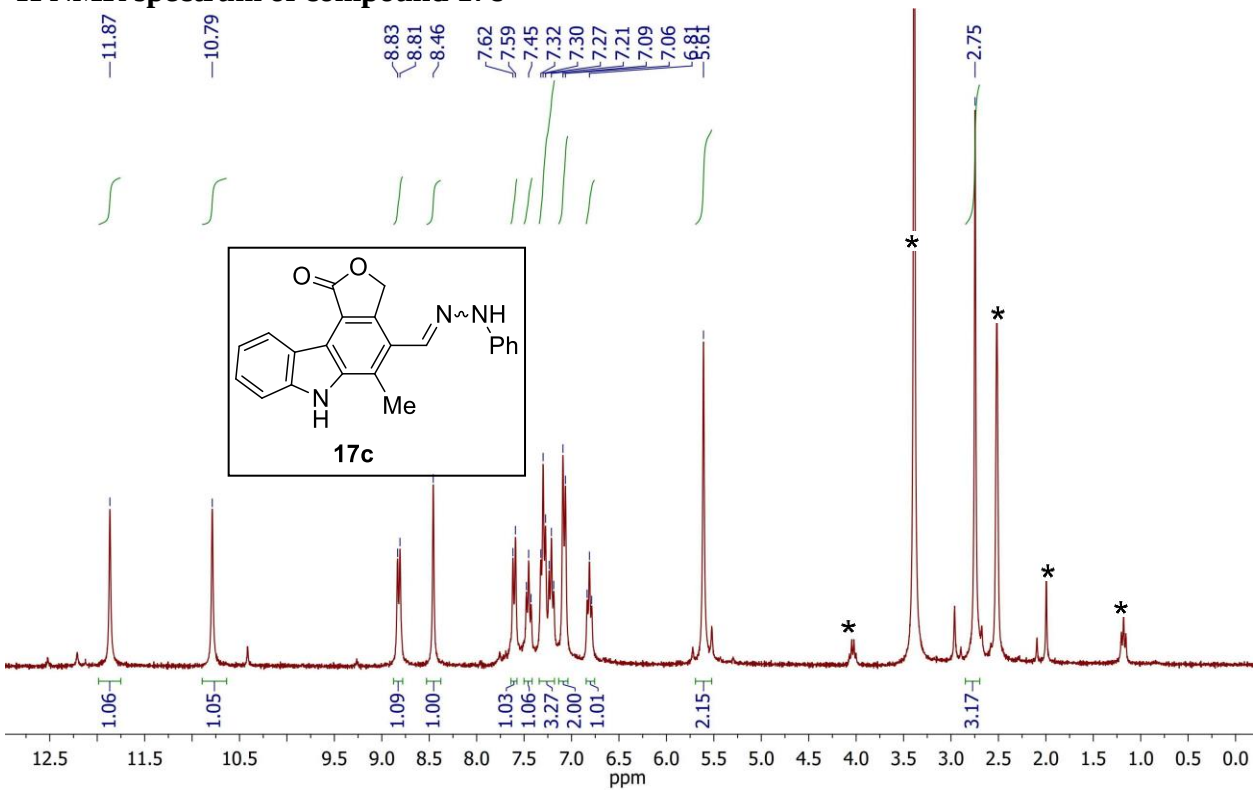


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 17b

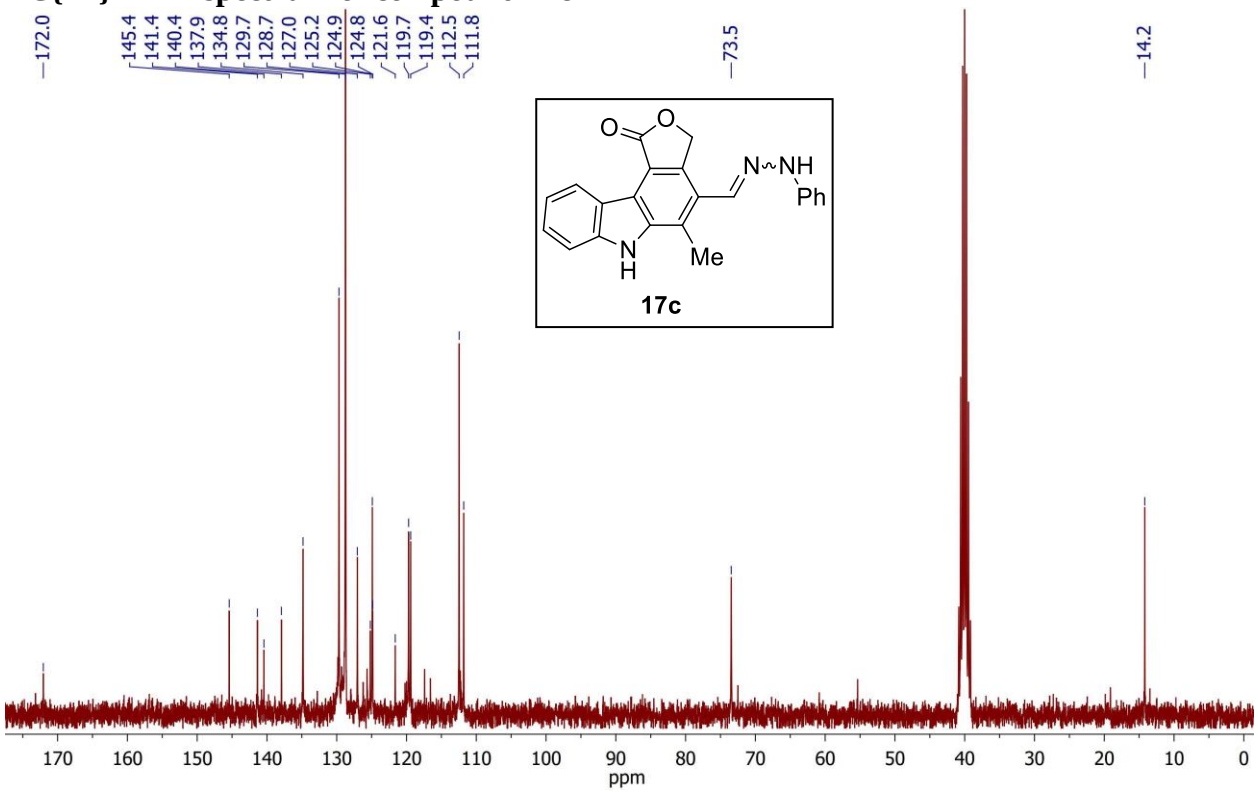


^{1}H NMR spectrum of compound 17c

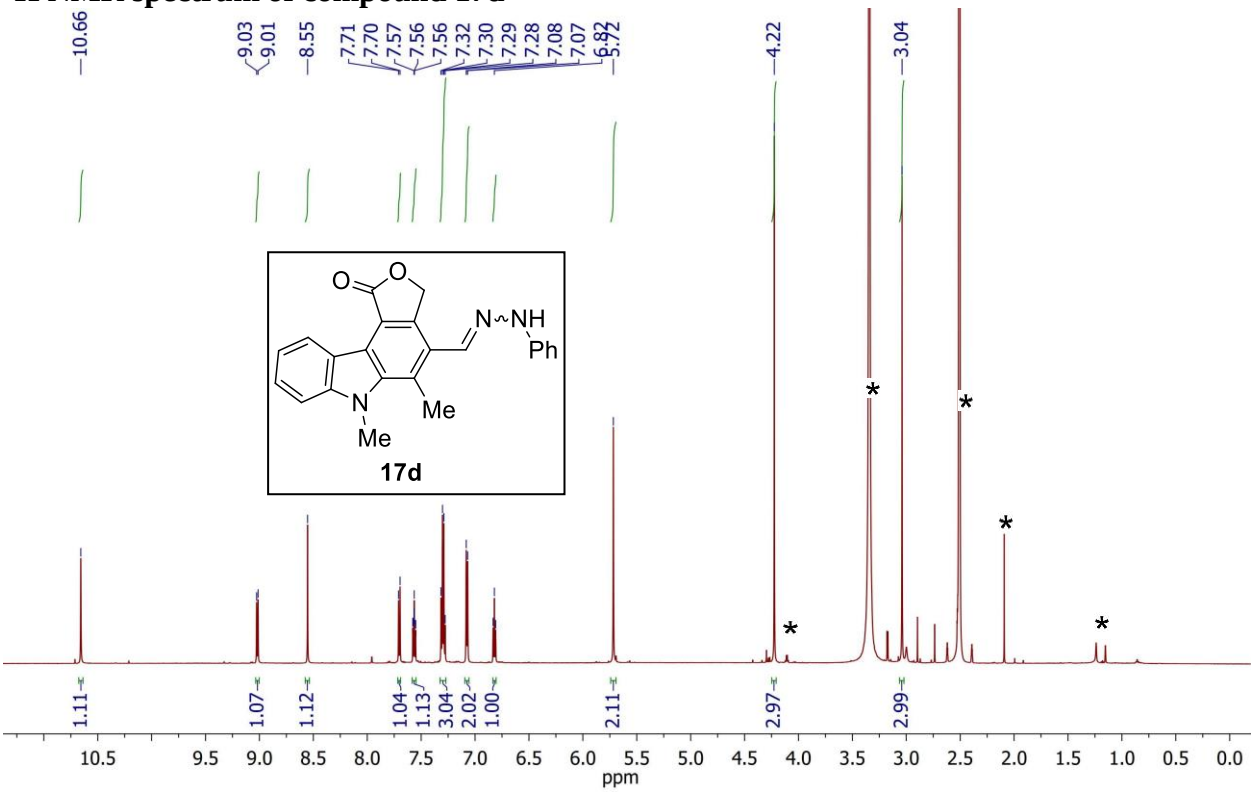


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 17c

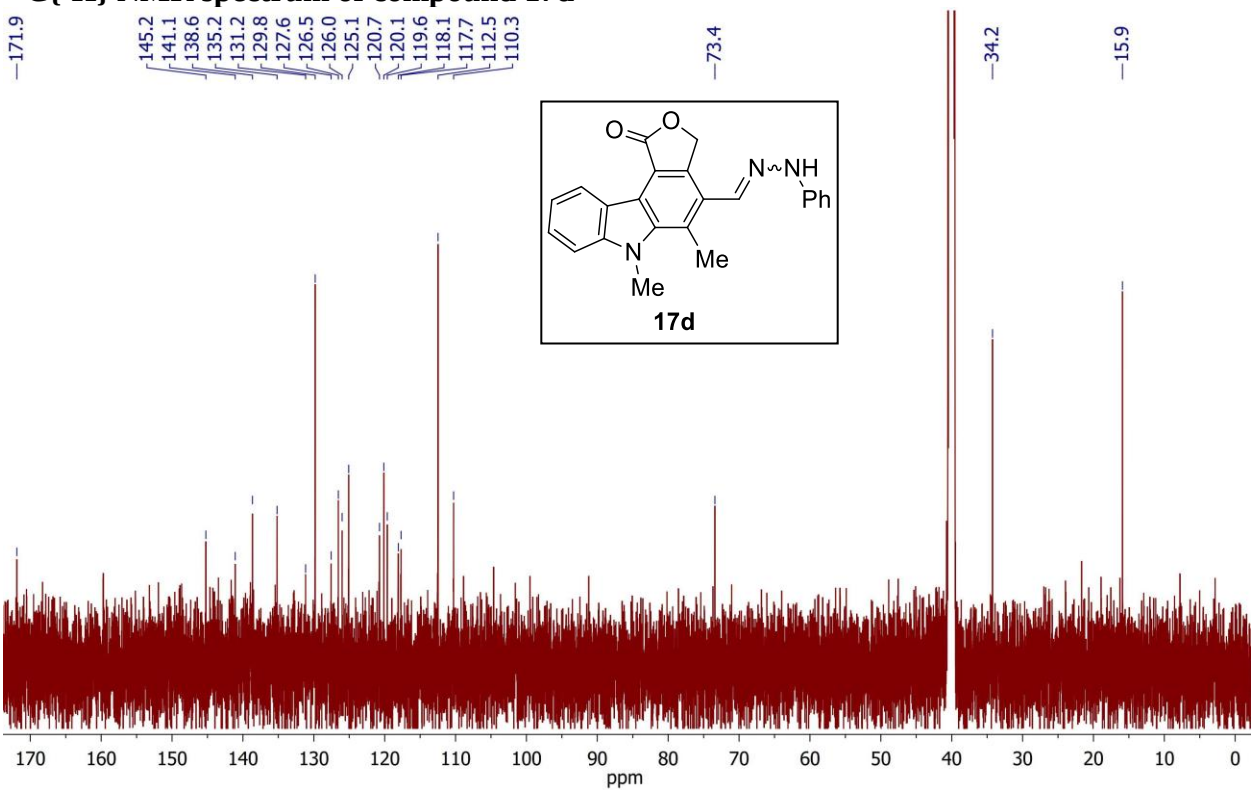


^{1}H NMR spectrum of compound 17d

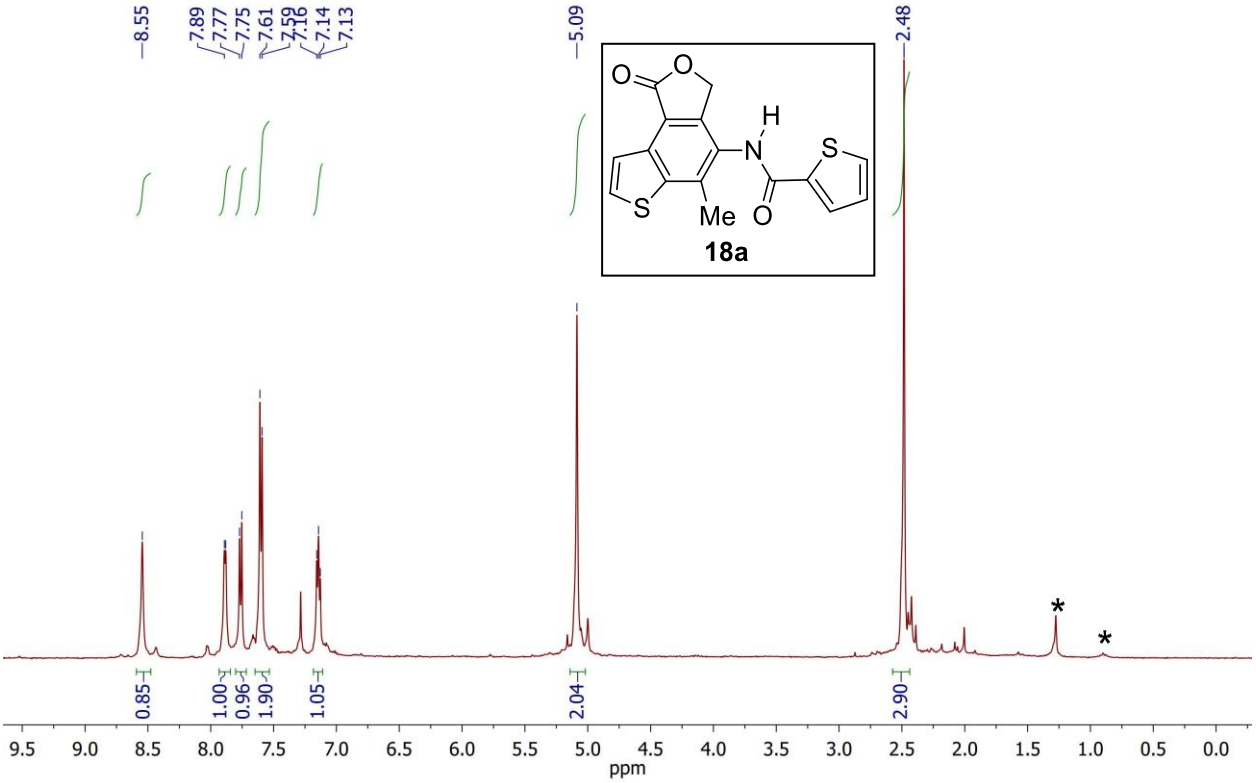


