Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Intramolecular Iron-Catalyzed Transannulation of Furans with *O*-Acetyl Oximes: Synthesis of Functionalized Pyrroles

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Supporting Information

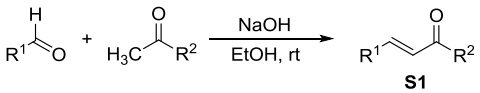
Table of Contents

1. GENERAL INFORMATION

^{1}H and ^{13}C NMR spectra were recorded with a «Bruker Avance III HD 400» (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm; [D_6] DMSO, ^{1}H: δ = 2.50 ppm, ^{13}C: δ = 39.52 ppm). Coupling constants (*J*) are given in Hertz. Splitting patterns of an apparent multiplets associated with an averaged coupling constants were designated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet), m (multiplet), dd (doublet of doublets) and br (broadened). High-resolution mass measurements were carried out using a BrukermicroTOF-QTM ESI-TOF (Electro Spray Ionization/Time of Flight) mass spectrometer. GC/MS analysis was performed on an «Agilent 7890B» interfaced to an «Agilent 5977A» mass selective detector. Melting points were determined with a «Stuart SMP 30. Data sets for X-Ray diffraction were collected with a «New Xcalibur, Ruby» diffractometer. ESR experiments were performed on Radiopan SE/X-2544 spectrometer in the Institute of Problems of Chemical Physics, RAS (IPCP RAS) in dioxane under air at 80 °C. Thermal analysis and differential scanning calorimetry were performed on NETZSCH STA 449F1 instrument at a scan rate of 10 °C/min under argon atmosphere. The electrochemical investigations were performed on potentiostat/galvanostat ZRA Interface 1000 in the standard three-electrode cell with a carbon-glass working electrode, a Pt wire as a counter electrode, and Ag/Ag^{+} reference electrode at room temperature at a scan rate of 100 mV s^{-1}. The potential of Ag/Ag^{+} reference electrode was internally calibrated using ferrocene/ferrocenium redox couple. The cyclic voltammetry measurements were performed in 1.0 mM solutions of studied compounds, Et_4NClO_4 (1 mM) was used as a supporting electrolyte. UV-Vis absorption spectra were recorded in acetonitrile (2×10^{-5} M) in standard 10 × 10 × 45 mm quartz cuvettes on Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were recorded in acetonitrile (2×10^{-5} M) in standard 10 × 10 × 45 mm quartz cuvettes on Shimadzu RF-5301pc spectrofluorimeter. Column chromatography was performed on silica gel Macherey Nagel (40-63 μm), unless otherwise noted. Pre-coated TLC sheets ALUGRAM SIL G/UV_{254} were used for thin-layer analytical chromatography. Starting substituted 2-(3-oxoalkyl)furans **3** [1-3] were synthesized according to known procedures. All the reactions were carried out using freshly distilled and dry solvents from solvent stills. All reagent-grade chemicals and solvents commercially available were used without further purification. $FeCl_3 \cdot 6H_2O$ (≥99%) was purchased from Sigma Aldrich and used as received.

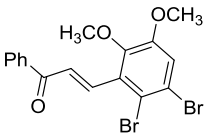
2. SYNTHESIS OF STARTING MATERIALS

General procedure for the synthesis of starting α,β-unsaturated ketones S1.



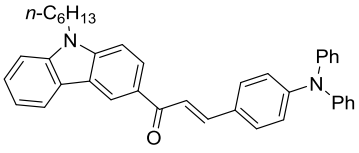
S1

To the solution of an aldehyde (10 mmol) and a methyl ketone (10 mmol) in EtOH (10 mL) was added aq. solution of NaOH (20%, 5 mL) at room temperature. The resulting mixture was stirred until full conversion of starting materials (TLC or GC control). Upon completion, the mixture was poured into water; the formed precipitate was filtered, washed with water, and dried. Crude α,β-unsaturated ketones were recrystallized from EtOH. If necessary, the product could be purified by column chromatography (eluent: petroleum ether/ethyl acetate, 9:1).



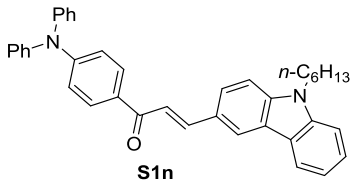
S1f

(2*E*)-3-(2,3-Dibromo-5,6-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**S1f**). Yield: 3365 mg, 79%; off-white solid; mp = 139−140 °C (EtOH). R_f = 0.45 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.02 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 15.9 Hz, 1H), 7.74 (d, *J* = 15.9 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.53 – 7.47 (m, 2H), 7.22 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 190.8, 152.8, 148.3, 140.0, 138.1, 133.1, 131.8, 129.8, 128.9 (2C), 128.8 (2C), 120.6, 118.3, 117.9, 60.8, 56.5. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}Br_2O_3^+$ 424.9382, found 424.9378.



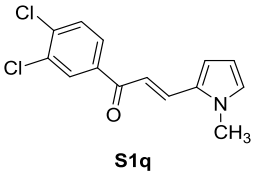
S1m

(2*E*)-3-(4-(Diphenylamino)phenyl)-1-(9-hexyl-9*H*-carbazol-3-yl)prop-2-en-1-one (**S1m**). Yield: 4439 mg, 81%; orange oil. R_f = 0.55 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.84 (br s, 1H), 8.23 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 15.5 Hz, 1H), 7.64 (d, *J* = 15.5 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.28 (m, 5H), 7.20 – 7.05 (m, 8H), 4.33 (t, *J* = 7.3 Hz, 2H), 2.01 – 1.79 (m, 2H), 1.54 – 1.19 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 189.7, 150.0, 147.2 (2C), 143.5, 143.3, 141.3, 130.1, 129.7 (2C), 129.6 (4C), 128.8, 126.8, 126.5, 125.5 (4C), 124.1 (2C), 123.5, 122.9, 122.1 (2C), 122.0, 120.8, 120.3, 120.0, 109.4, 108.6, 43.5, 31.7, 29.1, 27.1, 22.6, 14.1. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{39}H_{37}N_2O^+$ 549.2900, found 549.2905.



S1n

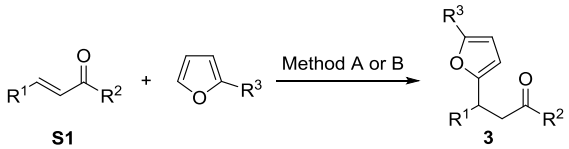
(2*E*)-1-(4-(Diphenylamino)phenyl)-3-(9-hexyl-9*H*-carbazol-3-yl)prop-2-en-1-one (**S1n**). Yield: 4548 mg, 83%; orange oil. R_f = 0.55 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.25 (br s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 15.5 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.66 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.48 (d, *J* = 15.5 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.32 – 7.15 (m, 7H), 7.10 – 6.95 (m, 8H), 4.18 (t, *J* = 7.3 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.31 – 1.17 (m, 6H), 0.77 (t, *J* = 7.0 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 188.5, 152.0, 146.9 (2C), 145.3, 142.0, 141.2, 131.6, 130.2 (2C), 129.7 (4C), 126.5, 126.4, 126.3, 126.0 (4C), 124.6 (2C), 123.6, 123.0, 121.4, 120.7, 120.3 (2C), 119.7, 119.2, 109.2, 109.1, 43.4, 31.7, 29.1, 27.1, 22.6, 14.1. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{39}H_{37}N_2O^+$ 549.2900, found 549.2904.



S1q

(2*E*)-1-(3,4-Dichlorophenyl)-3-(1-methyl-1*H*-pyrrol-2-yl)prop-2-en-1-one (**S1q**). Yield: 2240 mg, 80%; orange solid; mp = 119−120 °C (EtOH). R_f = 0.40 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.07 (br s, 1H), 7.87 – 7.77 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 15.1 Hz, 1H), 6.88 (d, *J* = 4.0 Hz, 1H), 6.85 (br s, 1H), 6.24 (br s, 1H), 3.77 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 187.4, 138.6, 136.9, 133.4, 133.3, 130.7, 130.4, 130.3, 128.7, 127.4, 115.4, 113.4, 110.3, 34.5. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{12}Cl_2NO^+$ 280.0290, found 280.0292.

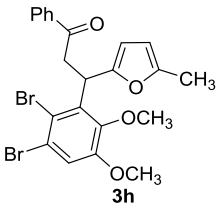
Michael addition of 2-substituted furans to α,β-unsaturated ketones.



S1 **3**

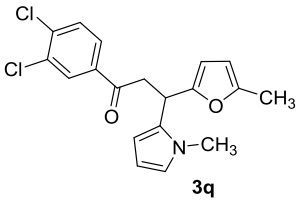
General method A

$CuBr_2$ (11.2 mg, 2.5 mol %) was added to a solution of α,β-unsaturated ketone (2 mmol) and furan (3 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature while controlling the reaction progress by TLC or GC. Upon completion, the mixture was concentrated at reduced pressure. The products were isolated by column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 19:1 to 10:1 to 5:1).



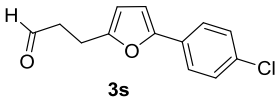
3h

3-(2,3-Dibromo-5,6-dimethoxyphenyl)-3-(5-methylfuran-2-yl)-1-phenylpropan-1-one (**3h**). Yield: 577 mg, 57%; pale yellow oil. R_f = 0.50 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.00 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.38 (m, 2H), 7.14 (s, 1H), 5.90 (d, *J* = 3.1 Hz, 1H), 5.87 (d, *J* = 3.1 Hz, 1H), 5.66 (t, *J* = 6.8 Hz, 1H), 4.13 (dd, *J* = 17.5, 7.7 Hz, 1H), 3.78 (s, 3H), 3.69 (dd, *J* = 17.5, 6.1 Hz, 1H), 3.56 (s, 3H), 2.19 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.5, 153.4, 152.5, 150.0, 147.9, 137.0, 136.9, 132.9, 128.4 (2C), 128.0 (2C), 116.3 (2C), 106.3 (2C), 105.9, 60.4, 55.9 (2C), 40.4, 13.4. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{21}Br_2O_4^+$ 506.9801, found 506.9785.



3q

1-(3,4-Dichlorophenyl)-3-(5-methylfuran-2-yl)-3-(1-methyl-1*H*-pyrrol-2-yl)propan-1-one (**3q**). Yield: 231 mg, 32%; pale yellow oil. R_f = 0.45 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.02 (d, *J* = 2.1 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 6.54 (s, 1H), 6.06 (d, *J* = 3.5 Hz, 1H), 6.01 (d, *J* = 3.5 Hz, 1H), 5.83 (d, *J* = 3.0 Hz, 1H), 5.79 (d, *J* = 3.0 Hz, 1H), 4.79 (t, *J* = 7.1 Hz, 1H), 3.66 (dd, *J* = 16.8, 7.1 Hz, 1H), 3.61 (s, 3H), 3.57 (dd, *J* = 16.8, 7.1 Hz, 1H), 2.23 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 195.7, 153.7, 151.2, 137.7, 136.7, 133.4, 132.2, 130.8, 130.2, 127.2, 122.0, 106.9, 106.8, 106.2, 105.8, 43.2, 33.8, 32.3, 13.6. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{18}Cl_2NO_2^+$ 362.0709, found 362.0718.

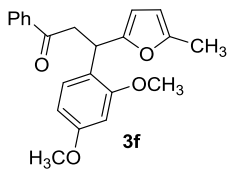


3s

3-[5-(4-Chlorophenyl)furan-2-yl]propanal (**3s**). Yield: 427 mg, 91%; pale yellow oil. R_f = 0.40 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): *δ* 9.75 (s, 1H), 7.67 – 7.60 (m, 2H), 7.48 – 7.40 (m, 2H), 6.85 (d, *J* = 3.3 Hz, 1H), 6.24 (d, *J* = 3.3 Hz, 1H), 2.97 (t, *J* = 7.1 Hz, 2H), 2.83 (t, *J* = 7.1 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): *δ* 201.9, 154.7, 150.4, 131.2, 129.2, 128.7, 124.6, 107.8, 107.2, 40.7, 20.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{12}ClO_2^+$ 235.0520, found 235.0516.

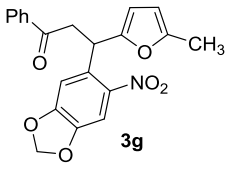
General method B

TMSCl (60 μL, 20 mol %) was added to a solution of α,β-unsaturated ketone (2 mmol) and 2-substituted furan (3 mmol) in CH_3CN (5 mL). The reaction vessel was placed into aluminium block preheated to 60 °C and stirred while controlling the reaction progress by TLC or GC. Upon completion, the mixture was concentrated at reduced pressure. The products were isolated by column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 19:1 to 10:1 to 5:1).



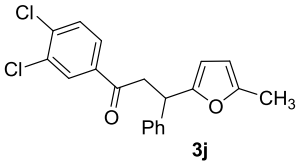
3f

3-(2,4-Dimethoxyphenyl)-3-(5-methylfuran-2-yl)-1-phenylpropan-1-one (**3f**). Yield: 637 mg, 91%; pale yellow oil. R_f = 0.45 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.03 – 7.97 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 – 7.42 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.96 (d, *J* = 3.0 Hz, 1H), 5.87 (d, *J* = 3.0 Hz, 1H), 5.16 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.72 (dd, *J* = 16.3, 8.5 Hz, 1H), 3.50 (dd, *J* = 16.3, 6.1 Hz, 1H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 198.2, 159.7, 157.6, 154.8, 150.5, 137.2, 132.7, 128.9, 128.4 (2C), 128.1 (2C), 123.2, 106.5, 106.0, 104.5, 98.8, 55.4, 55.2, 43.0, 33.9, 13.5. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{23}O_4^+$ 351.1591, found 351.1591.



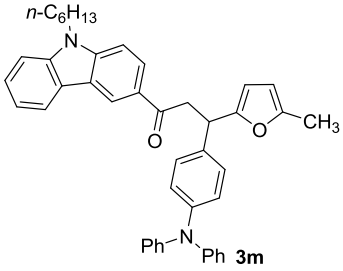
3g

3-(5-Methylfuran-2-yl)-3-(6-nitro-1,3-benzodioxol-5-yl)-1-phenylpropan-1-one (**3g**). Yield: 417 mg, 55%; pale yellow oil. R_f = 0.40 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 7.7 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.40 (m, 2H), 7.36 (s, 1H), 6.85 (s, 1H), 6.03 (d, J = 3.0 Hz, 1H), 6.01 (s, 2H), 5.86 (d, J = 3.0 Hz, 1H), 5.51 (t, J = 7.1 Hz, 1H), 3.76 (dd, J = 17.4, 7.6 Hz, 1H), 3.58 (dd, J = 17.4, 6.6 Hz, 1H), 2.21 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.5, 152.9, 151.6 (2C), 146.6, 143.3, 136.7, 133.9, 133.2, 128.6 (2C), 128.1 (2C), 108.5, 107.7, 106.3, 105.5, 102.9, 43.3, 35.3, 13.5. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NO_{6+}$ 380.1129, found 380.1135.



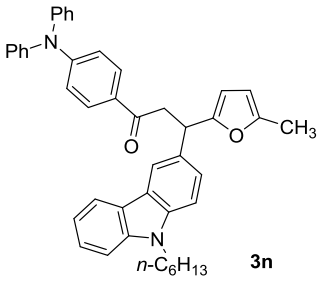
3j

1-(3,4-Dichlorophenyl)-3-(5-methylfuran-2-yl)-3-phenylpropan-1-one (**3j**). Yield: 452 mg, 63%; pale yellow oil. R_f = 0.65 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 2.1 Hz, 1H), 7.75 (dd, J = 8.4, 2.1 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 5.93 (d, J = 3.0 Hz, 1H), 5.88 (d, J = 3.0 Hz, 1H), 4.78 (t, J = 7.2 Hz, 1H), 3.77 (dd, J = 16.8, 7.2 Hz, 1H), 3.50 (dd, J = 16.8, 7.2 Hz, 1H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.6, 154.5, 151.2, 141.9, 137.6, 136.7, 133.3, 130.7, 130.2, 128.7 (2C), 127.9 (2C), 127.2, 127.0, 106.8, 106.2, 43.8, 40.7, 13.6. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}Cl_2O_2^+$ 359.0600, found 359.0590.



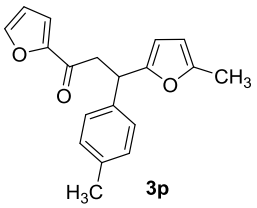
3m

3-[4-(Diphenylamino)phenyl]-1-(9-hexyl-9*H*-carbazol-3-yl)-3-(5-methylfuran-2-yl)propan-1-one (**3m**). Yield: 1054 mg, 84%; pale orange oil. R_f = 0.55 (ethyl acetate/petroleum ether = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, J = 1.7 Hz, 1H), 8.06 – 8.01 (m, 2H), 7.43 – 7.39 (m, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 8.7 Hz, 1H), 7.22 – 7.18 (m, 1H), 7.15 – 7.07 (m, 6H), 6.95 – 6.85 (m, 8H), 5.87 (d, J = 3.0 Hz, 1H), 5.75 (d, J = 3.0 Hz, 1H), 4.73 (t, J = 7.2 Hz, 1H), 4.21 (t, J = 7.3 Hz, 2H), 3.77 (dd, J = 16.4, 7.2 Hz, 1H), 3.56 (dd, J = 16.4, 7.2 Hz, 1H), 2.15 (s, 3H), 1.81 – 1.75 (m, 2H), 1.27 – 1.17 (m, 6H), 0.77 (t, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.3, 155.6, 151.1, 148.0 (2C), 146.4, 143.4, 141.3, 137.1, 129.3 (4C), 128.9, 128.8 (2C), 126.6, 126.4, 124.3 (4C), 124.2 (2C), 123.4, 122.8, 122.7 (2C), 121.8, 120.8, 120.1, 109.4, 108.4, 106.6, 106.1, 43.9, 43.5, 40.5, 31.7, 29.0, 27.1, 22.6, 14.1, 13.7. HRMS (ESI/TOF) m/z: $[M + Na]^+$ calcd for $C_{44}H_{42}N_2NaO_2^+$ 653.3138, found 653.3131.



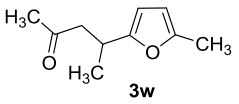
3n

1-[4-(Diphenylamino)phenyl]-3-(9-hexyl-9H-carbazol-3-yl)-3-(5-methylfuran-2-yl)propan-1-one (**3n**). Yield: 592 mg, 47%; pale orange oil. R_f = 0.55 (ethyl acetate/petroleum ether = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.17 – 7.12 (m, 6H), 7.01 – 6.96 (m, 7H), 6.81 (d, J = 8.5 Hz, 2H), 5.81 (d, J = 3.0 Hz, 1H), 5.71 (d, J = 3.0 Hz, 1H), 4.84 (t, J = 7.2 Hz, 1H), 4.07 (t, J = 7.4 Hz, 3H), 3.65 (dd, J = 16.5, 7.2 Hz, 1H), 3.44 (dd, J = 16.5, 7.2 Hz, 1H), 2.08 (s, 3H), 1.71 – 1.67 (m, 2H), 1.19 – 1.13 (m, 6H), 0.73 (t, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.3, 156.2, 152.1, 150.9, 146.6 (2C), 140.9, 139.5, 133.0, 130.0, 129.8 (2C), 129.6 (4C), 126.0 (4C), 125.9, 125.6, 124.6 (2C), 123.0, 122.9, 120.4, 119.8 (2C), 119.5, 118.6, 108.7, 108.6, 106.3, 106.1, 44.0, 43.2, 40.9, 31.6, 29.0, 27.0, 22.6, 14.0, 13.6. HRMS (ESI/TOF) m/z: $[M + Na]^+$ calcd for $C_{44}H_{42}N_2NaO_2^+$ 653.3138, found 653.3146.



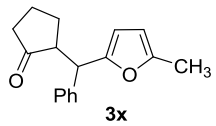
3p

1-Furan-2-yl-3-(5-methylfuran-2-yl)-3-(4-methylphenyl)propan-1-one (**3p**). Yield: 400 mg, 68%; pale yellow oil. R_f = 0.50 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 1.8 Hz, 1H), 7.27 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 3.6 Hz, 1H), 7.15 (d, J = 7.8 Hz, 2H), 6.50 (dd, J = 3.6, 1.8 Hz, 1H), 5.97 (d, J = 3.0 Hz, 1H), 5.88 (d, J = 3.0 Hz, 1H), 4.79 (t, J = 7.4 Hz, 1H), 3.66 (dd, J = 16.2, 7.4 Hz, 1H), 3.44 (dd, J = 16.2, 7.4 Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 186.7, 154.9, 152.9, 150.9, 146.2, 139.0, 136.2, 129.1 (2C), 127.7 (2C), 117.0, 112.1, 106.4, 105.9, 43.5, 40.0, 20.9, 13.4. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}O_3^+$ 295.1329, found 295.1328.



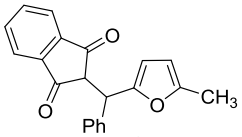
3w

4-(5-Methylfuran-2-yl)pentan-2-one (**3w**). Yield: 236 mg, 71%; pale yellow oil. R_f = 0.65 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84 (d, J = 3.0 Hz, 1H), 5.82 (d, J = 3.0 Hz, 1H), 3.38 – 3.27 (m, 1H), 2.82 (dd, J = 16.3, 6.0 Hz, 1H), 2.53 (dd, J = 16.3, 7.9 Hz, 1H), 2.24 (s, 3H), 2.11 (s, 3H), 1.23 (d, J = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.4, 157.4, 150.6, 105.9, 104.6, 49.7, 30.4, 29.2, 19.2, 13.6. HRMS (ESI/TOF) m/z: $[M + Na]^+$ calcd for $C_{10}H_{14}NaO_2^+$ 189.0886, found 189.0882.



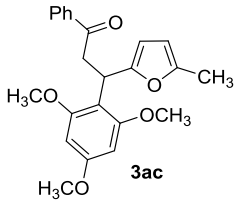
3x

2-[(5-Methylfuran-2-yl)(phenyl)methyl]cyclopentanone (**3x**) was isolated as a mixture of inseparable diastereomers in 1:1 ratio. Yield: 371 mg, 73%; pale yellow oil. R_f = 0.60 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.37 – 7.16 (m, 10H), 6.04 (d, *J* = 3.0 Hz, 1H), 5.92 (d, *J* = 3.0 Hz, 1H), 5.83 (d, *J* = 3.0 Hz, 1H), 5.78 (d, *J* = 3.0 Hz, 1H), 4.67 (d, *J* = 4.2 Hz, 1H), 4.64 (d, *J* = 4.0 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.68 – 2.57 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H), 2.42 – 2.09 (m, 6H), 2.00 – 1.61 (m, 8H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 218.7, 218.6, 154.7, 153.5, 151.1, 151.0, 141.4, 140.1, 129.2 (2C), 128.7 (2C), 128.6 (2C), 128.3 (2C), 126.9, 126.9, 108.8, 107.2, 106.0 (2C), 54.1, 53.1, 44.9, 44.0, 38.5, 38.4, 26.6, 26.5, 20.7, 20.6, 13.7, 13.6. HRMS (ESI/TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{18}NaO_2^+$ 277.1199, found 277.1199.



3ab

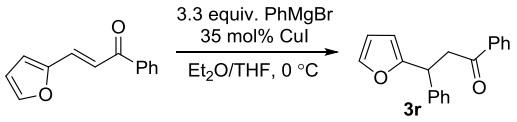
2-[(5-Methylfuran-2-yl)(phenyl)methyl]-1*H*-indene-1,3(2*H*)-dione (**3ab**). Yield: 575 mg, 91%; pale yellow oil. R_f = 0.35 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.93 – 7.87 (m, 2H), 7.77 – 7.73 (m, 2H), 7.41 – 7.36 (m, 2H), 7.26 – 7.16 (m, 3H), 5.96 (d, *J* = 3.1 Hz, 1H), 5.79 (d, *J* = 3.1 Hz, 1H), 4.98 (d, *J* = 3.2 Hz, 1H), 3.70 (d, *J* = 3.2 Hz, 1H), 2.03 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 198.8, 198.7, 152.3, 151.1, 142.9, 142.6, 138.7, 135.4 (2C), 129.3 (2C), 128.5 (2C), 127.4, 123.2, 123.1, 109.0, 106.3, 57.6, 44.4, 13.4. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}O_3^+$ 317.1172, found 317.1172.



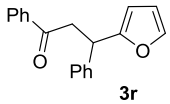
3ac

3-(2,4,6-Trimethoxyphenyl)-3-(5-methylfuran-2-yl)-1-phenylpropan-1-one (**3ac**). Yield: 388 mg, 51%; pale yellow oil. R_f = 0.45 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.94 (d, *J* = 7.7 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 6.12 (s, 2H), 5.79 (d, *J* = 3.0 Hz, 1H), 5.75 (d, *J* = 3.0 Hz, 1H), 5.34 (t, *J* = 7.3 Hz, 1H), 3.87 (dd, *J* = 16.4, 7.0 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 6H), 3.69 (dd, *J* = 16.4, 7.5 Hz, 1H), 2.19 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 199.4, 160.2, 159.5 (2C), 155.9, 149.6, 137.7, 132.6, 128.4 (2C), 128.3 (2C), 111.0, 106.0, 105.2, 91.8 (2C), 56.1 (2C), 55.3, 41.5, 30.3, 13.7. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{25}O_5^+$ 381.1697, found 381.1709.

Synthesis of 3-furan-2-yl-1,3-diphenylpropan-1-one (3r).



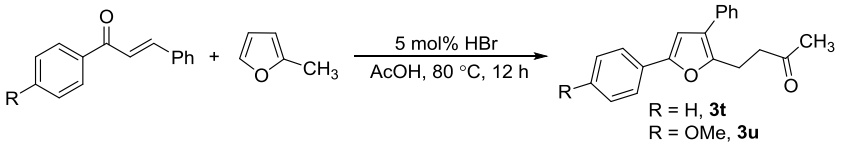
To a solution of PhMgBr in Et_2O/THF (3.3 mL of PhMgBr 1 M solution in Et_2O, 3.3 mmol, 3.3 equiv. and 3 mL THF) was added CuI (67 mg, 0.35 mmol) at 0 °C. To the resulting mixture was added (2*E*)-3-furan-2-yl-1-phenylprop-2-en-1-one (198 mg, 1 mmol) in THF (1 mL) over 1 min at 0 °C upon stirring. The reaction mixture was stirred at the same temperature for 1 h (TLC control), after which it was quenched with MeOH (2 mL). The mixture was dry-loaded on basic Al_2O_3 and subjected to column chromatography on basic Al_2O_3 (eluent: petroleum ether/ethyl acetate, gradient from 50:1 to 30:1).



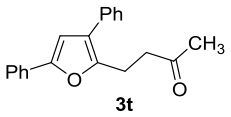
3r

3-Furan-2-yl-1,3-diphenylpropan-1-one (**3r**).[3] Yield: 171 mg, 62%; pale yellow oil. R_f = 0.55 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.99 – 7.93 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 7.35 – 7.30 (m, 5H), 7.26 – 7.22 (m, 1H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 4.87 (t, *J* = 7.0 Hz, 1H), 3.84 (dd, *J* = 17.0, 7.0 Hz, 1H), 3.58 (dd, *J* = 17.0, 7.0 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 197.6, 157.0, 141.7, 137.2, 133.2, 128.8 (2C), 128.7 (2C), 128.3, 128.2 (2C), 128.0 (2C), 127.0, 110.3, 106.0, 43.8, 40.5.

General procedure for the synthesis of substituted furans 3t,u

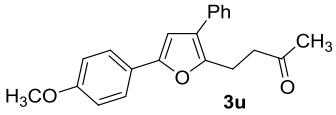


5 mL Wheaton microreaction vial equipped with a spinning bar and a Teflon cap was charged with *E*-chalcone for compound **3t** or (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one for compound **3u** (1 mmol), 2-methylfuran (135 µL, 1.5 mmol, 1.5 eq.), AcOH (5 mL), and 48% aq. HBr (8.4 mg, 5.6 µL, 5% mol.). The vial was closed and placed into an aluminum block preheated to 80 °C, and the mixture was stirred for 12 h (TLC control). Upon completion, the solvent was evaporated. The products were isolated by column chromatography (eluent: petroleum ether/CH_2Cl_2, 4:1).



3t

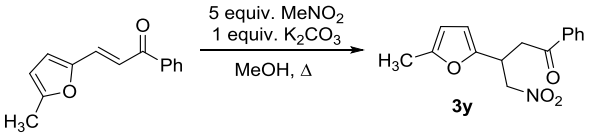
4-(3,5-Diphenylfuran-2-yl)butan-2-one (**3t**).[4] Yield: 249 mg, 86%; pale yellow oil. R_f = 0.45 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.24 (m, 3H), 6.77 (s, 1H), 3.17 (t, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H), 2.21 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.1, 152.1, 149.5, 133.8, 130.8, 128.8 (4C), 127.8 (2C), 127.3, 126.8, 123.6 (3C), 106.9, 41.8, 29.9, 21.5. HRMS (ESI$^+$) m/z: $[M + H]^+$ calcd for $C_{20}H_{19}O_2^+$ 291.1380, found 291.1384.



3u

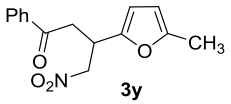
4-[5-(4-Methoxyphenyl)-3-phenylfuran-2-yl]butan-2-one (**3u**).[4] Yield: 288 mg, 90%; pale yellow oil. R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.31 – 7.27 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.62 (s, 1H), 3.84 (s, 3H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.18 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.3, 159.2, 152.3, 148.8, 134.0, 128.8 (2C), 127.9 (2C), 126.8, 125.1 (2C), 124.1, 123.6, 114.4 (2C), 105.4, 55.5, 42.0, 30.0, 21.6. HRMS (ESI$^+$) m/z: $[M + H]^+$ calcd for $C_{21}H_{21}O_3^+$ 321.1485, found 321.1495.

Synthesis of 3-(5-methylfuran-2-yl)-4-nitro-1-phenylbutan-1-one (3y).



3y

To a stirred solution of (2*E*)-3-(5-methylfuran-2-yl)-1-phenylprop-2-en-1-one (424 mg, 2.0 mmol) in MeOH (10 mL) was added nitromethane (540 µL, 10 mmol, 5 equiv.) and freshly calcined K_2CO_3 (276 mg, 2 mmol, 1 equiv.) at room temperature. The resulting mixture was refluxed up to the full conversion of the starting material (TLC or GC control). Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, 3:1).



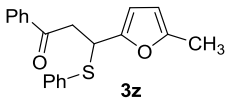
3y

3-(5-Methylfuran-2-yl)-4-nitro-1-phenylbutan-1-one (**3y**). Yield: 393 mg, 72%; pale yellow oil. R_f = 0.35 (ethyl acetate/petroleum ether = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.91 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.43 (m, 2H), 6.04 (d, *J* = 3.0 Hz, 1H), 5.85 (d, *J* = 3.0 Hz, 1H), 4.78 (dd, *J* = 12.5, 6.2 Hz, 1H), 4.72 (dd, *J* = 12.5, 7.2 Hz, 1H), 4.26 (p, *J* = 6.7 Hz, 1H), 3.50 (dd, *J* = 17.8, 6.1 Hz, 1H), 3.40 (dd, *J* = 17.8, 7.5 Hz, 1H), 2.23 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 196.8, 152.1, 150.1, 136.5, 133.7, 128.8 (2C), 128.2 (2C), 108.0, 106.4, 77.5, 39.2, 33.4, 13.6. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}NO_4^+$ 274.1074, found 274.1072.

Synthesis of 3-(5-methylfuran-2-yl)-1-phenyl-3-(phenylsulfanyl)propan-1-one (3z).

3z

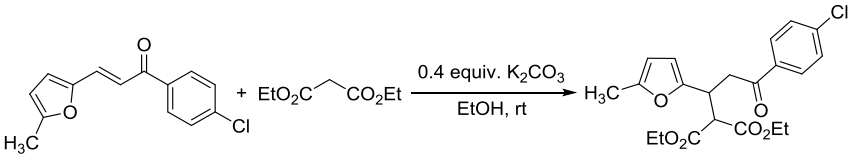
To a stirred solution of (2*E*)-3-(5-methylfuran-2-yl)-1-phenylprop-2-en-1-one (424 mg, 2.0 mmol) in CH_2Cl_2 (5 mL) was added thiophenol (245 µL, 2.4 mmol, 1.2 equiv.) and $FeCl_3$ (65 mg, 20 mol%) under argon at 0 °C. The resulting mixture was allowed to reach room temperature over 1 h and then stirred up to the full conversion of the starting material (TLC or GC control). Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 1:0 to 10:1 to 3:1).



3z

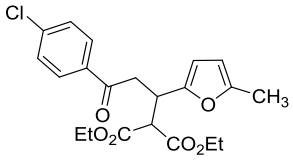
3-(5-Methylfuran-2-yl)-1-phenyl-3-(phenylsulfanyl)propan-1-one (**3z**). Yield: 187 mg, 29%; pale yellow oil. R_f = 0.60 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.96 – 7.92 (m, 2H), 7.60 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.41 – 7.36 (m, 2H), 7.30 – 7.27 (m, 3H), 5.93 (d, *J* = 3.1 Hz, 1H), 5.81 (d, *J* = 3.1 Hz, 1H), 4.96 (dd, *J* = 7.9, 6.2 Hz, 1H), 3.70 (dd, *J* = 17.0, 7.9 Hz, 1H), 3.52 (dd, *J* = 17.0, 6.2 Hz, 1H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 196.9, 151.8, 151.5, 137.0, 133.9 (2C), 133.8, 133.4, 128.9 (2C), 128.8 (2C), 128.3 (2C), 128.0, 108.3, 106.4, 42.4, 42.1, 13.7. HRMS (ESI/TOF) m/z: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_2S^+$ 345.0920, found 345.0928.

Synthesis of diethyl [3-(4-chlorophenyl)-1-(5-methylfuran-2-yl)-3-oxopropyl]propanedioate (3aa).



3aa

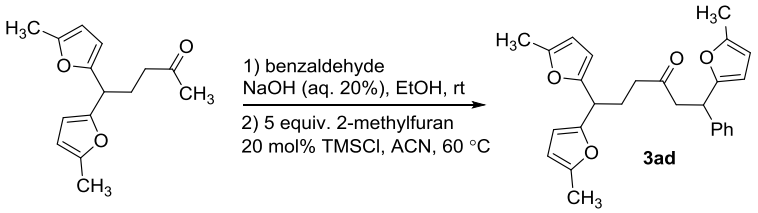
To a stirred solution of (2*E*)-1-(4-chlorophenyl)-3-(5-methylfuran-2-yl)prop-2-en-1-one (493 mg, 2.0 mmol) in EtOH (10 mL) was added diethylmalonate (340 µL, .2.2 mmol, 1.1 equiv.) and freshly calcined K_2CO_3 (55 mg, 0.8 mmol, 0.4 equiv.) at room temperature. The resulting mixture stirred up to the full conversion of the starting material (TLC or GC control). Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 19:1 to 9:1 to 1:1).



3aa

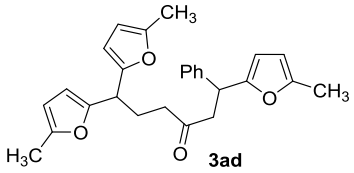
Diethyl [3-(4-chlorophenyl)-1-(5-methylfuran-2-yl)-3-oxopropyl]propanedioate (**3aa**). Yield: 455 mg, 56%; pale yellow oil. R_f = 0.50 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.79 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.85 (d, *J* = 3.1 Hz, 1H), 5.68 (d, *J* = 3.1 Hz, 1H), 4.17 – 4.05 (m, 3H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 8.0 Hz, 1H), 3.40 (dd, *J* = 16.7, 8.0 Hz, 1H), 3.33 (dd, *J* = 16.7, 5.0 Hz, 1H), 2.08 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): *δ* 196.4, 168.1, 167.8, 151.5, 151.1, 139.5, 135.3, 129.6, 128.9, 107.8, 106.1, 61.5, 61.4, 55.3, 39.9, 34.6, 14.0, 13.9, 13.4. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}ClO_6^+$ 407.1256, found 407.1266.

Synthesis of 1,6,6-tris(5-methylfuran-2-yl)-1-phenylhexan-3-one (3ad).



3ad

To the solution of 5,5-bis(5-methylfuran-2-yl)pentan-2-one[5] (1.23 g, 5 mmol) and benzaldehyde (510 µL, 5 mmol) in EtOH (2.5 mL) was added aqueous solution of NaOH (20%, 2.5 mL) at room temperature. The resulting mixture was stirred until full conversion of either aldehyde or ketone (TLC or GC control). Upon completion, the mixture was poured into water (50 mL) and extracted with ethyl acetate (2 × 30 mL). Combined organic fractions were washed with water (2 × 15 mL) and brine (20 mL). The combined organic fractions were dried with anhydrous $NaSO_4$, concentrated and subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 6:1 to 4:1). Unpolar major fraction that corresponded to α,β-unsaturated ketone was collected (R_f = 0.85, ethyl acetate/petroleum ether = 1:3; verified by GC and NMR), concentrated, and dissolved in acetonitrile (15 mL). To the resulting solution was added 2-methylfuran (885 µL, 10 mmol, 2 equiv.) and TMSCl (150 µL, 20 mol%), the reaction vessel was placed into aluminium block preheated to 60 °C and stirred while controlling the reaction progress by TLC or GC. Upon completion, the mixture was concentrated at reduced pressure. The product was isolated by column chromatography (eluent: petroleum ether/CH_2Cl_2, 9:1).

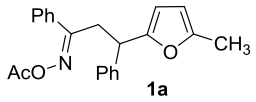


3ad

1,6,6-Tris(5-methylfuran-2-yl)-1-phenylhexan-3-one (**3ad**). Yield: 1373 mg, 66%; pale yellow oil. R_f = 0.70 (ethyl acetate/petroleum ether = 1:4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 – 7.03 (m, 5H), 5.77 (d, *J* = 3.0 Hz, 1H), 5.74 (d, *J* = 3.1 Hz, 1H), 5.73 – 5.68 (m, 4H), 4.42 (t, *J* = 7.4 Hz, 1H), 3.78 (t, *J* = 7.6 Hz, 1H), 3.00 (dd, *J* = 16.4, 7.4 Hz, 1H), 2.77 (dd, *J* = 16.4, 7.4 Hz, 1H), 2.28 – 2.17 (m, 2H), 2.09 (s, 6H), 2.07 (s, 3H), 2.06 – 2.02 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 207.6, 154.8, 153.2, 153.1, 151.0, 150.8 (2C), 142.1, 128.5 (2C), 127.8 (2C), 126.7, 106.6, 106.5, 106.4, 106.1, 106.0 (2C), 47.8, 40.9, 40.4, 38.1, 26.8, 13.5 (2C), 13.4. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{29}O_4^+$ 417.2060, found 417.2057.

Synthesis of *N*-(acetyloxy)-3-(5-methylfuran-2-yl)-1,3-diphenylpropan-1-imine (1a).

To a stirred solution of 3-(5-methylfuran-2-yl)-1,3-diphenylpropan-1-one (**3a**) (1.45 g, 5 mmol) in MeOH (50 ml) was added $NaOAc{\cdot}3H_2O$ (816 mg, 1.2 eq.) and $NH_2OH{\cdot}HCl$ (417 mg, 1.2 eq.). The resulting reaction mixture was refluxed until full conversion of **3a** by TLC was observed (ca. 8 h). Solvent was evaporated, water (20 ml) was added, the product was extracted with ethyl acetate (3 × 25 ml), and the extracts were dried with anhydrous Na_2SO_4. After filtration and evaporation of ethyl acetate, a mixture of stereoisomeric oximes was obtained as a pale yellow oil in nearly quantitative yield. Obtained mixture was dissolved in CH_2Cl_2 (30 ml), Ac_2O (710 µl, 1.5 eq.) was added in a single portion at room temperature and the reaction mixture was stirred up to the full conversion of the intermediate oximes (TLC control). Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 10:1 to 3:1).



1a

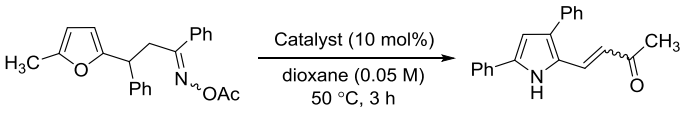
N-(Acetyloxy)-3-(5-methylfuran-2-yl)-1,3-diphenylpropan-1-imine (**1a**) was isolated as a mixture of inseparable diastereomers. Yield: 1648 mg, 95%; off-white solid; mp = 83−84 °C (ethyl acetate/petroleum ether). R_f = 0.60 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.52 (m, 2H), 7.44 – 7.36 (m, 3H), 7.29 – 7.21 (m, 5H), 5.92 (d, *J* = 3.0 Hz, 1H), 5.83 (d, *J* = 3.0 Hz, 1H), 4.23 (t, *J* = 7.8 Hz, 1H), 3.60 (dd, *J* = 13.2, 7.4 Hz, 1H), 3.52 (dd, *J* = 13.3, 8.3 Hz, 1H), 2.20 (s, 3H), 2.17 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.5, 164.3, 153.6, 151.3, 140.8, 133.8, 130.3, 128.4 (2C), 128.3 (2C), 127.7 (2C), 127.4 (2C), 127.0, 107.0, 105.9, 42.6, 33.8, 19.6, 13.4. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}NO_3^+$ 348.1594, found 348.1589.