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 17d

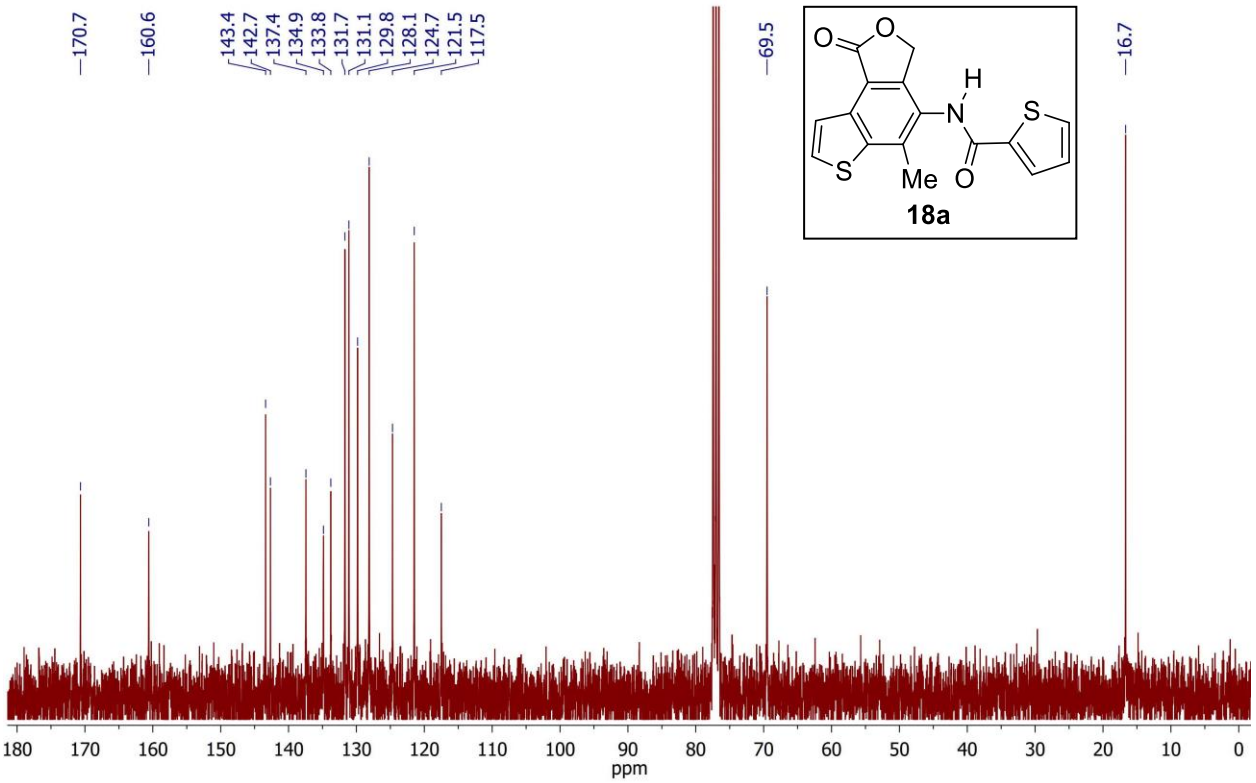


^{1}H NMR spectrum of compound 18a

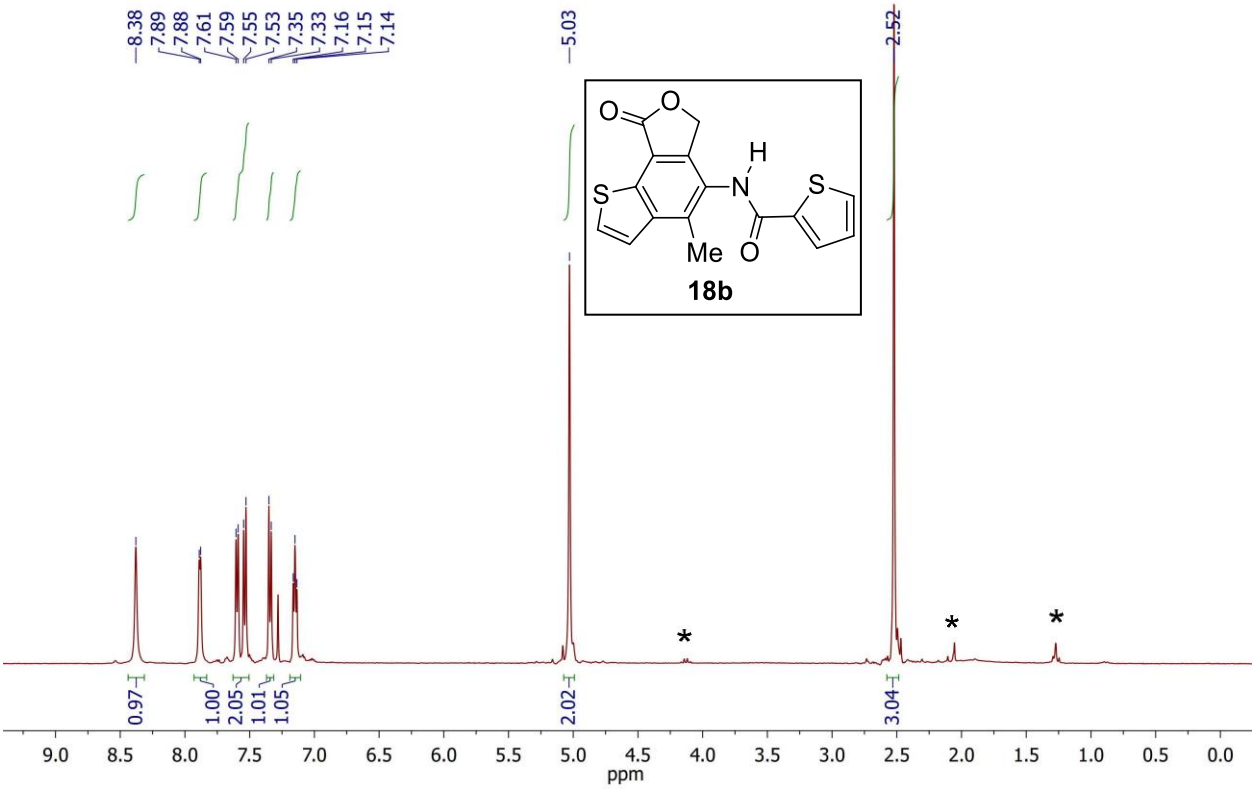


* Grease

^{13}C{^{1}H} NMR spectrum of compound 18a

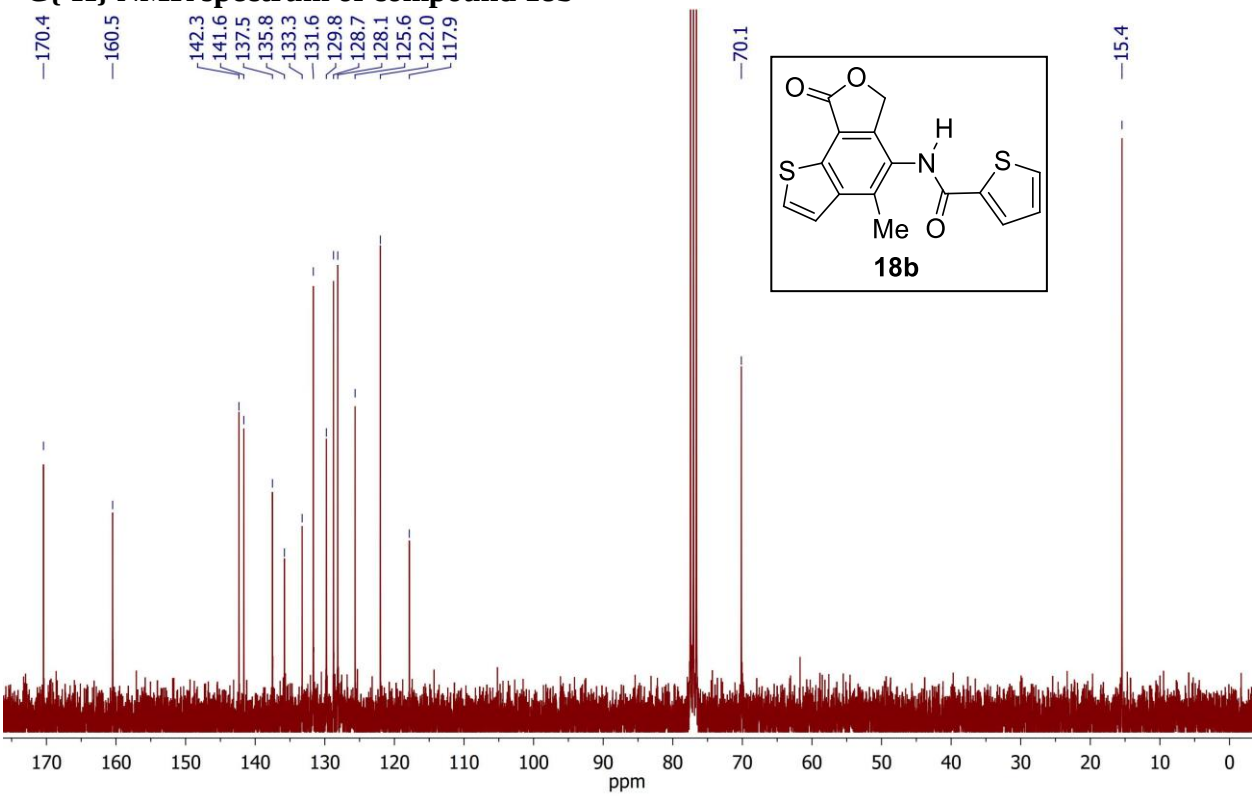


^{1}H NMR spectrum of compound 18b

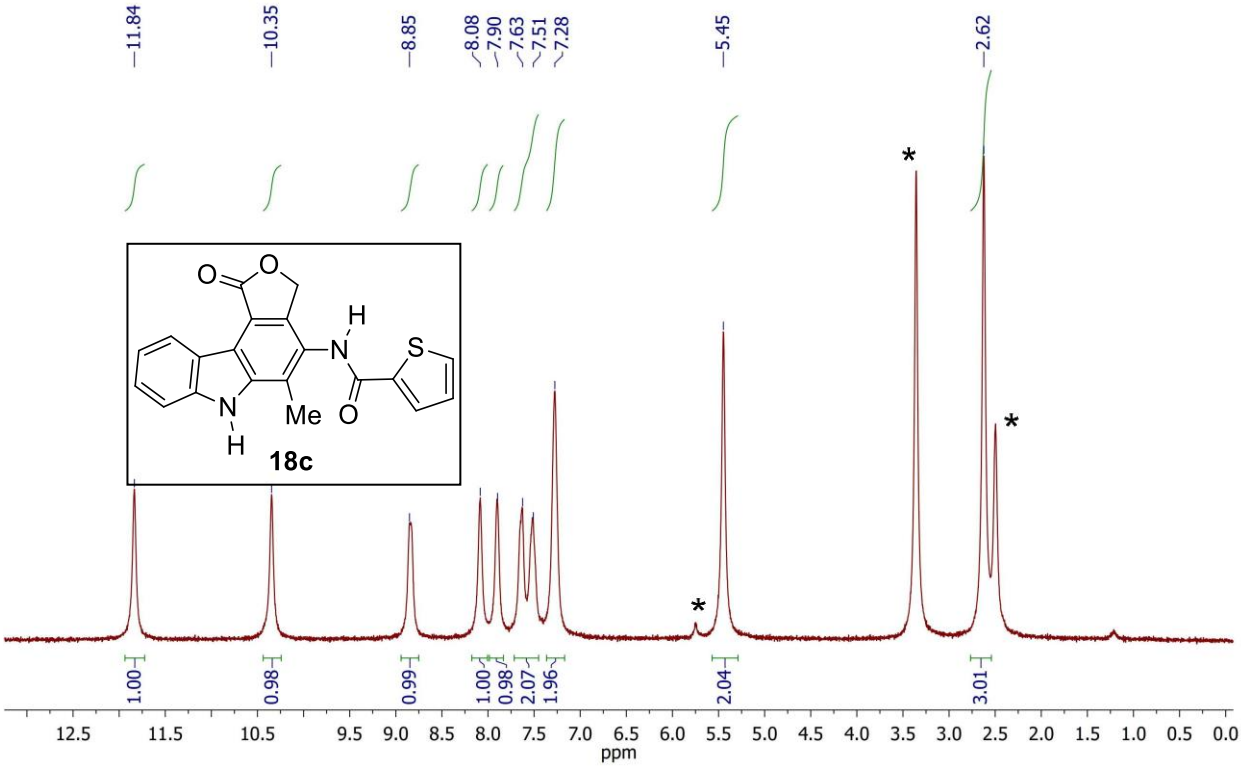


* Ethyl acetate

^{13}C{^{1}H} NMR spectrum of compound 18b

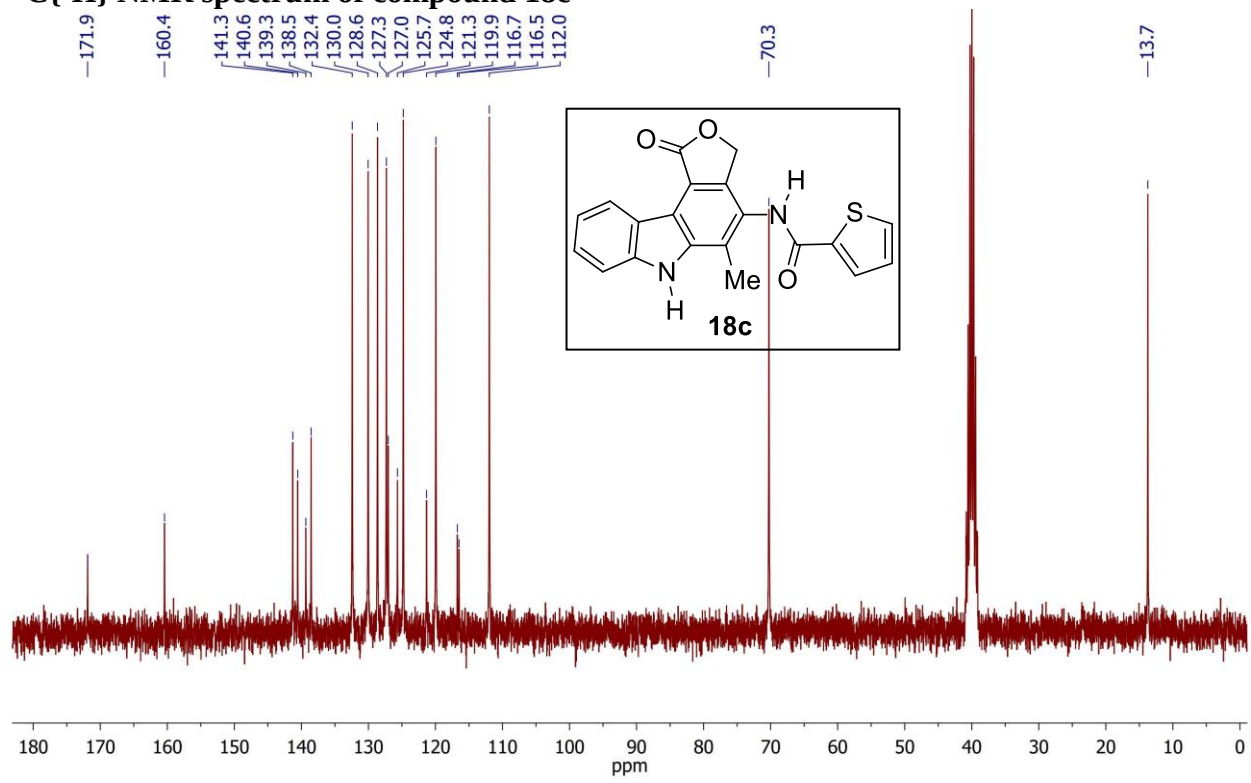


^{1}H NMR spectrum of compound 18c

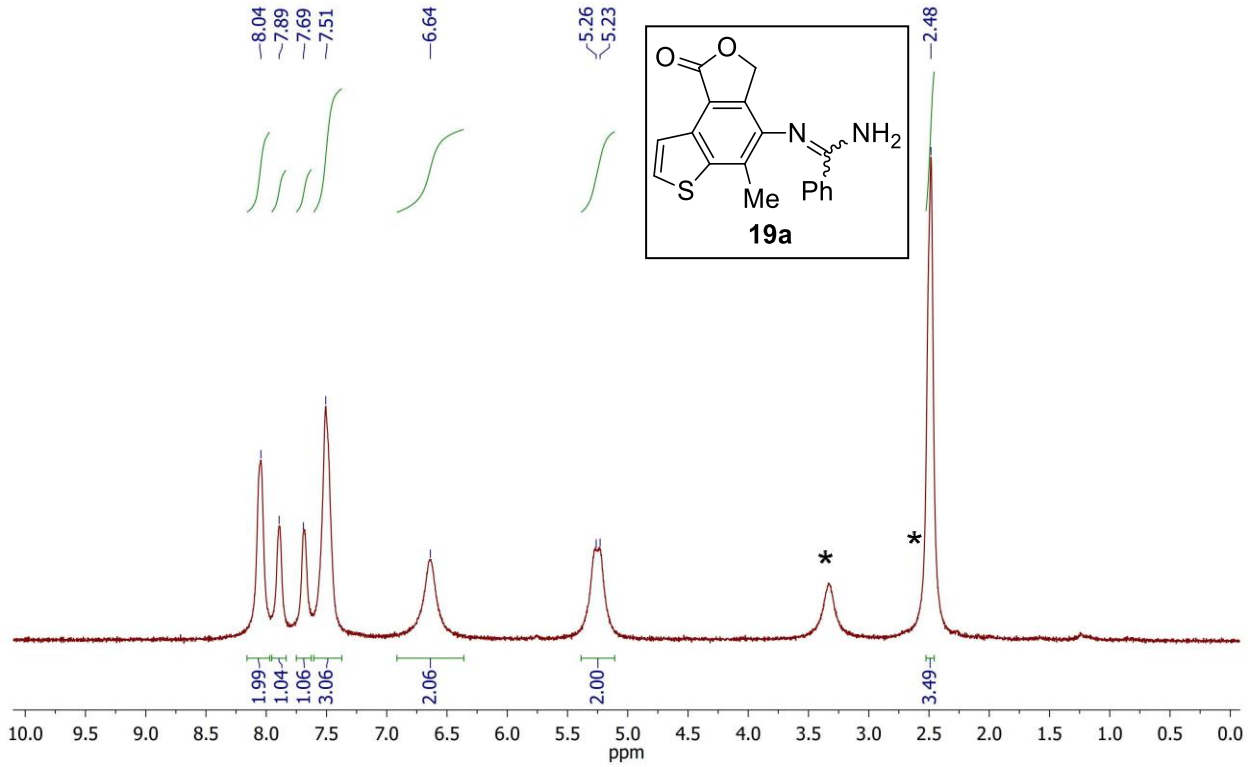


* Dichloromethane (5.76 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 18c

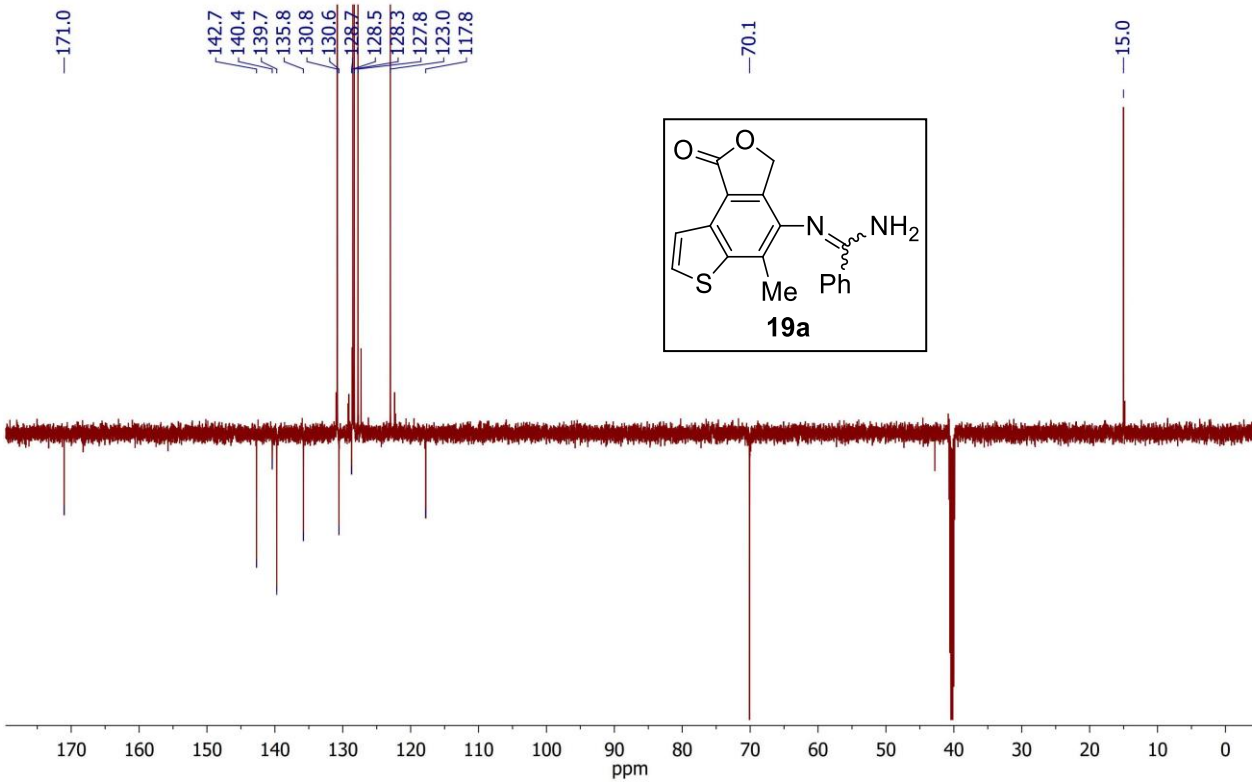


^{1}H NMR spectrum of compound 19a

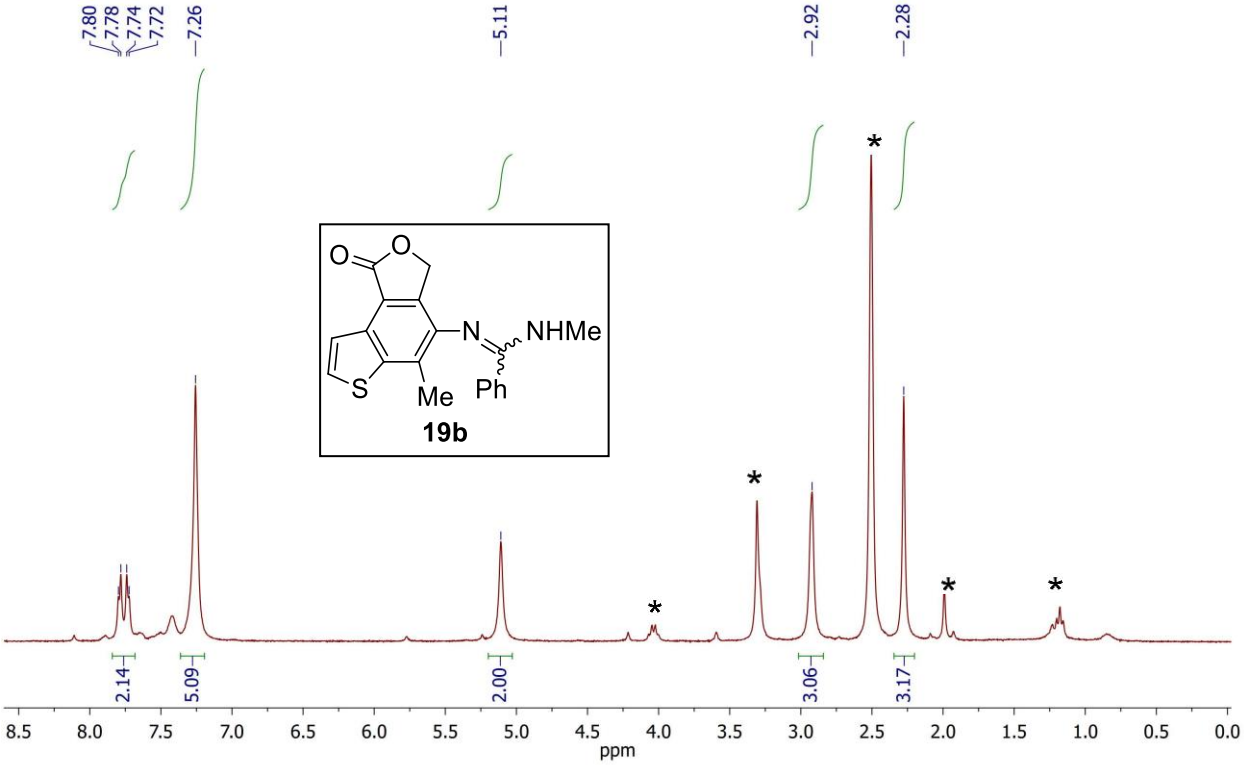


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} DEPT NMR spectrum of compound 19a