3. KEY OPTIMIZATION STUDIES

General notes.

All reactions, unless otherwise stated, were performed in a 3 mL Wheaton microreaction vials equipped with spinning bars and Teflon pressure caps. The vials were charged with reaction components under ambient conditions on air. Preheated aluminum blocks were used for heating the reaction vials.

Table S1. Screening of the catalyst.



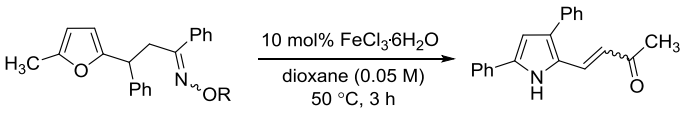
1a (*Z*/*E*)-**2a**

0.1 mmol scale

Entry	Catalyst	Combined yield of (*Z*/*E*)-**2a**, %[a]
1	$CuBr_2$	trace
2	$NiBr_2$	N/R[b]
3	HBr[d]	0[c]
4	CuCl	trace
5	$CuCl_2 \cdot 2H_2O$	N/R[b]
6	HCl[e]	0[c]
7	$Cu(OAc)_2 \cdot H_2O$	N/R[b]
8	$FeSO_4 \cdot 7H_2O$	N/R[b]
9	$CoSO_4 \cdot 7H_2O$	N/R[b]
10	$Sc(OTf)_3$	54
11	TfOH	0[c]
12	$FeCl_3$	94
13	**$FeCl_3 \cdot 6H_2O$**	**94**
14	$Fe(acac)_3$	75
15	$Pd(OAc)_2$	61
16	$PdCl_2$	49
17	TEMPO	N/R[b]
18	Blue LED[f]	N/R[b]

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard. [b] <5% conversion of **1a**. [c] Partial decomposition of **1a**. [d] Aqueous solution (48% w/w). [e] Aqueous solution (36% w/w). [f] Wavelength 465-475 nm.

Table S2. Screening of different oximes.



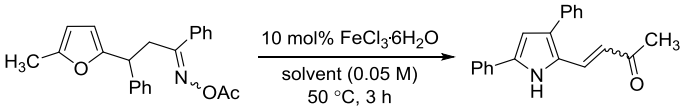
1 (*Z*/*E*)-**2a**

0.1 mmol scale

Entry	R	Combined yield of (*Z*/*E*)-**2a**, %[a]
1	H	N/R[b]
2	Me	N/R
3	**Ac**	**94**
4	Bz	51
5	^{F}Bz	N/R
6	Ms	26
7	Cl_3CO	43

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard. [b] <5% conversion of **1**.

Table S3. Screening of solvents.



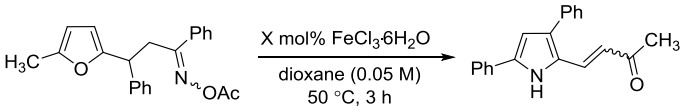
1a (*Z*/*E*)-**2a**

0.1 mmol scale

Entry	Solvent	Combined yield of (*Z*/*E*)-**2a**, %[a]
1	DCE	69
2	toluene	72
3	**Dioxane**	**94**
4	ethyl acetate	74
5	MeOH	N/R[b]

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard. [b] <5% conversion of **1a**.

Table S4. Screening of $FeCl_3 \cdot 6H_2O$ loading.



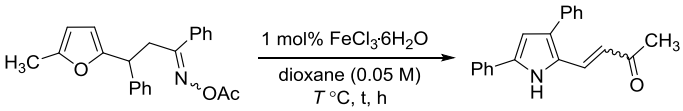
1a (*Z*/*E*)-**2a**

0.1 mmol scale

Entry	X	Combined yield of (*Z*/*E*)-**2a**, %[a]
1	10	94
2	5	89
3	2.5	85
4	**1**	**82**
5	0,5	68
6	0,1	45
7	0	N/R[b]

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard. [b] <5% conversion of **1a**.

Table S5. Screening of reaction conditions (temperature and time).



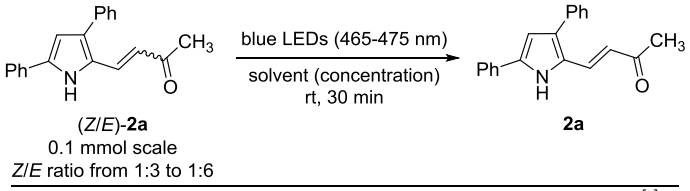
1a (*Z*/*E*)-**2a**

0.1 mmol scale

Entry	*T*,°C	t, h	Combined yield of (*Z*/*E*)-**2a**, %[a]
1	22 (rt)	24	35
2	50	5	89
3	60	5	91
4	**80**	**1.5**	**92**
5	100	1.5	92
6	80[b]	1.5	84
7	80[c]	1.5	88
8	80[d]	1.5	N/R[e]

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard. [b] 10 equiv. H_2O was added. [c] Reaction was performed under argon. [d] No $FeCl_3 \cdot 6H_2O$ was added. [e] <5% conversion of **1a**.

*Table S6. Isomerization of the (Z/E)-**2a** into **2a**.*



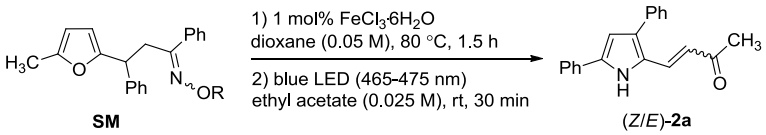
(*Z*/*E*)-**2a**
0.1 mmol scale
Z/*E* ratio from 1:3 to 1:6

2a

Entry	Solvent (concentration)	Yield of **2a**, %(*Z*/*E* ratio)[a]
1	dioxane (0.05M)	70 (1:12)
2	dioxane (0.025M)	78 (1:14)
3	$CHCl_3$ (0.025M)	Degrades over time
4	EtOAc (0.025M)	93 (>1:19)

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard.

Table S7. Screening of different oximes under optimal reaction conditions.



SM
0.1 mmol scale

(*Z*/*E*)-**2a**

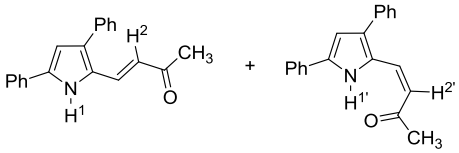
Entry	R	Combined yield of (*Z*/*E*)-**2a**, %[a]
1	**Ac**	**88**
2	Bz	64
3	Ms	37
4	CCl_3CO	50

[a] Analytical yield, determined by ^{1}H NMR with CH_2Br_2 as an internal standard.

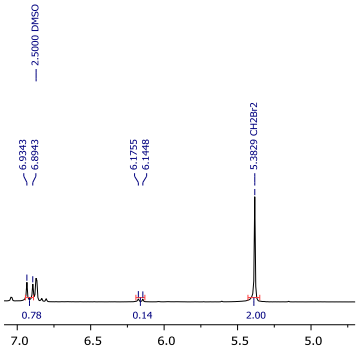
Example of the procedure for the optimization of reaction conditions for the synthesis of pyridine (*Z*/*E*)-2a (Table S5, entry 4)

3 mL Weaton microreactor was charged with oxime **1a** (35 mg, 0.1 mmol), dioxane (2 mL) and the solution of $FeCl_3 \cdot 6H_2O$ in dioxane (10 µL, 13.5 mg/mL, 1% mol.). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (80 ^oC) aluminum block. The reaction mixture was stirred for 1.5 h at this temperature. Then the reaction mixture was filtered through a pad of silica gel washed with ethyl acetate, concentrated *in vacuo*, dissolved in DMSO-d_6 (0.6 mL). CH_2Br_2 (7 µL, 0.1 mmol, 1 equiv) was added to the solution, and the resulting mixture was analyzed by ^{1}H NMR.

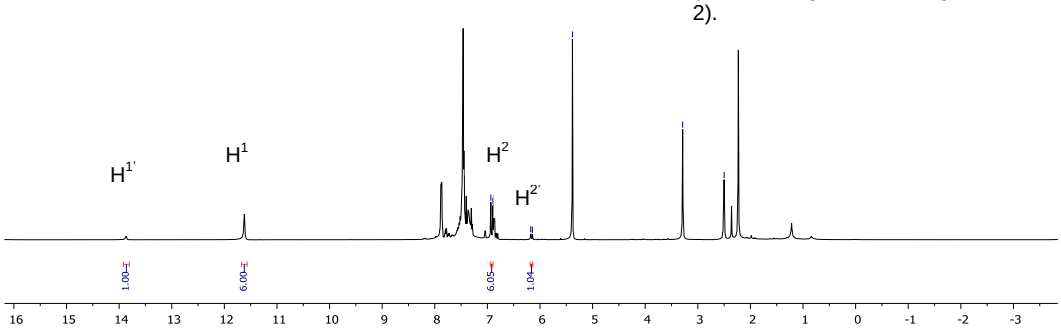
NMR ^{1}H (400 MHz, DMSO-d_6)
reaction mixture + CH_2Br_2 (1 equiv.)



Z/*E* = 1:6 by comparing integrals of H^1 vs $H^{1'}$ and H^2 vs $H^{2'}$

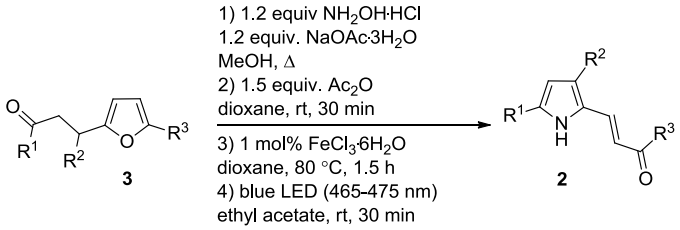


Analytical combined yield = 92% (CH_2Br_2 singlet was integrated as 2).



4. SYNTHESIS OF PRODUCTS

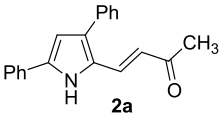
General procedure for the synthesis of pyrroles 2.



To a stirred solution of substrate **3** (0.5 mmol) and $NaOAc·3H_2O$ (81.6 mg, 0.6 mmol, 1.2 eq.) in MeOH (5 ml) was added $NH_2OH·HCl$ (41.7 mg, 0.6 mmol, 1.2 eq.), and the reaction mixture was refluxed until full conversion of the starting material by TLC was observed (typically 5-12 h). The reaction mixture was poured into water (60 mL), and the product was extracted with ethyl acetate (3×15 mL). Combined organic fractions were washed with water (2 × 15 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of ethyl acetate, a mixture of stereoisomeric oximes was obtained as a pale yellow oil. The resulting oil was dissolved in 1,4-dioxane (10 ml), Ac_2O (71 µL, 1.5 eq.) was added in a single portion at room temperature, and the reaction mixture was stirred for 30 min (TLC control). The solution of $FeCl_3·6H_2O$ in 1,4-dioxane (100 µL, 13.5 mg/mL, 1% mol.) was added, and stirring was continued at 80 ºC (aluminium block) for 1.5 h (TLC control). *The colour of the reaction mixture turns yellow almost right away, which indicates the beginning of the key rearrangement process. The colour of the reaction mixture gets dark yellow when the process is close to completion*. After that the reaction mixture was cooled to room temperature and filtered through a pad of silica gel, washed with mixture of petroleum ether/ethyl acetate, 1:1, dissolved in ethyl acetate (20 ml) and irradiated with blue LEDs (MOTOKO MTK-600B3528-12 LED strip, 12 V, 24 LEDs, 80 mW/LED, declared wavelength 465 – 475 nm) for 30 min at room temperature upon stirring (TLC control). *NOTE: prolonged irradiation leads to partial decomposition of the products!* Products were purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 5:1). *It is convenient to dry-load the reaction mixture on silica gel using* ethyl acetate *or CH_3CN solutions due to poor solubility of the products.* Alternatively, the products could be purified via recrystallization from ethyl acetate or CH_3CN as yellow amorphous solids, needles, or plates. The yields of the products are referred to isolated yields after column chromatography.

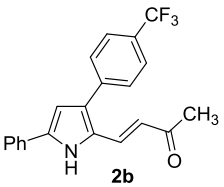
Blue LED step setup:

The inner diameter of a 600 mL glass beaker (outer diameter = 90 mm, height = 150 mm) was lined with a blue LED strip and placed onto magnetic stirring plate. A 50 mL round-bottom flask charged with a magnetic stirring bar and a mixture of isomeric pyrroles in ethyl acetate (20 mL) was placed in the middle of the beaker (the distance between the reaction flask and LED is ca. 15-20 mm, cotton could be used to support the flask). The beaker was covered with aluminium foil for additional eye protection.



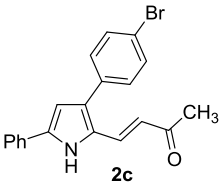
2a

(3*E*)-4-(3,5-Diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**). Yield: 123 mg, 86%; yellow solid; mp = 196−197 °C (ethyl acetate). R_f = 0.25 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): 11.62 (s, 1H), 7.89 – 7.86 (m, 2H), 7.50 – 7.39 (m, 8H), 7.37 – 7.29 (m, 2H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.87 (d, *J* = 2.5 Hz, 1H), 2.23 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.7, 136.4, 134.9, 132.7, 131.1, 130.7, 128.7 (2C), 128.6 (2C), 128.5 (2C), 127.3, 126.8, 125.6, 124.9 (2C), 121.4, 108.8, 27.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO^+$ 288.1383, found 288.1373.



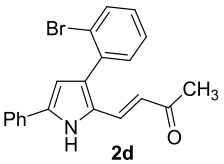
2b

(3*E*)-4-{5-Phenyl-3-[4-(trifluoromethyl)phenyl]-1*H*-pyrrol-2-yl}but-3-en-2-one (**2b**). Yield: 133 mg, 75%; yellow solid; mp = 200−201 °C (ethyl acetate). R_f = 0.20 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.74 (br s, 1H), 7.91 – 7.85 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.41 (d, *J* = 16.2 Hz, 1H), 7.35 – 7,28 (m, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.9, 139.1, 136.6, 130.9, 130.6, 130.2, 129.0 (2C), 128.7 (2C), 127.4, 127.1 (q, $^2J_{C\text{-}F}$ = 32 Hz), 126.1, 125.5 (q, $^3J_{C\text{-}F}$ = 4 Hz, 2C), 124.9 (2C) 124.3 (q, $^1J_{C\text{-}F}$ = 272 Hz), 122.4, 108.9, 27.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}F_3NO^+$ 356.1257, found 356.1266.



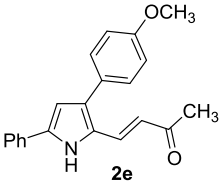
2c

(3*E*)-4-[3-(4-Bromophenyl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2c**). Yield: 117 mg, 64%; yellow solid; mp = 215−216 °C (ethyl acetate). R_f = 0.20 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.65 (br s, 1H), 7.90 – 7.83 (m, 2H), 7.68 – 7.62 (m, 2H), 7.47 – 7.40 (m, 4H), 7.37 (d, *J* = 16.1 Hz, 1H), 7.34 – 7.29 (m, 1H), 6.90 (d, *J* = 16.1 Hz, 1H), 6.88 (br s, 1H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.8, 136.5, 134.1, 131.5 (2C), 131.1, 130.9, 130.4 (2C), 130.3, 128.7 (2C), 127.4, 125.7, 124.9 (2C), 121.9, 120.0, 108.7, 27.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}BrNO^+$ 366.0488, found 366.0493.



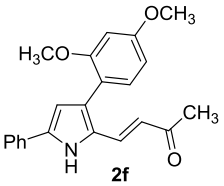
2d

(3*E*)-4-[3-(2-Bromophenyl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2d**). Yield: 148 mg, 81%; yellow solid; mp = 162−163 °C (ethyl acetate). R_f = 0.25 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.73 (br s, 1H), 7.89 – 7.82 (m, 2H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.39 – 7.28 (m, 3H), 7.05 (d, *J* = 16.1 Hz, 1H), 6.80 (br s, 1H), 6.77 (d, *J* = 16.1 Hz, 1H), 2.17 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.8, 135.8, 135.7, 132.9, 132.5, 131.2, 131.1, 130.7, 129.4, 128.8 (2C), 127.7, 127.4, 126.5, 124.8 (2C), 123.5, 121.1, 110.2, 27.6. λ_{max}(acetonitrile)/nm 274 (ε/dm^3 mol^{-1} cm^{-1} 14 100), 382 (27 300). HRMS (ESI$^+$) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}BrNO^+$ 366.0488, found 366.0493.



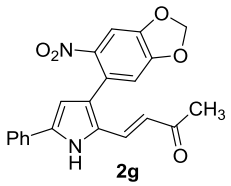
2e

(3*E*)-4-[3-(4-Methoxyphenyl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2e**). Yield: 105 mg, 66%; yellow solid; mp = 201−202 °C (ethyl acetate). R_f = 0.15 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.53 (br s, 1H), 7.90 – 7.82 (m, 2H), 7.46 – 7.36 (m, 5H), 7.32 – 7.28 (m, 1H), 7.07 – 7.01 (m, 2H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 3.81 (s, 3H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.7, 158.4, 136.4, 132.7, 131.1, 130.9, 129.6 (2C), 128.7 (2C), 127.3 (2C), 125.4, 124.8 (2C), 120.9, 114.2 (2C), 108.7, 55.1, 27.3. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{20}NO_2^+$ 318.1489, found 318.1478.



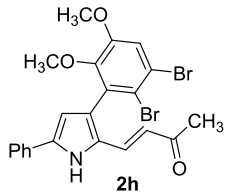
2f

(3*E*)-4-[3-(2,4-Dimethoxyphenyl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2f**). Yield: 108 mg, 62%; yellow solid; mp = 183−184 °C (ethyl acetate). R_f = 0.20 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.50 (br s, 1H), 7.86 – 7.79 (m, 2H), 7.46 – 7.39 (m, 2H), 7.31 – 7.25 (m, 1H), 7.19 (d, *J* = 16.1 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 16.1 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 2.18 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.8, 160.1, 157.5, 135.8, 131.9, 131.8, 131.4, 129.2, 128.7 (2C), 127.1, 126.6, 124.7 (2C), 120.2, 116.1, 110.4, 105.0, 98.9, 55.4, 55.2, 27.2. HRMS (ESI$^+$) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}NO_3^+$ 348.1594, found 348.1585.



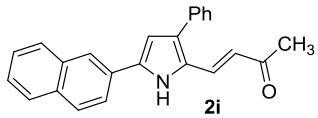
2g

(3*E*)-4-[3-(6-Nitro-1,3-benzodioxol-5-yl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2g**). Yield: 133 mg, 71%; yellow solid; mp = 254−255 °C (ethyl acetate). R_f = 0.15 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.70 (br s, 1H), 7.85 – 7.79 (m, 2H), 7.64 (s, 1H), 7.47 – 7.41 (m, 2H), 7.33 – 7.28 (m, 1H), 7.04 (d, J = 16.3 Hz, 1H), 7.02 (s, 1H), 6.75 (d, J = 16.3 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 6.27 (s, 2H), 2.18 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.6, 150.6, 147.1, 143.5, 136.2, 130.8, 129.6, 128.7 (2C), 127.3, 127.2, 126.4, 124.7 (2C), 121.6, 111.1, 109.1, 104.9, 103.2, 66.2, 27.2. HRMS (ESI/TOF) m/z: [M + H]$^+$ calcd for $C_{21}H_{17}N_2O_5^+$ 377.1132, found 377.1143.



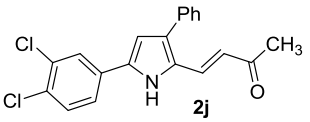
2h

(3*E*)-4-[3-(2,3-Dibromo-5,6-dimethoxyphenyl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2h**). Yield: 177 mg, 70%; yellow solid; mp = 195−196 °C (ethyl acetate). R_f = 0.15 (ethyl acetate/petroleum ether = 1:4). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (br s, 1H), 7.86 – 7.80 (m, 2H), 7.53 (s, 1H), 7.47 – 7.40 (m, 2H), 7.32 – 7.26 (m, 1H), 6.92 (d, J = 16.0 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H), 3.89 (s, 3H), 3.51 (s, 3H), 2.16 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.7, 152.5, 147.2, 135.9, 132.3, 131.1, 130.4, 128.8 (2C), 127.9, 127.3, 126.6, 124.6 (2C), 120.8, 118.9, 117.5, 117.2, 110.0, 60.4, 56.4, 27.8. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{22}H_{20}Br_2NO_3^+$ 503.9804, found 503.9806.



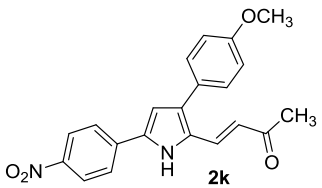
2i

(3*E*)-4-(5-Naphthalen-2-yl-3-phenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2i**). Yield: 142 mg, 84%; yellow solid; mp = 202−203 °C (ethyl acetate). R_f = 0.25 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.77 (br s, 1H), 8.44 (d, J = 1.8 Hz, 1H), 8.02 (dd, J = 8.6, 1.8 Hz, 1H), 7.97 (d, J = 8.6 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.58 – 7.48 (m, 7H), 7.45 (d, J = 16.0 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.04 (d, J = 2.5 Hz, 1H), 6.97 (d, J = 16.0 Hz, 1H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.8, 136.4, 134.9, 133.1, 132.8, 132.1, 130.7, 128.6 (2C), 128.5, 128.4 (2C), 128.2, 127.7, 127.6, 126.8, 126.6, 126.0, 125.9, 123.5, 122.7, 121.6, 109.5, 27.4. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{24}H_{20}NO^+$ 338.1539, found 338.1547.



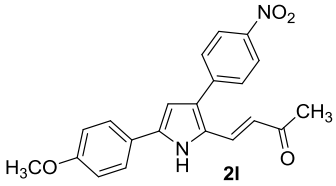
2j

(3*E*)-4-[5-(3,4-Dichlorophenyl)-3-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2j**). Yield: 141 mg, 79%; yellow solid; mp = 235−236 °C (ethyl acetate). R_f = 0.50 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.67 (br s, 1H), 8.19 (d, J = 2.1 Hz, 1H), 7.84 (dd, J = 8.5, 2.1 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.49 – 7.36 (m, 6H), 7.02 (d, J = 2.4 Hz, 1H), 6.88 (d, J = 16.1 Hz, 1H), 2.24 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.8, 134.6, 133.5, 132.5, 131.7, 131.6, 130.8, 130.5, 129.2, 128.6 (2C), 128.4 (2C), 126.9, 126.5, 126.0, 124.8, 122.2, 110.1, 27.3. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{20}H_{16}Cl_2NO^+$ 356.0603, found 356.0613.



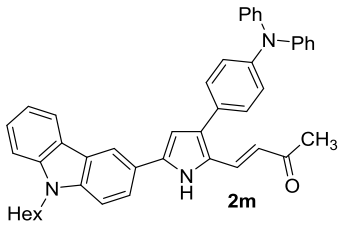
2k

(3*E*)-4-[3-(4-Methoxyphenyl)-5-(4-nitrophenyl)-1*H*-pyrrol-2-yl]but-3-en-2-one (**2k**). Yield: 94 mg, 52%; canary solid; mp = 276−277 °C (ethyl acetate). R_f = 0.20 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.79 (br s, 1H), 8.27 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.09 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 16.1 Hz, 1H), 3.81 (s, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.9, 158.5, 145.5, 137.3, 133.6, 132.6, 130.4, 129.6 (2C), 127.6, 126.7, 125.1 (2C), 124.1 (2C), 122.8, 114.2 (2C), 111.6, 55.1, 27.3. λ_{max}(acetonitrile)/nm 350 (ε/dm^3 mol^{-1} cm^{-1} 30 450), 423 (44 780). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{21}H_{19}N_2O_4^+$ 363.1339, found 363.1349.

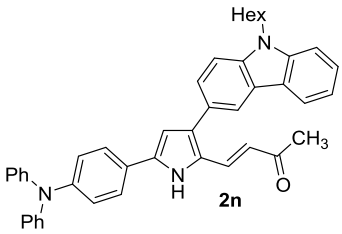


2l

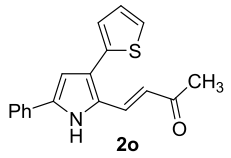
(3*E*)-4-[5-(4-Methoxyphenyl)-3-(4-nitrophenyl)-1*H*-pyrrol-2-yl]but-3-en-2-one (**2l**). Yield: 134 mg, 74%; red solid; mp = 254−255 °C (ethyl acetate). R_f = 0.10 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.69 (br s, 1H), 8.30 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 16.0 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 16.0 Hz, 1H), 6.89 (d, J = 2.2 Hz, 1H), 3.81 (s, 3H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.9, 159.0, 145.8, 142.0, 137.1, 130.1, 129.9, 129.1 (2C), 126.4 (2C), 125.9, 123.8 (2C), 123.5, 122.4, 114.2 (2C), 107.9, 55.2, 27.2. λ_{max}(acetonitrile)/nm 363 (ε/dm^3 mol^{-1} cm^{-1} 30 980). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{21}H_{19}N_2O_4^+$ 363.1339, found 363.1346.



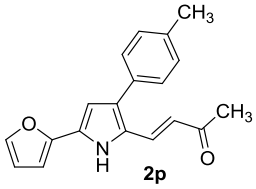
(3*E*)-4-{3-[4-(Diphenylamino)phenyl]-5-(9-hexyl-9*H*-carbazol-3-yl)-1*H*-pyrrol-2-yl}but-3-en-2-one (**2m**). Yield: 223 mg, 71%; orange solid; mp = 178−179 °C (ethyl acetate). R_f = 0.25 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.56 (br s, 1H), 8.68 (br s, 1H), 8.18 (d, *J* = 7.7 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.41 (m, 4H), 7.35 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 7.10 – 7.04 (m, 8H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 4.39 (t, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.84 – 1.71 (m, 2H), 1.32 – 1.19 (m, 6H), 0.80 (t, *J* = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.5, 147.1 (3C), 146.0, 140.4, 139.5, 138.2, 132.8, 130.8, 129.4 (4C), 129.3 (2C), 125.9, 124.8, 124.0 (4C), 123.4, 123.3 (2C), 123.0 (2C), 122.3, 122.2, 122.1, 120.1, 120.0, 118.9, 116.8, 109.4, 107.9, 42.3, 30.8, 28.4, 27.4, 26.0, 21.9, 13.7. λ_{max}(acetonitrile)/nm 276 (ε/dm^3 mol^{-1} cm^{-1} 25 700), 414 (27 000). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{44}H_{42}N_3O^+$ 628.3322, found 628.3323.



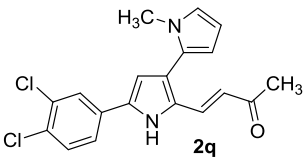
(3*E*)-4-(5-(4-(Diphenylamino)phenyl)-3-(9-hexyl-9H-carbazol-3-yl)-1H-pyrrol-2-yl)but-3-en-2-one (**2n**). Yield: 201 mg, 64%; deep orange solid; mp = 106−107 °C (ethyl acetate). R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.48 (br s, 1H), 8.24 – 8.17 (m, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.35 – 7.30 (m, 4H), 7.22 – 7.18 (m, 1H), 7.10 – 7.03 (m, 8H), 6.87 (d, *J* = 15.5 Hz, 1H), 6.85 (d, *J* = 2.4 Hz, 1H), 4.39 (t, *J* = 7.2 Hz, 2H), 2.20 (s, 3H), 1.82 – 1.76 (m, 2H), 1.32 – 1.22 (m, 6H), 0.81 (t, *J* = 6.9 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.5, 146.9 (2C), 146.4, 140.3, 139.1, 136.5, 134.3, 131.4, 129.5 (4C), 126.6, 126.1 (2C), 125.7, 125.6, 125.5, 125.3, 124.3, 124.0 (4C), 123.2 (2C), 123.1 (2C), 122.4, 122.0, 120.3, 120.0, 118.7, 109.3, 109.2, 108.6, 42.3, 30.8, 28.4, 27.1, 26.0, 21.9, 13.7. λ_{max}(acetonitrile)/nm 304 (ε/dm^3 mol^{-1} cm^{-1} 32 700), 330 (31 900), 416 (26 050). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{44}H_{42}N_3O^+$ 628.3322, found 628.3335.



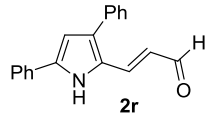
(3*E*)-4-(5-Phenyl-3-thiophen-2-yl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2o**). Yield: 113 mg, 77%; yellow solid; mp = 191−192 °C (ethyl acetate). R_f = 0.25 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.63 (br s, 1H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 16.0 Hz, 1H), 7.56 (d, *J* = 5.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.34 – 7.29 (m, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.18 – 7.15 (m, 1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.92 (br s, 1H), 2.28 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d6): δ 196.8, 136.7, 136.4, 130.8, 130.1, 128.7 (2C), 127.9, 127.5, 125.7, 125.4, 125.2, 125.1, 124.9 (2C), 121.8, 108.5, 27.2. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{18}H_{16}NOS^+$ 294.0947, found 294.0956.



(3*E*)-4-[5-Furan-2-yl-3-(4-methylphenyl)-1*H*-pyrrol-2-yl]but-3-en-2-one (**2p**). Yield: 103 mg, 71%; yellow solid; mp = 171−172 °C (ethyl acetate). R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.75 (br s, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.38 (d, *J* = 16.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 3.4 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.65 – 6.58 (m, 2H), 2.35 (s, 3H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.6, 146.7, 142.4, 136.2, 132.4, 131.7, 130.6, 129.2 (2C), 128.3 (2C), 128.0, 125.1, 121.2, 111.9, 107.6, 105.8, 27.3, 20.6. λ_{max}(acetonitrile)/nm 280 (ε/dm^3 mol^{-1} cm^{-1} 26 550), 395 (26 400). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{19}H_{18}NO_2^+$ 292.1332, found 292.1337.

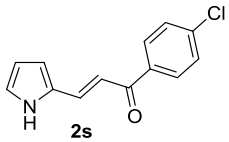


(3*E*)-4-[5'-(3,4-dichlorophenyl)-1-methyl-1*H*,1'*H*-2,3'-bipyrrol-2'-yl]but-3-en-2-one (**2q**). Yield: >5 mg, traces; yellow oil. R_f = 0.40 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.68 (br s, 1H), 8.18 (d, *J* = 2.2 Hz, 1H), 7.85 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 16.2 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 6.13 – 6.07 (m, 1H), 6.01 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.60 (s, 3H), 2.22 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.0, 133.5, 131.8, 131.7, 130.9, 130.8, 129.2, 128.1, 126.1, 126.0, 124.9, 123.8, 123.7, 121.6, 110.4, 109.7, 107.4, 34.5, 27.2. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{19}H_{17}Cl_2N_2O^+$ 359.0712, found 359.0706.



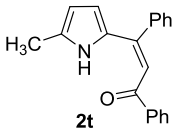
2r

(2*E*)-3-(3,5-Diphenyl-1*H*-pyrrol-2-yl)prop-2-enal (**2r**). Yield: 98 mg, 72%; yellow solid; mp = 209−210 °C (ethyl acetate). R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.68 (br s, 1H), 9.52 (d, J = 7.9 Hz, 1H), 7.93 – 7.84 (m, 2H), 7.52 – 7.43 (m, 7H), 7.40 – 7.31 (m, 2H), 6.92 (d, J = 2.5 Hz, 1H), 6.88 (dd, J = 15.6, 7.9 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 193.3, 139.9, 137.5, 134.6, 133.5, 130.8, 128.7 (2C), 128.6 (2C), 128.5 (2C), 127.6, 126.9, 125.8, 125.0 (2C), 123.0, 109.2. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{19}H_{16}NO^+$ 274.1226, found 274.1218.



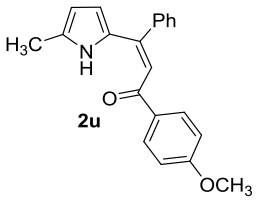
2s

(2*E*)-1-(4-Chlorophenyl)-3-(1*H*-pyrrol-2-yl)prop-2-en-1-one (**2s**). Yield: 51 mg, 44%; yellow solid; mp = 164−165 °C (ethyl acetate). R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.68 (br s, 1H), 8.06 – 8.00 (m, 2H), 7.65 – 7.58 (m, 3H), 7.52 (d, J = 15.4 Hz, 1H), 7.17 – 7.12 (m, 1H), 6.78 – 6.72 (m, 1H), 6.26 – 6.20 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 187.2, 137.3, 137.0, 134.6, 129.7 (2C), 129.0, 128.7 (2C), 124.4, 116.4, 114.2, 110.6. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{13}H_{11}ClNO_+$ 232.0524, found 232.0530.



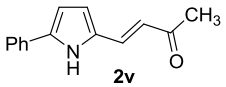
2t

(2*Z*)-3-(5-Methyl-1*H*-pyrrol-2-yl)-1,3-diphenylprop-2-en-1-one (**2t**). Yield: 60 mg, 42%; yellow oil. R_f = 0.70 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.03 (br s, 1H), 8.05 – 7.98 (m, 2H), 7.55 – 7.40 (m, 8H), 6.57 (s, 1H), 6.23 (d, J = 3.1 Hz, 1H), 6.11 (d, J = 3.1 Hz, 1H), 2.50 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 189.5, 150.4, 143.3, 141.0, 135.8, 132.0, 131.0, 129.2 (2C), 128.5 (2C), 128.4, 128.2 (2C), 128.0 (2C), 122.6, 112.6, 111.4, 14.1. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{20}H_{18}NO^+$ 288.1383, found 288.1375.



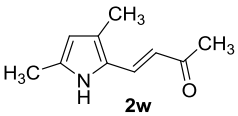
2u

(2*Z*)-1-(4-Methoxyphenyl)-3-(5-methyl-1*H*-pyrrol-2-yl)-3-phenylprop-2-en-1-one (**2u**). Yield: 62 mg, 39%; yellow oil. R_f = 0.70 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.95 (br s, 1H), 8.03 – 7.99 (m, 2H), 7.51 – 7.47 (m, 2H), 7.44 – 7.40 (m, 3H), 6.96 – 6.92 (m, 2H), 6.54 (s, 1H), 6.15 (d, J = 3.8 Hz, 1H), 6.06 (d, J = 3.8 Hz, 1H), 3.87 (s, 3H), 2.47 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 188.3, 162.9, 149.7, 143.5, 135.3, 133.5, 130.9, 130.5 (2C), 129.2 (2C), 128.3, 128.0 (2C), 122.0, 113.8 (2C), 112.7, 111.0, 55.6, 14.0. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{21}H_{20}NO_2^+$ 318.1489, found 318.1490.



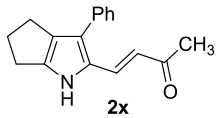
2v

(3*E*)-4-(5-Phenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2v**). Yield: 79 mg, 75%; yellow solid; mp = 169−170 °C (ethyl acetate). R_f = 0.20 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.59 (br s, 1H), 7.80 – 7.74 (m, 2H), 7.45 – 7.38 (m, 3H), 7.29 – 7.23 (m, 1H), 6.72 – 6.66 (m, 3H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.9, 136.6, 132.9, 131.4, 129.8, 128.7 (2C), 126.9, 124.4 (2C), 121.0, 116.7, 108.7, 26.8. λ_{max}(acetonitrile)/nm 263 (ε/dm^3 mol^{-1} cm^{-1} 5 800), 375 (28 050). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{14}H_{14}NO^+$ 212.1070, found 212.1066.



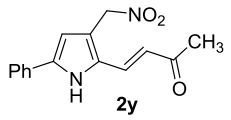
2w

(3*E*)-4-(3,5-Dimethyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2w**). Yield: 57 mg, 70%; greenish solid; mp = 191−192 °C (ethyl acetate). R_f = 0.20 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.95 (br s, 1H), 7.32 (d, J = 15.9 Hz, 1H), 6.28 (d, J = 15.9 Hz, 1H), 5.77 (d, J = 2.4 Hz, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 2.10 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.4, 134.1, 130.7, 127.2, 123.9, 117.1, 110.8, 26.7, 12.7, 11.0. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{10}H_{14}NO^+$ 164.1070, found 164.1068.

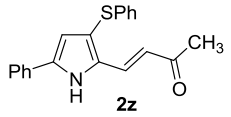


2x

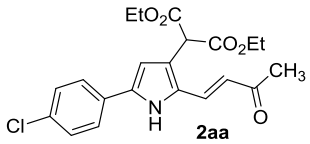
(3*E*)-4-(3-Phenyl-1,4,5,6-tetrahydrocyclopenta[*b*]pyrrol-2-yl)but-3-en-2-one (**2x**). Yield: 84 mg, 67%; yellow solid; mp = 176−177 °C (ethyl acetate). R_f = 0.10 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.43 (br s, 1H), 7.45 – 7.40 (m, 2H), 7.37 – 7.28 (m, 4H), 6.49 (d, J = 15.8 Hz, 1H), 2.74 (t, J = 7.2 Hz, 2H), 2.64 (t, J = 7.0 Hz, 2H), 2.42 – 2.35 (m, 2H), 2.16 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.2, 143.8, 135.0, 132.1, 128.5 (2C), 128.4 (2C), 128.0, 127.5, 126.6, 126.2, 118.3, 28.3, 27.1, 24.8, 24.4. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{17}H_{18}NO^+$ 252.1383, found 252.1393.



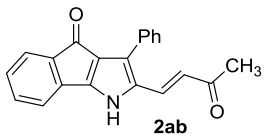
(3*E*)-4-[3-(Nitromethyl)-5-phenyl-1*H*-pyrrol-2-yl]but-3-en-2-one (**2y**). Yield: 97 mg, 72%; yellow solid; mp = 173−174 °C (ethyl acetate). R_f = 0.25 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.72 (br s, 1H), 7.80 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 16.2 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.33 – 7.27 (m, 1H), 6.86 (d, J = 16.2 Hz, 1H), 6.81 (d, J = 2.4 Hz, 1H), 5.82 (s, 2H), 2.31 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 197.4, 136.1, 130.8, 129.7, 129.1, 128.7 (2C), 127.4, 124.7 (2C), 123.0, 119.5, 110.4, 71.4, 26.8. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{15}H_{15}N_2O_3^+$ 271.1077, found 271.1075.



(3*E*)-4-[5-Phenyl-3-(phenylsulfanyl)-1*H*-pyrrol-2-yl]but-3-en-2-one (**2z**). Yield: 64 mg, 40%; yellow solid; mp = 181−182 °C (ethyl acetate). R_f = 0.35 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.98 (br s, 1H), 7.86 – 7.78 (m, 2H), 7.51 – 7.40 (m, 3H), 7.36 – 7.24 (m, 3H), 7.19 – 7.11 (m, 3H), 6.95 (d, J = 16.2 Hz, 1H), 2.23 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.9, 138.0, 136.8, 131.9, 130.6, 129.1 (2C), 128.8, 128.7 (2C), 127.6, 126.2 (2C), 125.4, 124.7 (2C), 122.7, 116.9, 114.3, 27.4. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{20}H_{18}NOS^+$ 320.1104, found 320.1108.



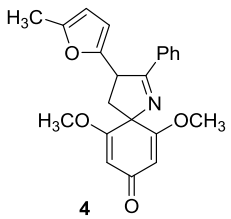
Diethyl {5-(4-chlorophenyl)-2-[(1*E*)-3-oxobut-1-en-1-yl]-1*H*-pyrrol-3-yl}propanedioate (**2aa**). Yield: 177 mg, 88%; yellow solid; mp = 214−215 °C (ethyl acetate). R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.54 (br s, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.54 – 7.44 (m, 3H), 6.76 (d, J = 16.1 Hz, 1H), 6.71 (d, J = 2.4 Hz, 1H), 5.16 (s, 1H), 4.21 – 4.12 (m, 4H), 2.28 (s, 3H), 1.20 (t, J = 7.1 Hz, 6H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 197.4, 167.7 (2C), 134.5, 131.6, 130.3, 129.8, 128.7 (2C), 127.9, 126.3 (2C), 122.3, 122.2, 109.7, 61.2 (2C), 49.2, 26.6, 13.8 (2C). HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{21}H_{23}ClNO_5^+$ 404.1259, found 404.1255.