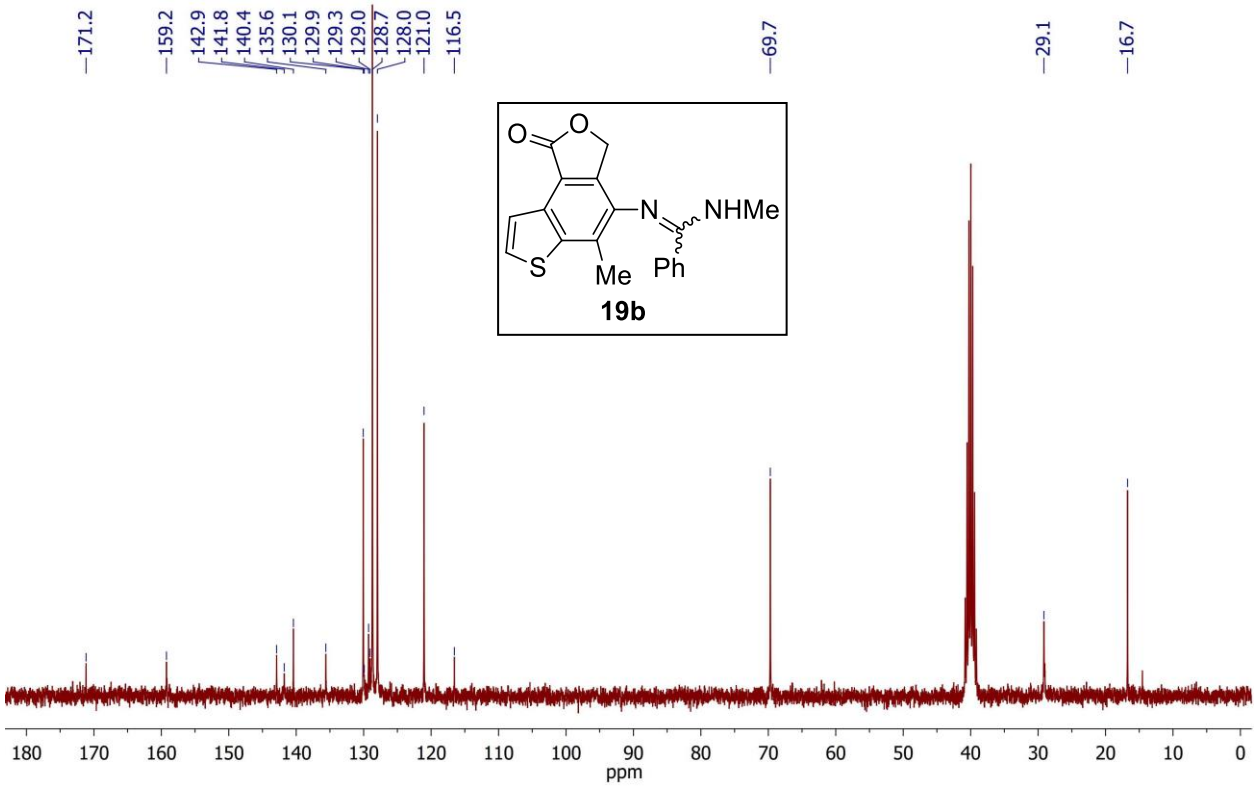


^{1}H NMR spectrum of compound 19b

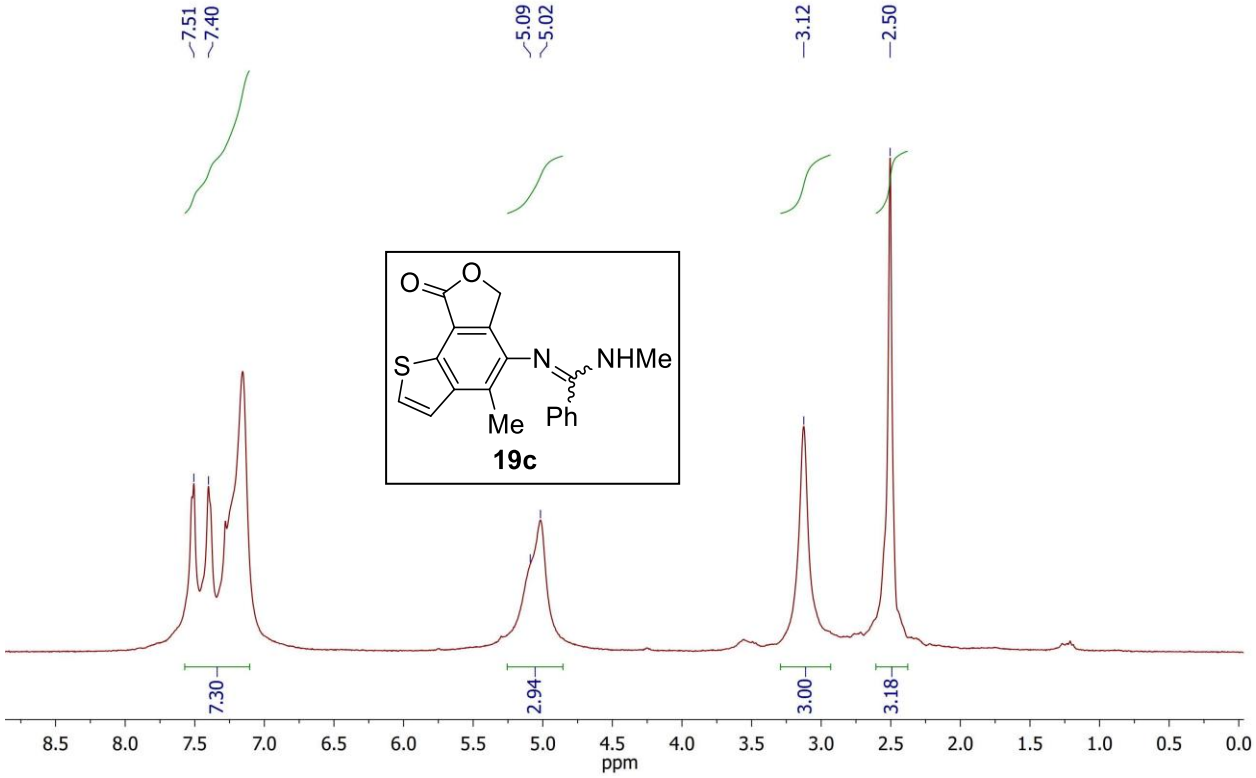


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

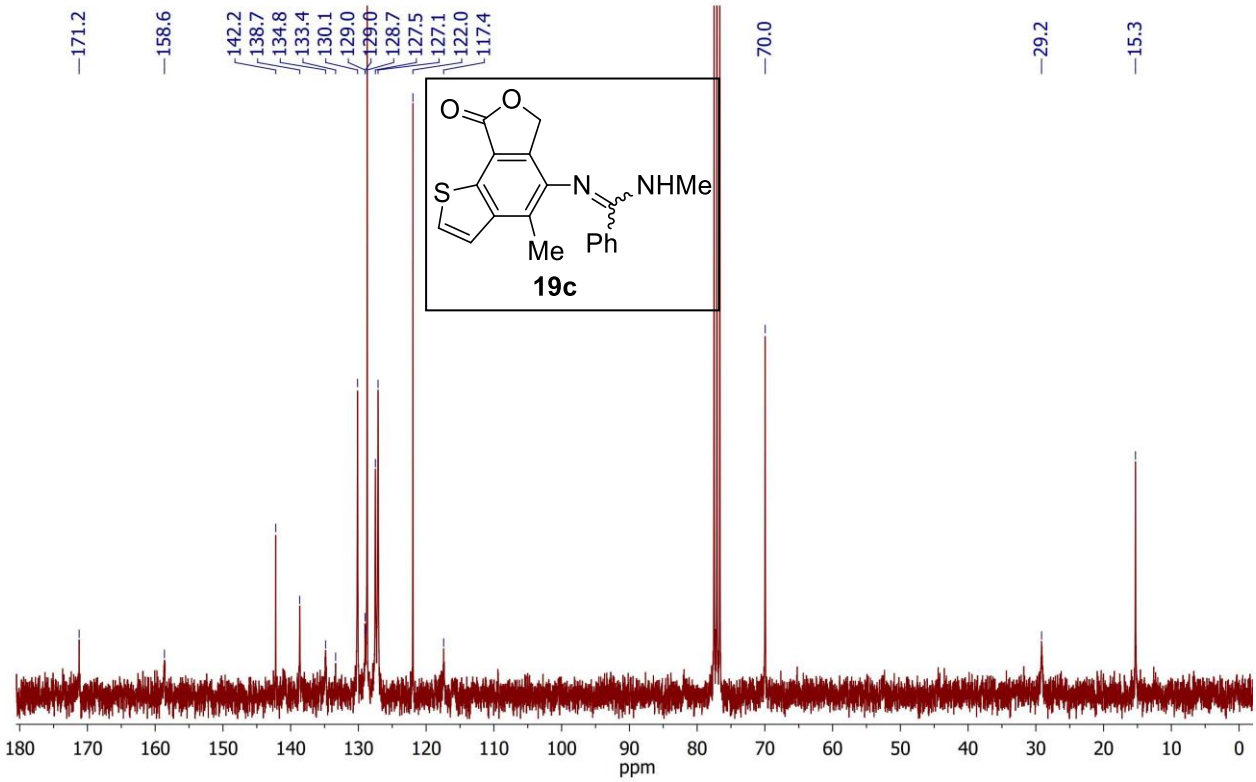
^{13}C{^{1}H} NMR spectrum of compound 19b



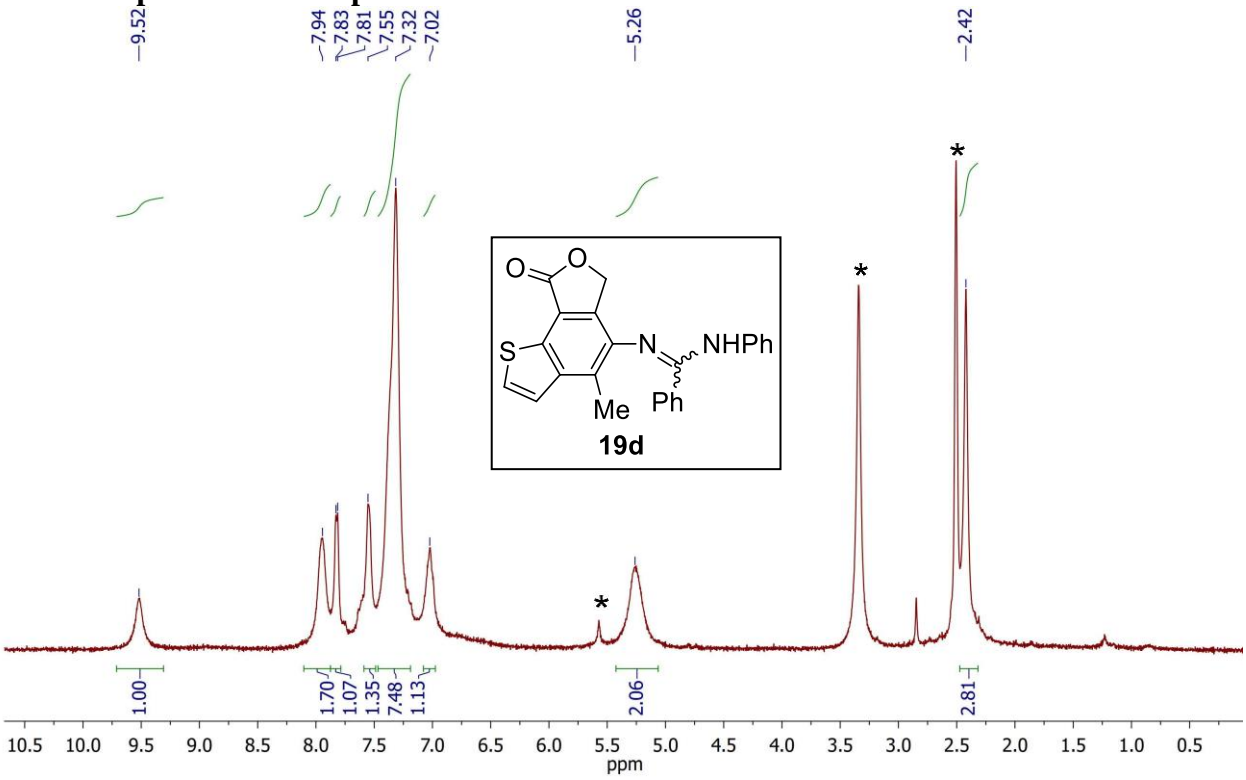
^{1}H NMR spectrum of compound 19c



^{13}C{^{1}H} NMR spectrum of compound 19c

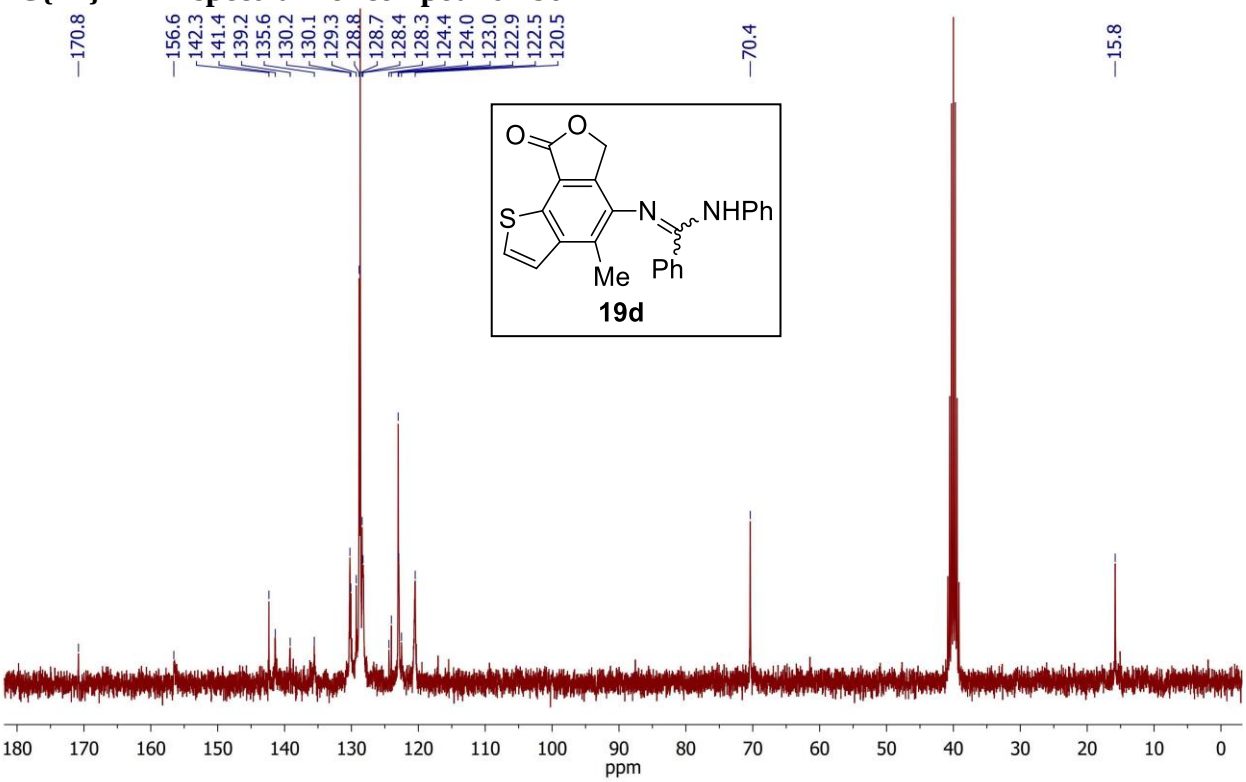


^{1}H NMR spectrum of compound 19d

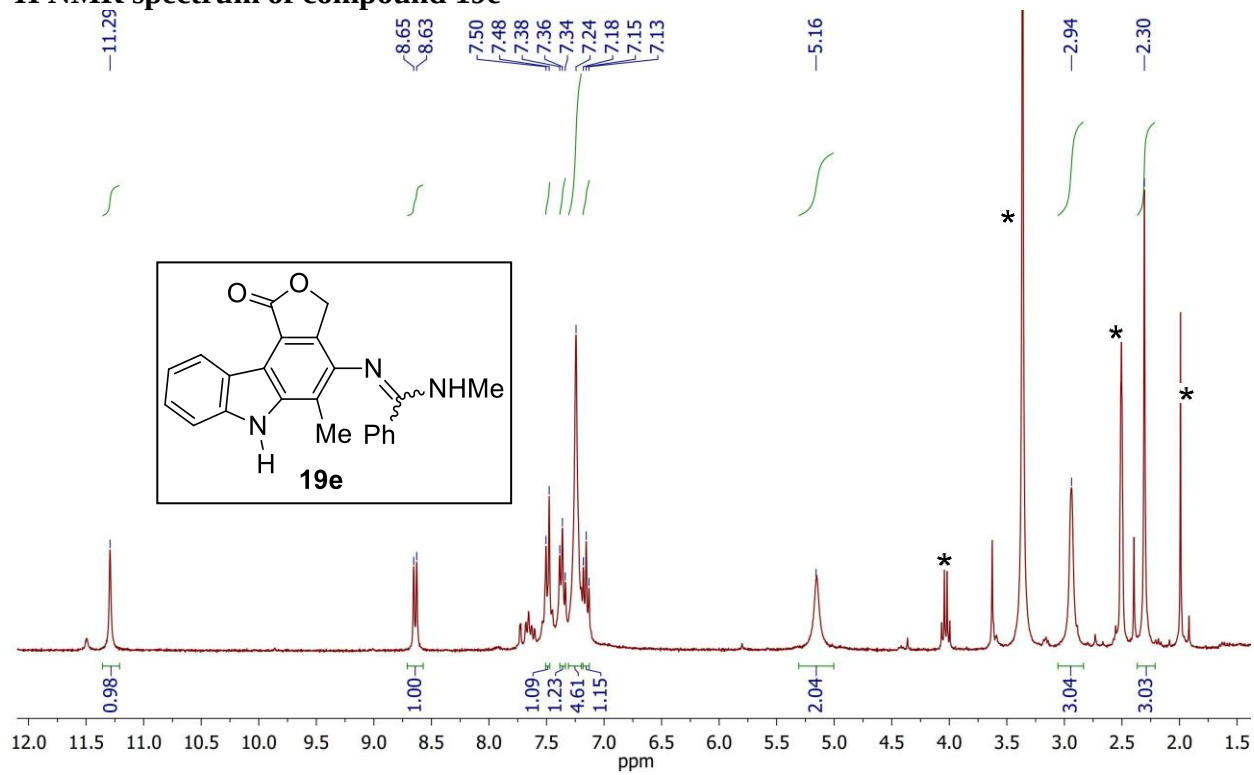


* Dichloromethane (5.76 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 19d

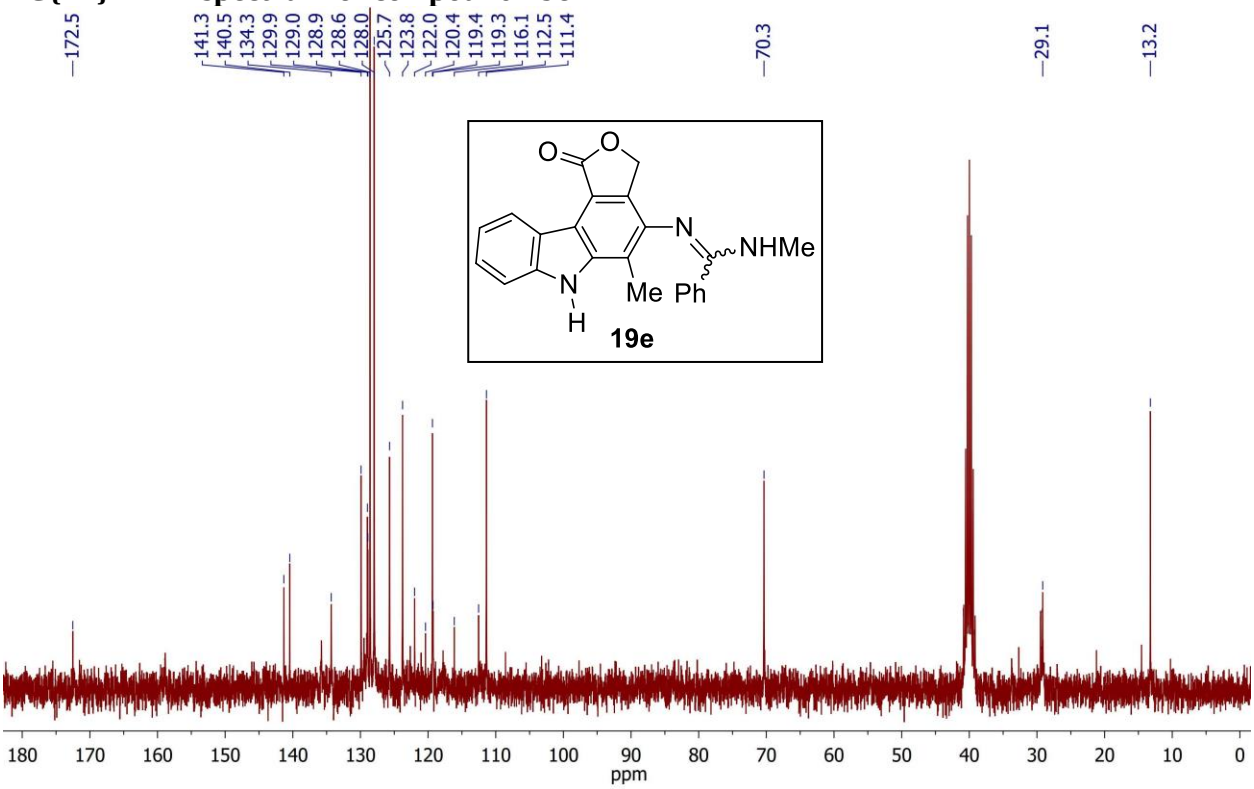


^{1}H NMR spectrum of compound 19e

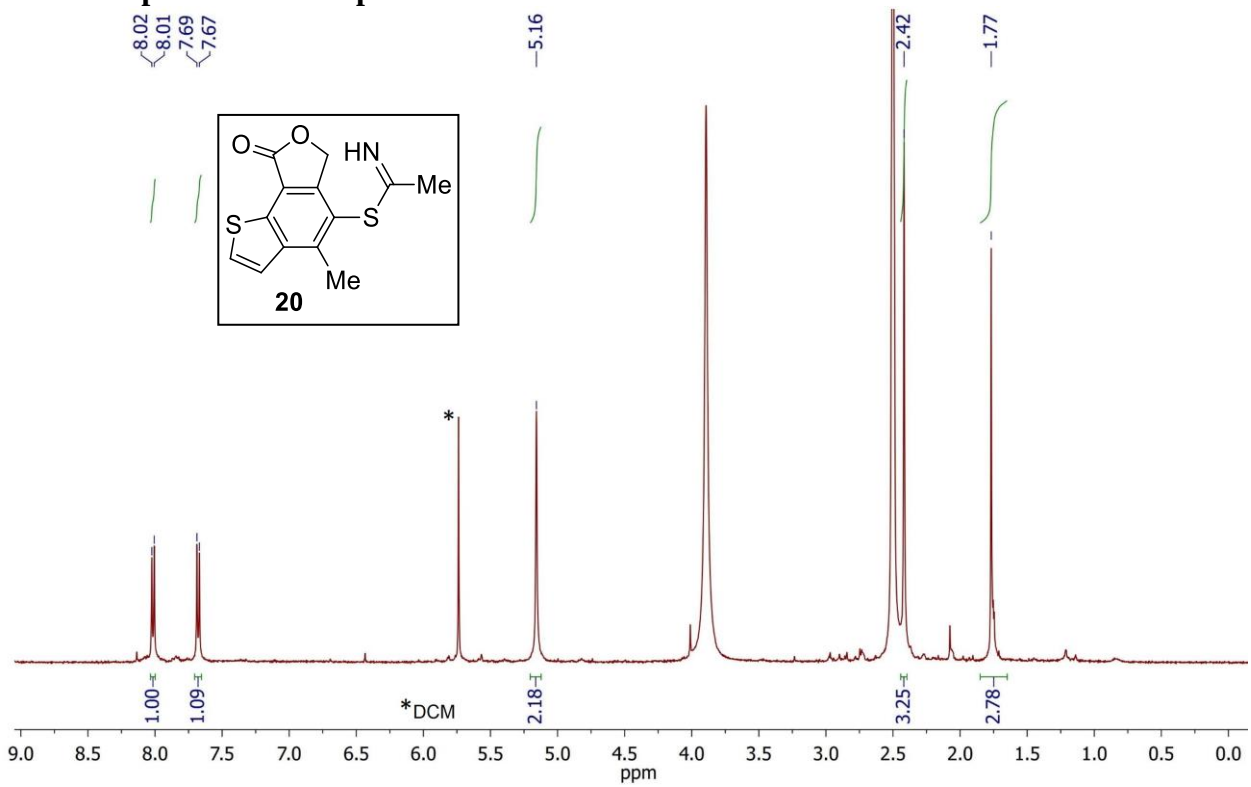


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

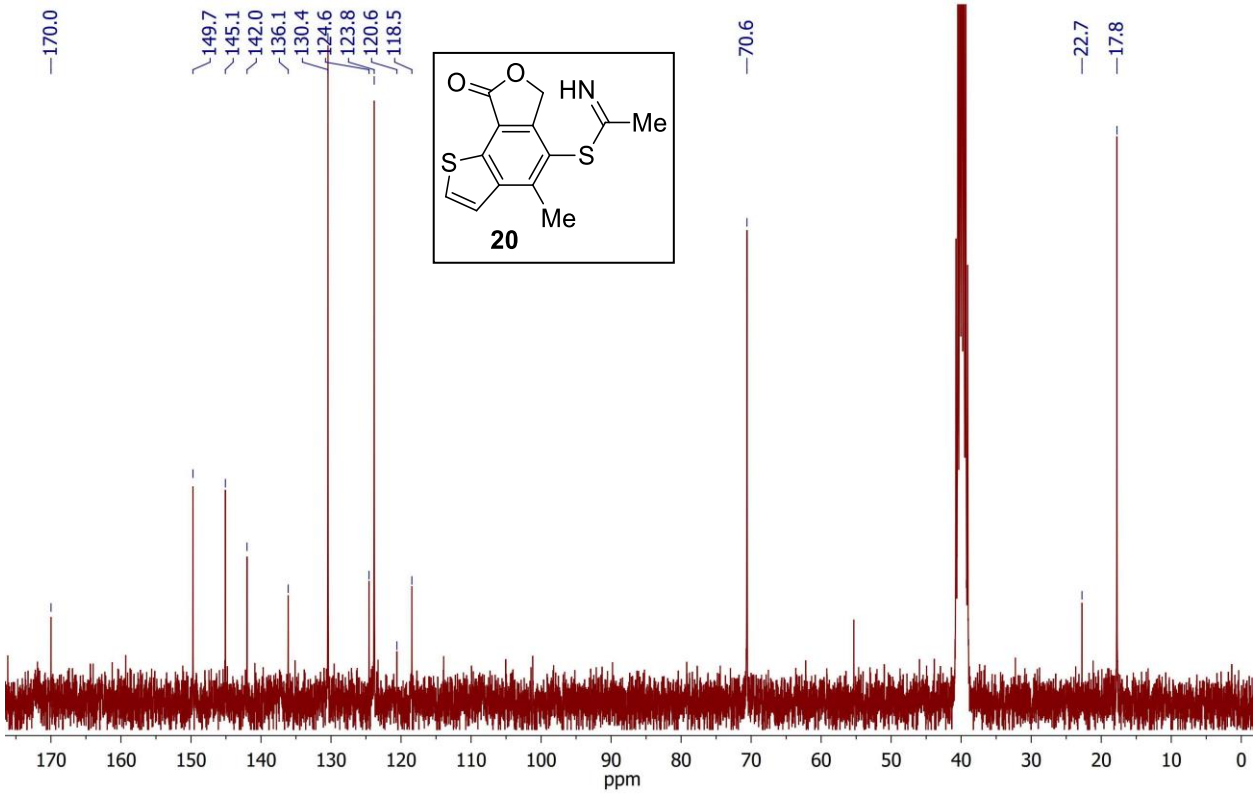
^{13}C{^{1}H} NMR spectrum of compound 19e