2-[(1*E*)-3-Oxobut-1-en-1-yl]-3-phenylindeno[1,2-*b*]pyrrol-4(1*H*)-one (**2ab**). Yield: 59 mg, 38%; yellow solid; mp = 270−271 °C (ethyl acetate). R_f = 0.15 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.65 (br s, 1H), 7.59 (d, J = 7.1 Hz, 2H), 7.52 – 7.35 (m, 6H), 7.32 – 7.24 (m, 2H), 6.65 (d, J = 16.0 Hz, 1H), 2.26 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 196.5, 184.7, 153.3, 139.6, 134.1, 133.4, 131.8, 130.6, 130.5, 129.1, 129.0 (2C), 128.5 (2C), 127.8, 127.7, 123.0, 122.7, 121.5, 118.7, 27.4. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{21}H_{16}NO_2^+$ 314.1176, found 314.1184.

Synthesis of 6,10-dimethoxy-3-(5-methylfuran-2-yl)-2-phenyl-1-azaspiro[4.5]deca-1,6,9-trien-8-one (4).

The product was obtained following the general protocol for the synthesis of pyrroles **2**.



6,10-Dimethoxy-3-(5-methylfuran-2-yl)-2-phenyl-1-azaspiro[4.5]deca-1,6,9-trien-8-one (**4**). Yield: 131 mg, 72%; pale yellow oil. R_f = 0.45 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.5 Hz, 2H), 7.51 – 7.43 (m, 3H), 5.93 (d, J = 3.0 Hz, 1H), 5.81 (d, J = 3.0 Hz, 1H), 5.60 (s, 1H), 5.20 (s, 1H), 4.14 (t, J = 10.0 Hz, 1H), 3.79 (s, 3H), 3.62 (dd, J = 16.6, 10.0 Hz, 1H), 3.50 (dd, J = 16.6, 10.0 Hz, 2H), 3.43 (s, 3H), 2.17 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 188.0, 178.0, 170.8, 169.8, 151.6, 149.2, 133.3, 131.8, 128.7, 128.5, 107.7, 106.2, 101.6, 101.5, 81.6, 56.5, 55.7, 46.6, 40.5, 13.6. HRMS (ESI$^+$) m/z: [M + H]$^+$ calcd for $C_{22}H_{22}NO_4^+$ 364.1543, found 364.1554.

5. ORTEP-DIAGRAM OF PYRROLE 2a

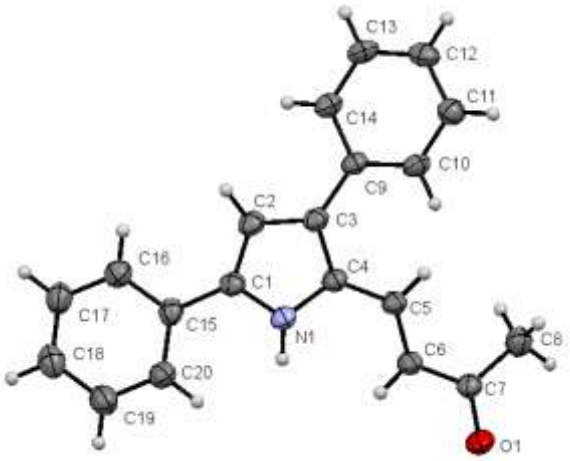


Figure S1. Structure of (3*E*)-4-(3,5-diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**) according to the X-ray diffraction data; non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

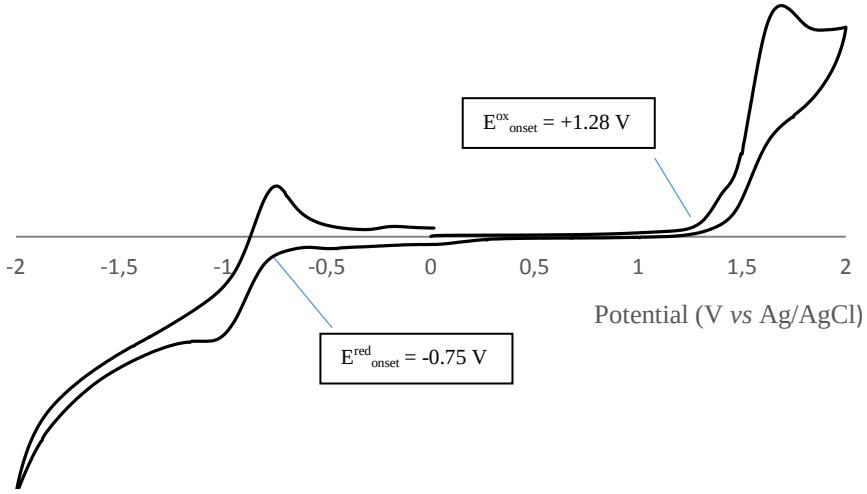
6. Synthesis (5 mmol scale) of (3*E*)-4-(3,5-diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (2a).

To a stirred solution of compound **3a** (1.45 g, 5 mmol) and $NaOAc \cdot 3H_2O$ (816 mg, 6 mmol, 1.2 eq.) in MeOH (50 ml) was added $NH_2OH \cdot HCl$ (417 mg, 6 mmol, 1.2 eq.), and the reaction mixture was refluxed until full conversion of the starting material by TLC was observed (ca. 8 h). The reaction mixture was poured into water (200 mL), and the product was extracted with ethyl acetate (3 × 40 mL). Combined organic fractions were washed with water (2 × 40 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of ethyl acetate, a mixture of stereoisomeric oximes was obtained as a pale yellow oil that solidified upon drying. The crude oxime was dissolved in dioxane (100 ml), Ac_2O (710 µl, 1.5 eq.) was added in a single portion at room temperature, and the reaction mixture was stirred for 60 min (TLC control). The solution of $FeCl_3 \cdot 6H_2O$ in 1,4-dioxane (1 mL, 13.5 mg/ml, 1% mol.) was added, and stirring was continued at 80ºC (aluminium block) for 3 h (TLC control). After that the reaction mixture was cooled to room temperature and filtered through a pad of SiO_2, washed with mixture of petroleum ether/ethyl acetate (1:1), dissolved in ethyl acetate (200 ml) and irradiated with blue LEDs (MOTOKO MTK-600B3528-12 LED strip, 12 V, 24 LEDs, 80 mW/LED, declared wavelength 465 – 475 nm) for 30 min at room temperature upon stirring (TLC control). Product was isolated by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 5:1) with 78 % yield (1.12 g).

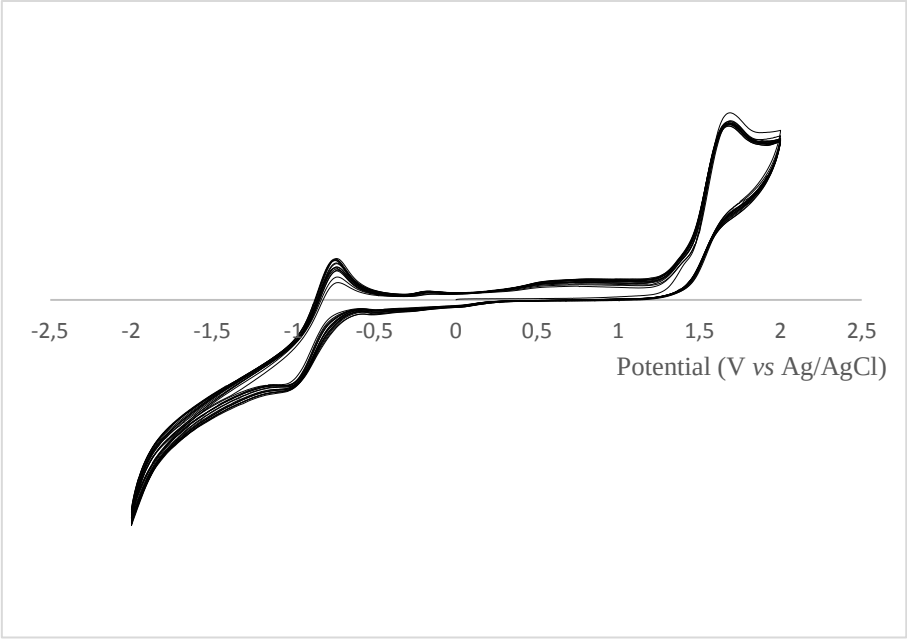
7. MECHANISTIC STUDIES

CV curve of oxime 1a (mixture of isomers, 5:1)

1 cycle

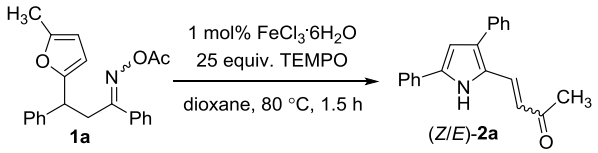


15 cycles



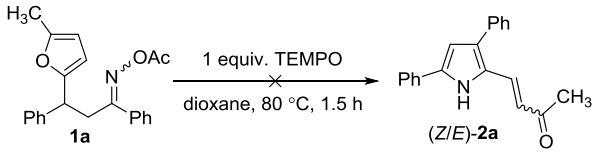
Mechanistic experiments with TEMPO

Experiment A



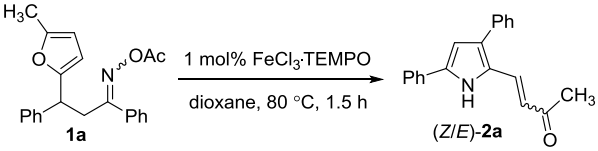
To the solution of *O*-acetyl oxime **1a** (104 mg, 0.3 mmol) in dioxane (6 mL) was added the solution of $FeCl_3 \cdot 6H_2O$ in 1,4-dioxane (60 µl, 13.5 mg/ml, 1% mol.) and TEMPO (1.17 g, 7.5 mmol, 25 equiv). The resulting mixture was stirred at 80 °C (aluminium block) for 1.5 h. After 1.5 h the reaction mixture was concentrated under reduced pressure. The major portion of TEMPO was removed by vacuum distillation on rotary evaporator at 80 °C under reduced pressure (*ca.* 15 mBar), and the residue was subjected to column chromatography (eluent: petroleum ether/ethyl acetate, gradient from 1:0 to 15:1 to 5:1). The product (*Z*/*E*)-**2a** was isolated with 77 mg, 89% combined yield, *Z*/*E* = 5:1.

Experiment B



To the solution of *O*-acetyl oxime **1a** (104 mg, 0.3 mmol) in dioxane (6 mL) was added TEMPO (47 mg, 0.3 mmol, 1 equiv). The resulting mixture was stirred at 80 °C (aluminium block) for 1.5 h. After 1.5 h the reaction mixture was concentrated under reduced pressure. The major portion of TEMPO was removed by vacuum distillation on rotary evaporator at 80 °C under reduced pressure (*ca.* 15 mBar), and the residue was subjected to column chromatography (eluent: petroleum ether/ethyl acetate, gradient from 1:0 to 15:1 to 5:1).The starting *O*-acetyl oxime **1a** was recovered (98 mg, conversion < 5%).

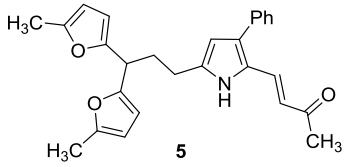
$FeCl_3(\eta^1$-TEMPO)-catalyzed synthesis of (*Z*/*E*)-2a.



To the solution of *O*-acetyl oxime **1a** (104 mg, 0.3 mmol) in dioxane (6 mL) was added $FeCl_3(\eta^1$-TEMPO)[6] (47 mg, 0.3 mmol, 1 equiv). The resulting mixture was stirred at 80 °C (aluminium block) for 1.5 h. After 1.5 h the reaction mixture was cooled to room temperature, concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/ethyl acetate, gradient from 1:0 to 15:1 to 5:1). The starting *O*-acetyl oxime **1a** was recovered (98 mg, conversion < 5%).

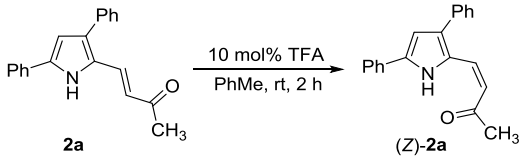
Synthesis of (3,3-bis(5-methylfuran-2-yl)propyl)-3-phenyl-1H-pyrrol-2-yl)but-3-en-2-one (5).

The product was obtained following the general protocol for the synthesis of pyrroles **2**. Pyrrole **5** was isolated by column chromatography (eluent: petroleum ether/ethyl acetate, gradient from 15:1 to 5:1)



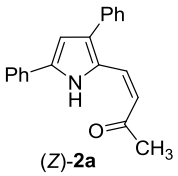
(*E*)-4-{5-[3,3-bis(5-methylfuran-2-yl)propyl]-3-phenyl-1*H*-pyrrol-2-yl}but-3-en-2-one (**5**). Yield: 171 mg, 83%; pale yellow oil. R_f = 0.30 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (br s, 1H), 7.39 (d, *J* = 16.1 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.16 (m, 1H), 6.41 (d, *J* = 16.1 Hz, 1H), 6.06 (d, *J* = 2.5 Hz, 1H), 5.86 (d, *J* = 3.1 Hz, 2H), 5.75 (d, *J* = 3.0 Hz, 2H), 3.93 (t, *J* = 7.6 Hz, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 2.14 (s, 3H), 2.13 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 199.0, 153.4 (2C), 151.0 (2C), 139.2, 135.7, 133.6, 133.5, 128.9 (2C), 128.7 (2C), 126.9, 123.9, 120.2, 109.7, 106.7 (2C), 106.2 (2C), 38.6, 32.6, 26.0, 25.9, 13.6 (2C). HRMS (ESI$^+$) m/z: $[M + H]^+$ calcd for $C_{27}H_{28}NO_3^+$ 414.2064, found 414.2071.

8. Synthesis of (3*Z*)-4-(3,5-diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (*Z*)-2a.



2a (*Z*)-**2a**

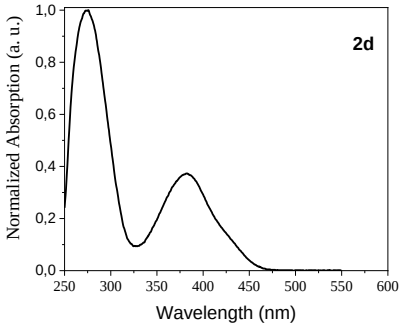
(3*E*)-4-(3,5-Diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**) (0.2 mmol, 57.4 mg) was dissolved in hot toluene (5 ml) and cooled to room temperature, then TFA (1.5 µl, 10% mol.) was added, and the resulting solution was stirred for 2 h at room temperature. Filtration through a pad of silica gel and washing it with mixture of petroleum ether/ethyl acetate 19:1 afforded (*Z*)-**2a** in 50% yield (44% of starting material was recovered).

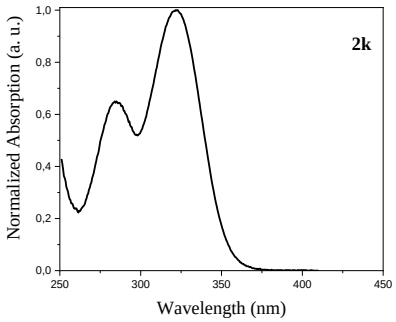


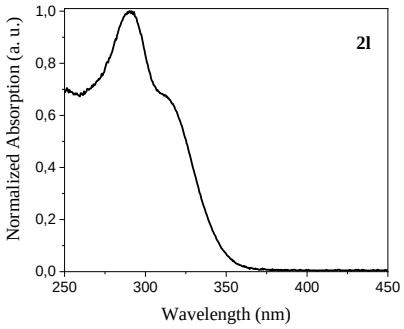
(*Z*)-**2a**

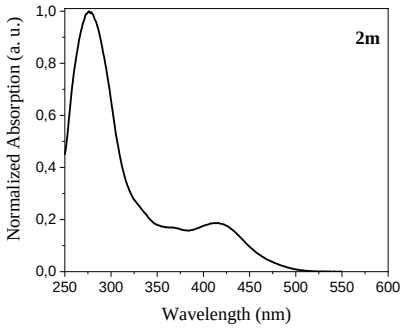
(3*Z*)-4-(3,5-Diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one [Z-(**2a**)]. Yield: 29 mg, 50%; yellow solid; mp = 186−187 °C (ethyl acetate). R_f = 0.55 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.86 (br s, 1H), 7.82 – 7.74 (m, 2H), 7.56 – 7.42 (m, 6H), 7.41 – 7.32 (m, 2H), 7.03 (d, J = 2.4 Hz, 1H), 6.80 (d, J = 12.2 Hz, 1H), 6.14 (d, J = 12.2 Hz, 1H), 2.35 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 199.2, 134.7, 134.5, 134.1, 131.4, 130.5, 129.2 (2C), 128.8 (2C), 128.6 (2C), 127.8, 127.1, 127.0, 124.0 (2C), 116.2, 109.4, 31.0. HRMS (ESI$^+$) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}NO^+$ 288.1383, found 288.1383.

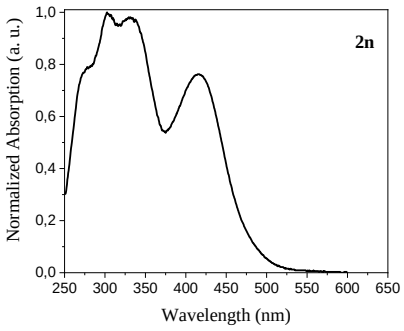
9. UV/VIS SPECTRA OF COMPOUNDS 2d,k-n,p,v

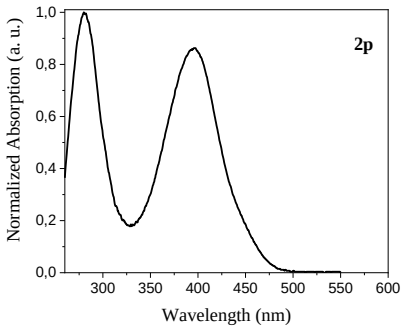


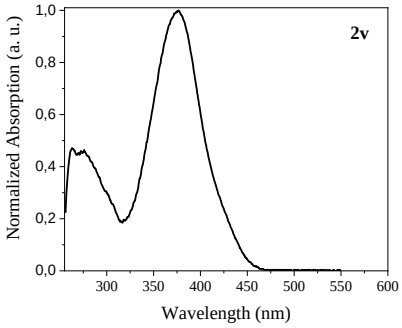


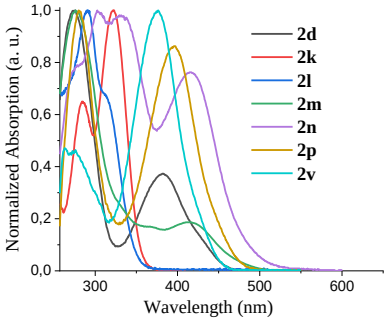




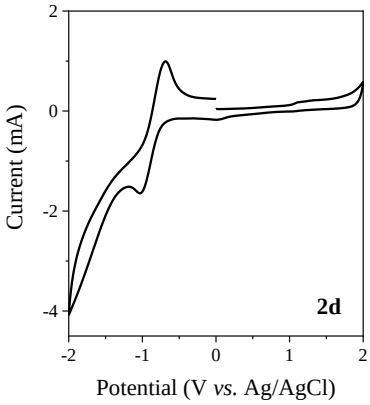


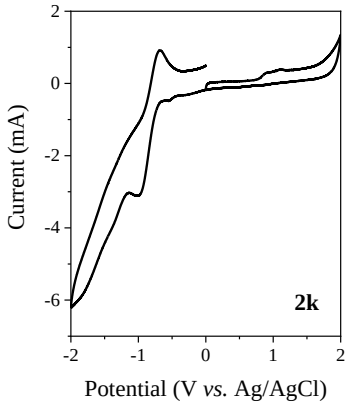


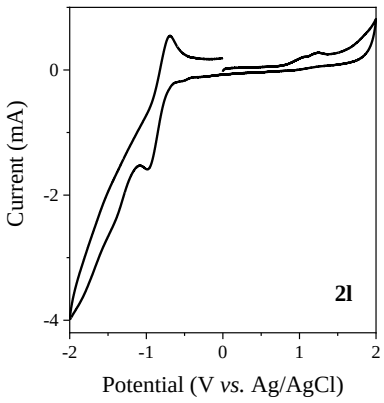


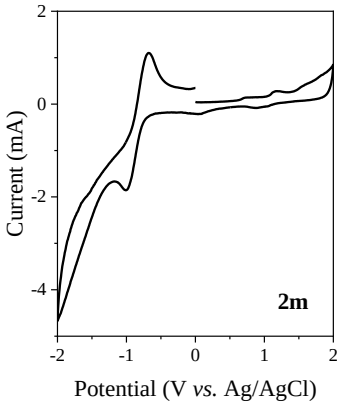


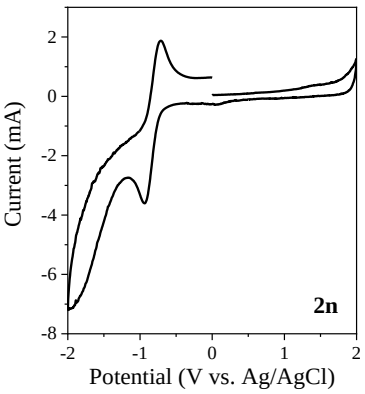
10. CV CURVES OF COMPOUNDS 2d,k-n,p,v

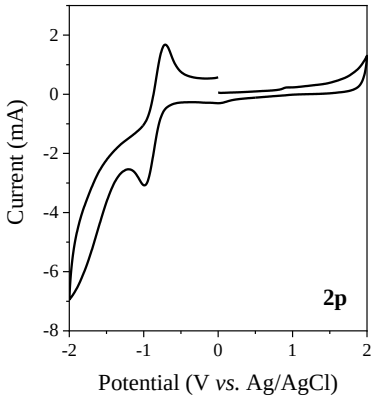












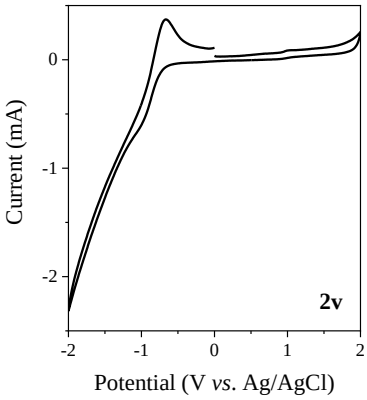
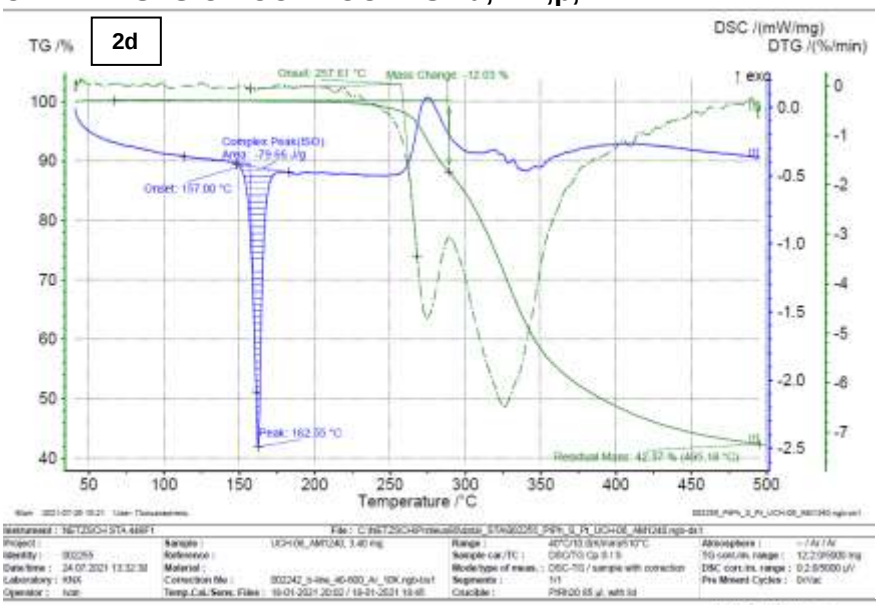


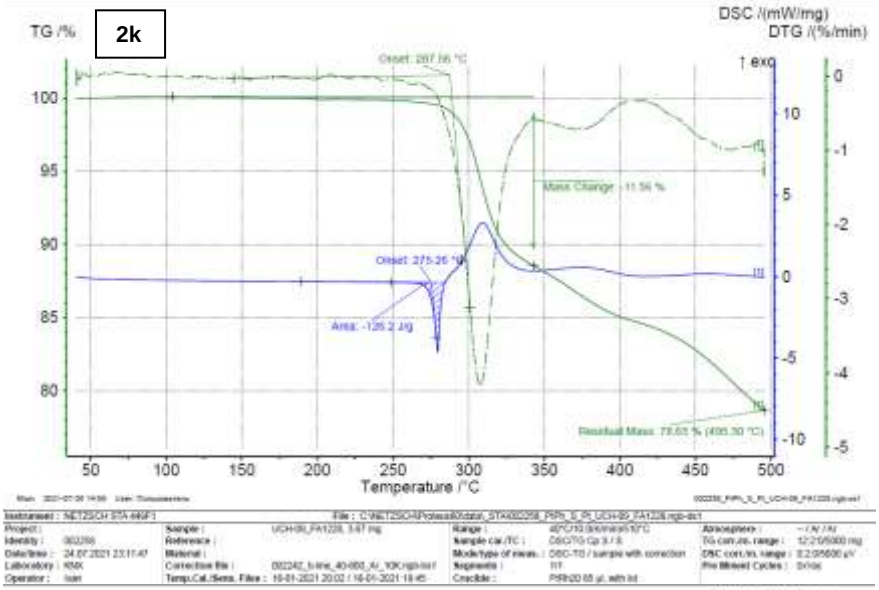
*Table S8. Physicochemical properties of selected pyrroles **2***

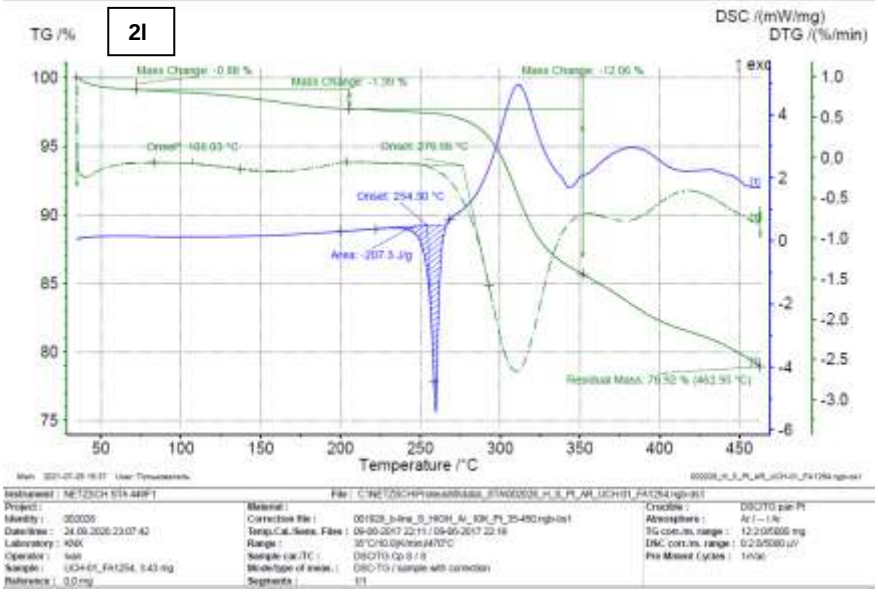
Compound	λ_{max}, nm (ε, $dm^3\ mol^{-1}cm^{-1}$)	λ_{onset}, nm	E^{opt}_g, eV[a]	E^{red}_{onset}, V	HOMO, eV[b]	LUMO, eV[c]	Melting point, °C[d]
2d	274 (14 100) 382 (27 300)	458	2.70	- 0.70	- 6.35	- 3.65	162-163
2k	350 (30 450) 423 (44 780)	500	2.48	- 0.67	- 6.17	- 3.69	276-277
2l	363 (30 980)	487	2.54	- 0.71	- 6.19	- 3.65	254-255
2n	304 (32 700) 330 (31 900) 416 (26 050)	500	2.48	- 0.68	- 6.15	- 3.67	178-179
2p	280 (26 550) 395 (26 400)	475	2.61	- 0.66	- 6.30	- 3.69	171-172
2v	263 (5 800) 375 (28 050)	455	2.72	- 0.70	- 6.37	- 3.65	169-170

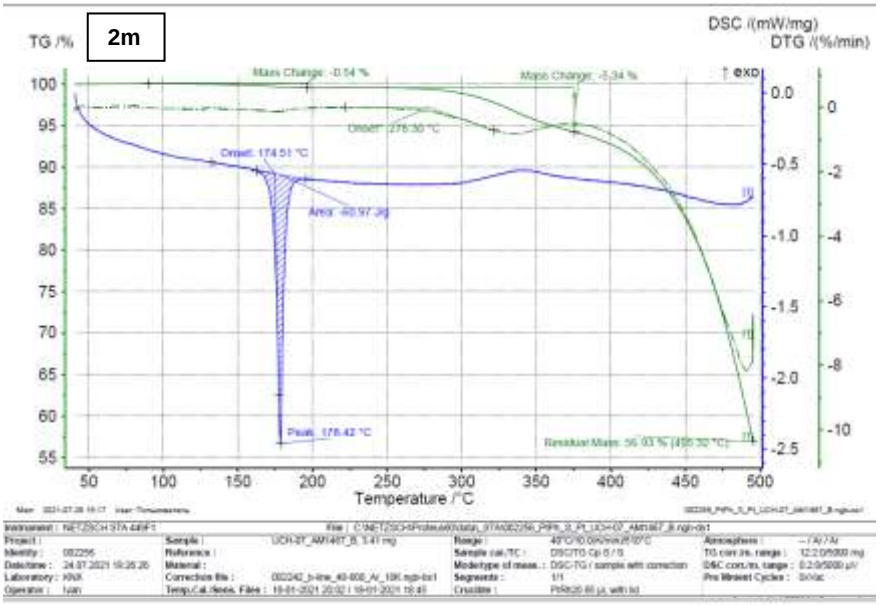
[a] $E^{opt}_g = 1240/\lambda_{onset}$, λ_{onset} is the long-wavelength absorption edge. [b] $E_{HOMO} = E^{opt}_g - E_{LUMO}$. [c] $E_{LUMO} = [-e(E^{red}_{onset\ vs\ Ag/AgCl} - E_{Fc\ vs\ Ag/AgCl} + 4.80)]$, where 4.8 eV is the energy level of ferrocene below the vacuum level. [d] Based on DTG-DSC studies.

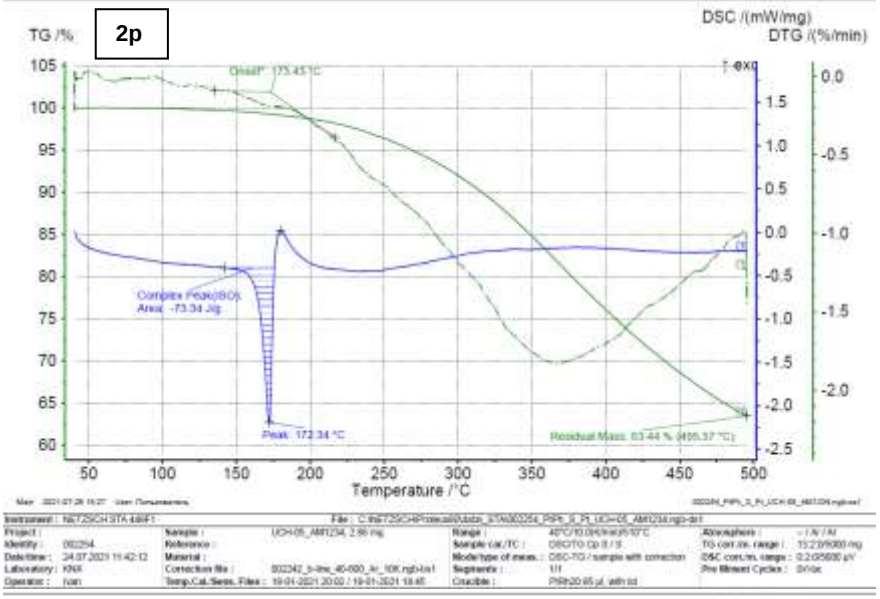
11. DTG AND DSC ANALYSES OF COMPOUNDS 2d,k-m,p,v

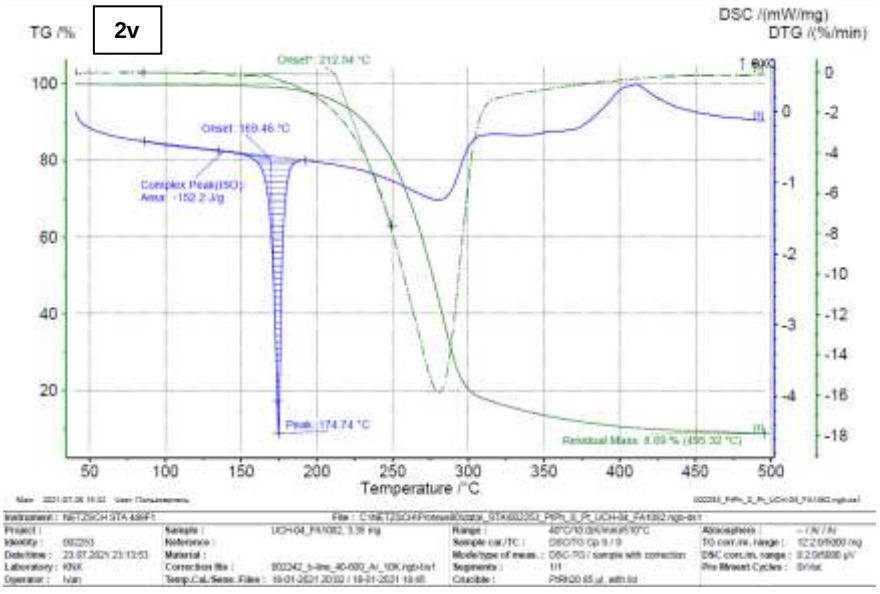






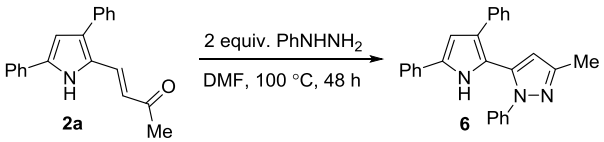

2m
TG /%
DSC /(mW/mg)
DTG /(%/min)
Mass Change: -0.54 %
Mass Change: -5.34 %
↑ exo
Onset: 276.30 °C
Onset: 174.51 °C
Area: -60.97 J/g
Peak: 178.42 °C
Residual Mass: 56.03 % (495.32 °C)
Temperature /°C


2p
TG /%
DSC /(mW/mg)
DTG /(%/min)
Onset: 175.45 °C
↑ exo
Complex Peak(ISO)
Area: -73.34 J/g
Peak: 172.34 °C
Residual Mass: 63.44 % (495.37 °C)
Temperature /°C

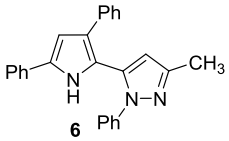

2v
TG /%
DSC /(mW/mg)
DTG /(%/min)
Onset: 212.34 °C
↑ exo
Onset: 169.46 °C
Complex Peak(ISO)
Area: -152.2 J/g
Peak: 174.74 °C
Residual Mass: 8.69 % (495.32 °C)
Temperature /°C

12. FURTHER TRANSFORMATIONS OF PYRROLE 2a

Synthesis of 5-(3,5-diphenyl-1*H*-pyrrol-2-yl)-3-methyl-1-phenyl-1*H*-pyrazole (6).

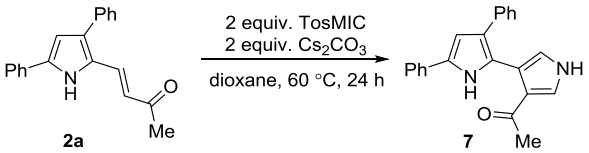


The mixture of (3*E*)-4-(3,5-diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**) (58 mg, 0.2 mmol) and $PhNHNH_2$ (44 µL, 0.4 mmol, 2 equiv.) in DMF (1 mL) was stirred at 100 °C (aluminium block) for 48 h (TLC or GC control). Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/ethyl acetate, gradient from 20:1 to 15:1).

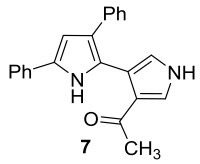


5-(3,5-Diphenyl-1*H*-pyrrol-2-yl)-3-methyl-1-phenyl-1*H*-pyrazole (**6**). Yield: 68 mg, 91%; pale yellow oil. R_f = 0.40 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (br s, 1H), 7.30 – 7.22 (m, 5H), 7.09 – 7.03 (m, 10H), 6.54 (d, J = 2.8 Hz, 1H), 6.18 (s, 1H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.8, 140.0 (2C), 135.6, 135.4, 133.2, 132.0, 129.1 (2C), 128.8 (2C), 128.3 (2C), 127.6 (2C), 127.0, 126.9, 126.2, 124.0 (2C), 123.9 (2C), 118.2, 109.0, 107.2, 13.8. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{22}N_3^+$ 376.1808, found 376.1818.

Synthesis of 1-(3,5-diphenyl-1*H*,1'*H*-2,3'-bipyrrol-4'-yl)ethanone (7).



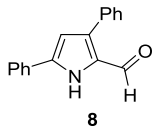
The mixture of (3*E*)-4-(3,5-diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**) (115 mg, 0.4 mmol), TosMIC (157 mg, 0.8 mmol, 2 equiv.), and Cs_2CO_3 (260 mg, 0.8 mmol, 2 equiv.) in dioxane (3 mL) was stirred at 60 °C (aluminium block) for 24 h (TLC or GC control). Upon completion, the reaction mixture was concentrated under reduced pressure and subjected to column chromatography (eluent: petroleum ether/ ethyl acetate, gradient from 15:1 to 10:1).



1-(3,5-Diphenyl-1*H*,1'*H*-2,3'-bipyrrol-4'-yl)ethanone (**7**). Yield: 129 mg, 79%; off-white solid; mp = 178−179 °C (ethyl acetate). R_f = 0.15 (ethyl acetate/petroleum ether = 1:2). ^{1}H NMR (400 MHz, , DMSO-d_6): δ 12.15 (br s, 1H), 11.55 (br s, 1H), 7.75 (br s, 1H), 7.69 (d, J = 7.9 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.32 – 7.27 (m, 2H), 7.20 – 7.14 (m, 2H), 6.72 (d, J = 2.9 Hz, 1H), 6.69 (br s, 1H), 2.34 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, , DMSO-d_6): δ 194.2, 137.5, 132.5, 129.3, 128.7 (2C), 128.1 (2C), 127.7 (2C), 127.4, 125.3, 125.2, 123.7, 122.9 (2C), 122.6, 122.5, 119.3, 115.5, 107.1, 27.8. HRMS (ESI/TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{19}N_2O^+$ 327.1492, found 327.1489.

Synthesis of 3,5-diphenyl-1*H*-pyrrole-2-carbaldehyde (8).

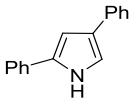
To the mixture of (3*E*)-4-(3,5-diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**) (115 mg, 0.4 mmol) was added ethanolic solution of KOH (0.3 g/mL, 5 mL, *ca.* 65 equiv. of KOH) at room temperature. The reaction mixture was refluxed for 1 h (TLC control). Upon completion, the mixture was poured into water (50 mL) and extracted with ethyl acetate (2 × 15 mL) Combined organic fractions were washed with water (2 × 10 mL) and brine (10 mL). The combined organic fractions were dried with anhydrous $NaSO_4$, concentrated and subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 2:1 to 1:1).



3,5-Diphenyl-1*H*-pyrrole-2-carbaldehyde (**8**).[7] Yield: 92 mg, 93%; off-white solid; mp = 154−155 °C (ethyl acetate). R_f = 0.40 (ethyl acetate/petroleum ether = 1:4). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.38 (br s, 1H), 9.62 (s, 1H), 7.98 (d, J = 7.8 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.50 – 7.39 (m, 4H), 7.39 – 7.32 (m, 2H), 6.94 (d, J = 2.4 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ 178.5, 138.7, 136.8, 133.6, 130.5, 129.1, 128.9 (2C), 128.7 (2C), 128.5 (2C), 128.1, 127.4, 125.7 (2C), 109.0.

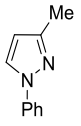
Synthesis of 2,4-diphenyl-1*H*-pyrrole (9) and 3-methyl-1-phenyl-1*H*-pyrazole (10).