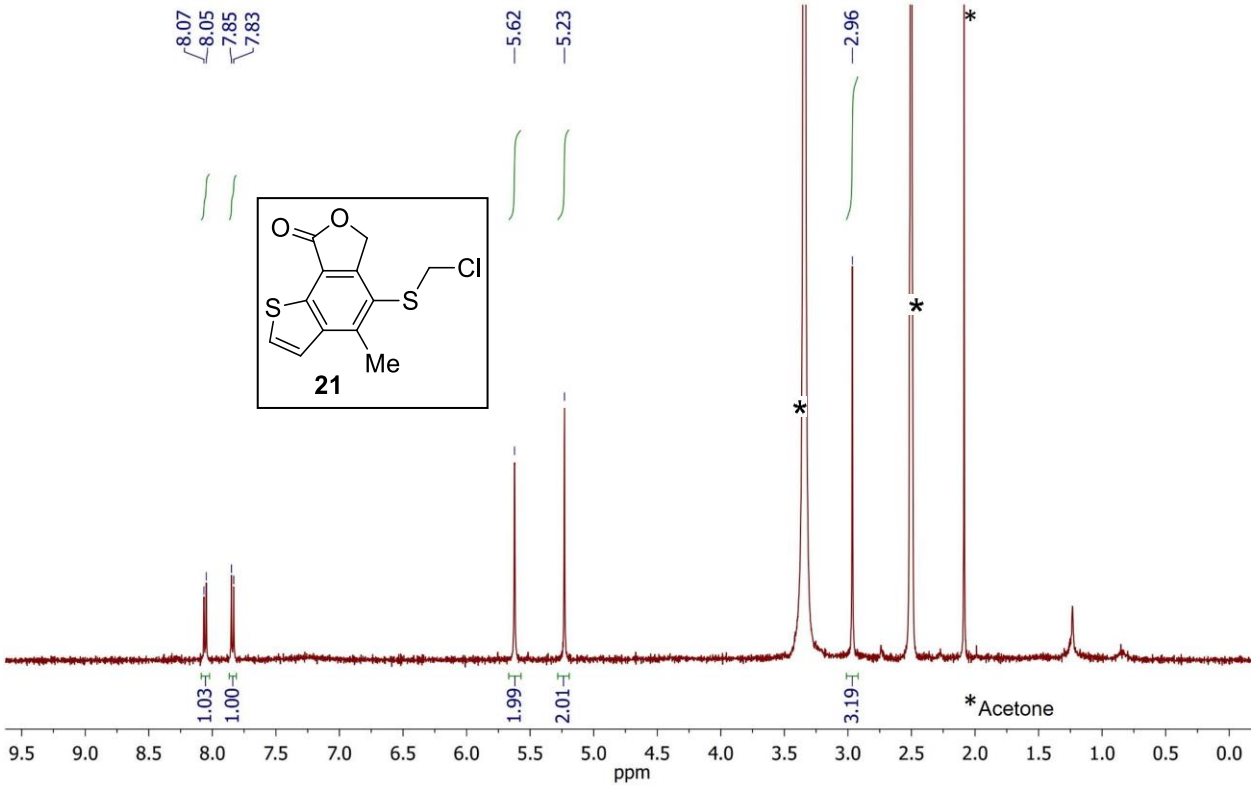
^{1}H NMR spectrum of compound 20



^{13}C{^{1}H} NMR spectrum of compound 20

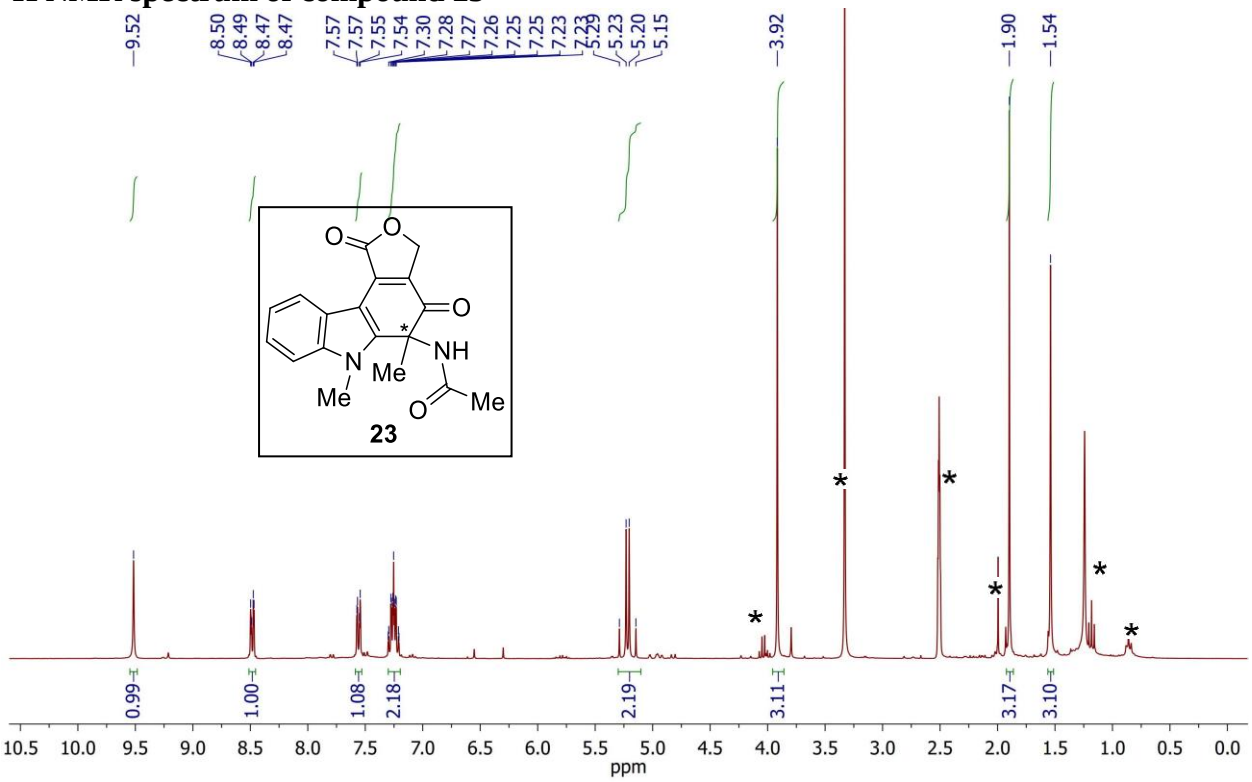


^{1}H NMR spectrum of compound 21



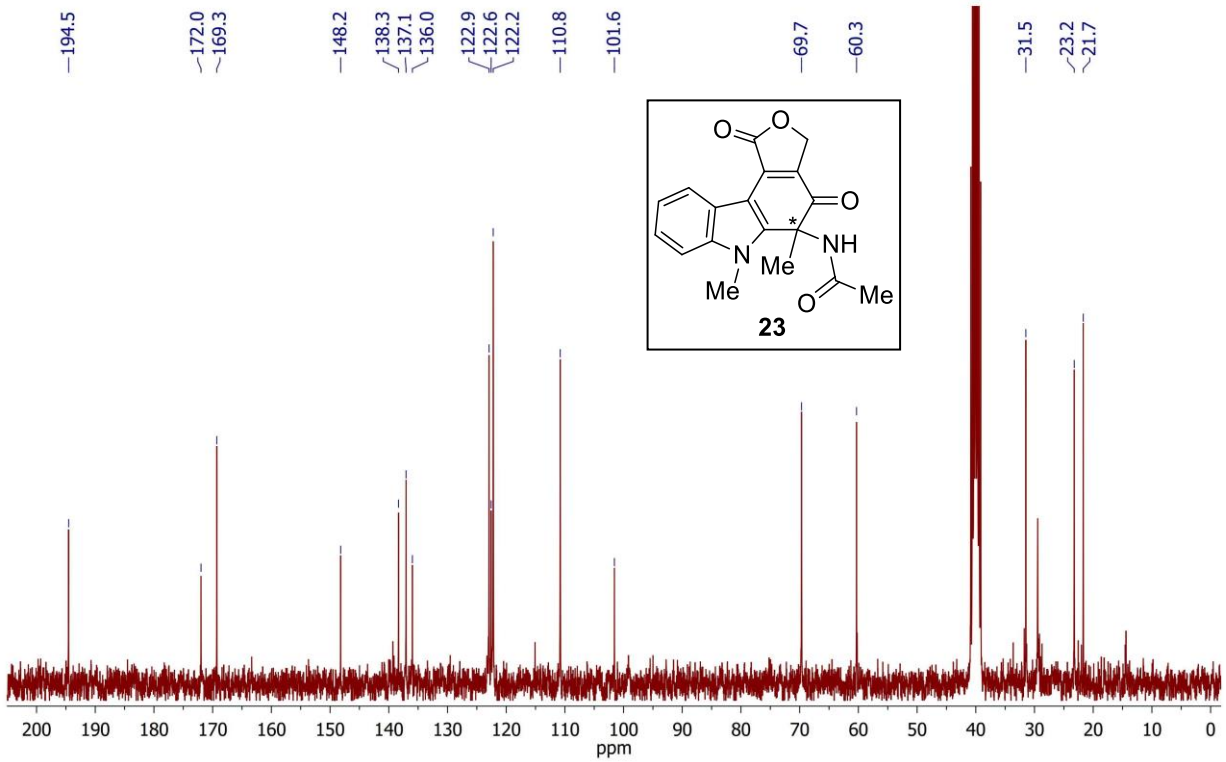
* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{1}H NMR spectrum of compound 23

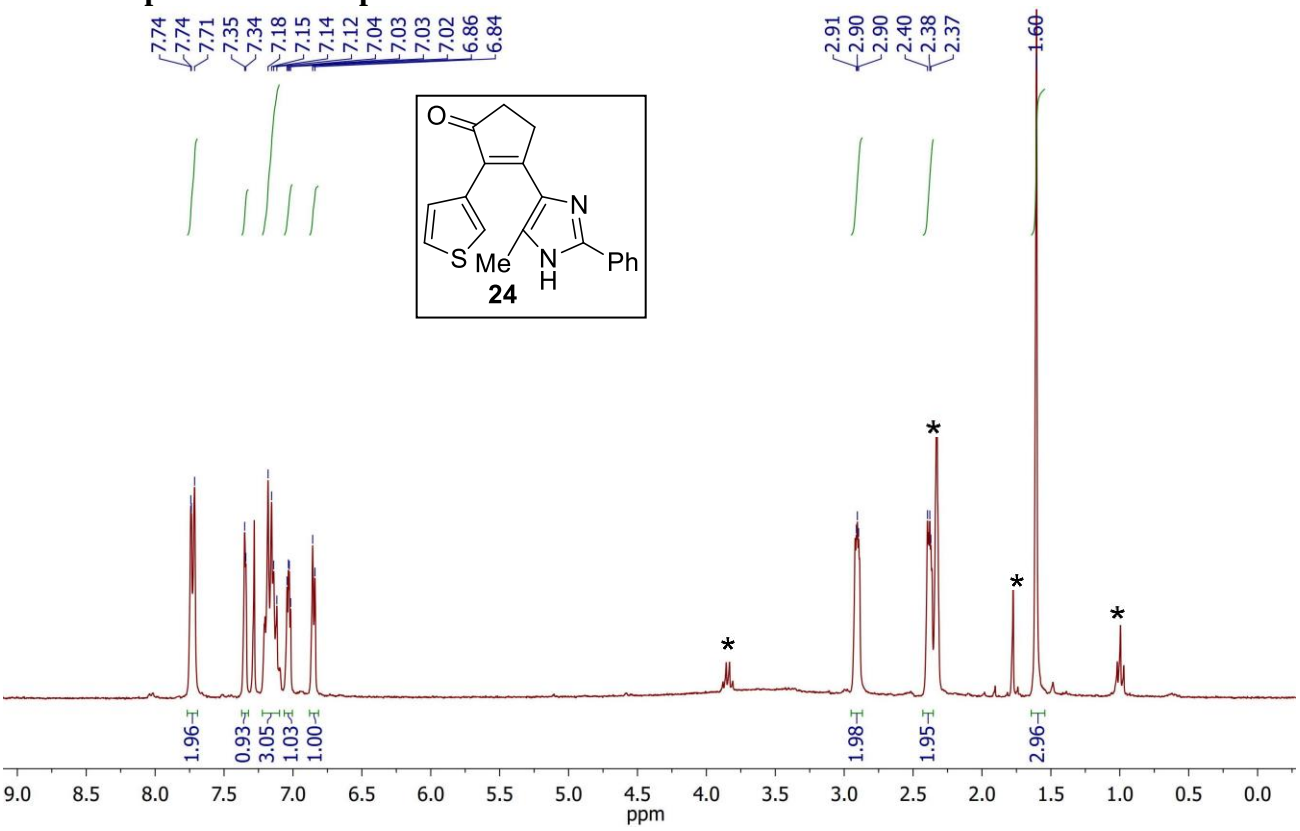


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm), DMSO (2.50 ppm) and grease (0.86 and 1.26 ppm).

^{13}C{^{1}H} NMR spectrum of compound 23

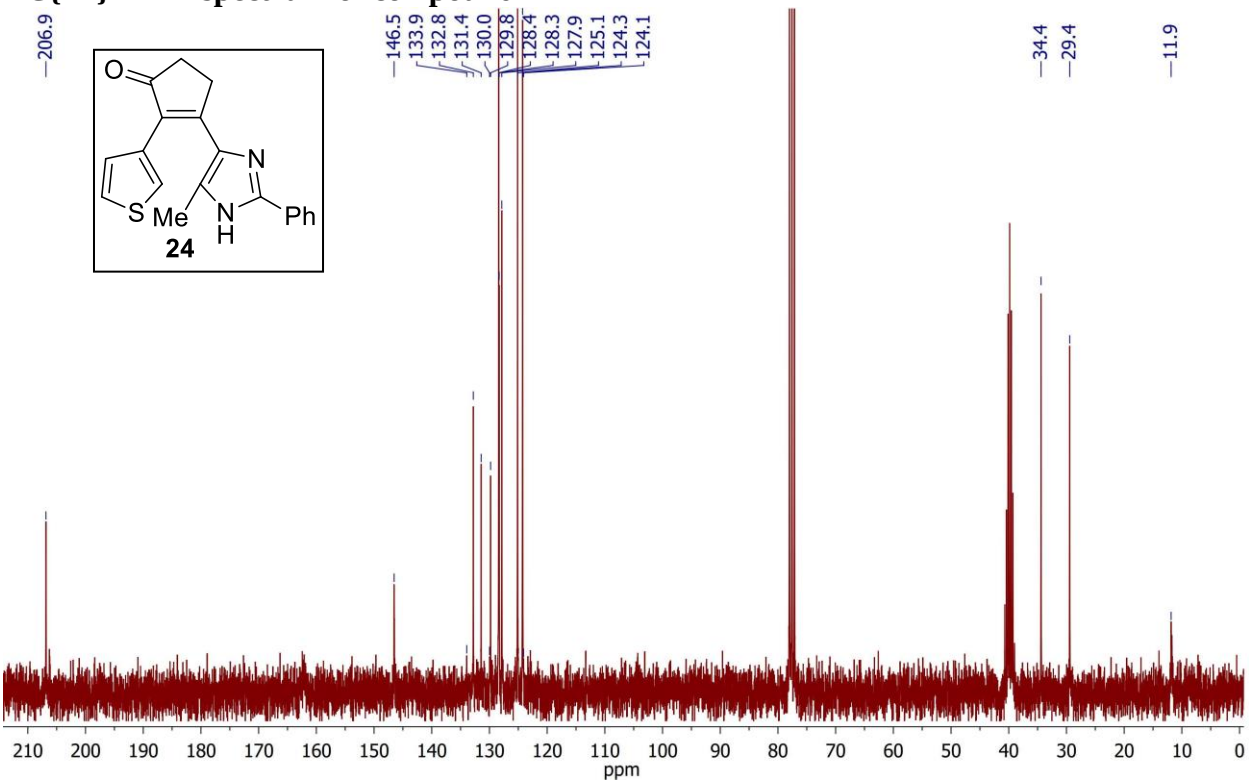


^{1}H NMR spectrum of compound 24

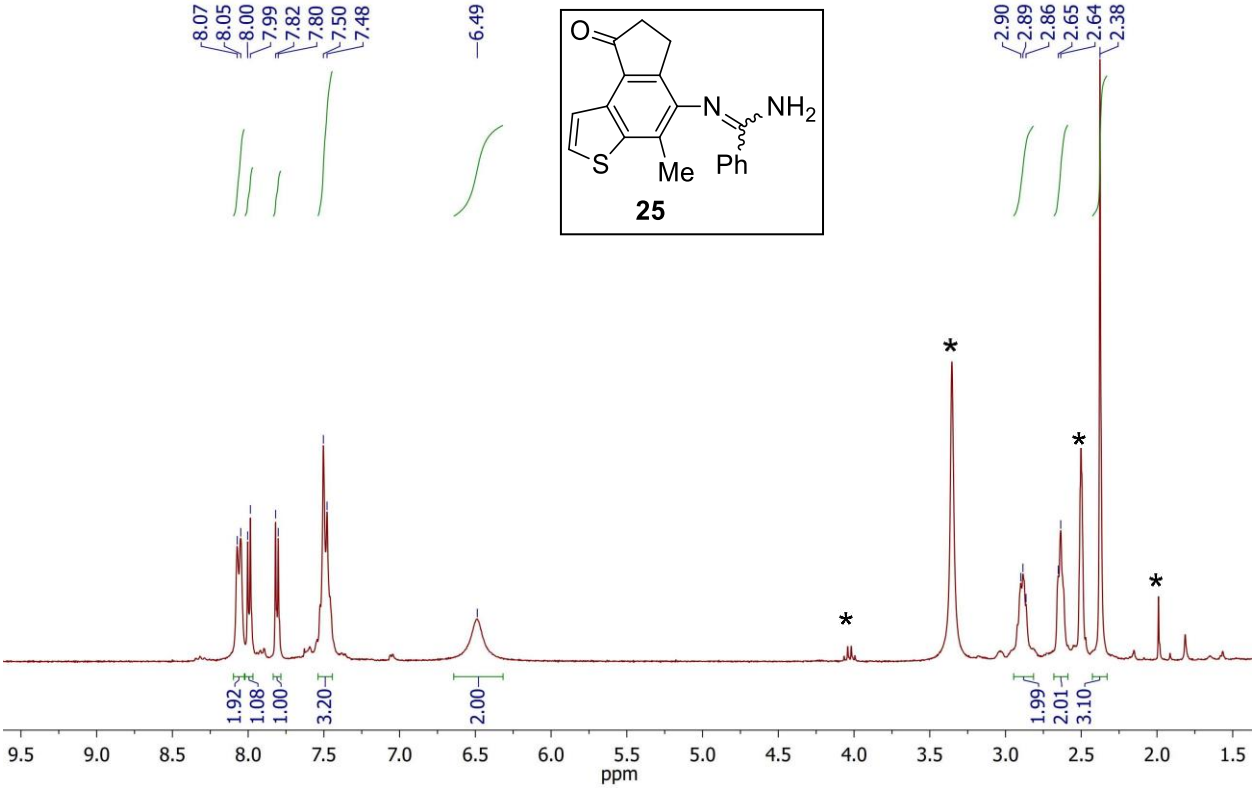


* Ethyl acetate and DMSO

^{13}C{^{1}H} NMR spectrum of compound 24

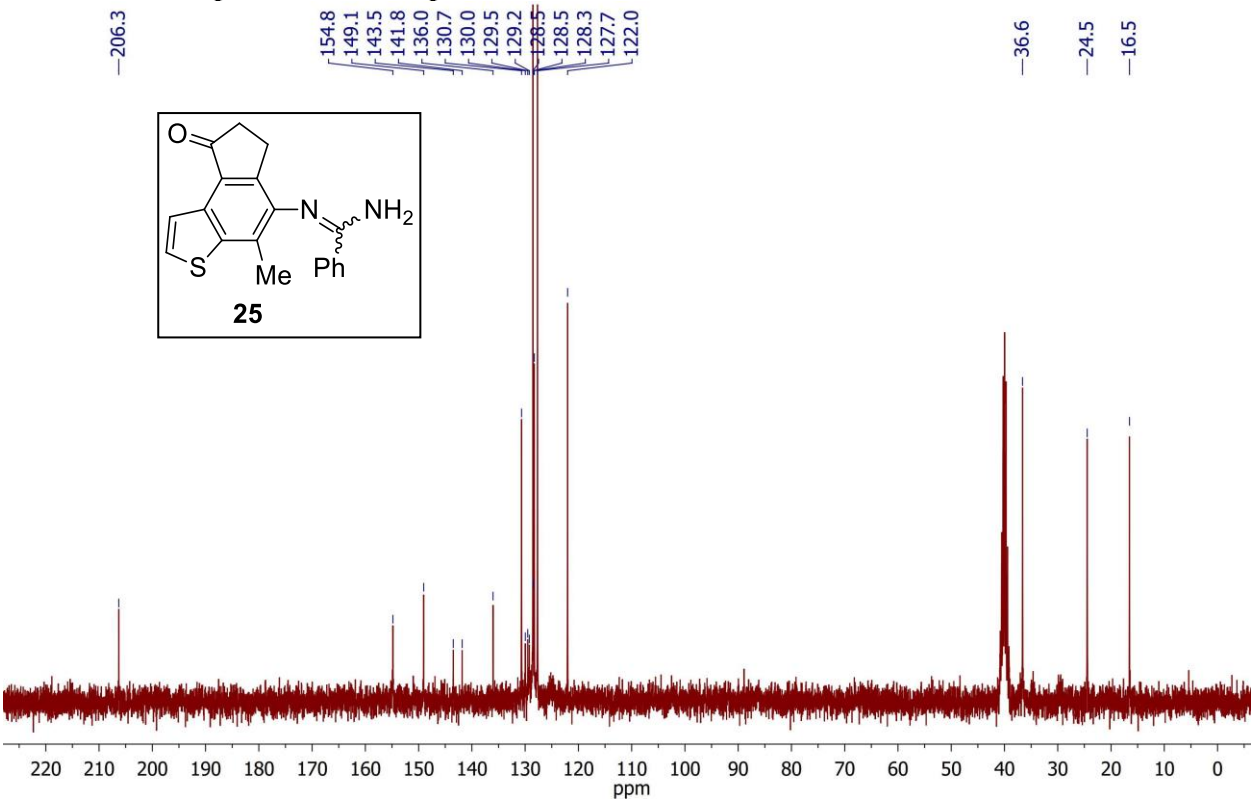


^{1}H NMR spectrum of compound 25

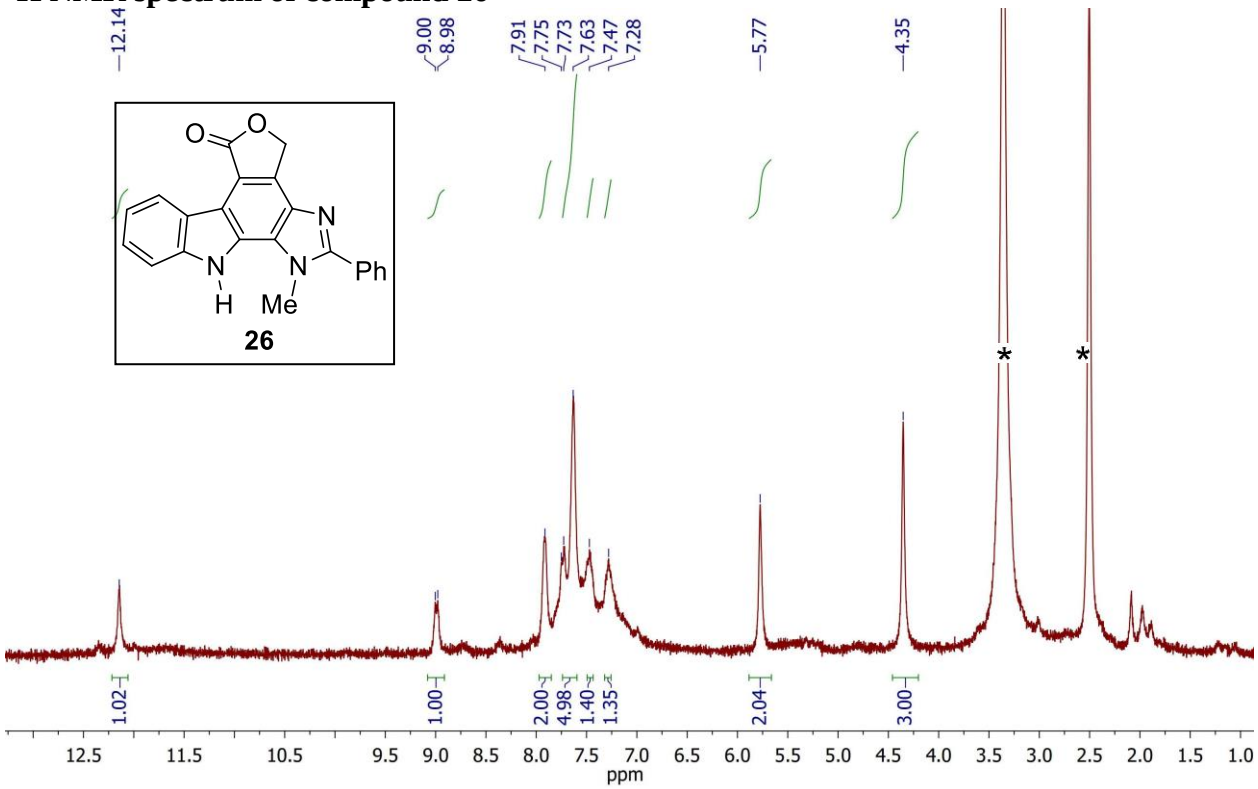


* Ethyl acetate (4.03, 1.99, 1.17 ppm), H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 25

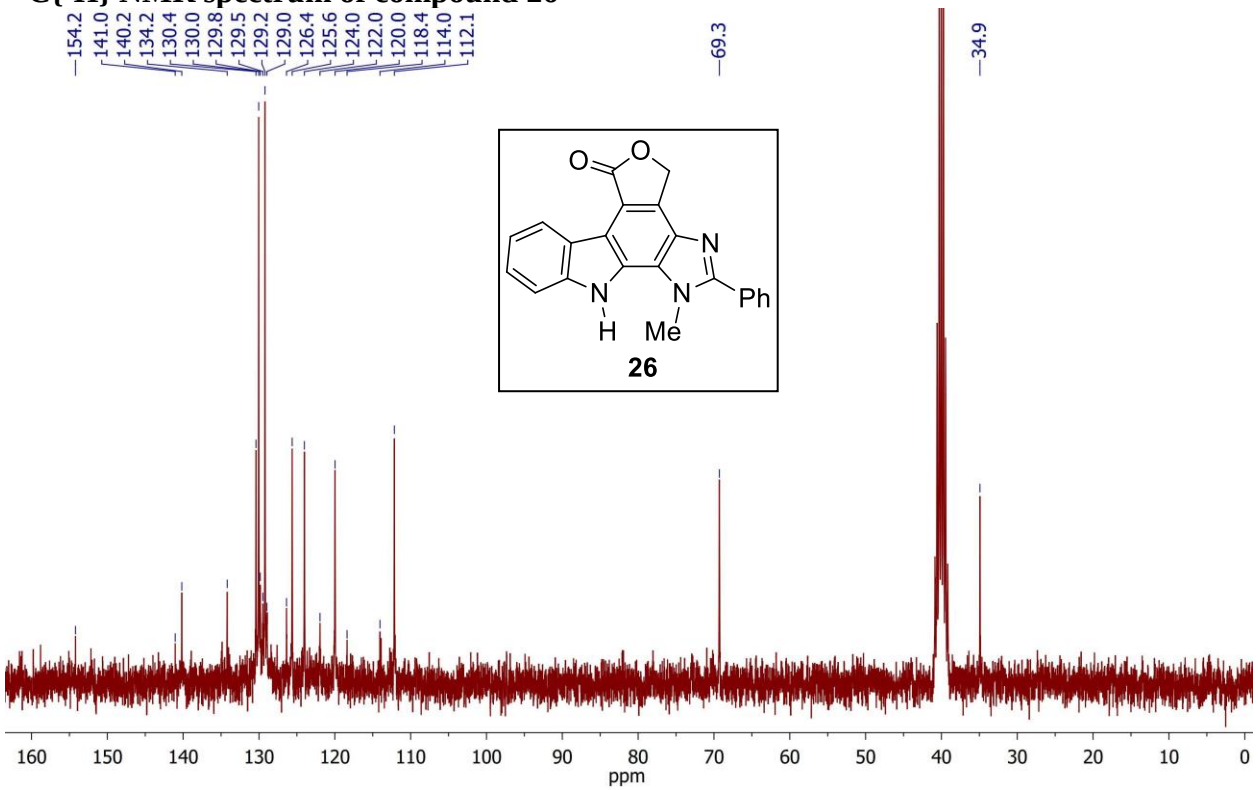


^{1}H NMR spectrum of compound 26

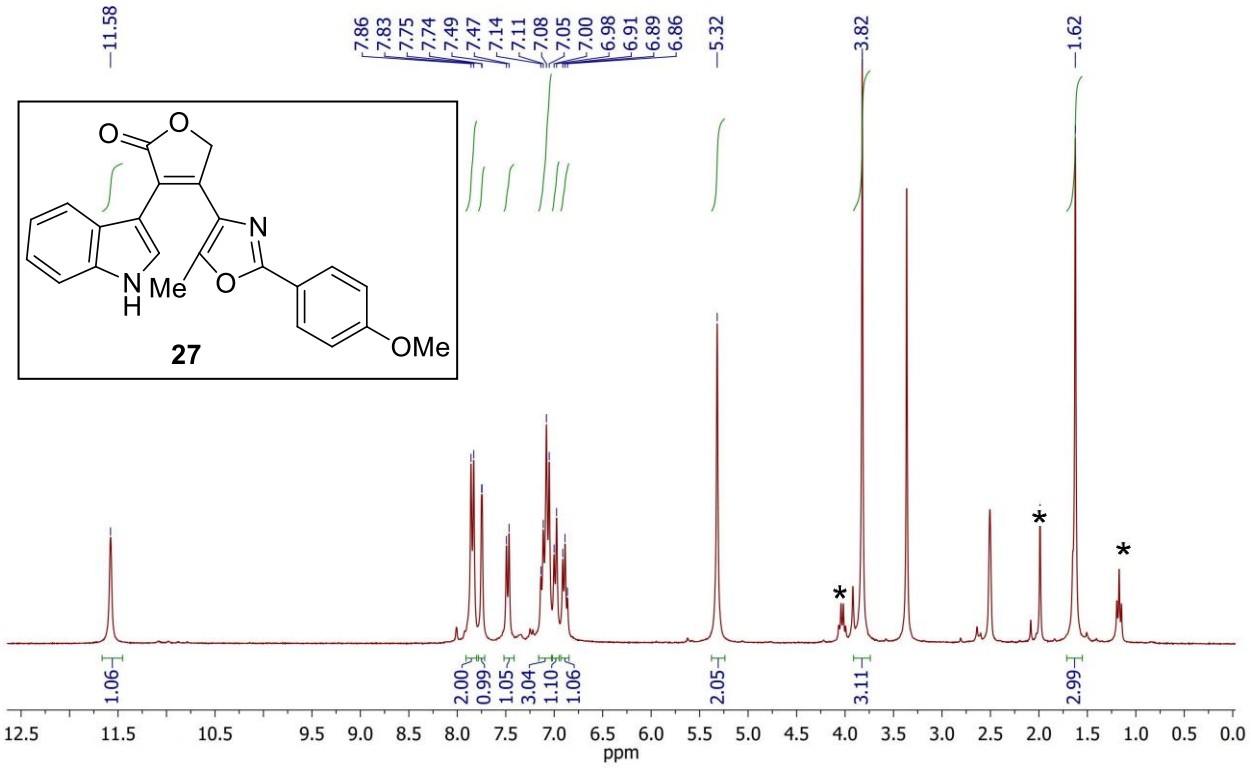


* H_2O (3.33 ppm) and DMSO (2.50 ppm)