(3*E*)-4-(3,5-Diphenyl-1*H*-pyrrol-2-yl)but-3-en-2-one (**2a**) (86 mg, 0.3 mmol) was dissolved in a solution of $PhNHNH_2$ in DMF (1.2 mL, 32.4 mg/mL, 1.2 eq. of $PhNHNH_2$) under argon. TFA as a solution in DMF was added (0.4 ml, 22.8 mg/ml, 0.2 eq. of TFA), and the reaction mixture was stirred at 150ºC (aluminium block) for 30 min (TLC control). *The colour of the reaction mixture changes from yellowish red to dark brown.* Upon completion, the reaction mixture was cooled to room temperature, poured into aqueous citric acid (25 mL, 5 mg/mL), extracted with ethyl acetate (3 x 5 mL), washed with water (2 × 15 mL) and dried with anhydrous Na_2SO_4. The extract was filtered and evaporated to dryness at 65 ºC under reduced pressure. The residue was subjected to column chromatography (eluent: petroleum ether/CH_2Cl_2, gradient from 10:1 to 6:1 to 4:1). *NOTE: 3-Methyl-1-phenyl-1H-pyrazole (**10**) could be distilled from concentrated crude reaction mixture on rotary evaporator. We observed nearly complete removal of pyrazole (**10**) at ca. 85 °C, 15 mbar in ca. 1 h.*



9

2,4-Diphenyl-1*H*-pyrrole (**9**).[8] Yield: 62 mg, 94%; off-white solid; mp = 178−179 °C (ethyl acetate). R_f = 0.50 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (br s, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.37 (m, 4H), 7.28 – 7.22 (m, 2H), 7.11 (br s, 1H), 6.86 (d, *J* = 2.6 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): 135.5, 132.5, 128.9 (4C), 128.7 (4C), 126.5, 125.8, 125.2, 123.9, 115.6, 104.1.



10

3-Methyl-1-phenyl-1*H*-pyrazole (**10**).[9] Yield: 45 mg, 94%; colorless oil. R_f = 0.65 (ethyl acetate/petroleum ether = 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 2.3 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.26 – 7.20 (m, 1H), 6.23 (d, *J* = 2.3 Hz, 1H), 2.39 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.6, 140.4, 129.4 (2C), 127.4, 126.0, 119.0 (2C), 107.6, 13.8.

13. REFERENCES

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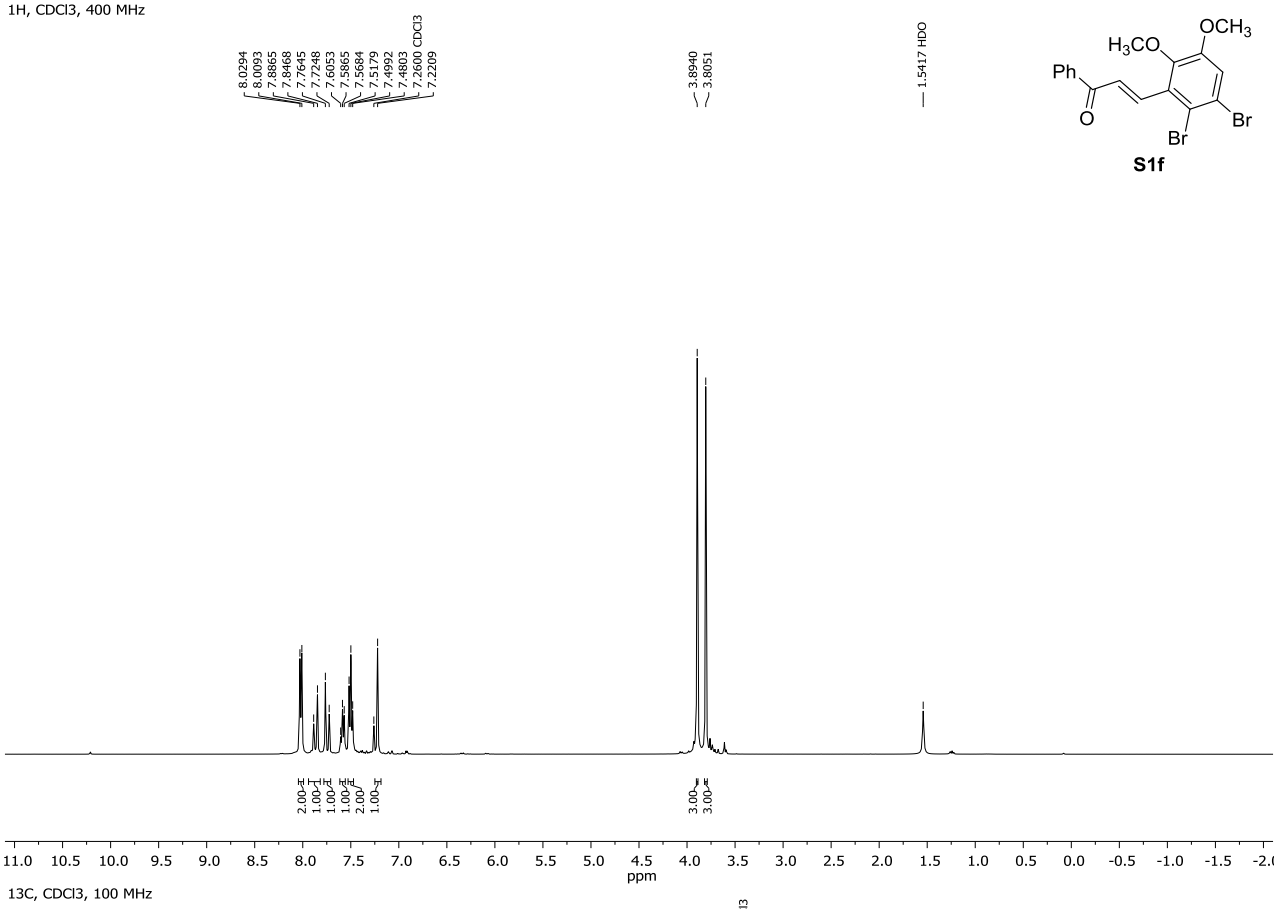
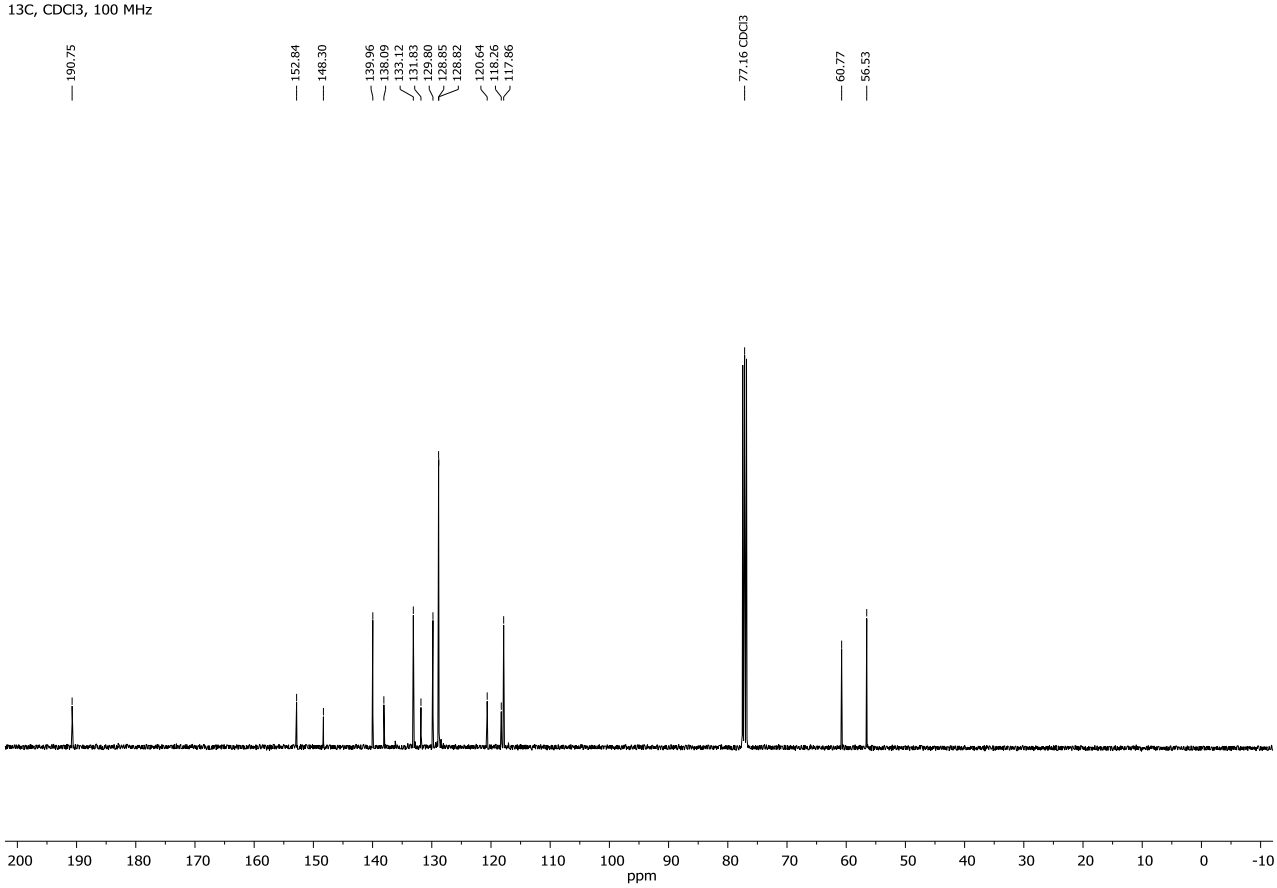
14. COPIES OF NMR SPECTRA

1H, CDCl3, 400 MHz



S1f

13C, CDCl3, 100 MHz



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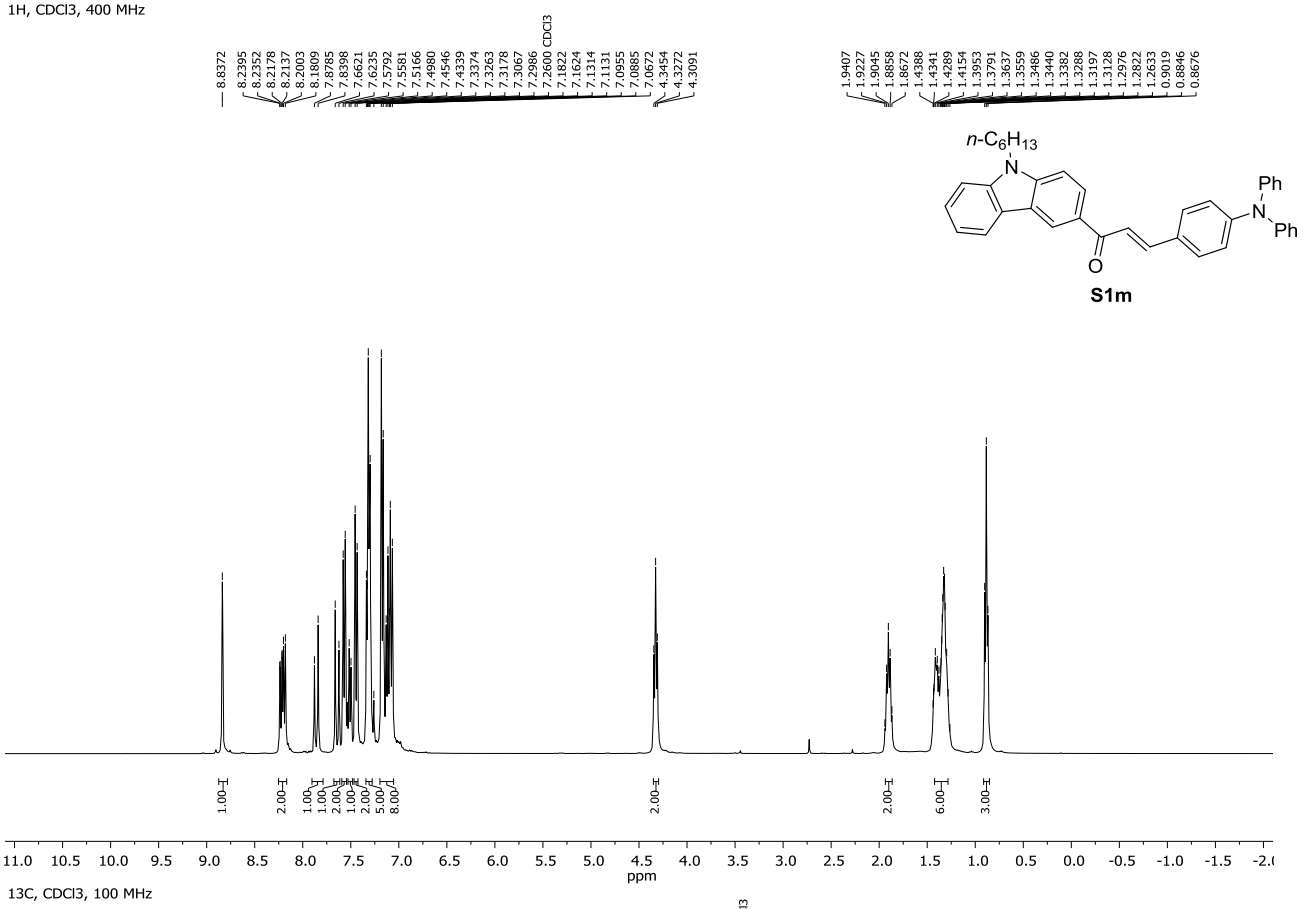

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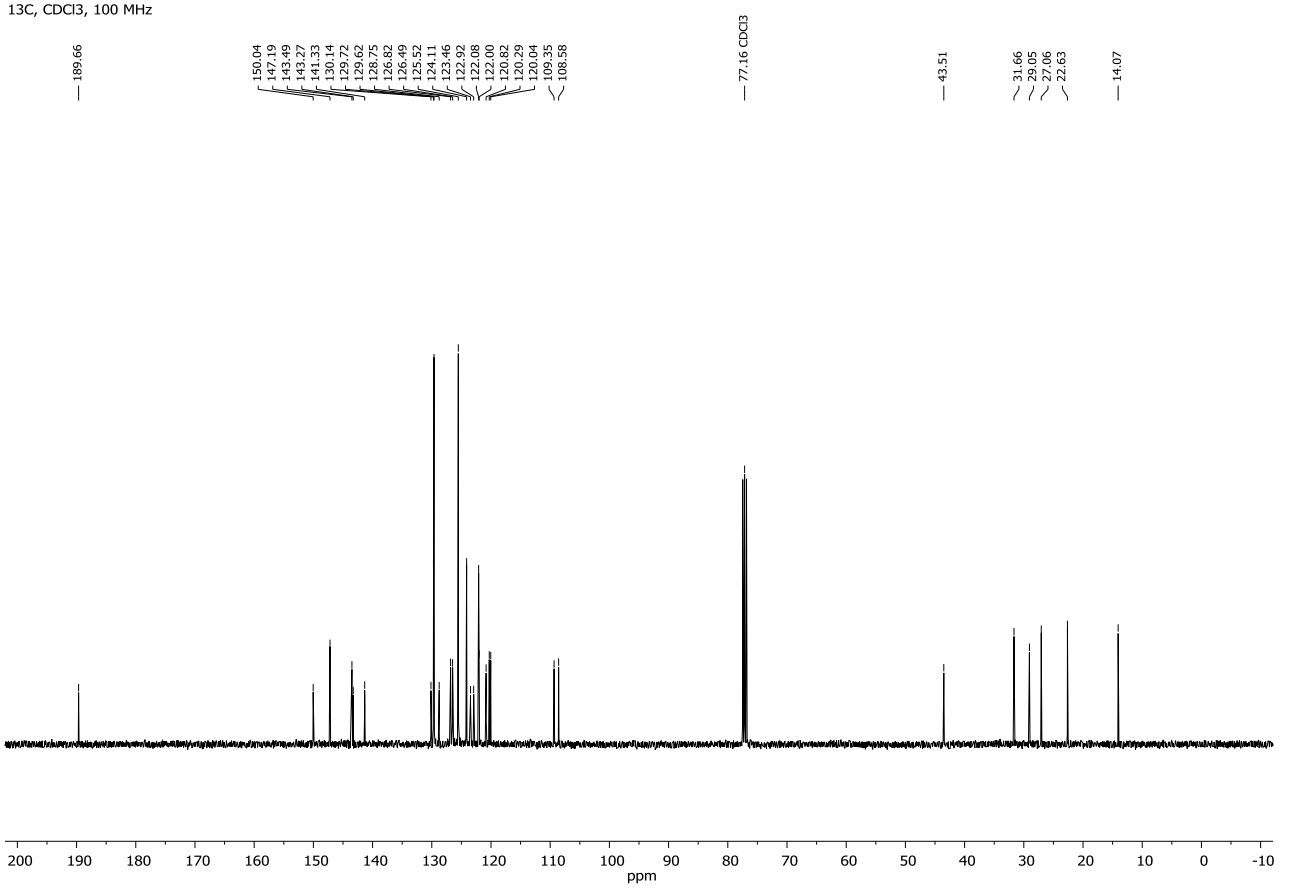

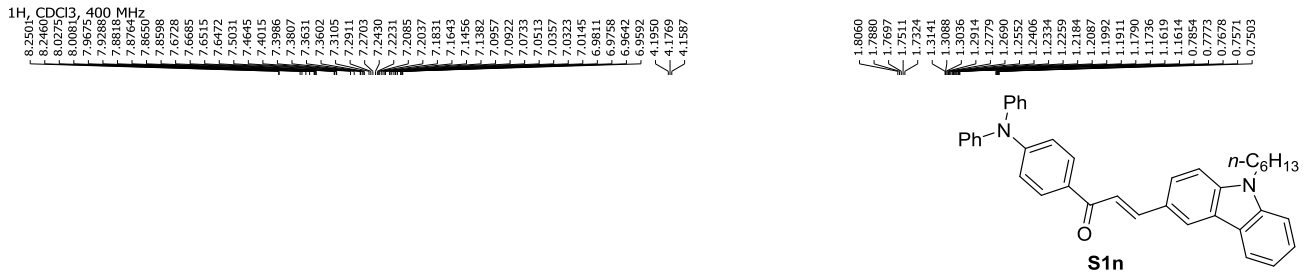
1H, CDCl3, 400 MHz
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7.8764
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7.8598
7.6728
7.6685
7.6515
7.6472
7.5031
7.4645
7.4015
7.3986
7.3807
7.3631
7.3602
7.3105
7.2911
7.2703
7.2430
7.2231
7.2085
7.2037
7.1831
7.1643
7.1456
7.1382
7.0957
7.0922
7.0733
7.0513
7.0357
7.0323
7.0145
6.9811
6.9758
6.9642
6.9592
4.1950
4.1769
4.1587
1.8060
1.7880
1.7697
1.7511
1.7324
1.3141
1.3088
1.3036
1.2914
1.2779
1.2690
1.2552
1.2406
1.2334
1.2259
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1.1619
1.1614
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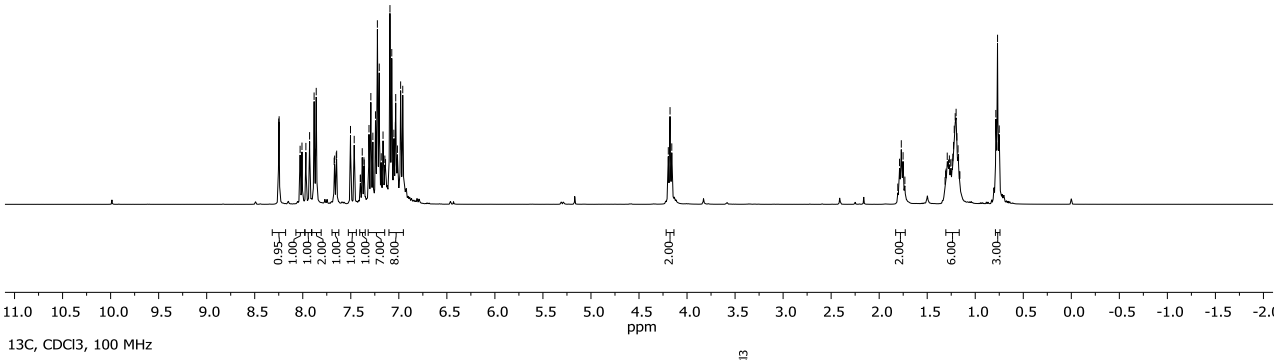
Ph
N
Ph
n-C6H13
N
O

S1n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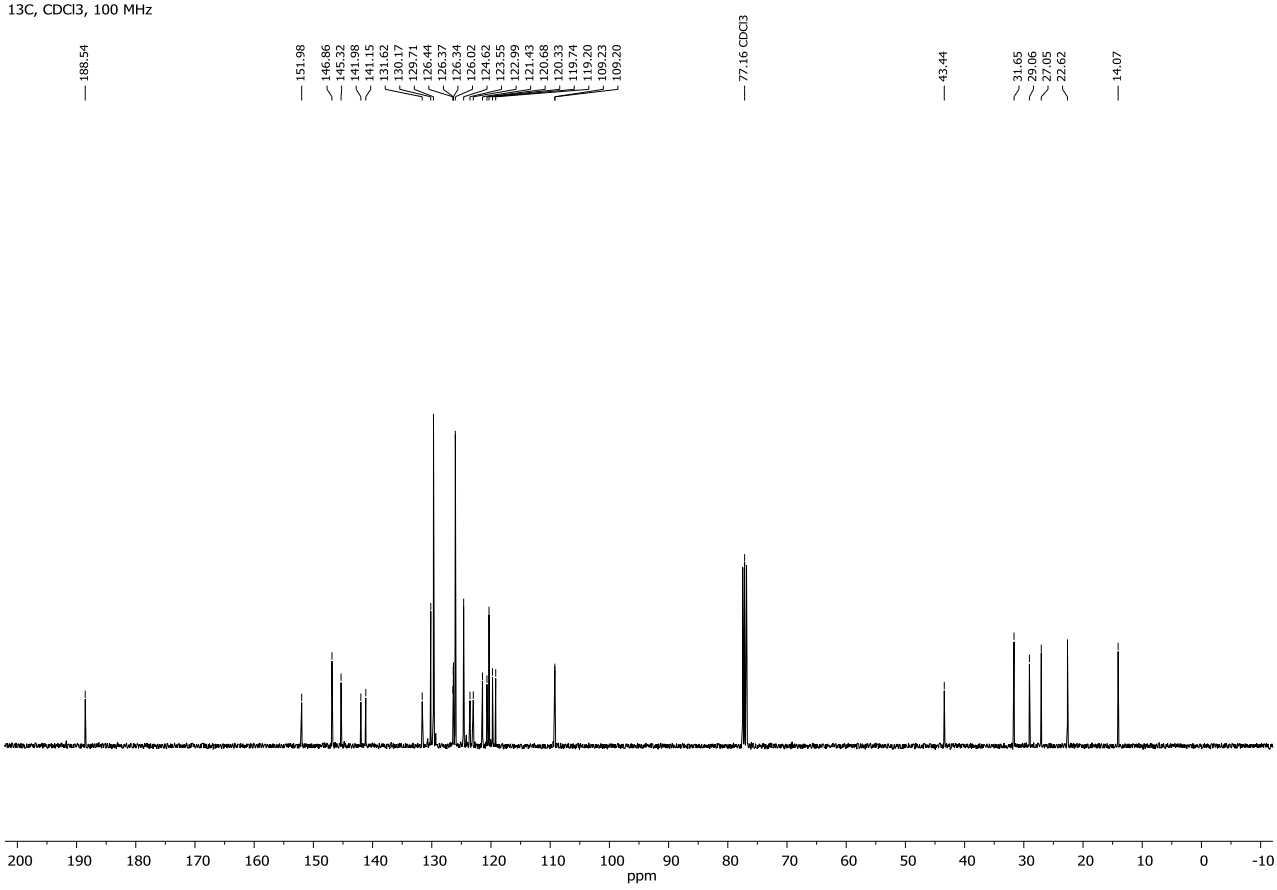
1.00
7.00
8.00
2.00
2.00
6.00
3.00
ppm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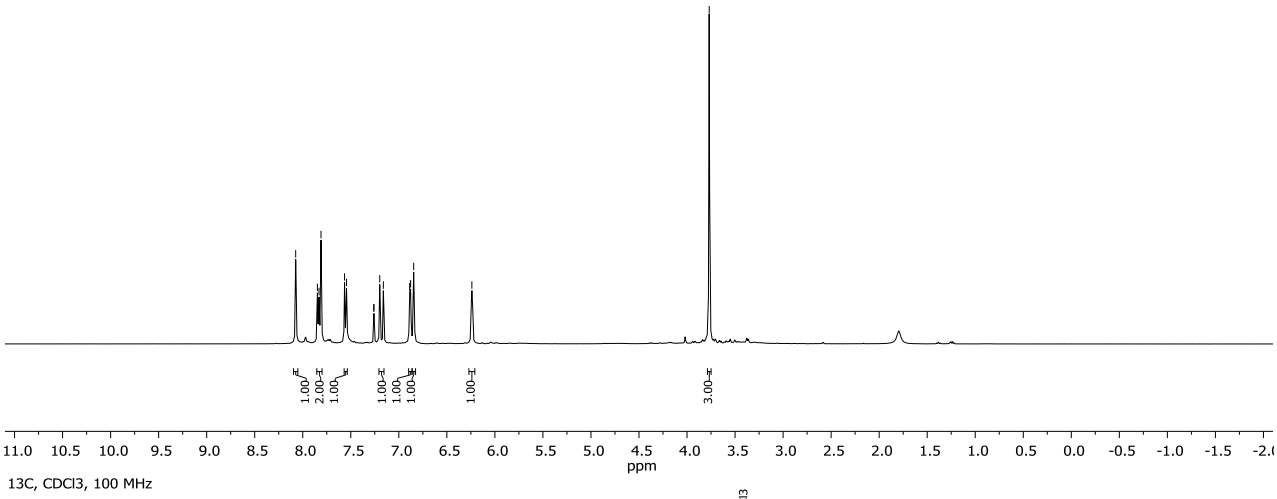
145.32
141.98
141.15
131.62
130.17
129.71
126.44
126.37
126.34
126.02
124.62
123.55
122.99
121.43
120.68
120.33
119.74
119.20
109.23
109.20
77.16 CDCl3
43.44
31.65
29.06
27.05
22.62
14.07
ppm

1H, CDCl3, 400 MHz

S1q



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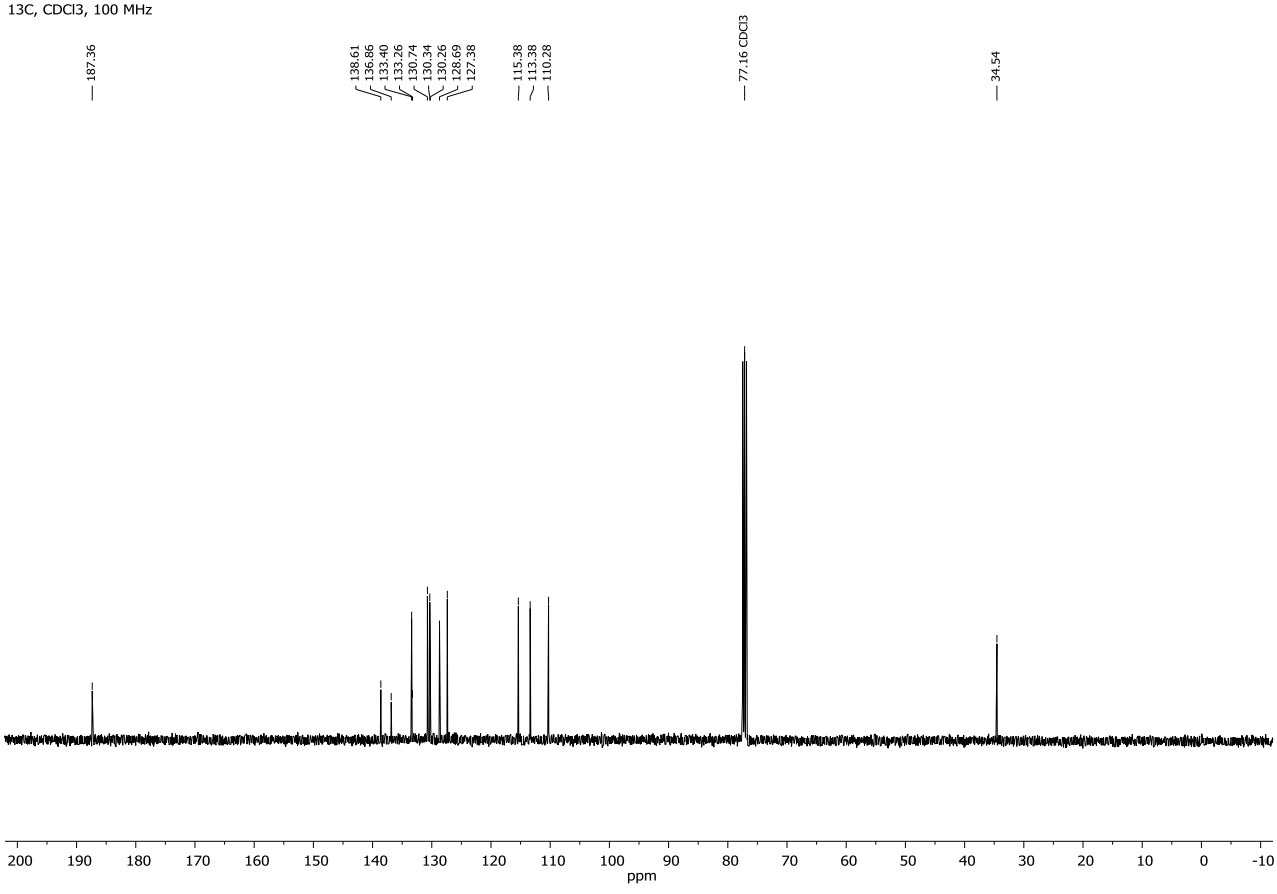

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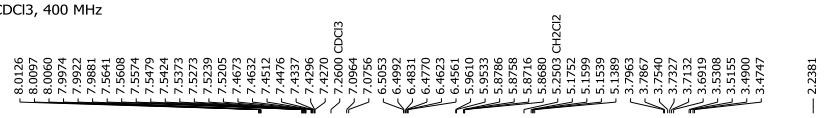

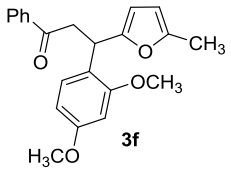

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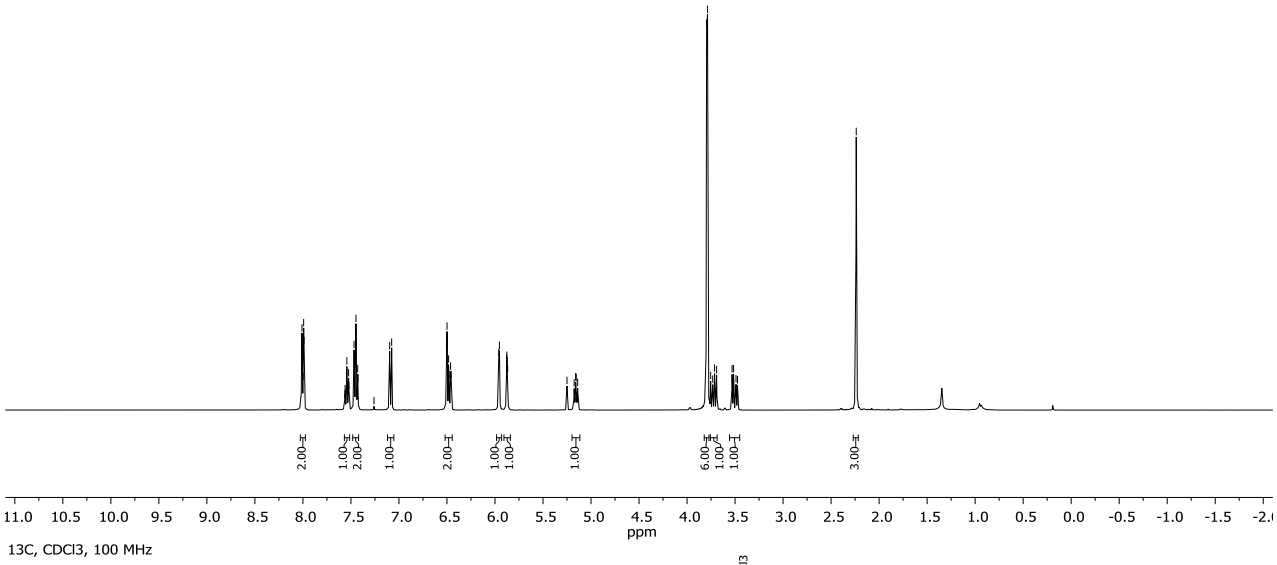

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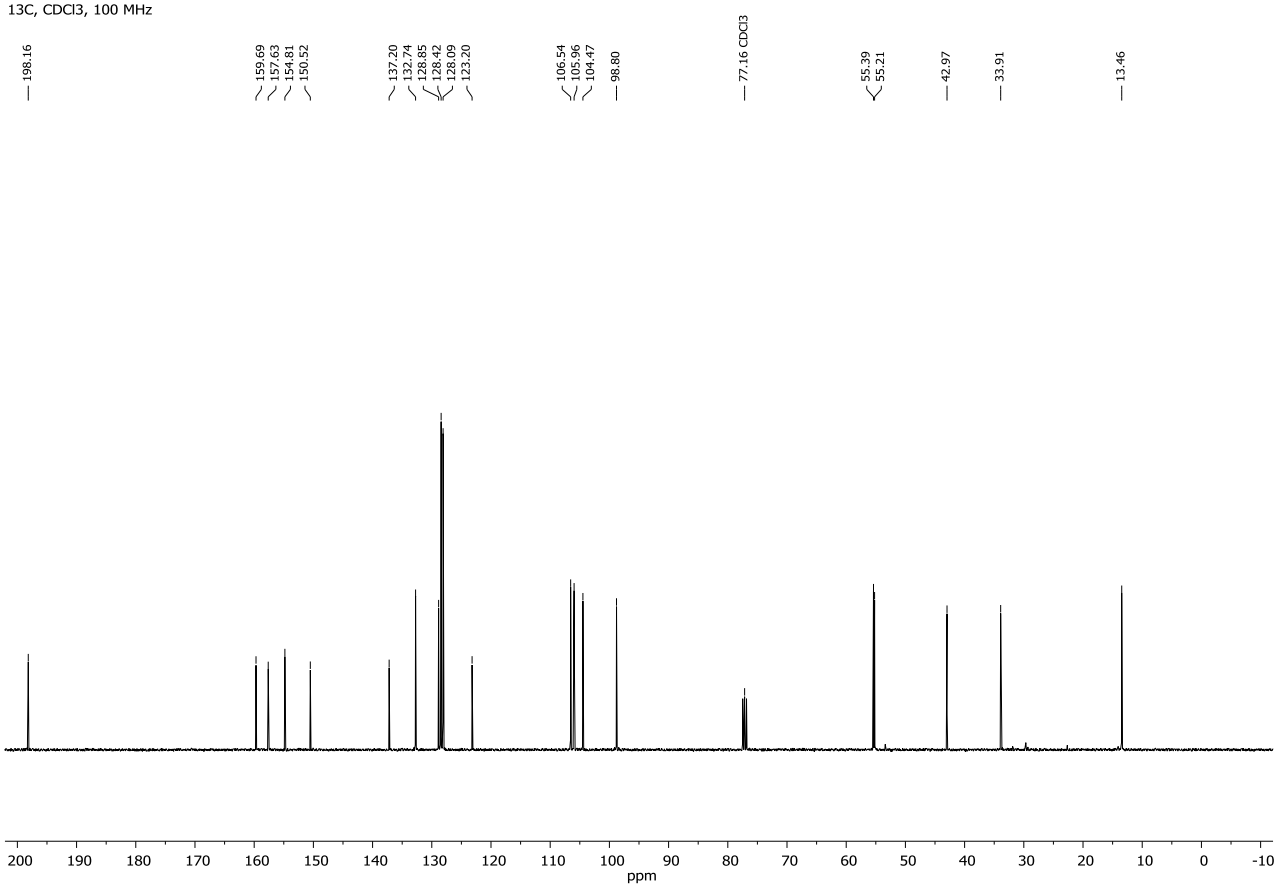

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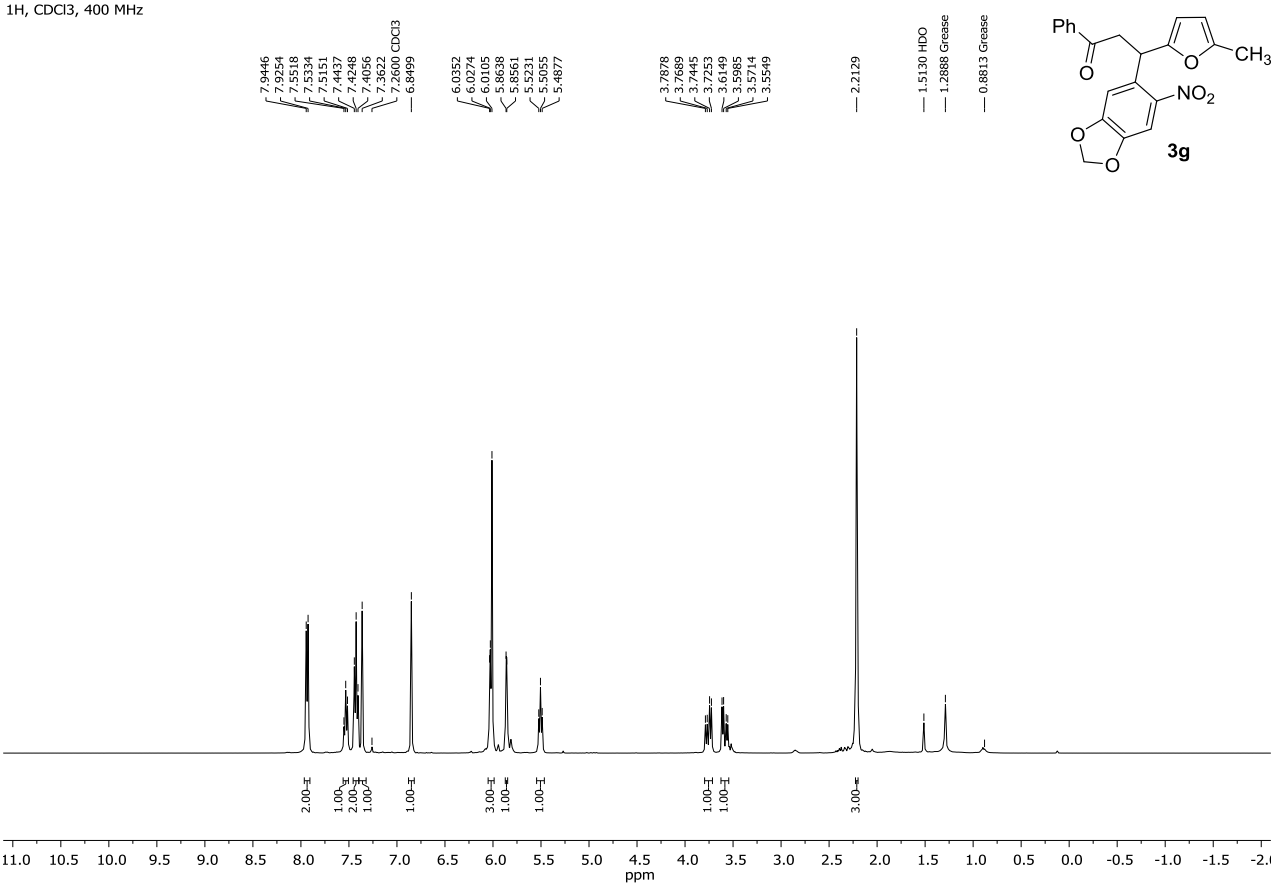

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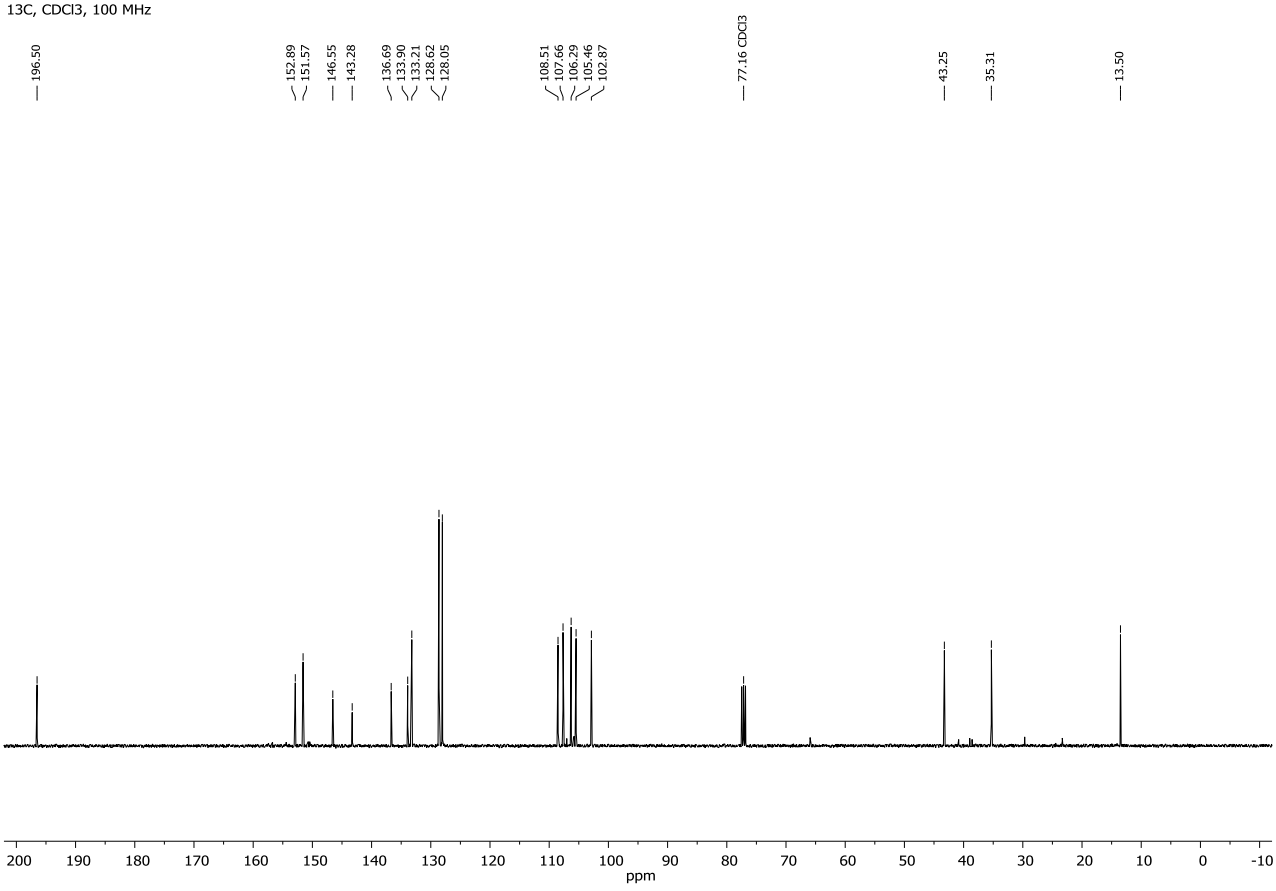

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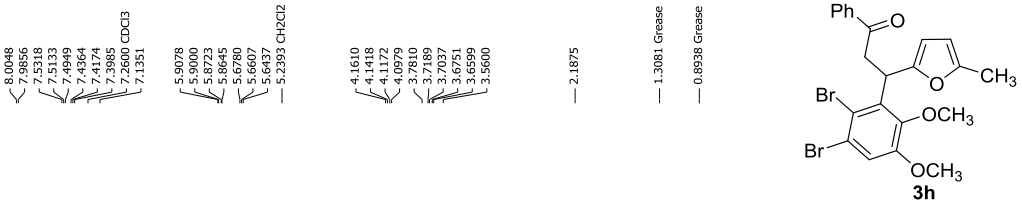

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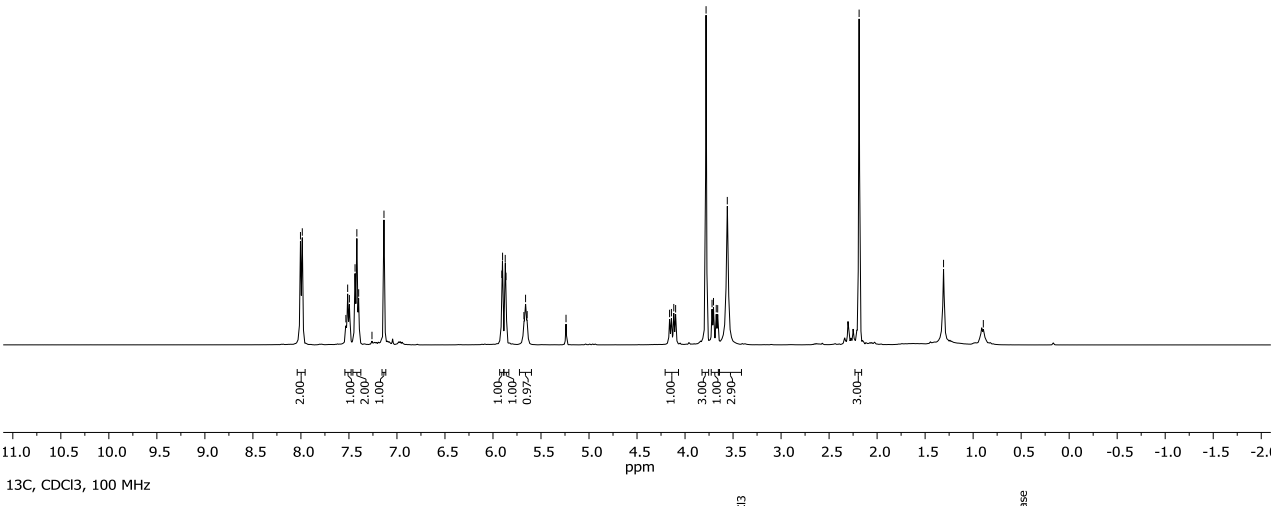

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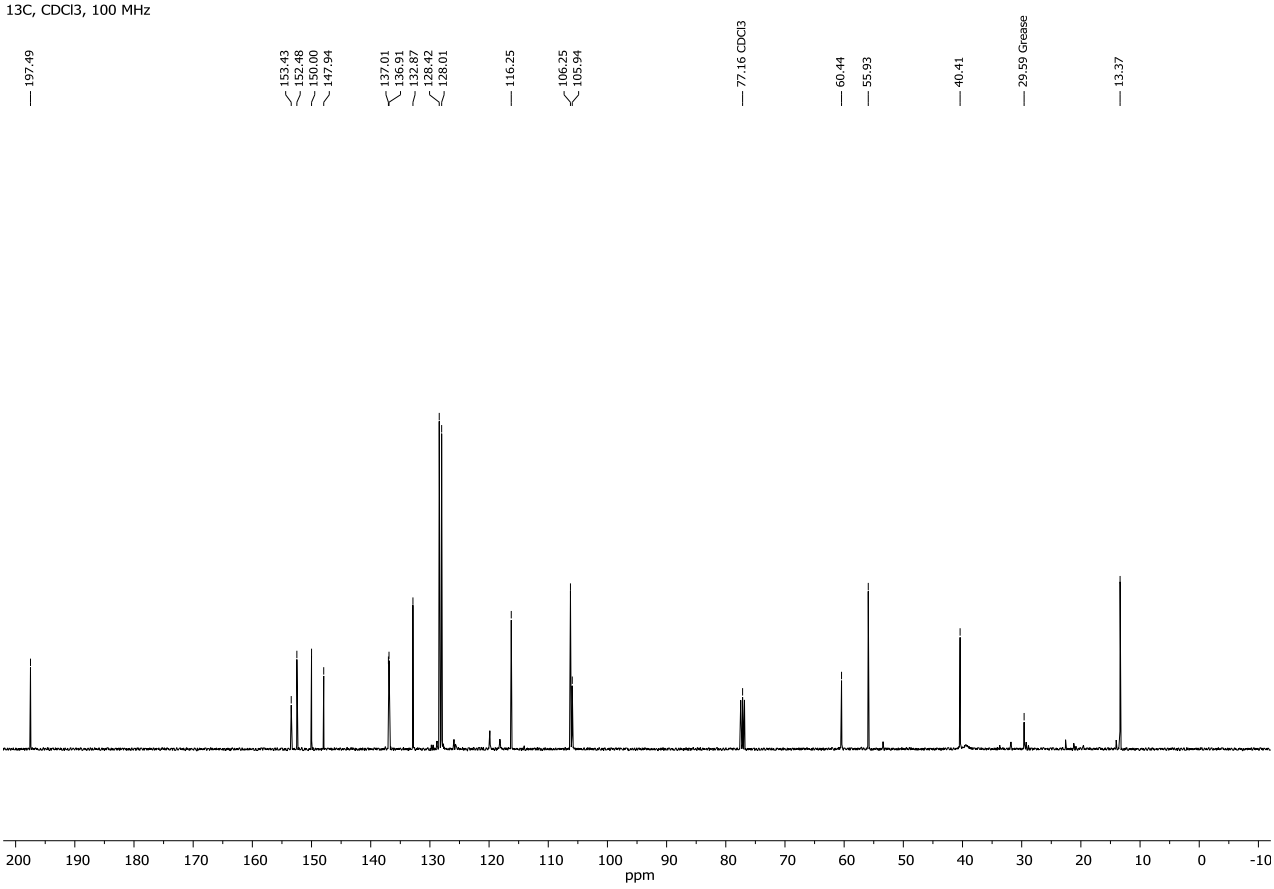

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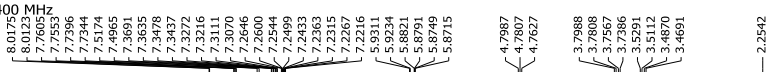

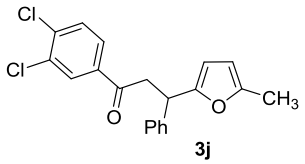

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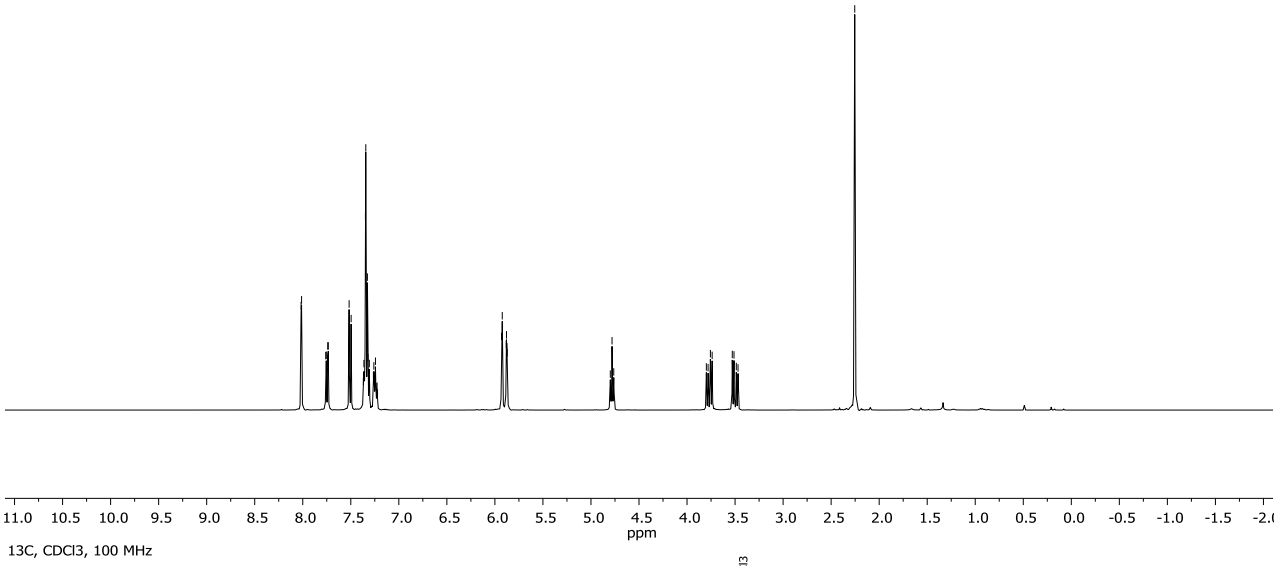

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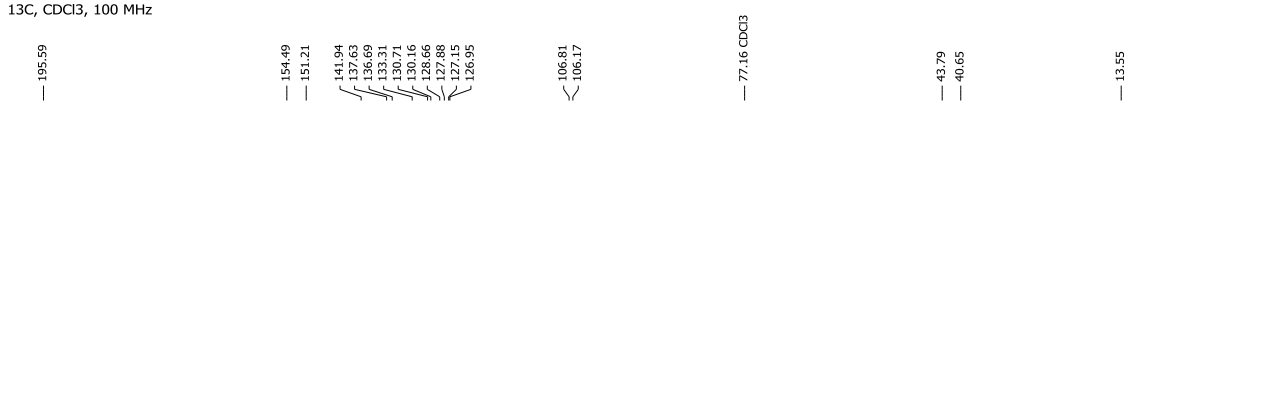

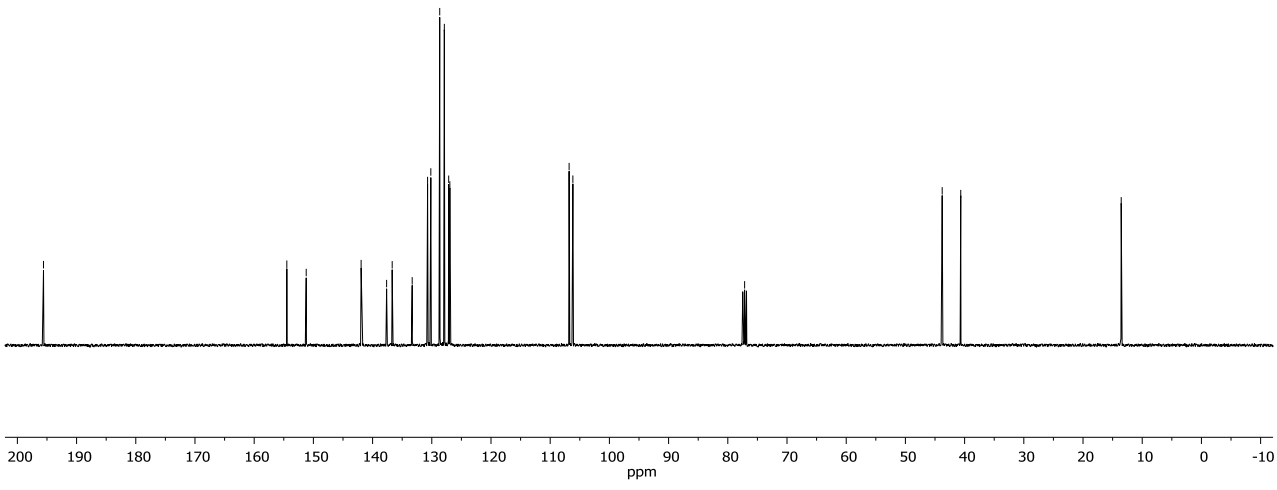

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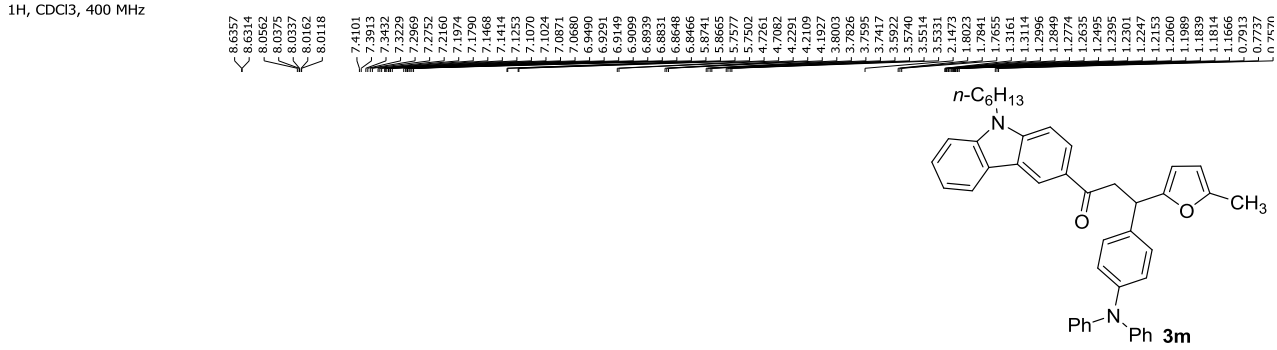

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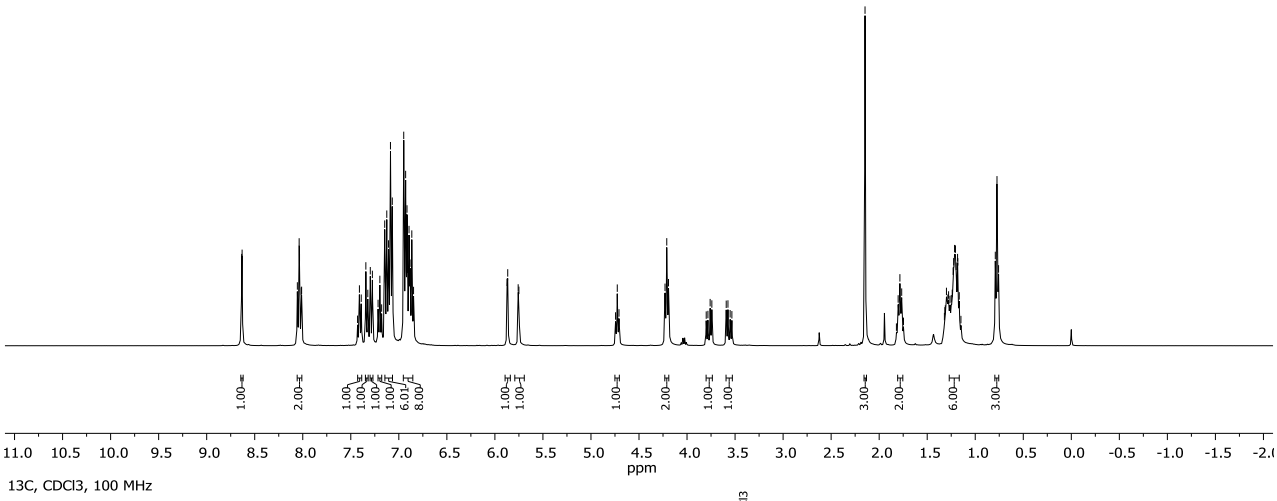

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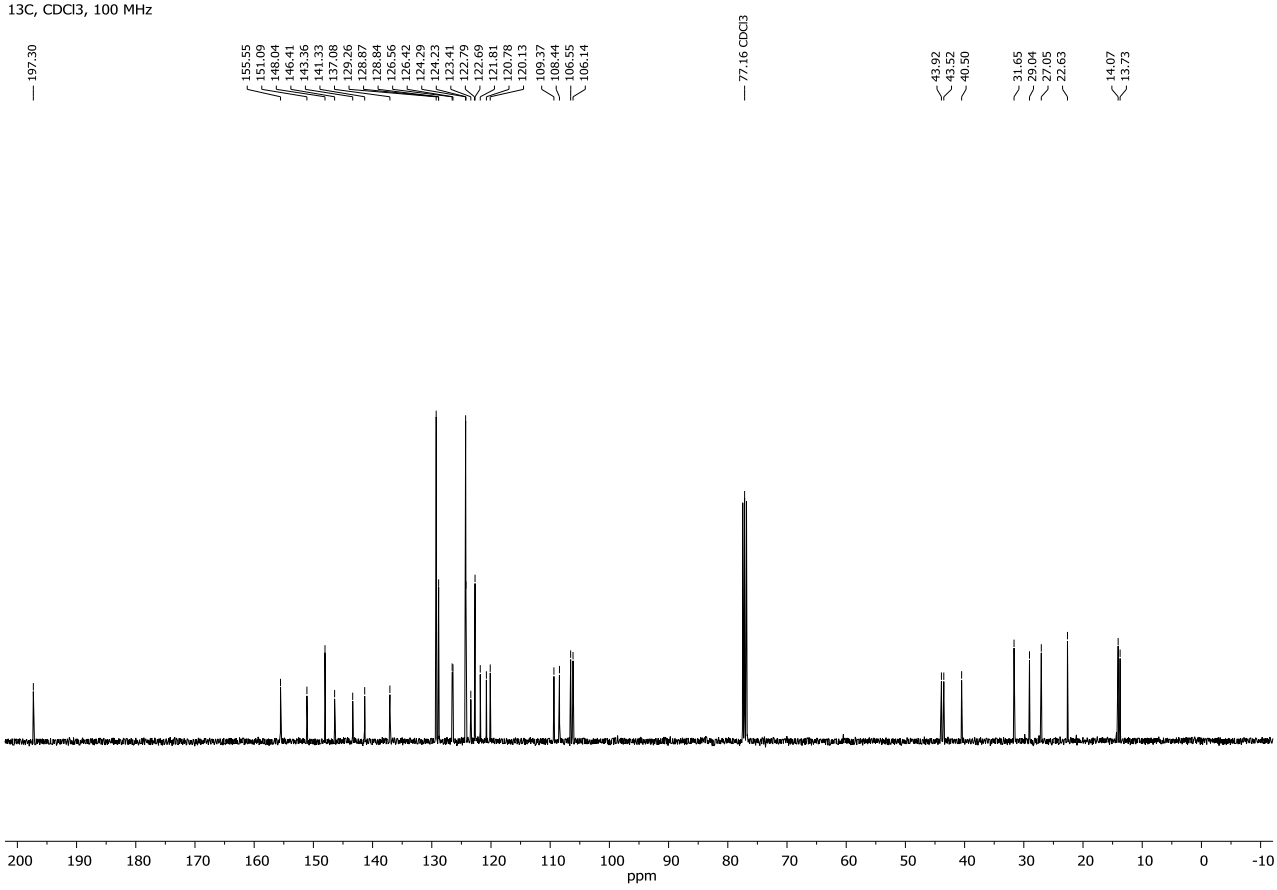

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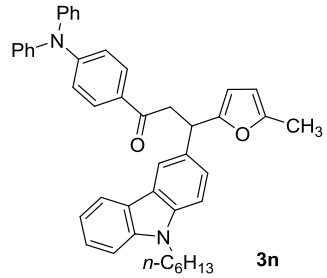

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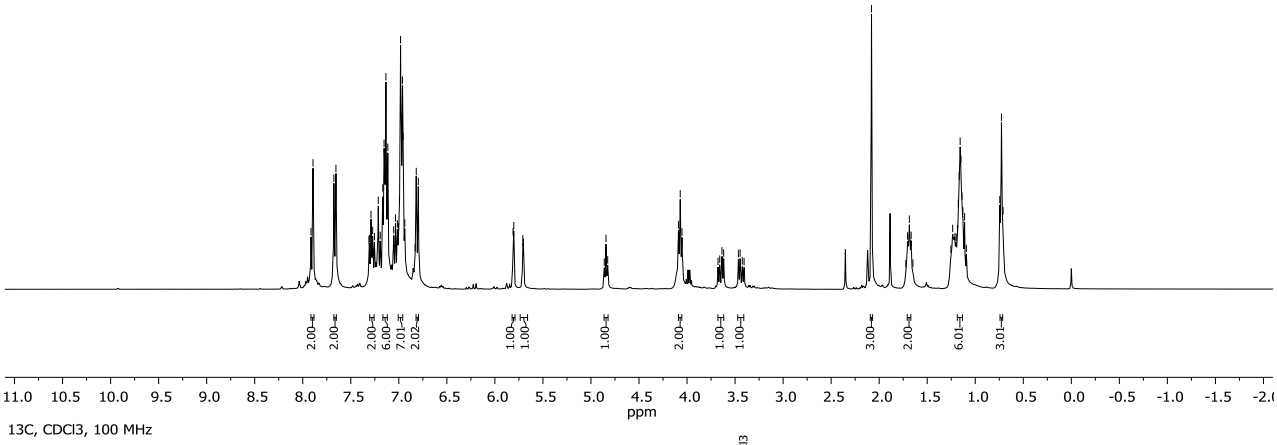

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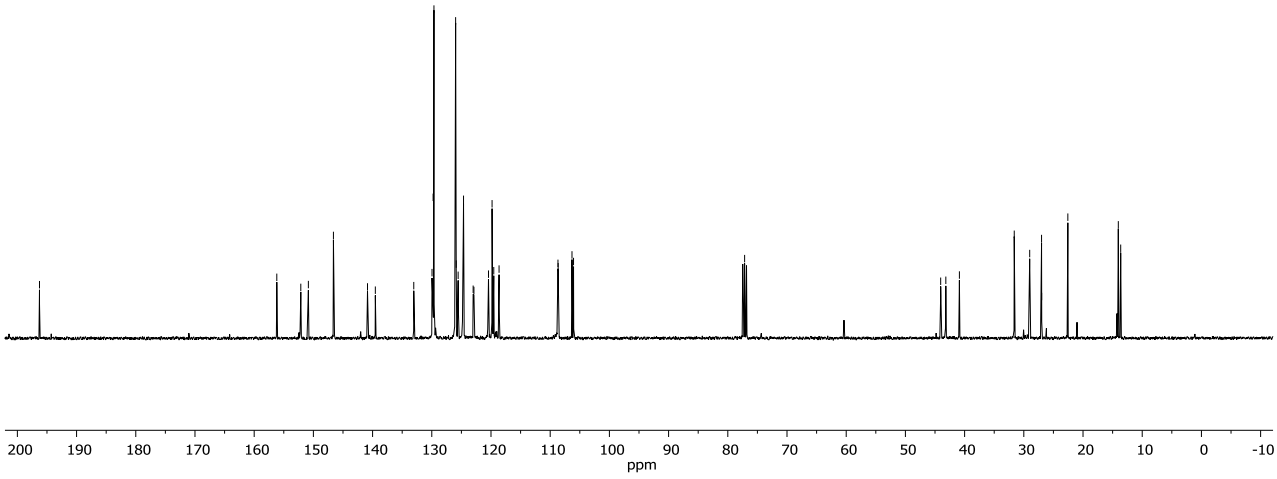

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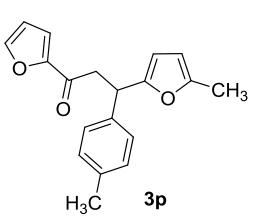

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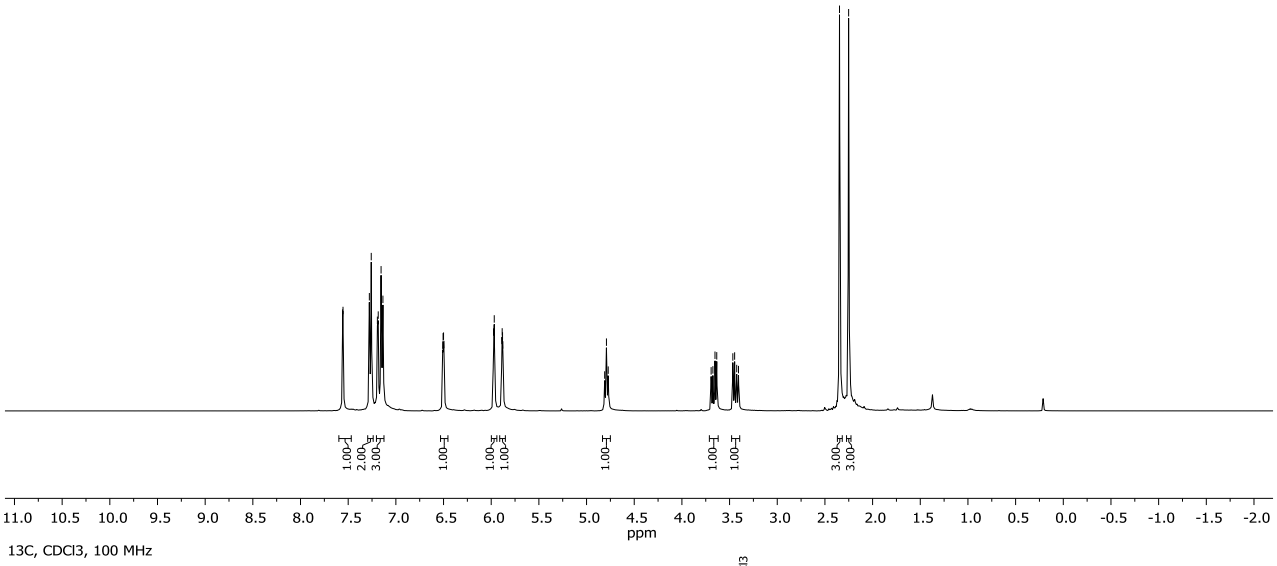

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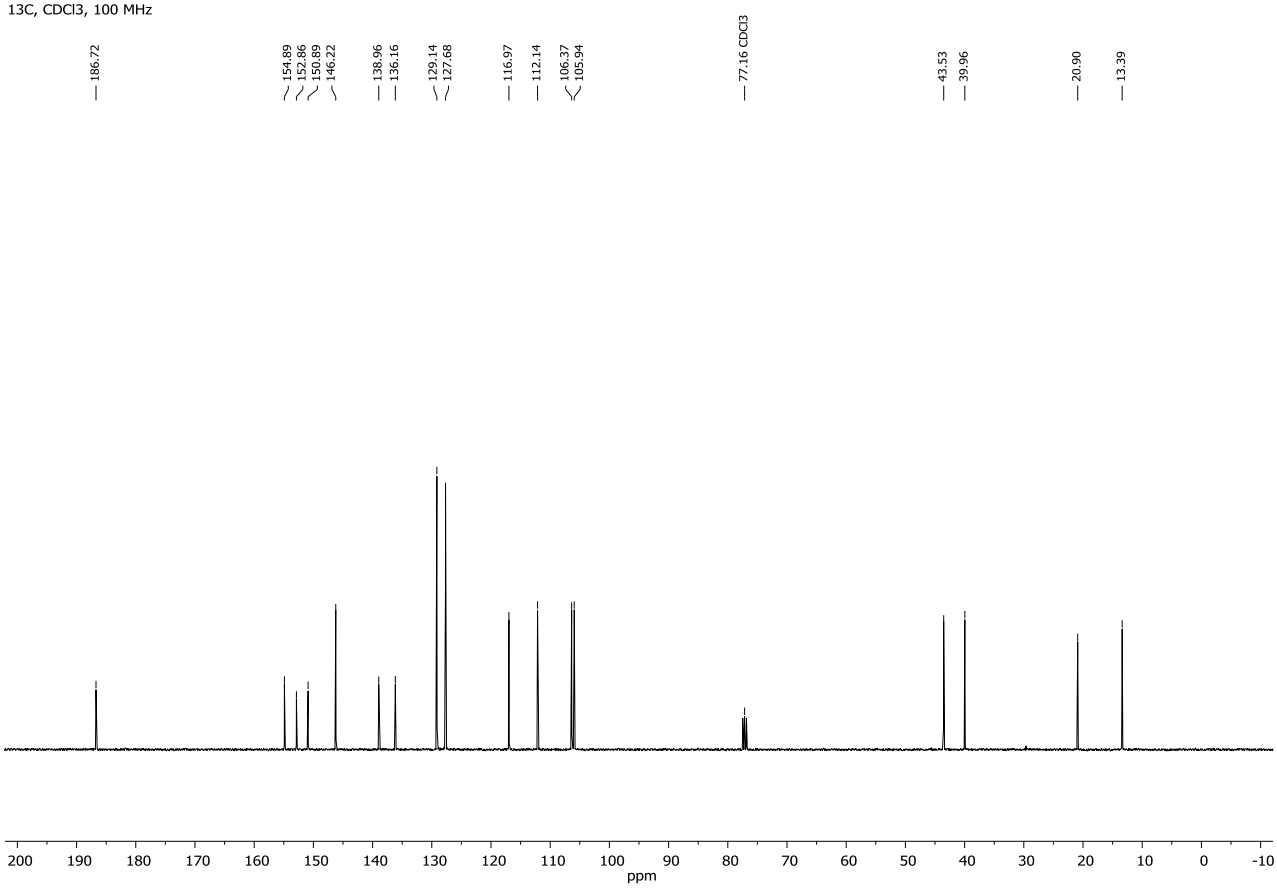

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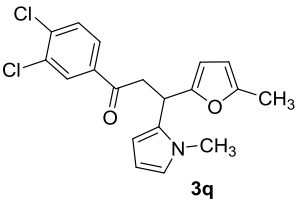

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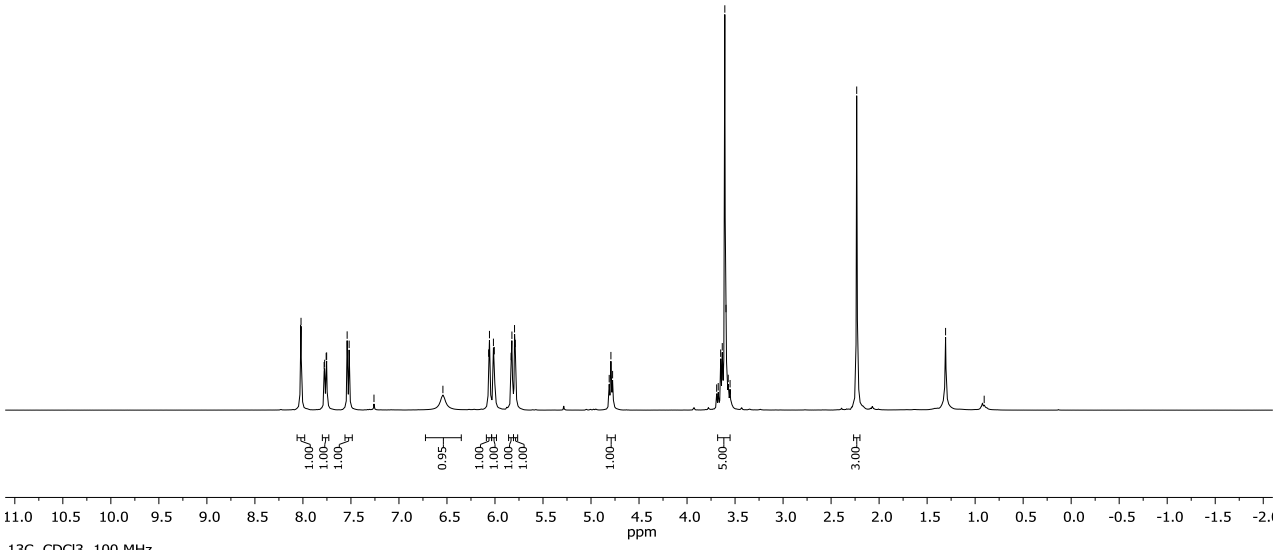

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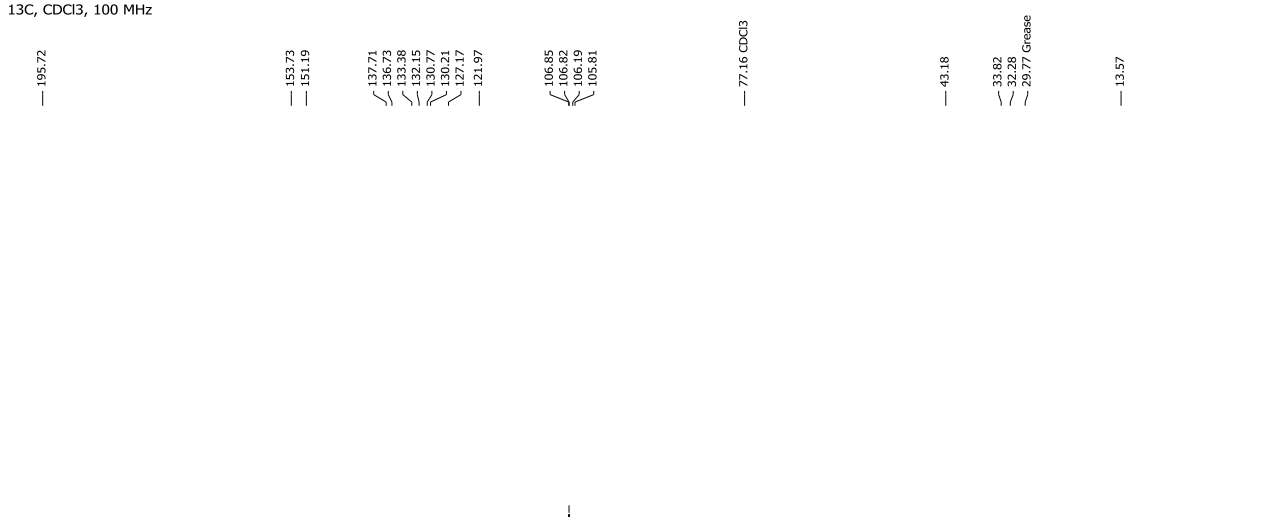

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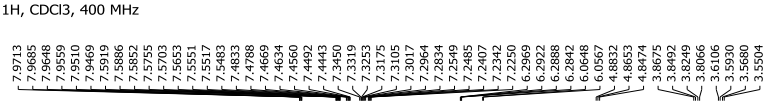

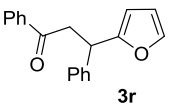

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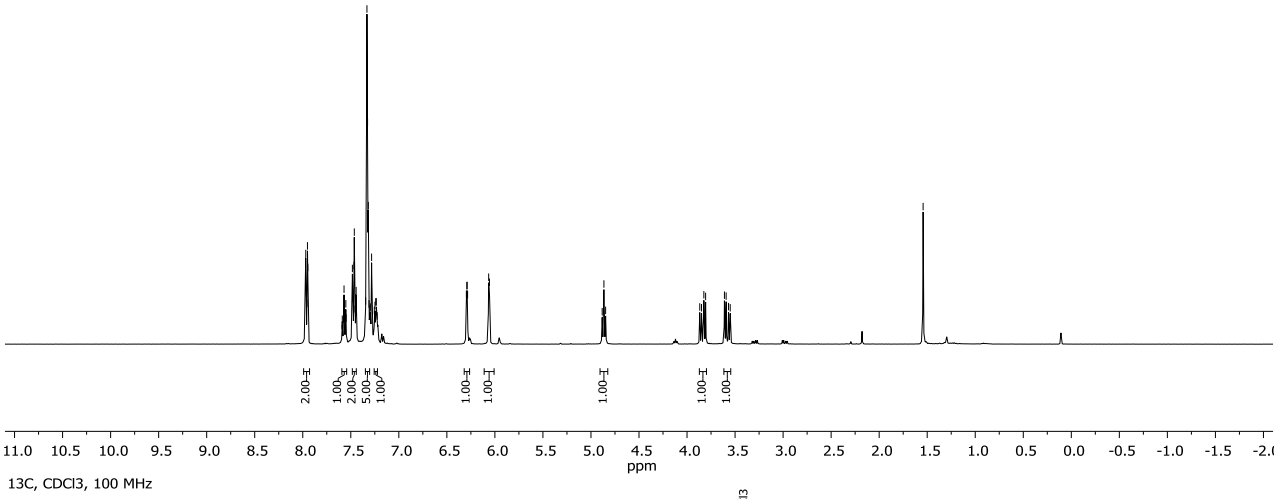
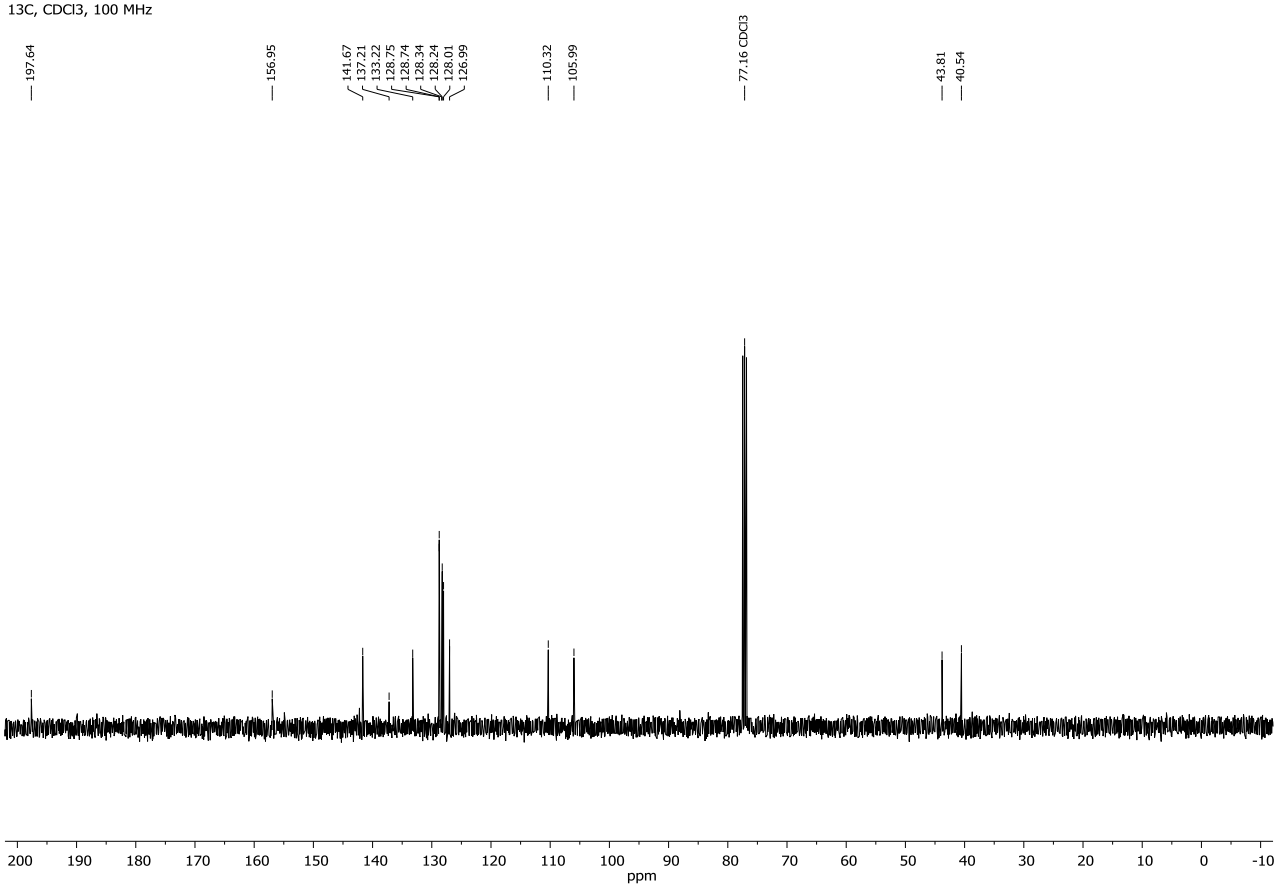
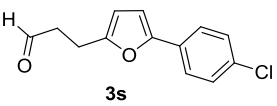