^{13}C{^{1}H} NMR spectrum of compound 26

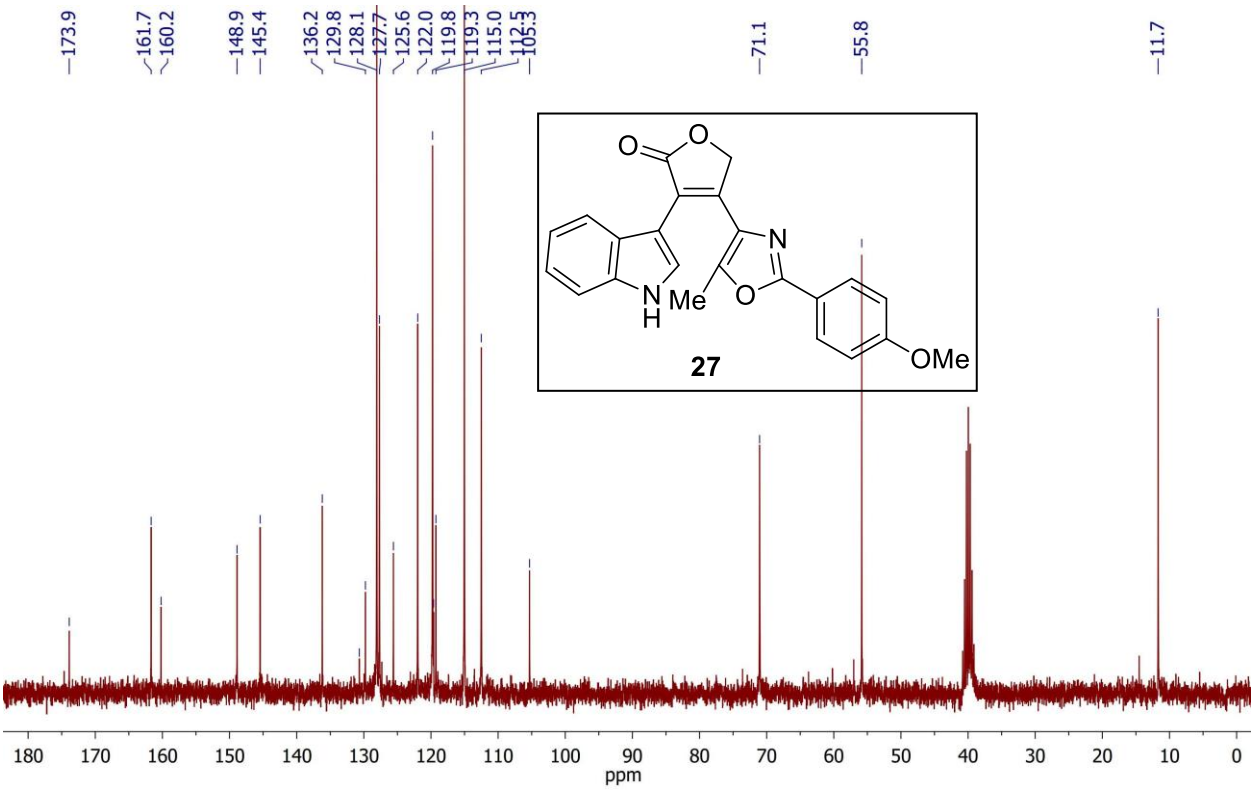


^{1}H NMR spectrum of compound 27

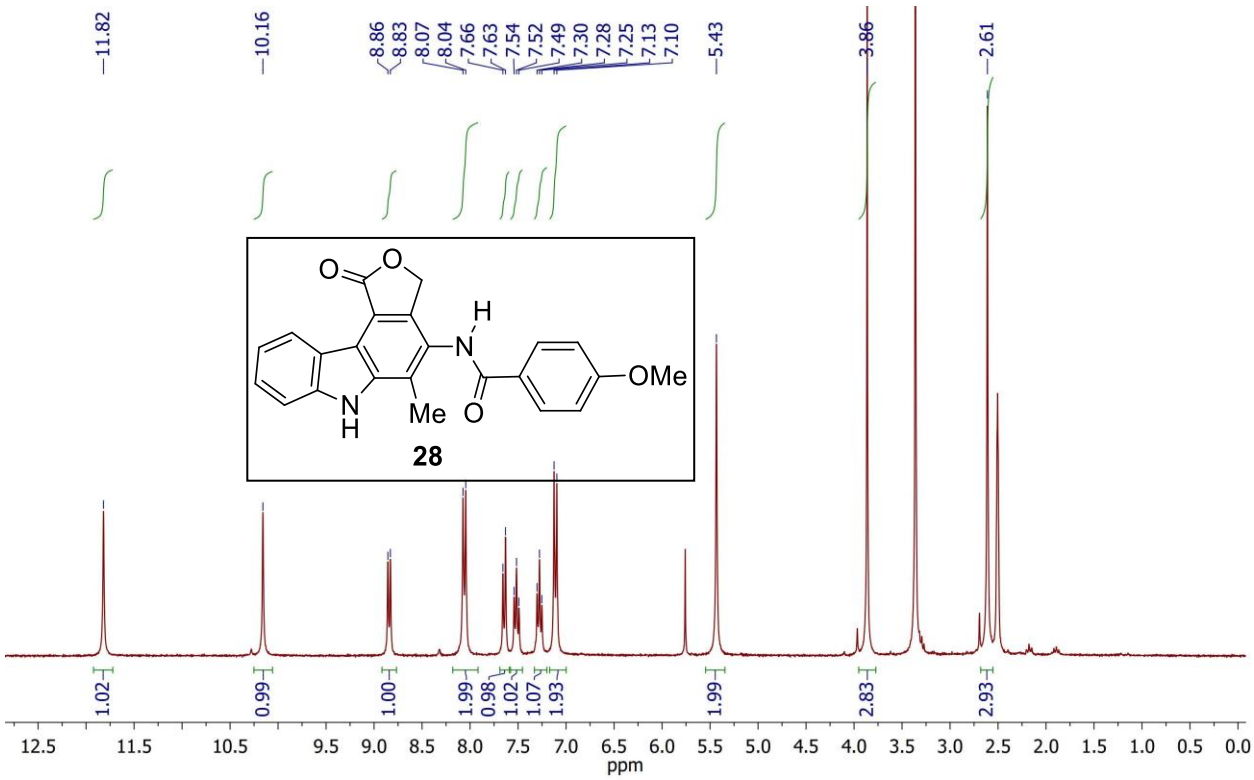


* Ethyl acetate

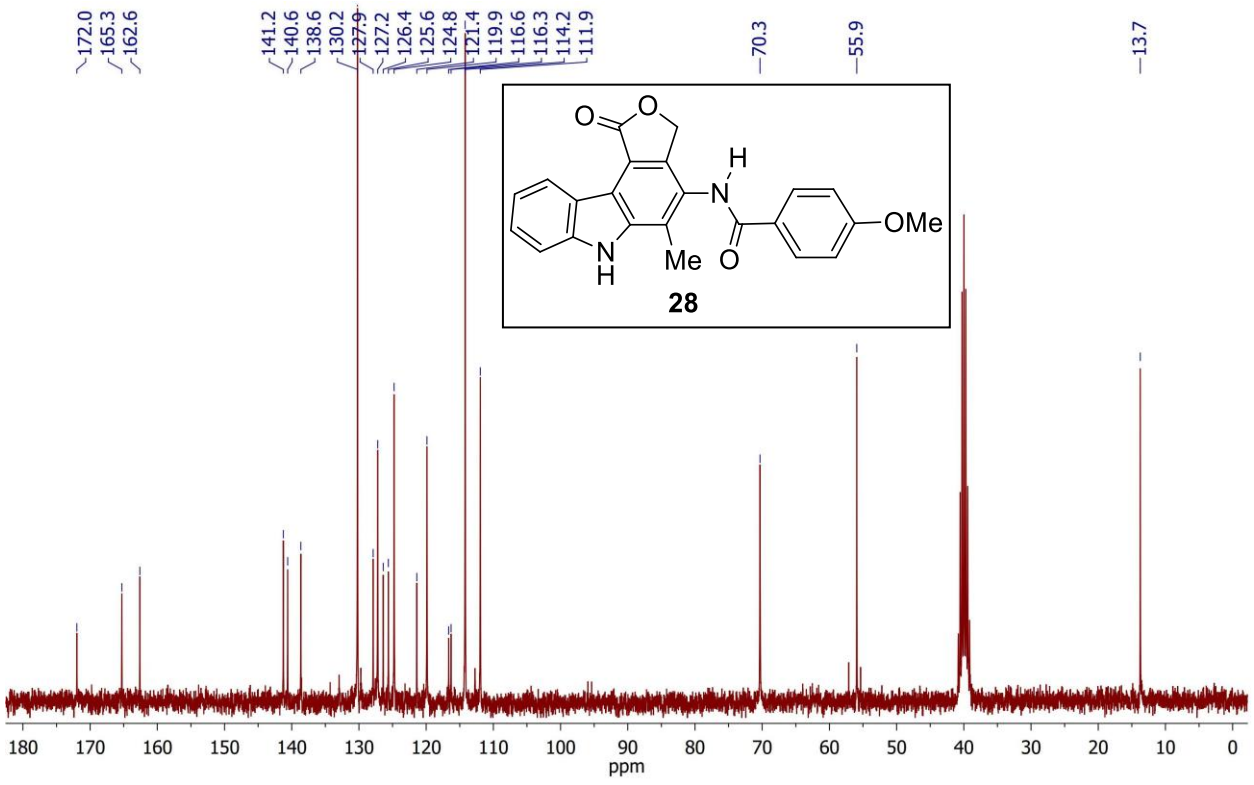
^{13}C{^{1}H} NMR spectrum of compound 27



^{1}H NMR spectrum of compound 28



^{13}C{^{1}H} NMR spectrum of compound 28



X. References

[1] Bruker. APEXII. Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

[2] G. M. Sheldrick, SADABS. University of Göttingen, Germany, 1997.

[3] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

[4] (a) G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122. (b) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

[6] V. Z. Shirinian, A. A. Shimkin, D. V. Lonshakov, A. G. Lvov, M. M. Krayushkin, *J. Photochem. Photobiol. A*, 2012, **233**, 1.

[7] a) S. Samori, M. Hara, T.-I. Ho, S. Tojo, K. Kawai, M. Endo, M. Fujitsuka, T. Majima, *J. Org. Chem.*, 2005, **70**, 2708–2712; b) E. M. Glebov, N. V. Ruban, I. P. Pozdnyakov, V. P. Grivin, V. F. Plyusnin, A. G. Lvov, A. V. Zakharov, V. Z. Shirinian, *J. Phys. Chem. A*, 2018, **122**, 7107−7117.

[8] (a) T.-I. Ho, J.-Y. Wu, S.-L. Wang, *Angew. Chem., Int. Ed.*, 1999, **38**, 2558-2560; (b) T.-I. Ho, J.-H. Ho, J.-Y. Wu, *J. Am. Chem. Soc.*, 2000, **122**, 8575-8576; (c) A. G. Lvov, V. Z. Shirinian, V. V. Kachala, A. M. Kavun, I. V. Zavarzin, M. M. Krayushkin, *Org. Lett.*, 2014, **16**, 4532-4535; (d) A. G. Lvov, V. Z. Shirinian, A. V. Zakharov, M. M. Krayushkin, V. V. Kachala, I. V. Zavarzin, *J. Org. Chem.*, 2015, **80**, 11491-11500; (e) O. Galangau, T. Nakashima, F. Maurel, T. Kawai, *Chem. Eur. J.*, 2015, **21**, 8471-8482. (f) A. V. Zakharov, E. B. Gaeva, A. G. Lvov, A. V. Metelitsa, V. Z. Shirinian, *J. Org. Chem.*, 2017, **82**, 8651-8661. (g) J. Fan, T. Wang, C. Li, R. Wang, X. Lei, Y. Liang, Z. Zhang, *Org. Lett.*, 2017, **19**, 5984-5987. (h) S. Jing, Y. He, T. Wang, J. Zhang, A. Cheng, Y. Liang, Z. Zhang, *Synlett*, 2018, **29**, 1578–1582.

[9] For review see: M. Stratakis and M. Orfanopoulos, *Tetrahedron*, 2000, **56**, 1595–1615.

[10] M. Auzias, D. Häussinger, M. Neuburger, H. A. Wegner, *Org. Lett.*, 2011, **13**, 474-477.

[11] (a) Li, X.; Ma, Y.; Wang, B.; Li, G. *Org. Lett.*, 2008, **10**, 3639. (b) Wu, Y.; Chen, S.; Yang, Y.; Zhang, Q.; Xie, Y.; Tian, H.; Zhu, W. *Chem. Commun.*, 2012, **48**, 528. (c) Wu, Y.; Zhu, W.; Wan, W.; Xie, Y.; Tian, H.; Li, A.D.Q. *Chem. Commun.*, 2014, **50**, 14205.

[12] O. A. Fedorova, Yu. V. Fedorov, E. N. Andryukhina, S. P. Gromov, M. V. Alfimov, R. Lapouyade, *Org. Lett.*, 2003, **5**, 4533.

[13] E. N. Gulakova, D. V. Berdnikova, T. M. Aliyeu, Yu. V. Fedorov, I. A. Godovikov, O. A. Fedorova, *J. Org. Chem.*, 2014, **79**, 5533).

[14] T. Nakashima, R. Fujii, T. Kawai, *Chem. Eur. J.*, 2011, **17**, 10951.

[15] S. Fukumoto, T. Nakashima, T. Kawai, *Angew. Chem., Int. Ed.*, 2011, **50**, 1565.

[16] Galangau, O.; Nakashima, T.; Maurel, F.; Kawai, T. *Chem. Eur. J.*, 2015, **21**, 8471.

[17] Lvov, A. G.; Kavun, A. M.; Kachala, V. V.; Nelyubina, Y. V.; Metelitsa, A. V.; Shirinian, V. Z. *J. Org. Chem.*, 2017, **82**, 1477.

[18] Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.*, 2002, 2804.

[19] Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. *Chem. Commun.*, 1999, 747.

[20] Herder, M.; Schmidt, B. M.; Grubert, L.; Païzel, M.; Schwarz, J.; Hecht, S. *J. Am. Chem. Soc.*, 2015, **137**, 2738.