13C, CDCl3, 100 MHz



1H, DMSO-d6, 400 MHz



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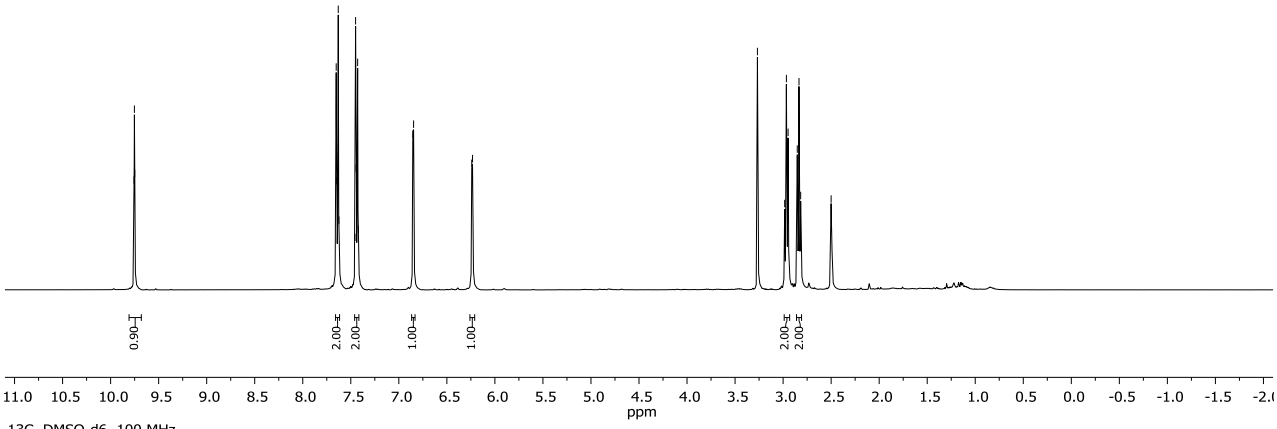
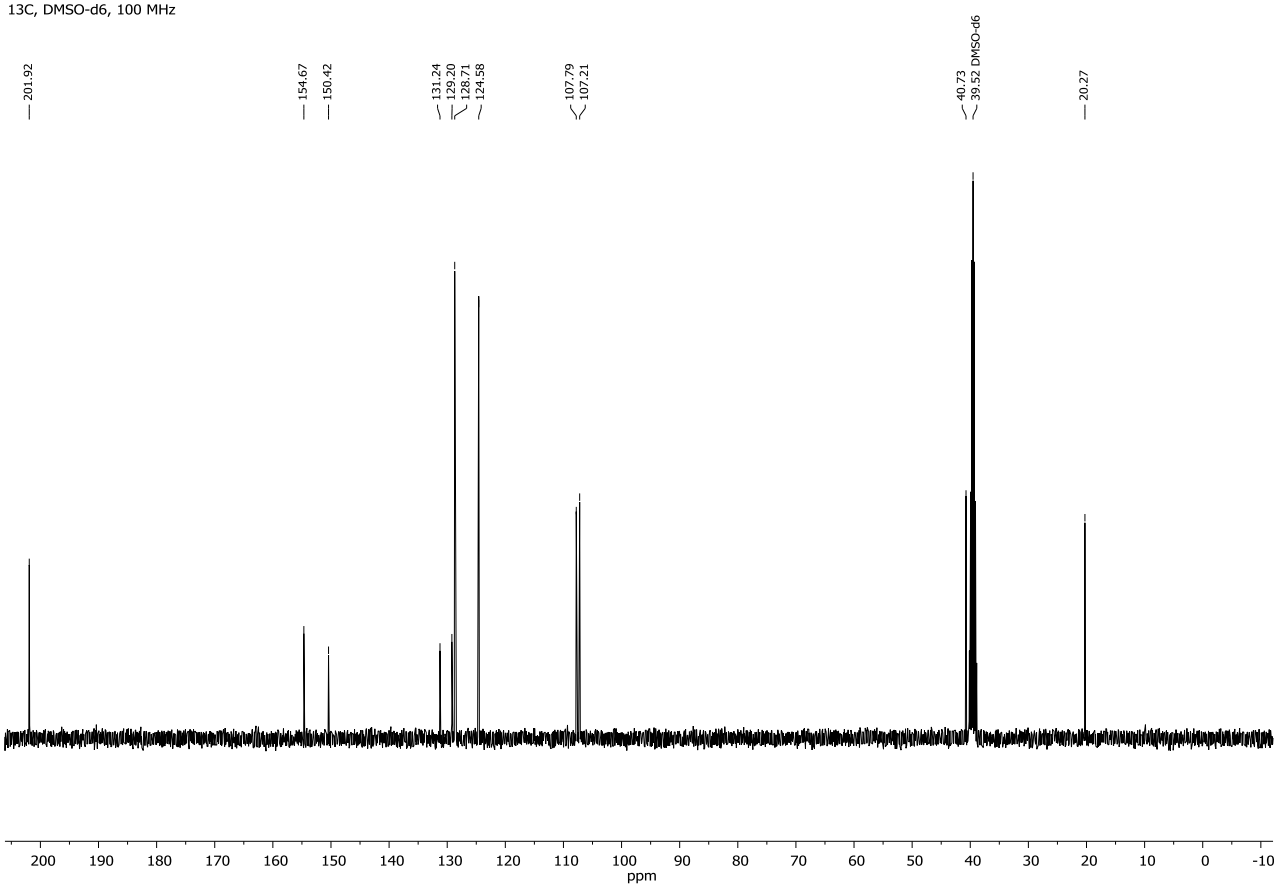
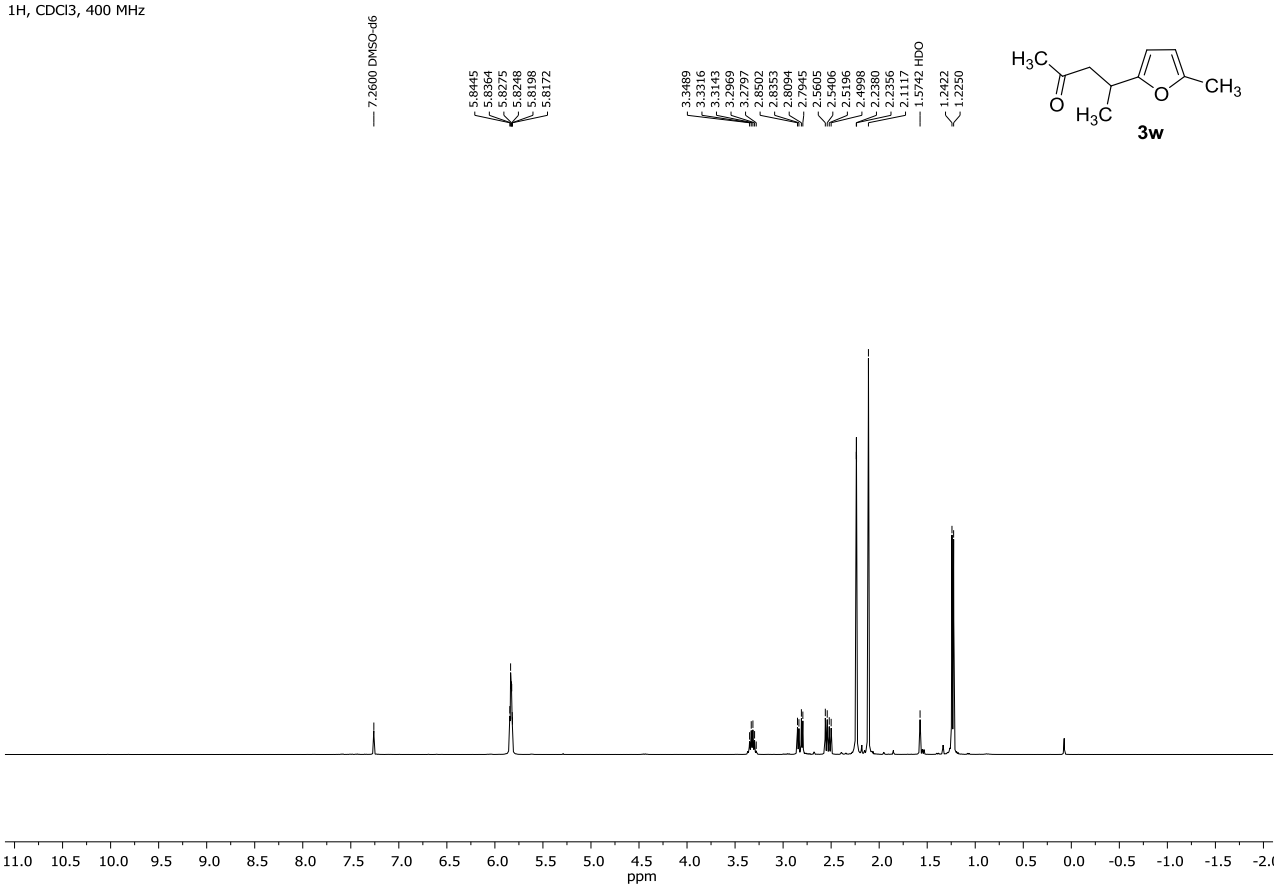


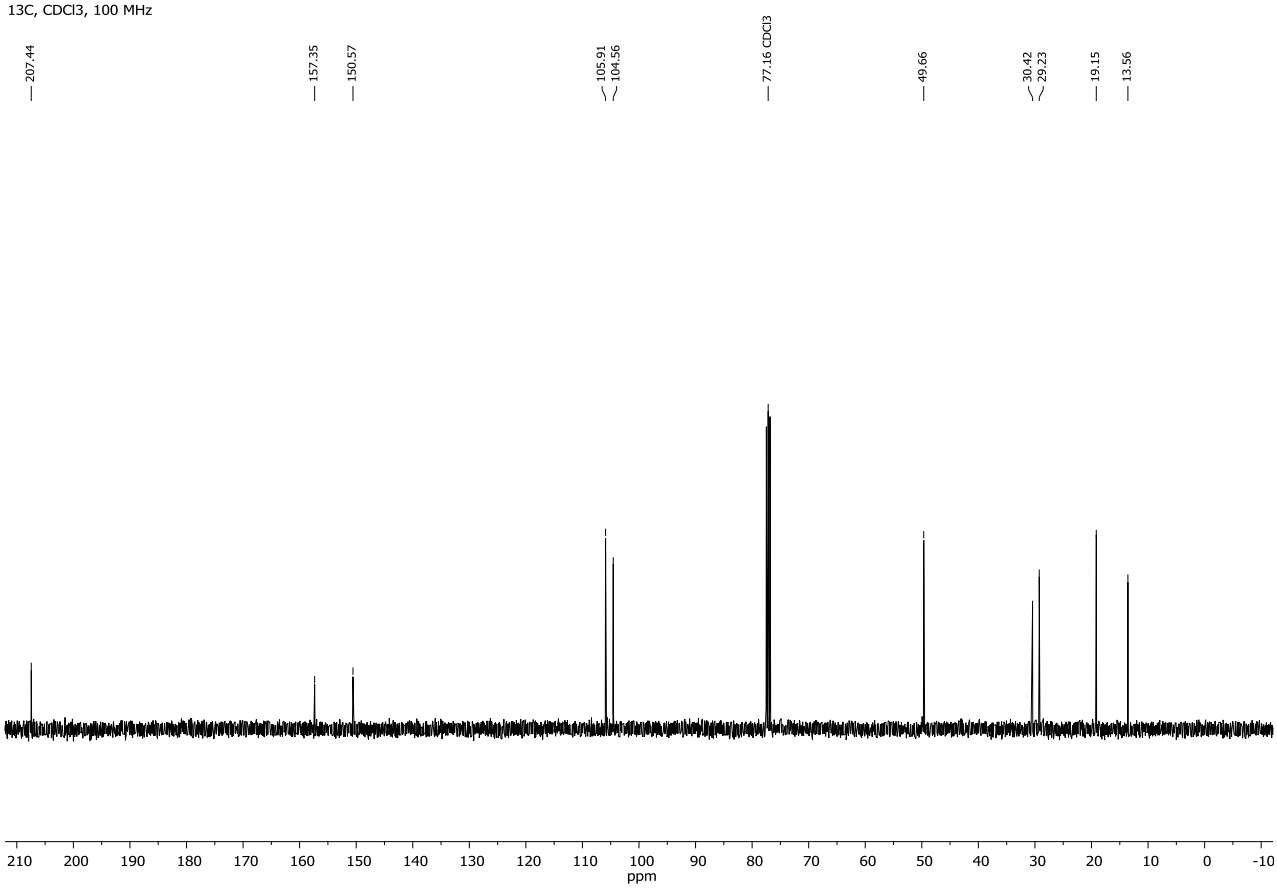
13C, DMSO-d6, 100 MHz

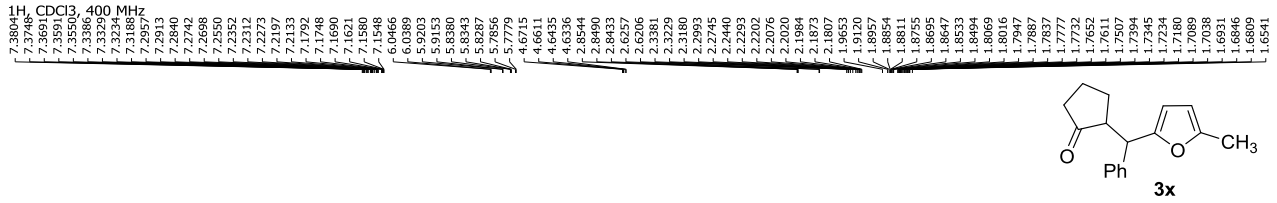


1H, CDCl3, 400 MHz



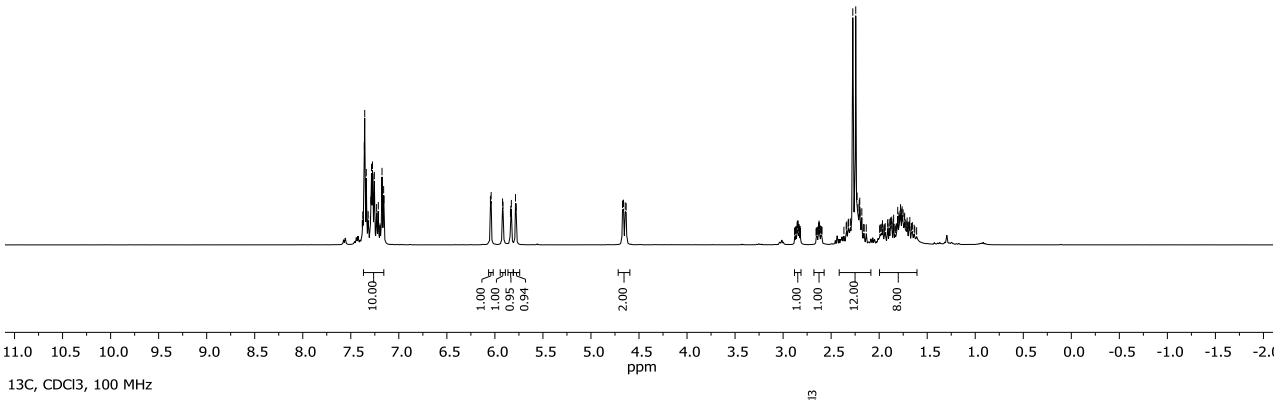
13C, CDCl3, 100 MHz

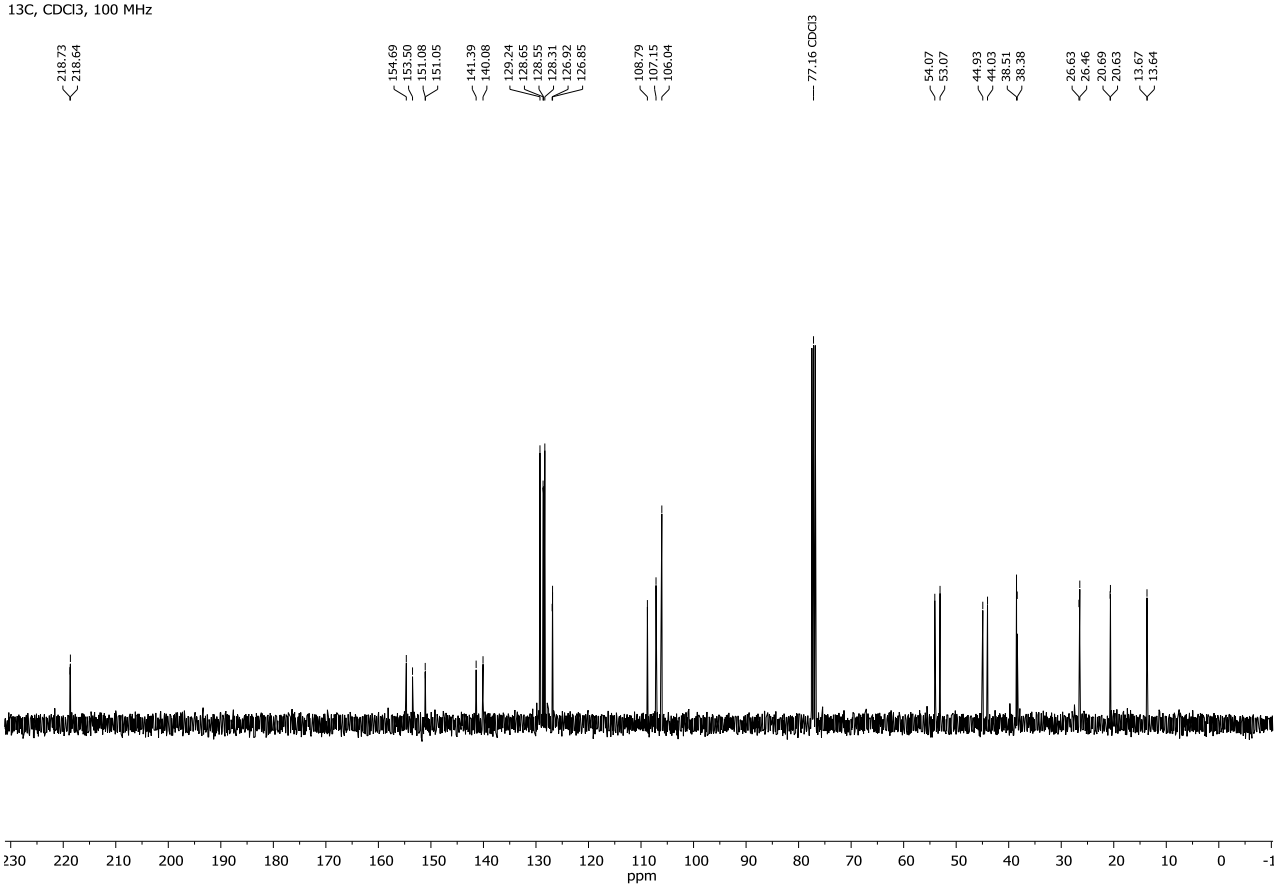



1H, CDCl3, 400 MHz
7.3804
7.3748
7.3691
7.3591
7.3550
7.3386
7.3329
7.3234
7.3188
7.2957
7.2913
7.2840
7.2742
7.2698
7.2550
7.2352
7.2312
7.2273
7.2197
7.2133
7.1792
7.1748
7.1690
7.1621
7.1580
7.1548
6.0466
6.0389
5.9203
5.9153
5.8380
5.8343
5.8287
5.7856
5.7779
4.6715
4.6611
4.6435
4.6336
2.8544
2.8490
2.8433
2.6257
2.6206
2.3381
2.3229
2.3180
2.2993
2.2745
2.2440
2.2293
2.2202
2.2076
2.2020
2.1984
2.1873
2.1807
1.9653
1.9120
1.8957
1.8854
1.8811
1.8755
1.8695
1.8647
1.8533
1.8494
1.8069
1.8016
1.7947
1.7887
1.7837
1.7777
1.7732
1.7652
1.7611
1.7507
1.7394
1.7345
1.7234
1.7180
1.7089
1.7038
1.6931
1.6846
1.6809
1.6541

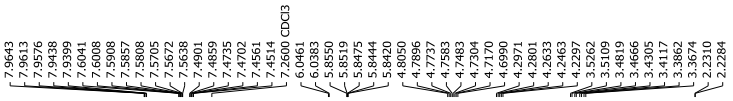
O
Ph
O
CH3

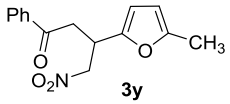
3x


10.00
1.00
1.00
0.95
0.94
2.00
1.00
1.00
12.00
8.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
ppm

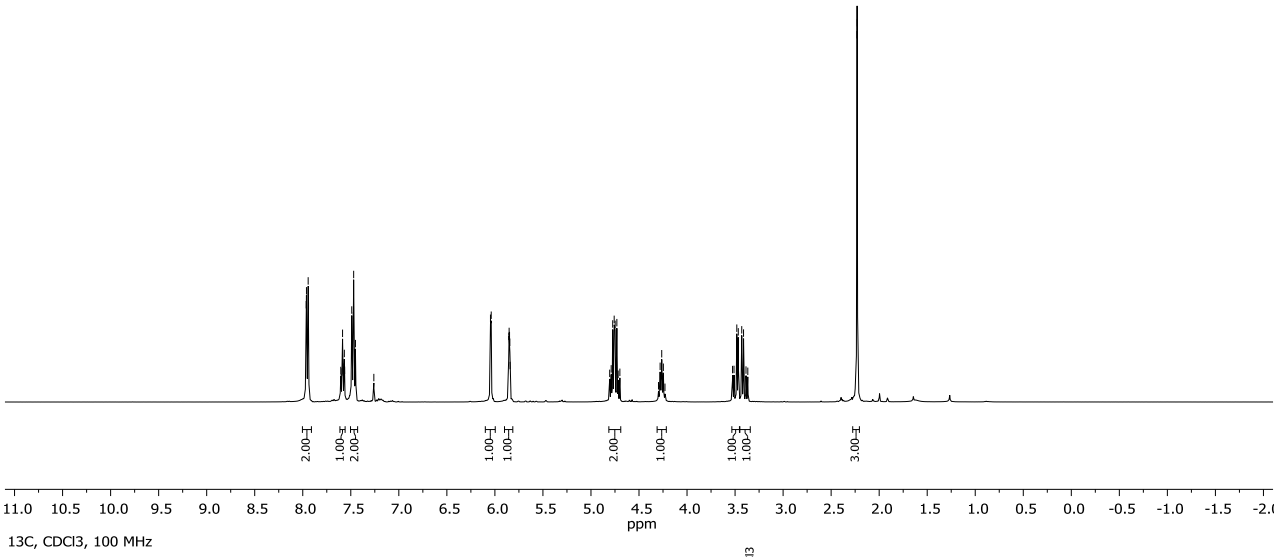

13C, CDCl3, 100 MHz
218.73
218.64
154.69
153.50
151.08
151.05
141.39
140.08
129.24
128.65
128.55
128.31
126.92
126.85
108.79
107.15
106.04
77.16 CDCl3
54.07
53.07
44.93
44.03
38.51
38.38
26.63
26.46
20.69
20.63
13.67
13.64
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm

1H, CDCl3, 400 MHz

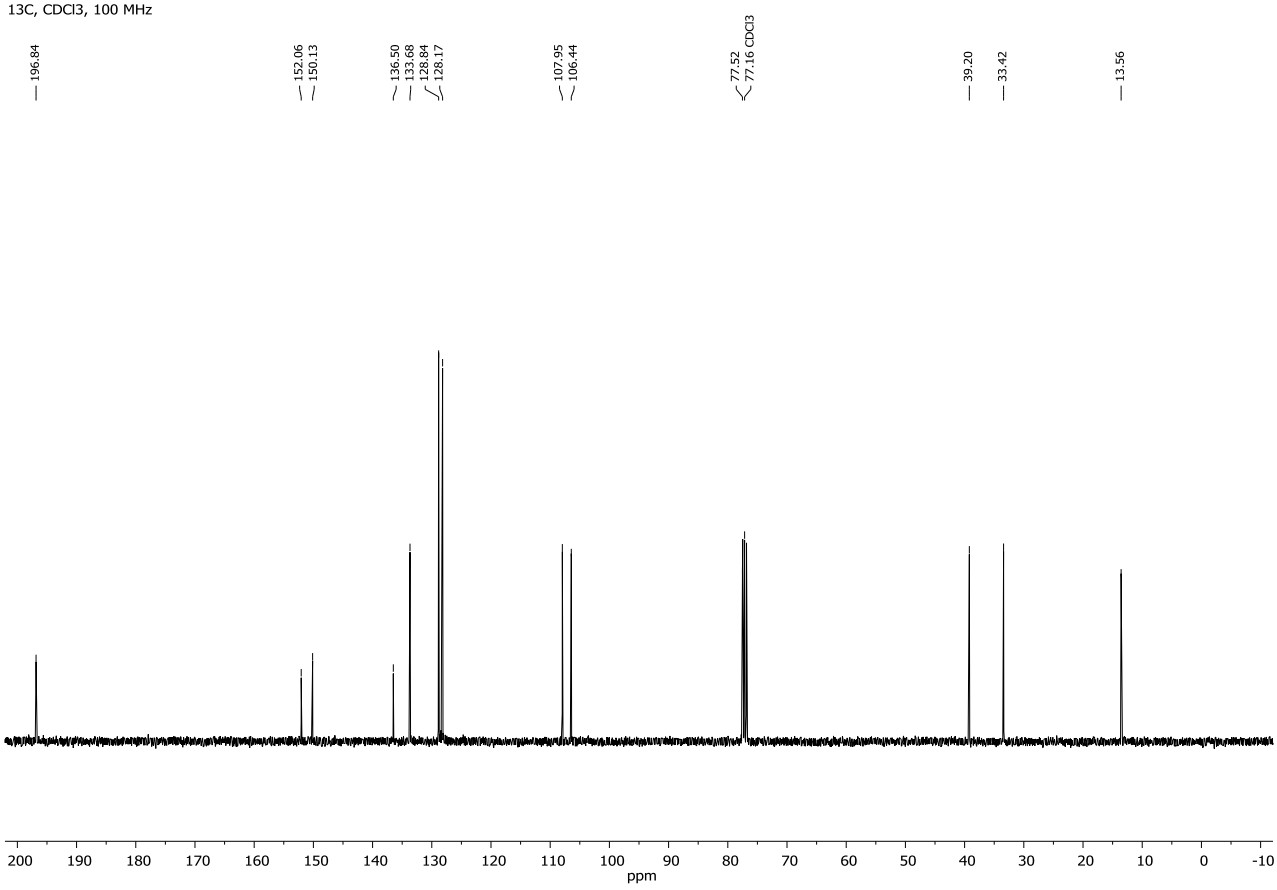




3y

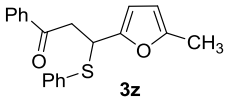


13C, CDCl3, 100 MHz

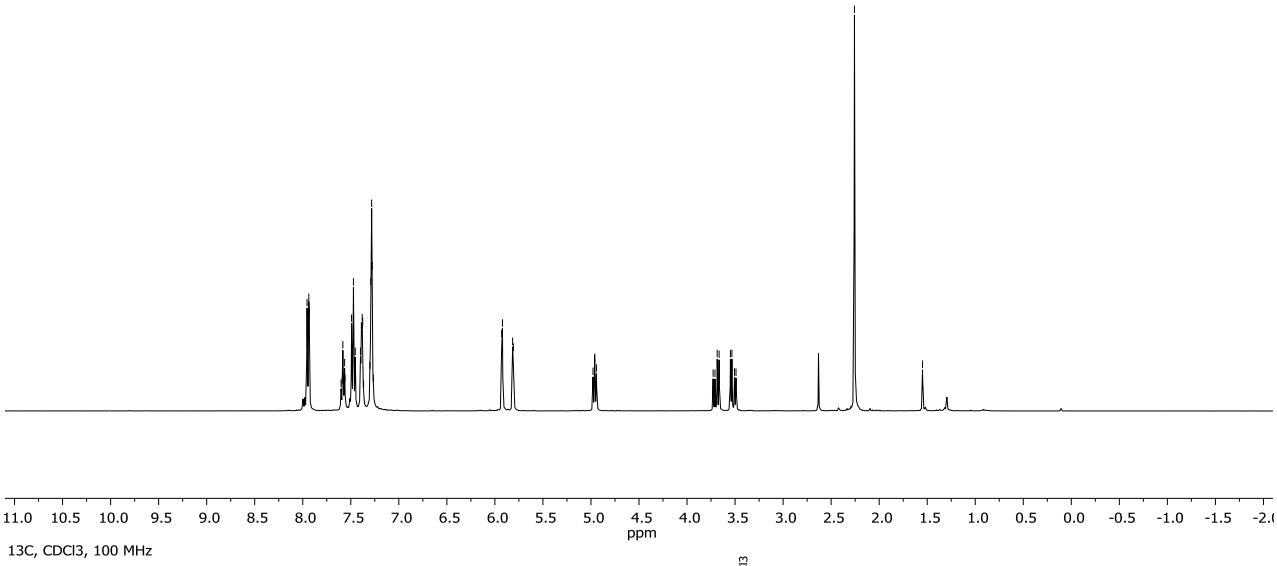


1H, CDCl3, 400 MHz

7.9553
7.9370
7.9331
7.6012
7.5883
7.5824
7.5680
7.5642
7.5604
7.4918
7.4880
7.4722
7.4533
7.3997
7.3902
7.3813
7.3757
7.3667
7.3005
7.2920
7.2828
7.2757
7.2661
5.9291
5.9213
5.8155
5.8079
4.9786
4.9631
4.9590
4.9433
3.7285
3.7088
3.6859
3.6662
3.5483
3.5327
3.5057
3.4901
2.2573
1.5487 HDO



3z

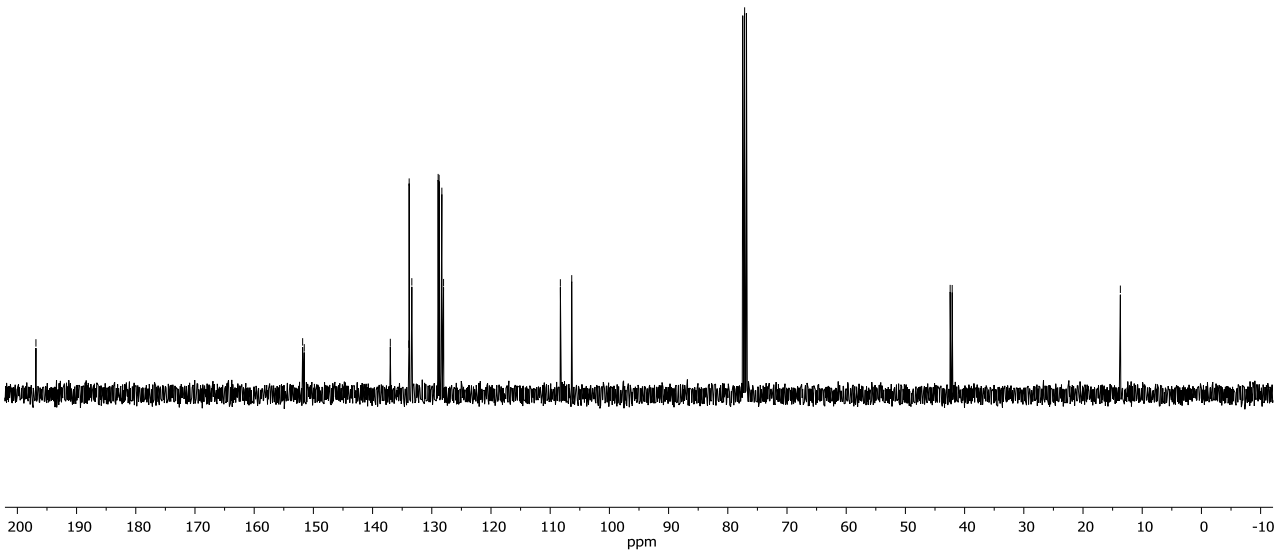


11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0

ppm

13C, CDCl3, 100 MHz

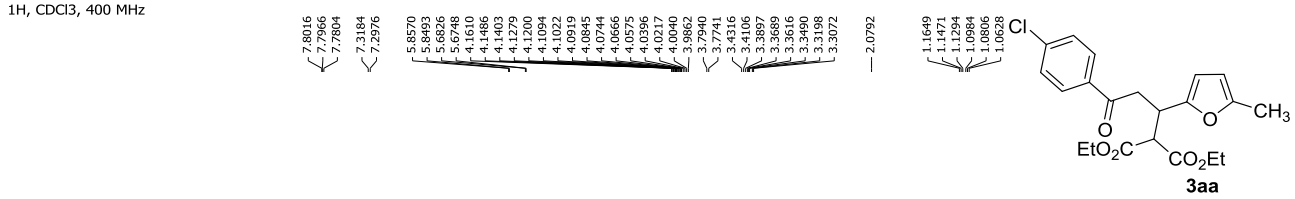
196.86
151.81
151.54
137.01
133.87
133.82
133.37
128.93
128.77
128.30
128.01
108.28
106.36
77.16 CDCl3
42.44
42.10
13.69



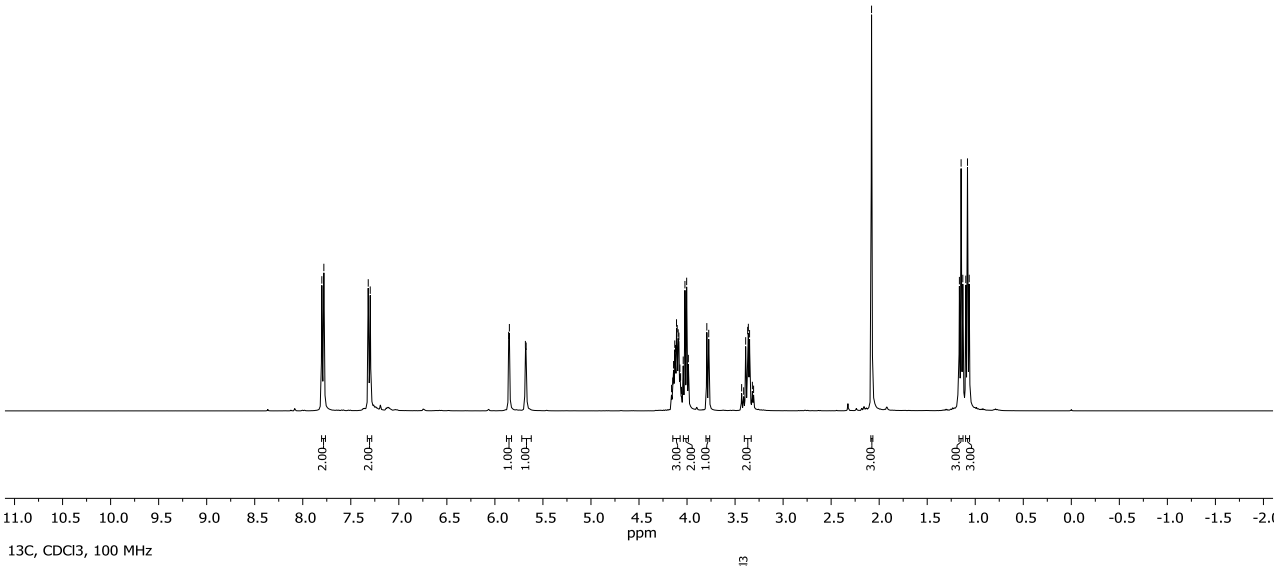
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

ppm

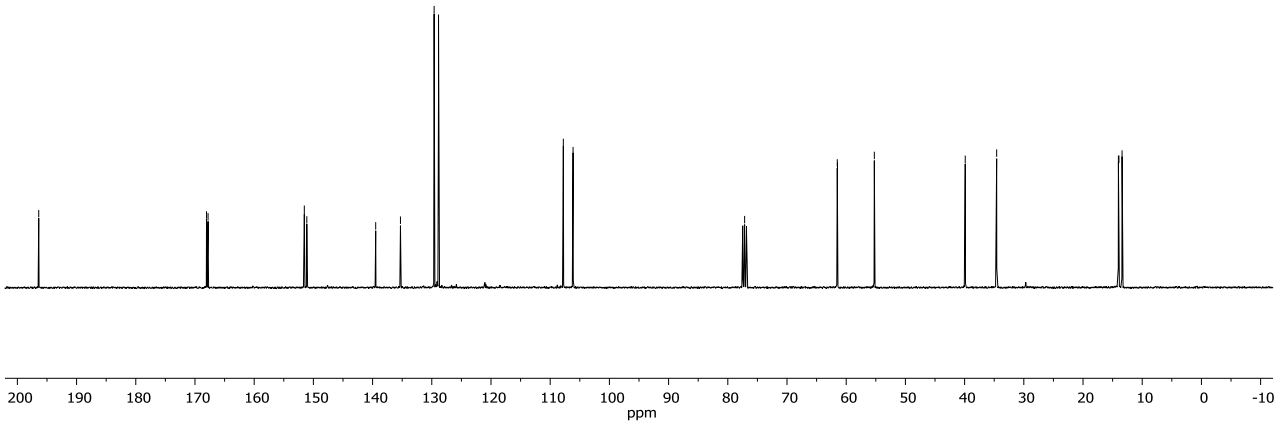
1H, CDCl3, 400 MHz



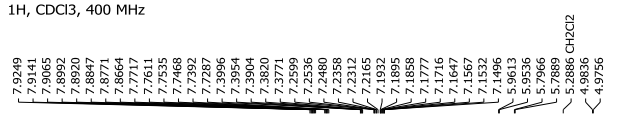
3aa

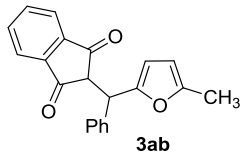


13C, CDCl3, 100 MHz

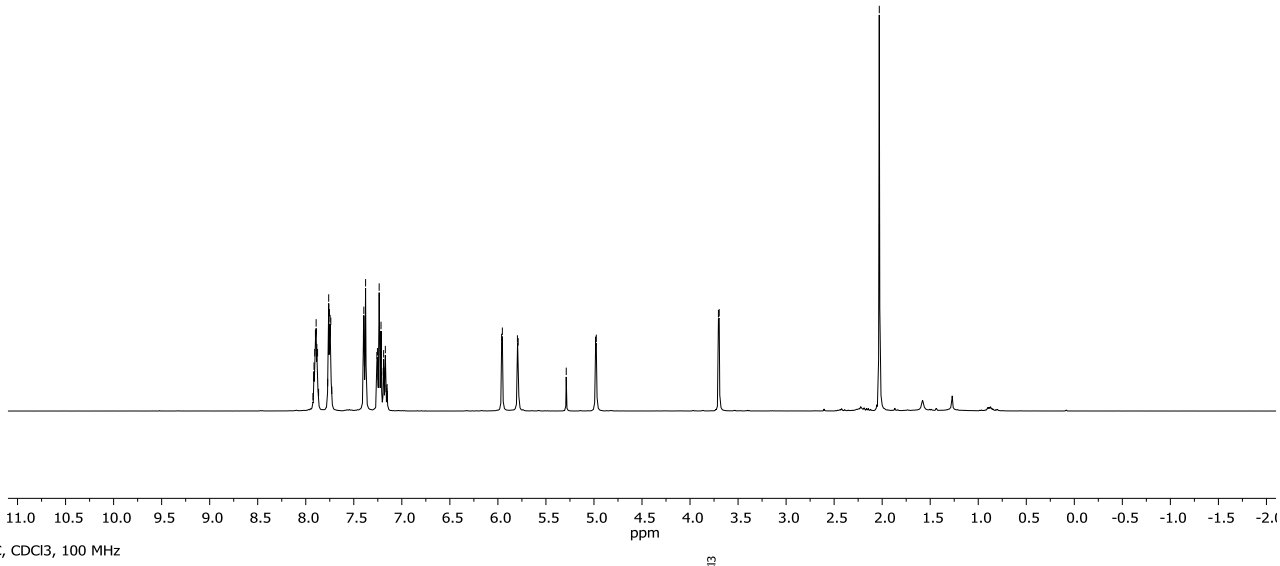


1H, CDCl3, 400 MHz

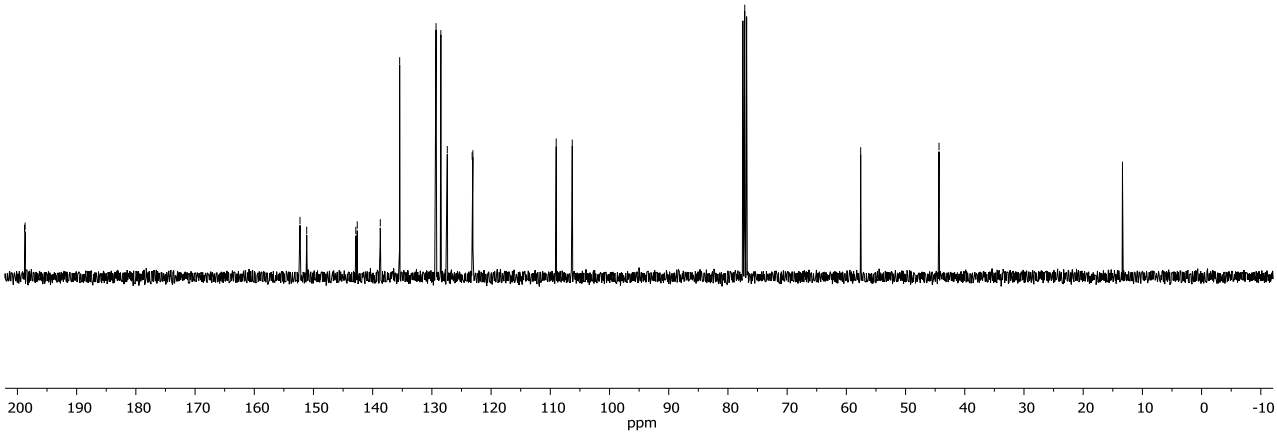




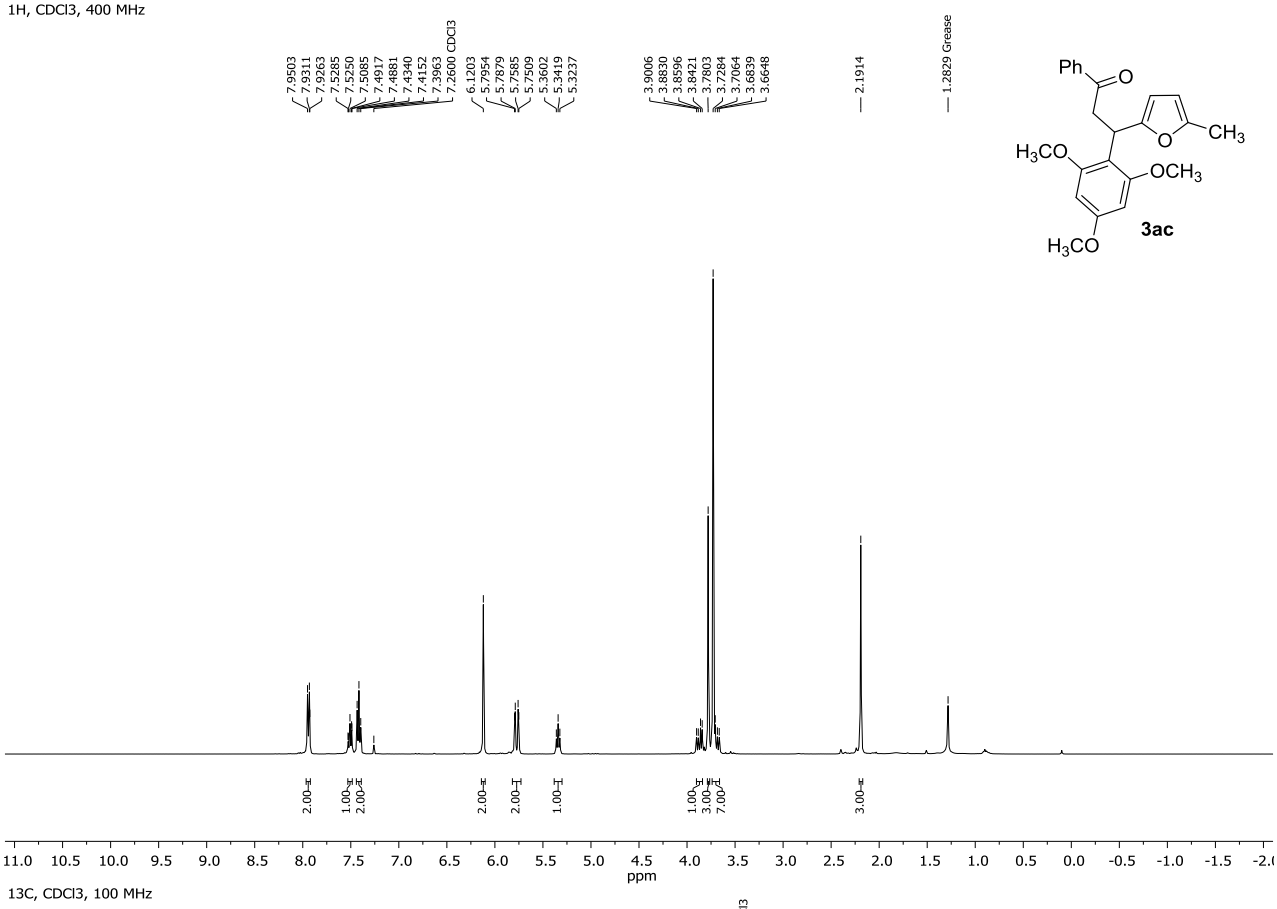
3ab



13C, CDCl3, 100 MHz

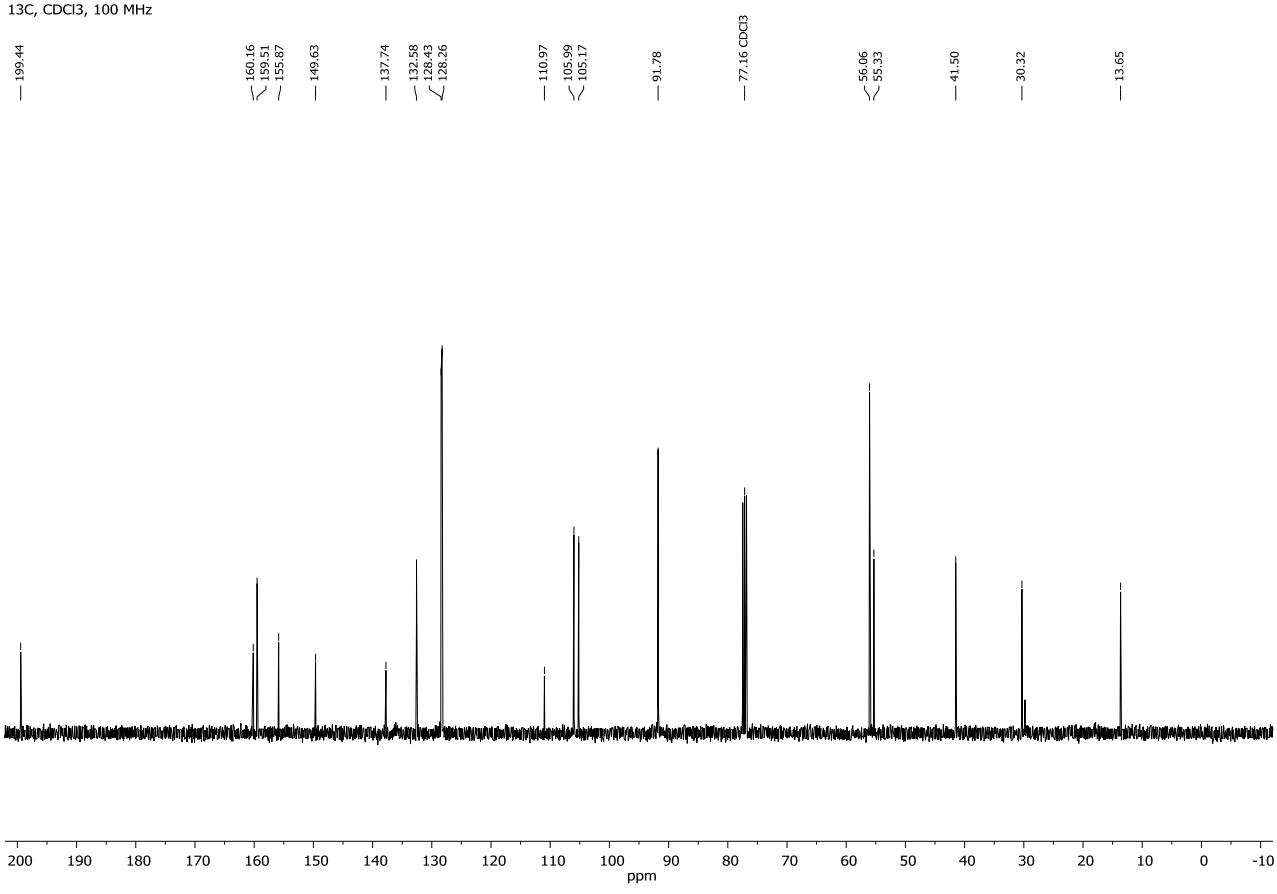


1H, CDCl3, 400 MHz

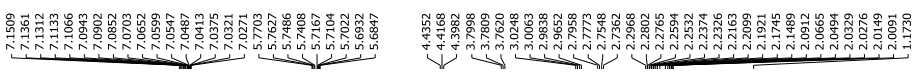


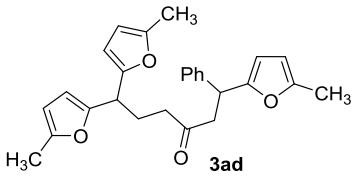
3ac

13C, CDCl3, 100 MHz

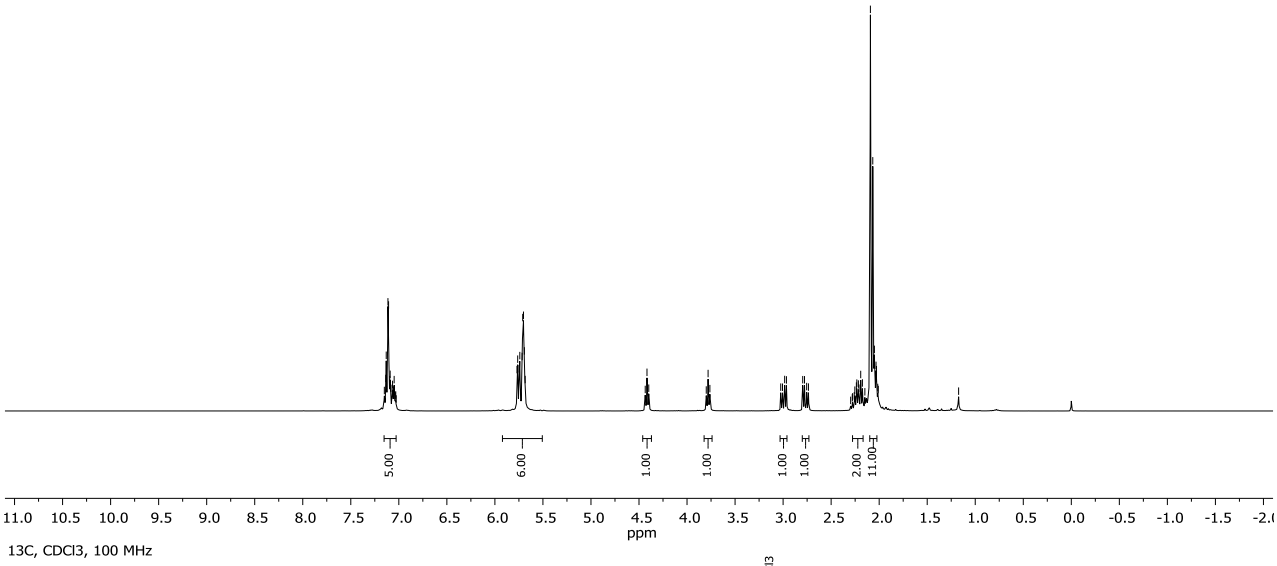


1H, CDCl3, 400 MHz

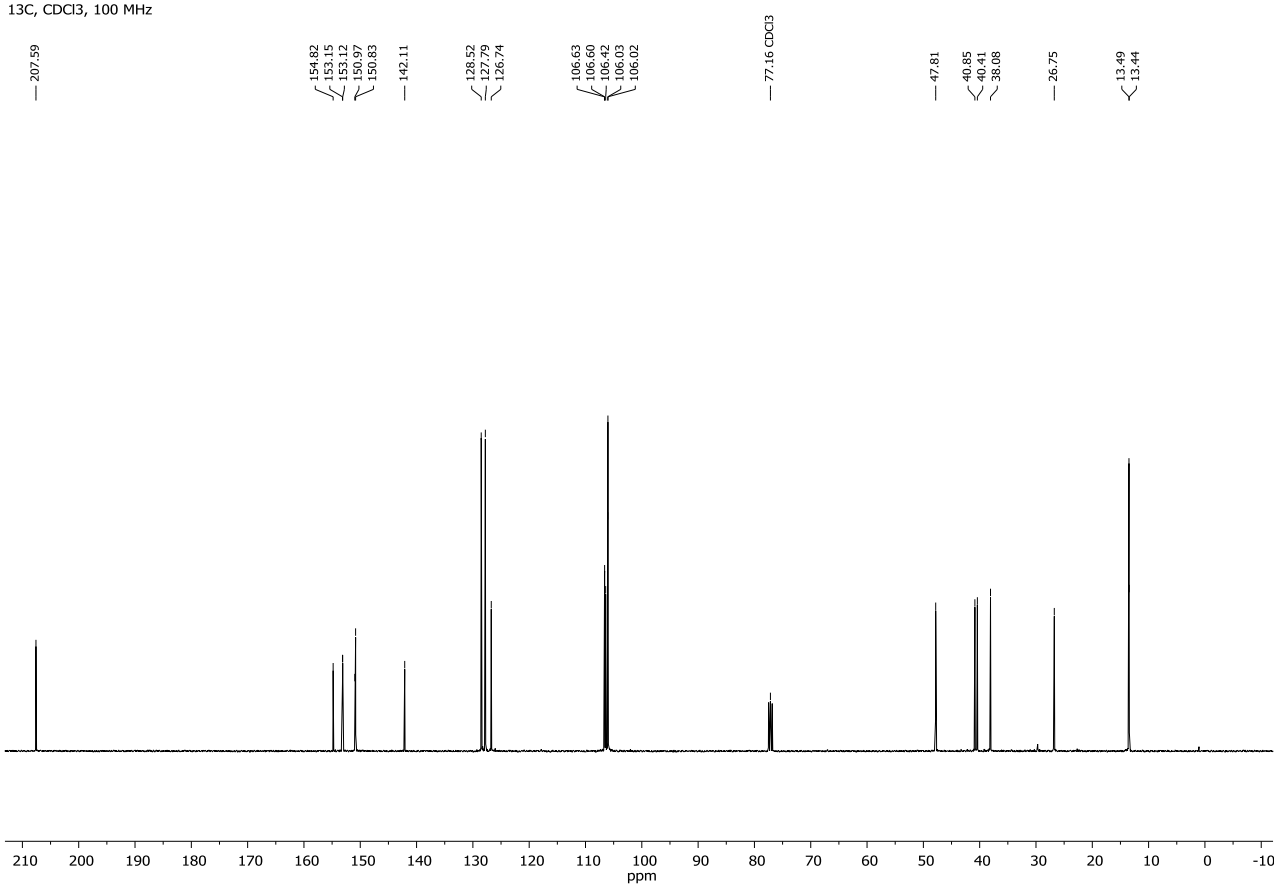




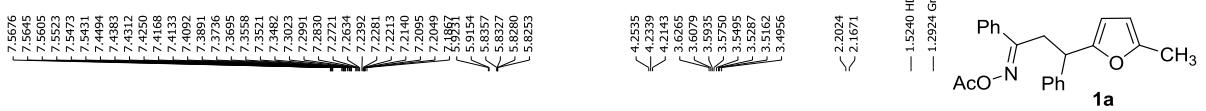
3ad

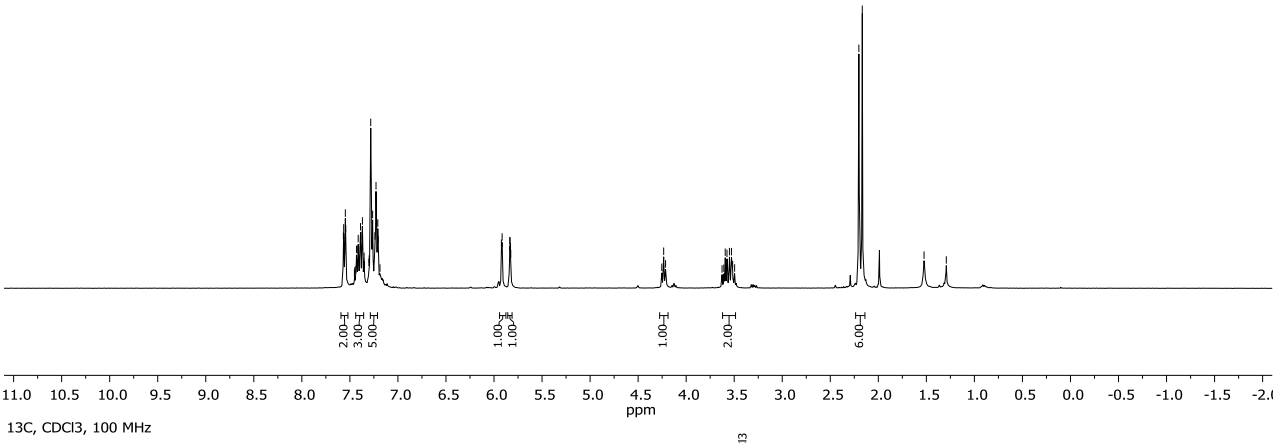


13C, CDCl3, 100 MHz

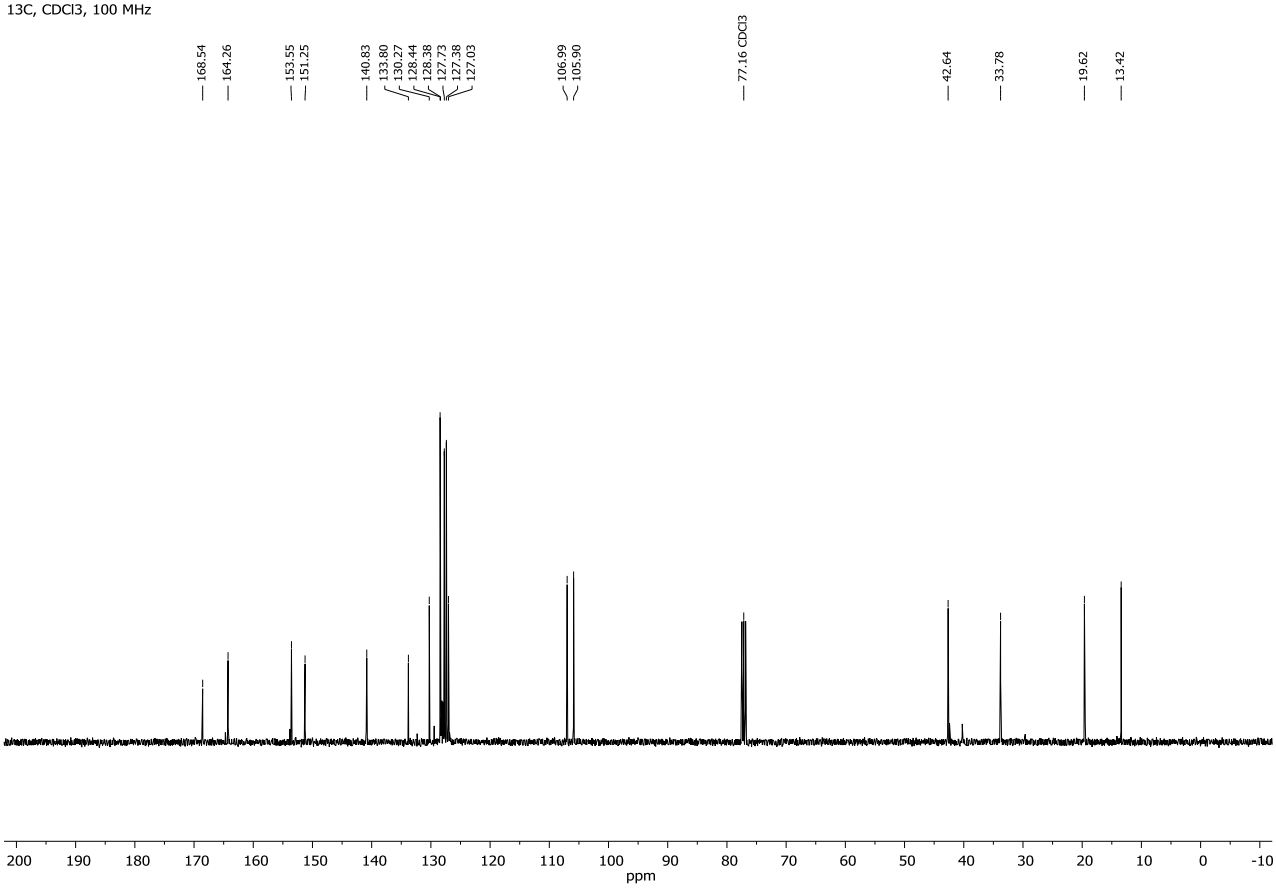


1H, CDCl3, 400 MHz

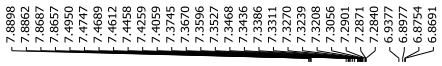


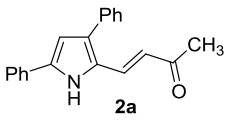


13C, CDCl3, 100 MHz

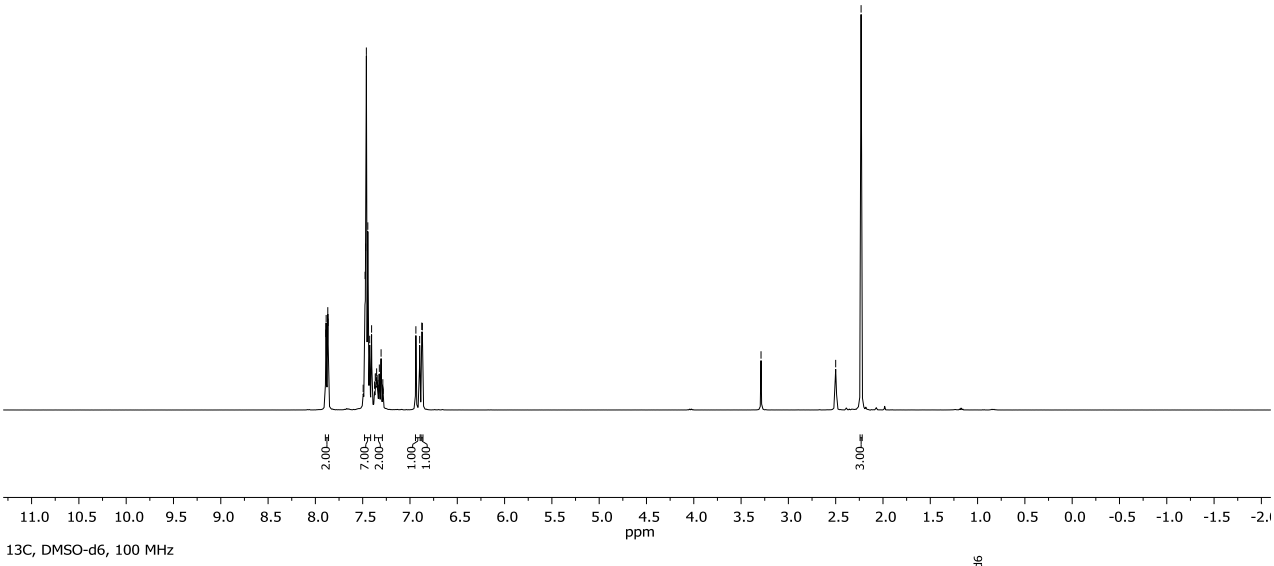


1H, DMSO-d6, 400 MHz

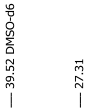


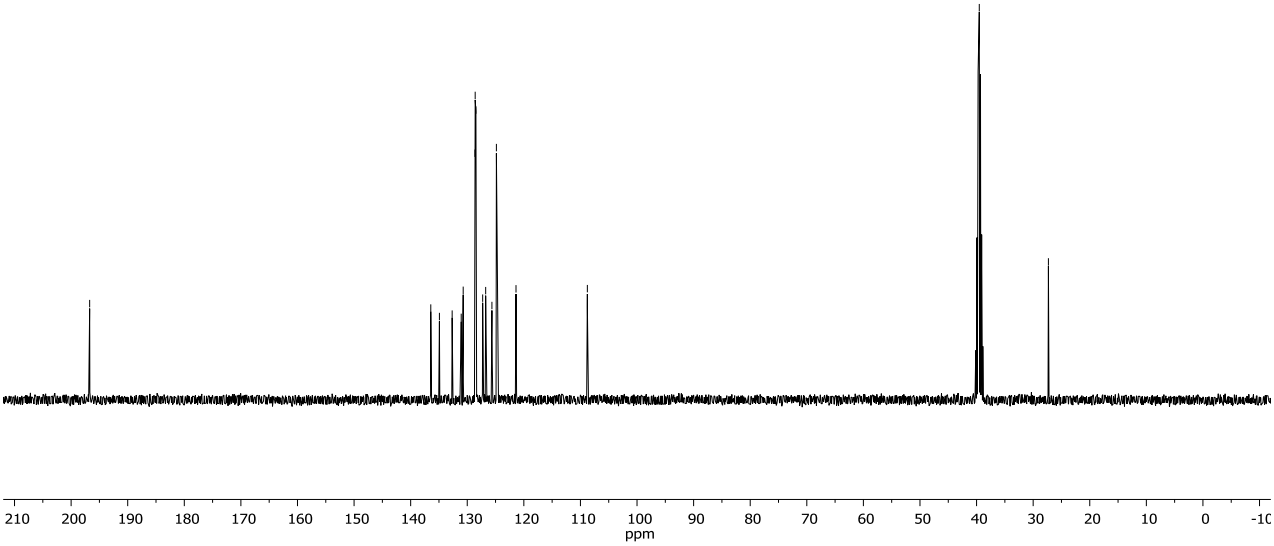


2a

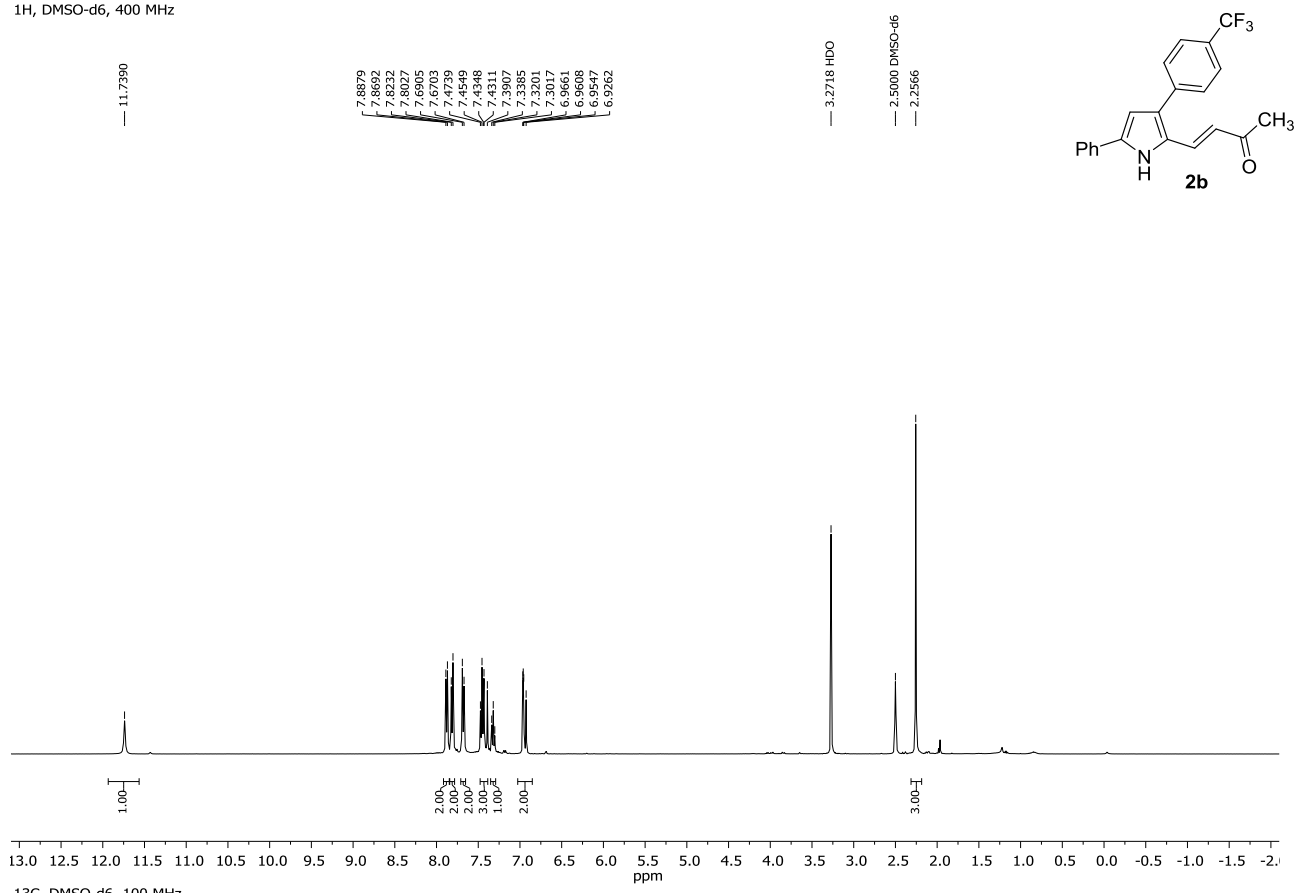


13C, DMSO-d6, 100 MHz



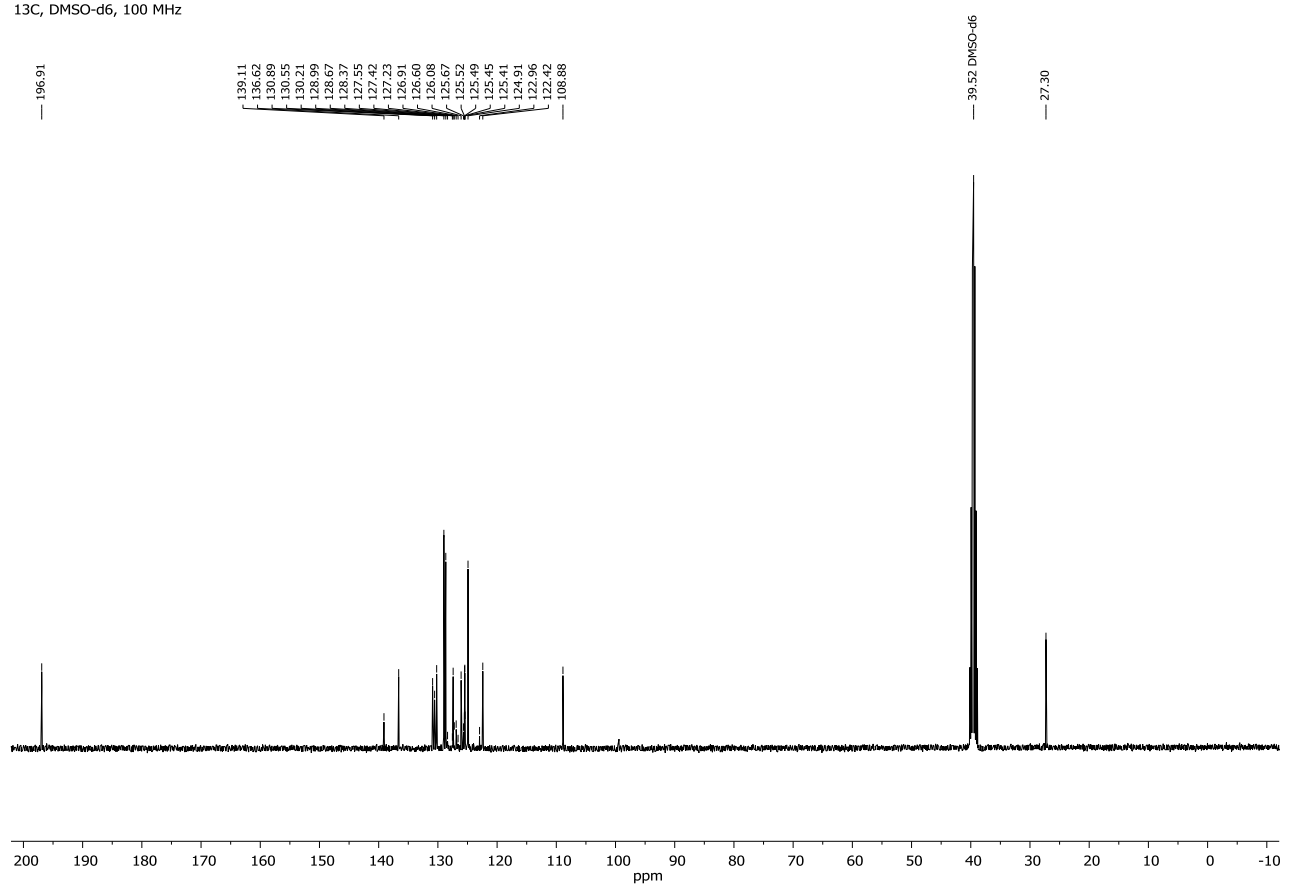


1H, DMSO-d6, 400 MHz

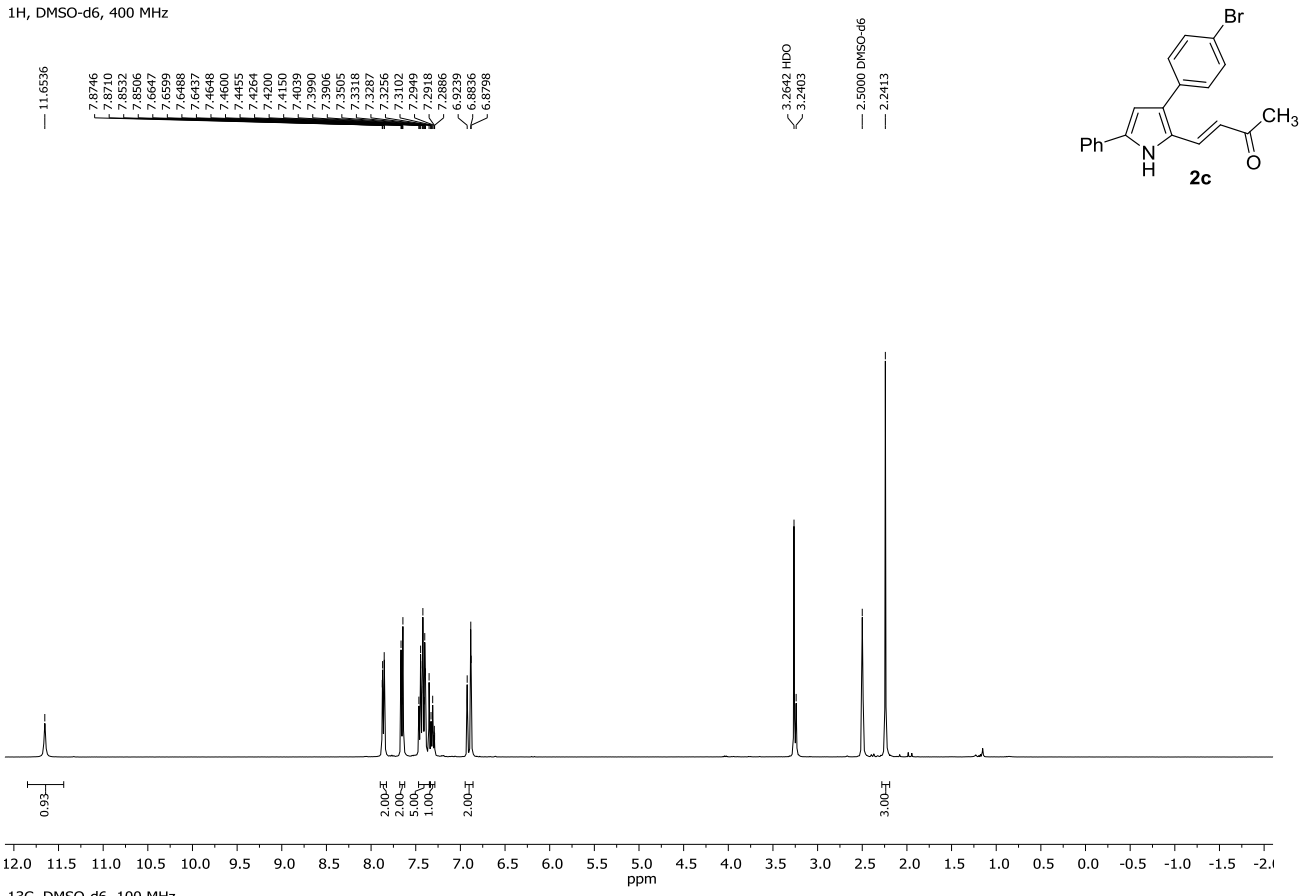


2b

13C, DMSO-d6, 100 MHz

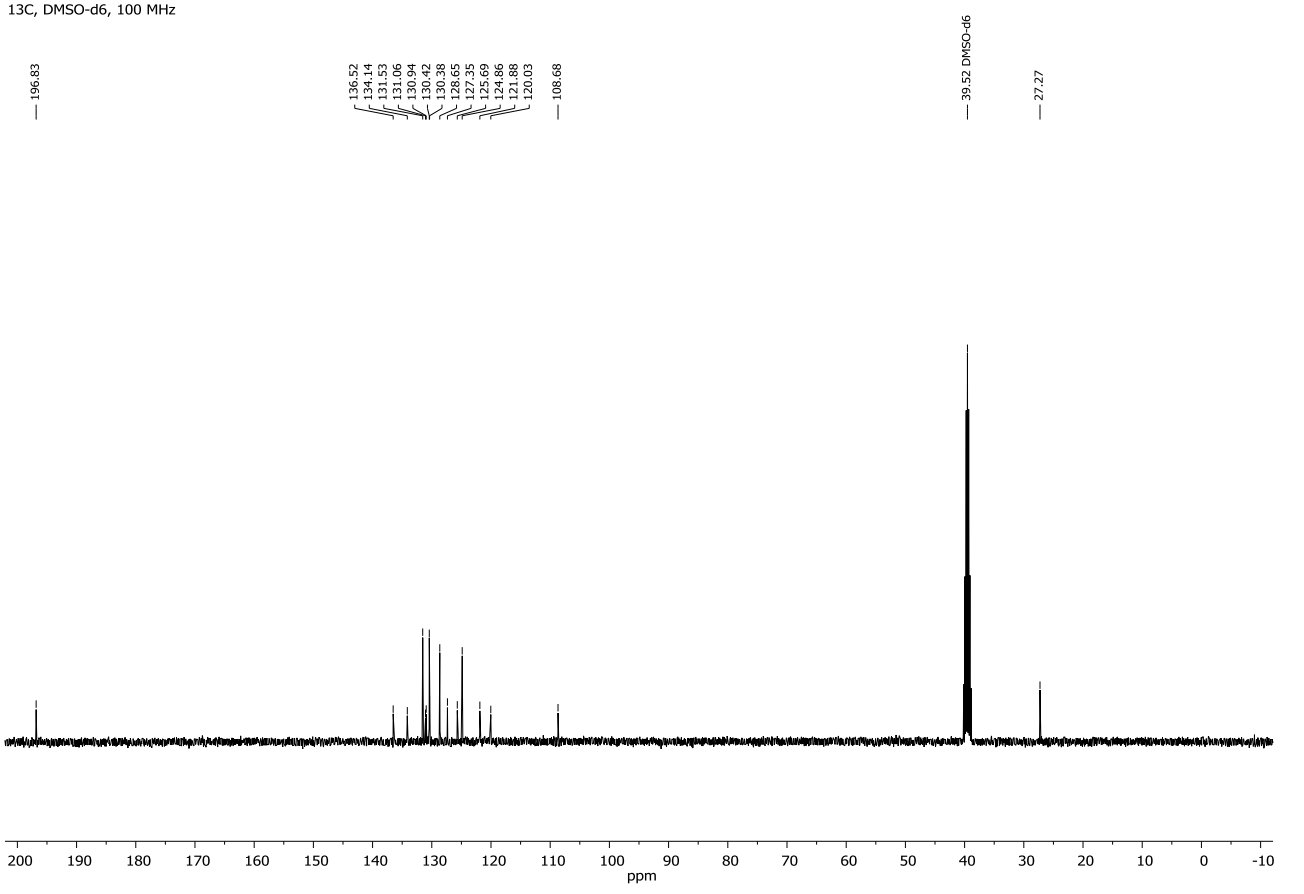


1H, DMSO-d6, 400 MHz

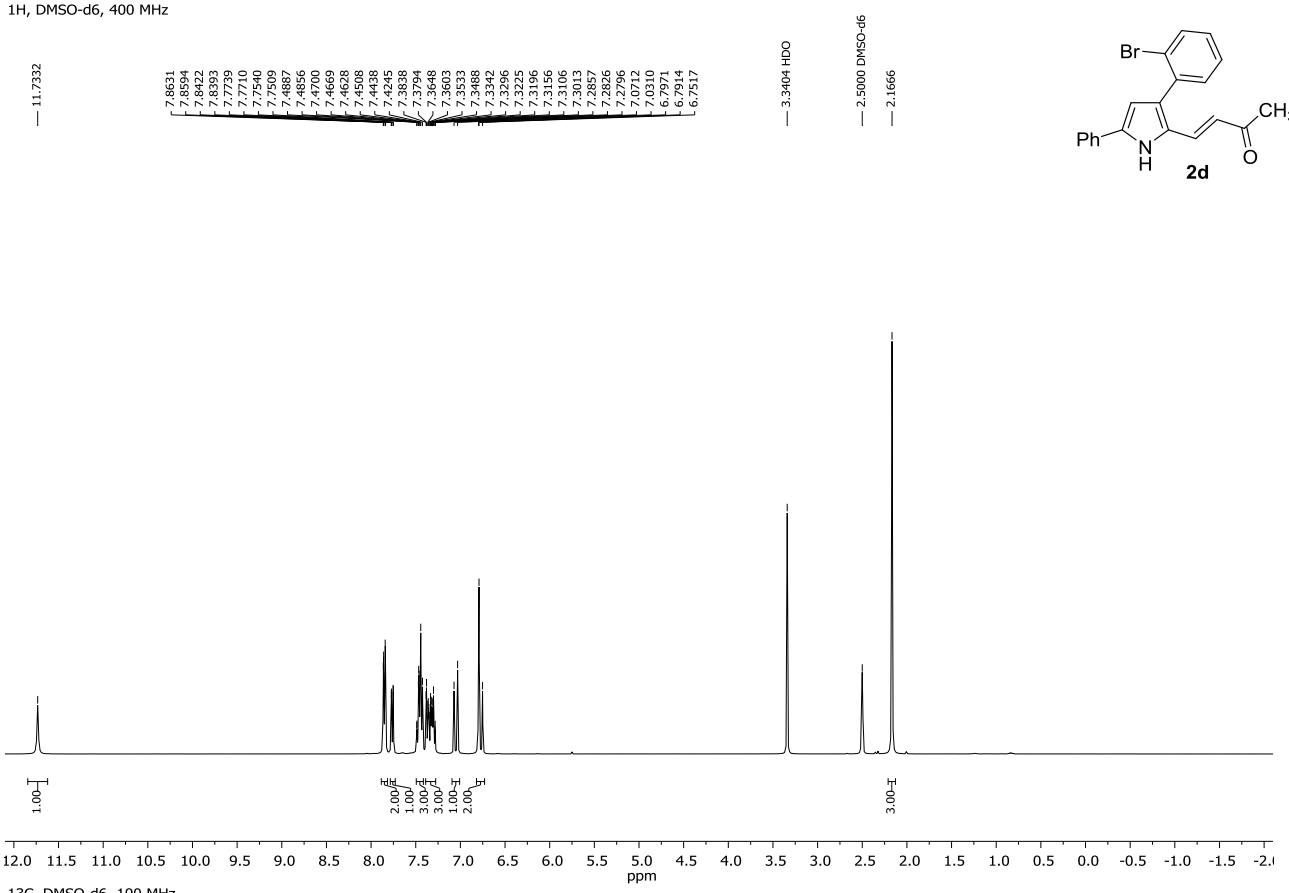


2c

13C, DMSO-d6, 100 MHz

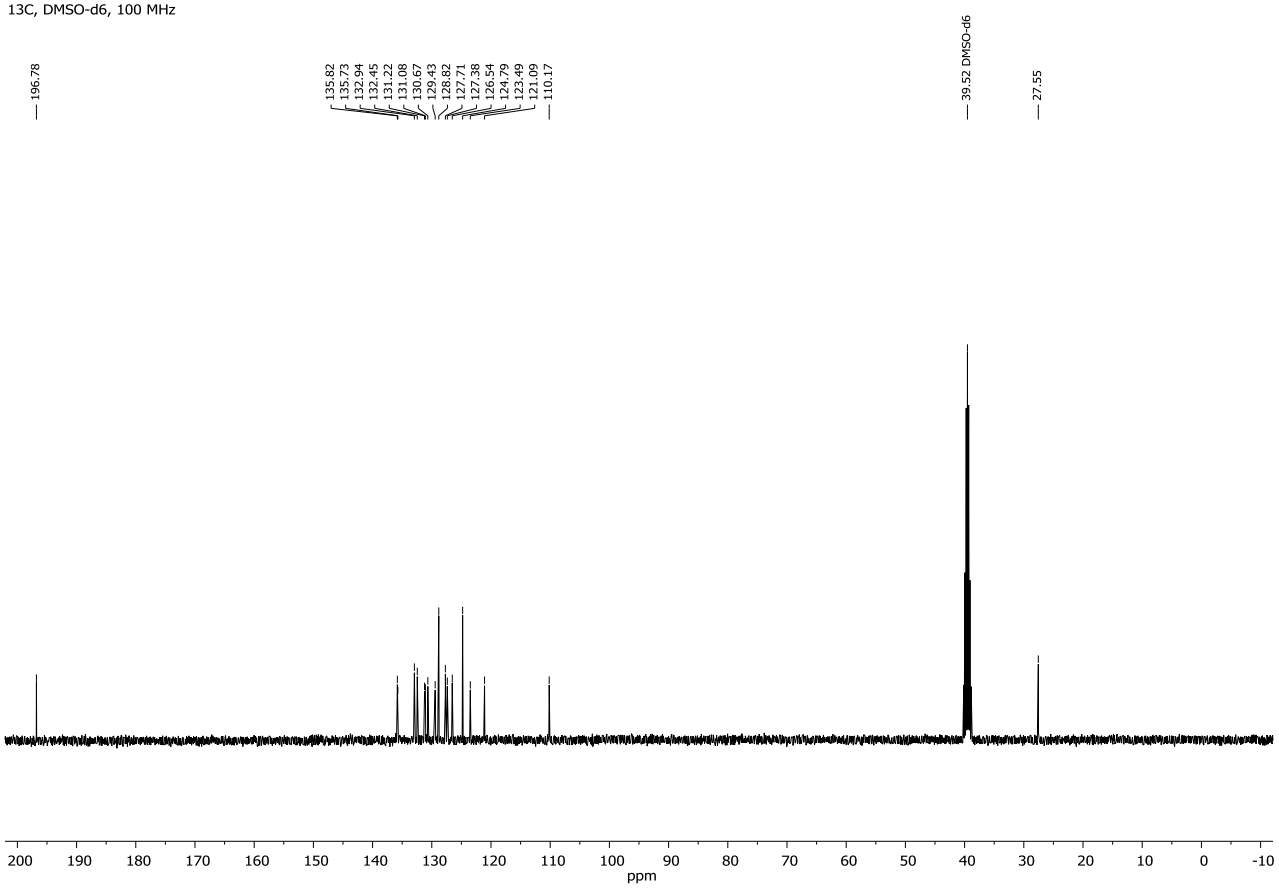


1H, DMSO-d6, 400 MHz

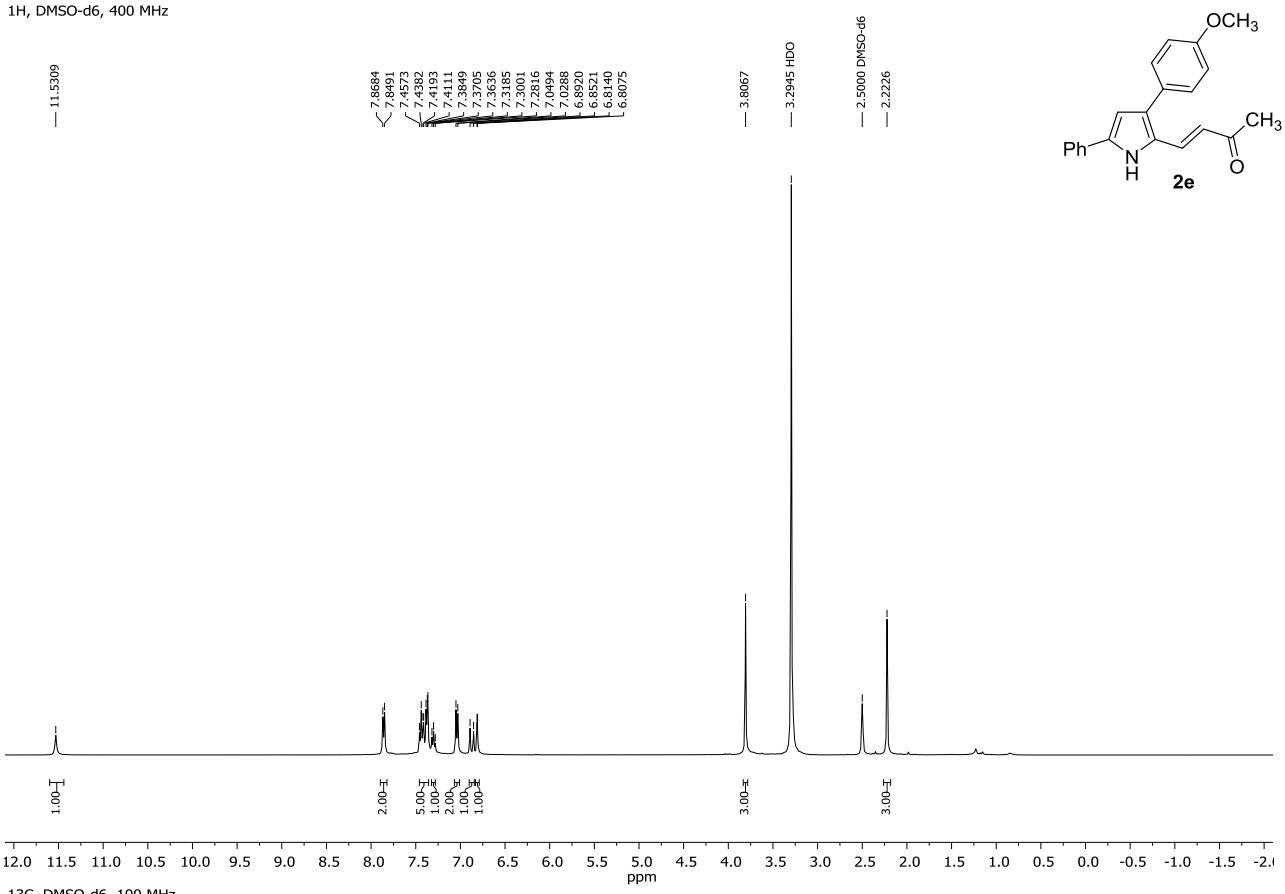


2d

13C, DMSO-d6, 100 MHz

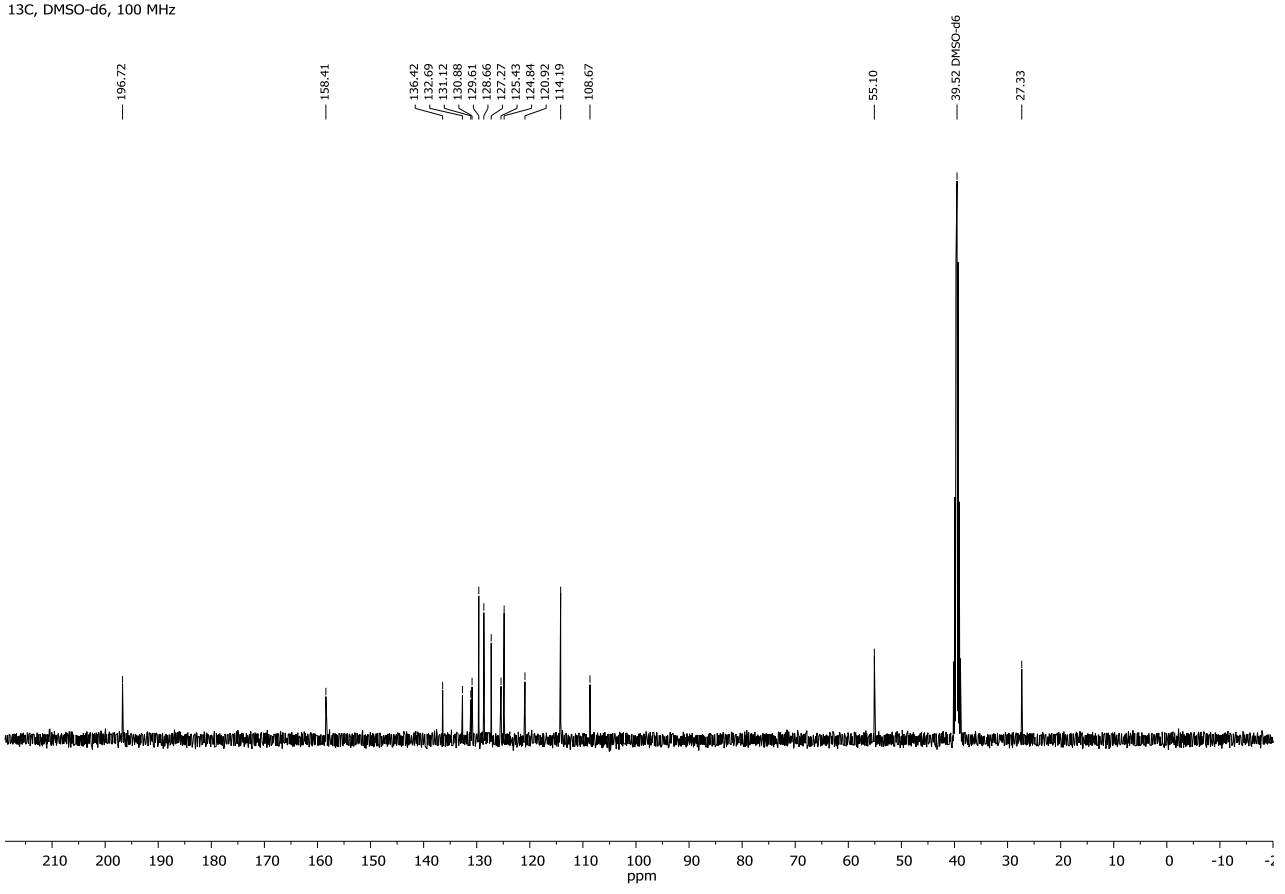


1H, DMSO-d6, 400 MHz

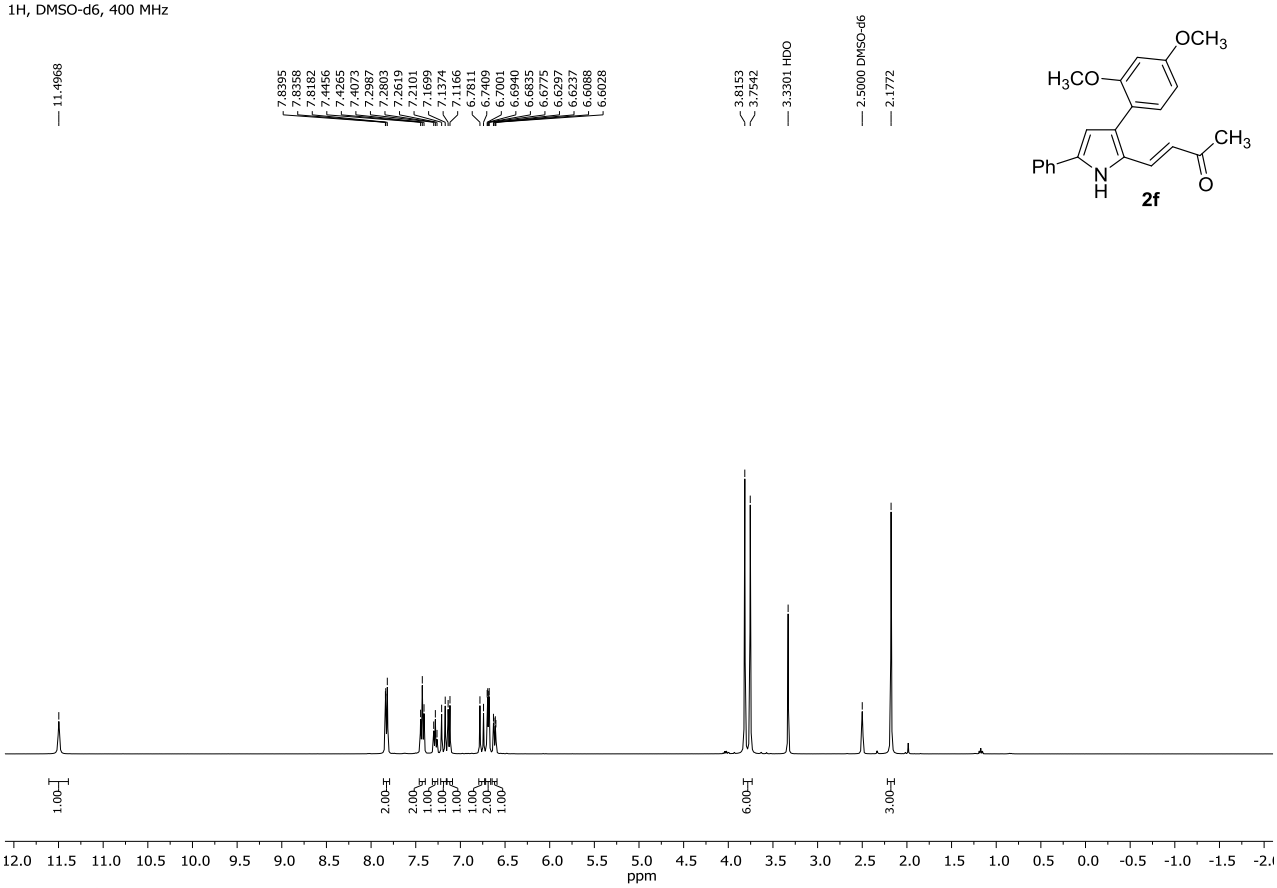


2e

13C, DMSO-d6, 100 MHz

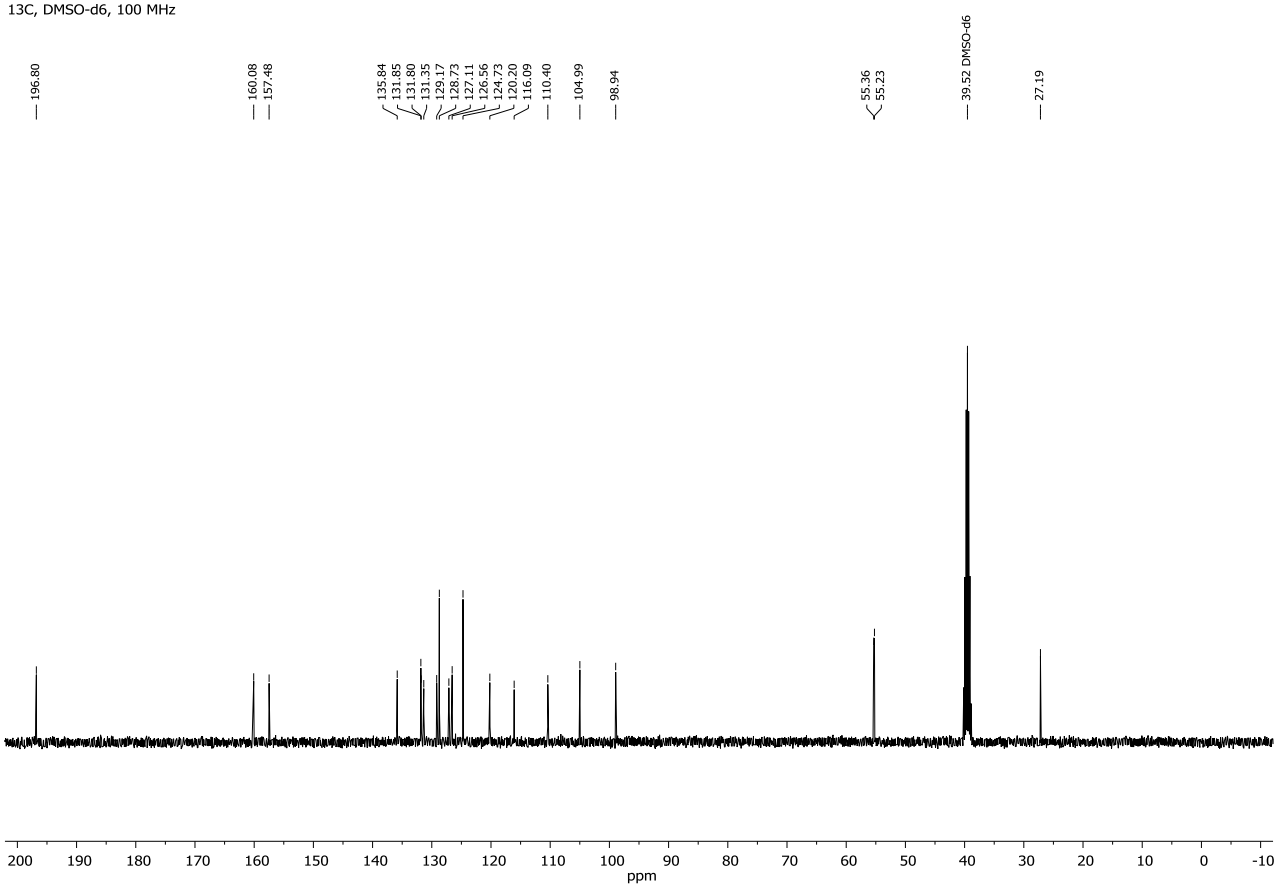


1H, DMSO-d6, 400 MHz

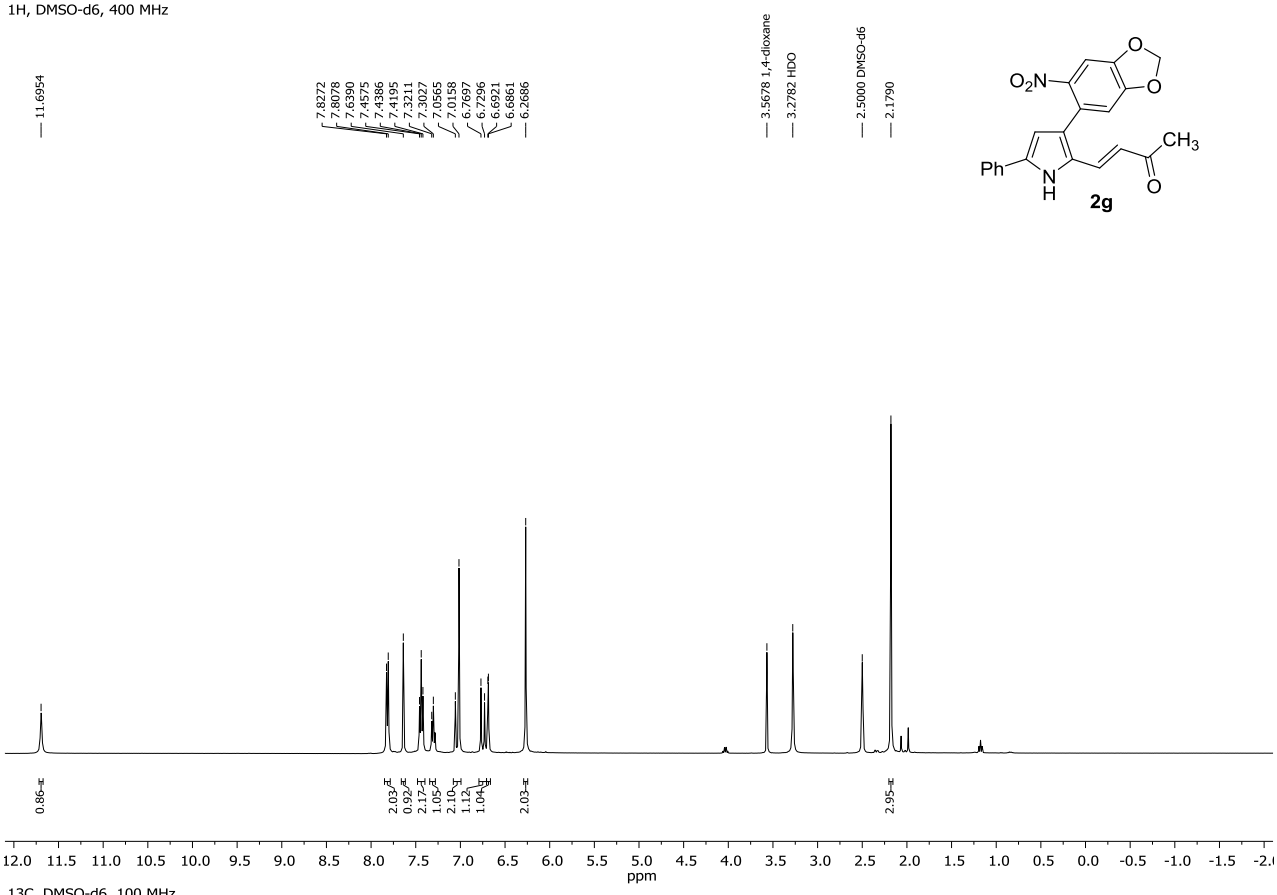


2f

13C, DMSO-d6, 100 MHz

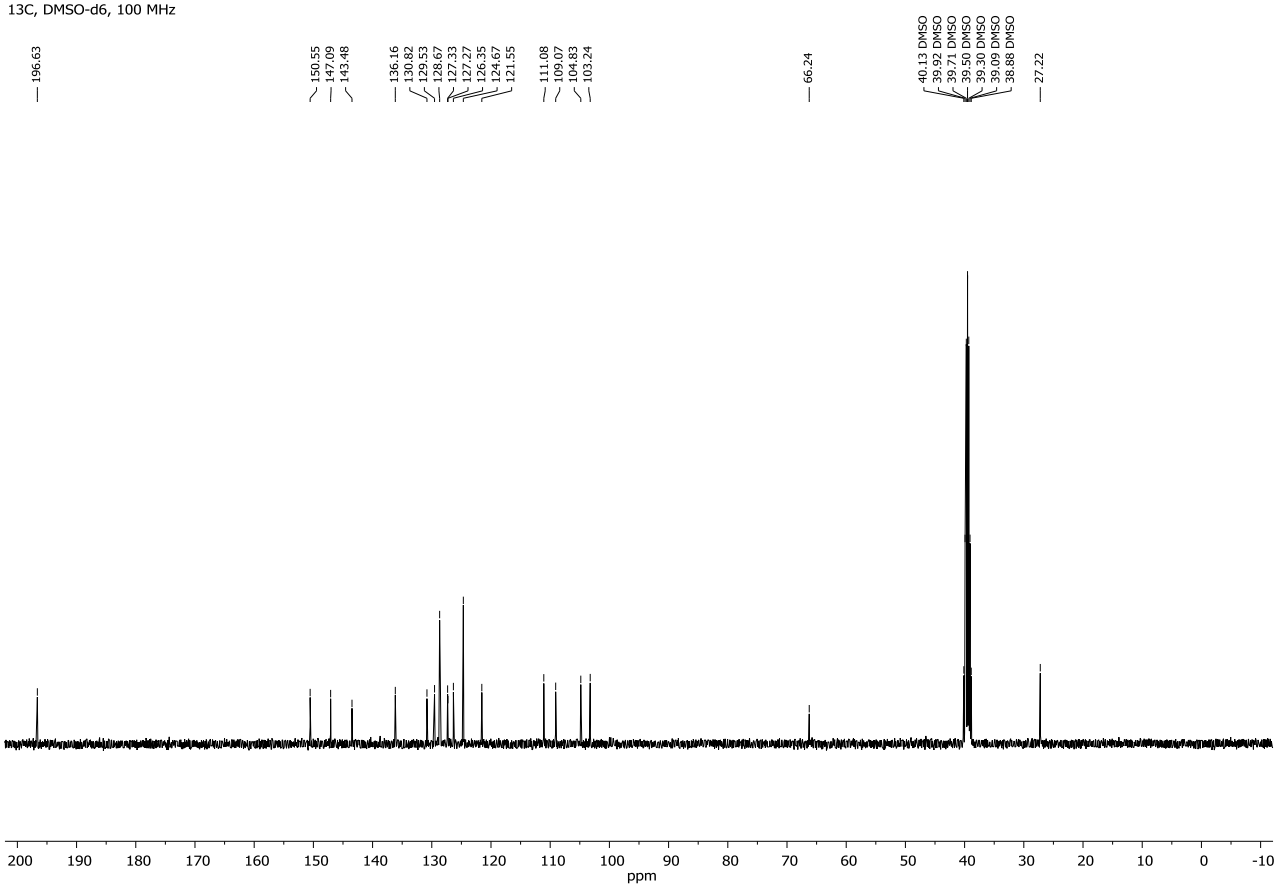


1H, DMSO-d6, 400 MHz

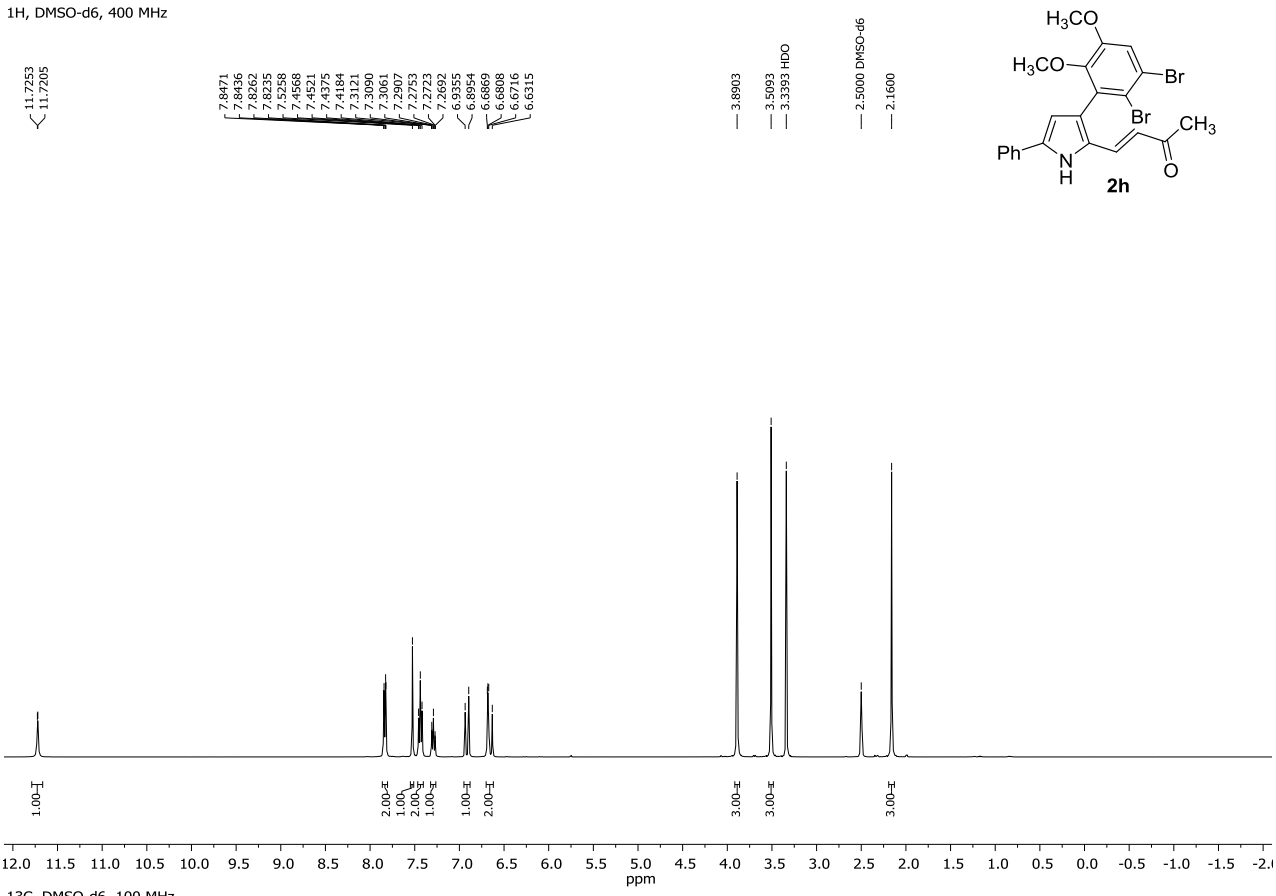


2g

13C, DMSO-d6, 100 MHz

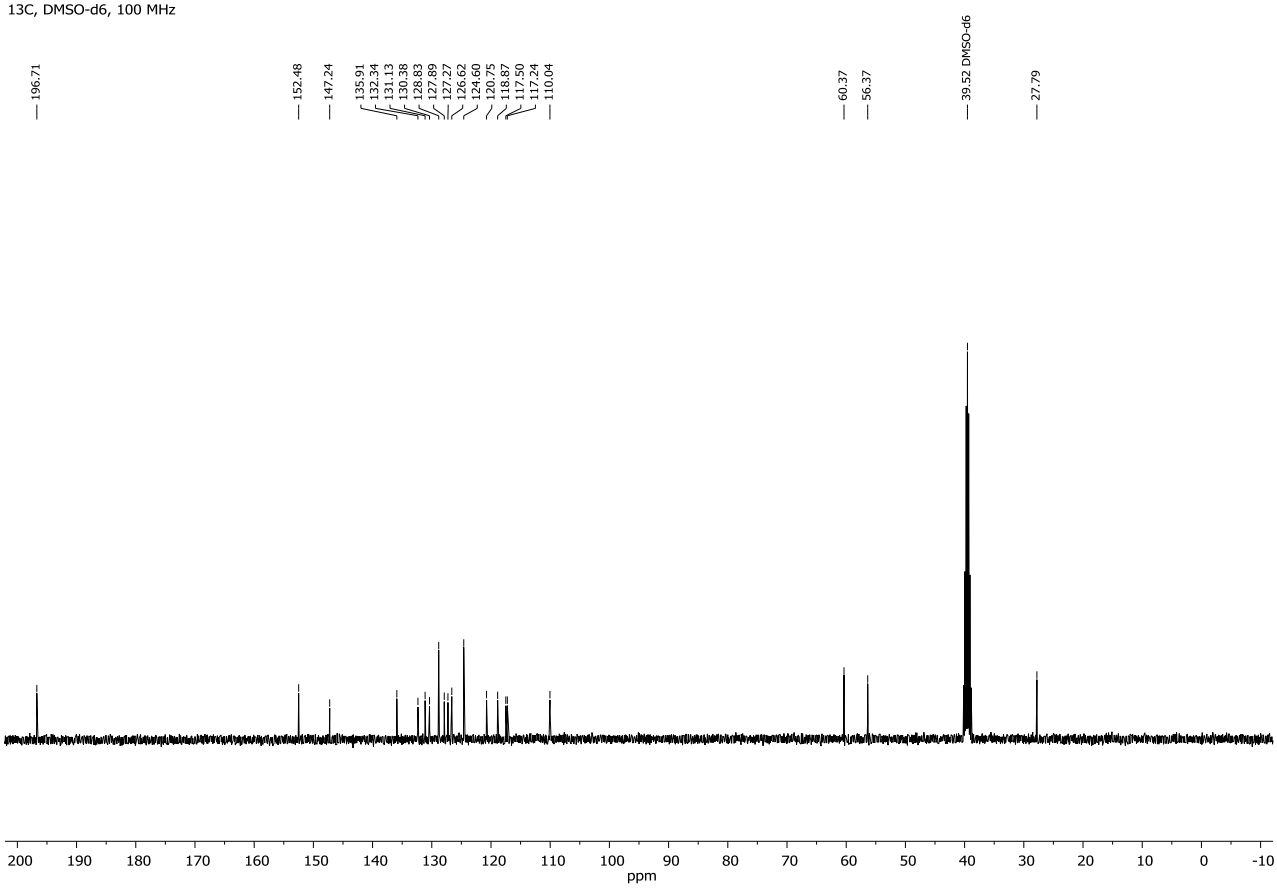


1H, DMSO-d6, 400 MHz

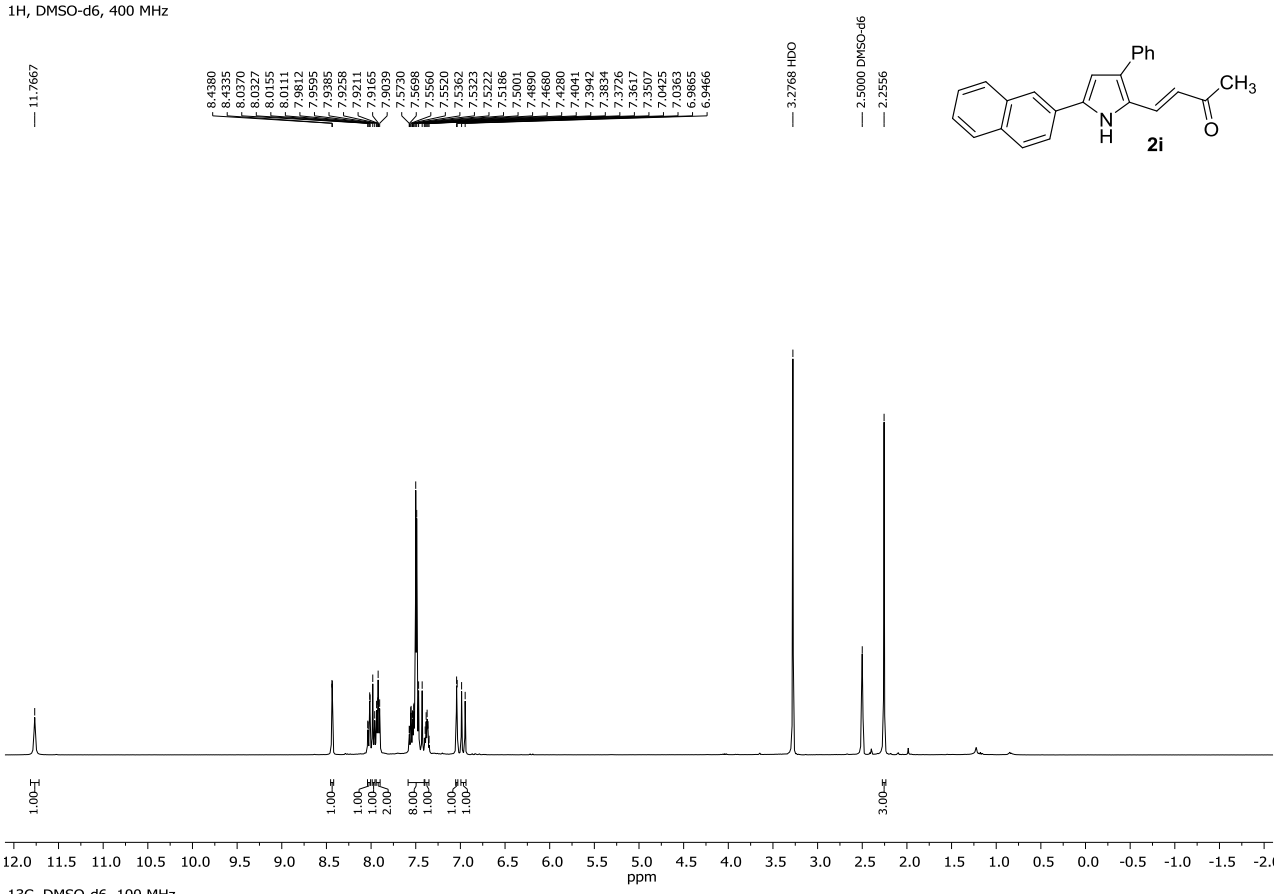


2h

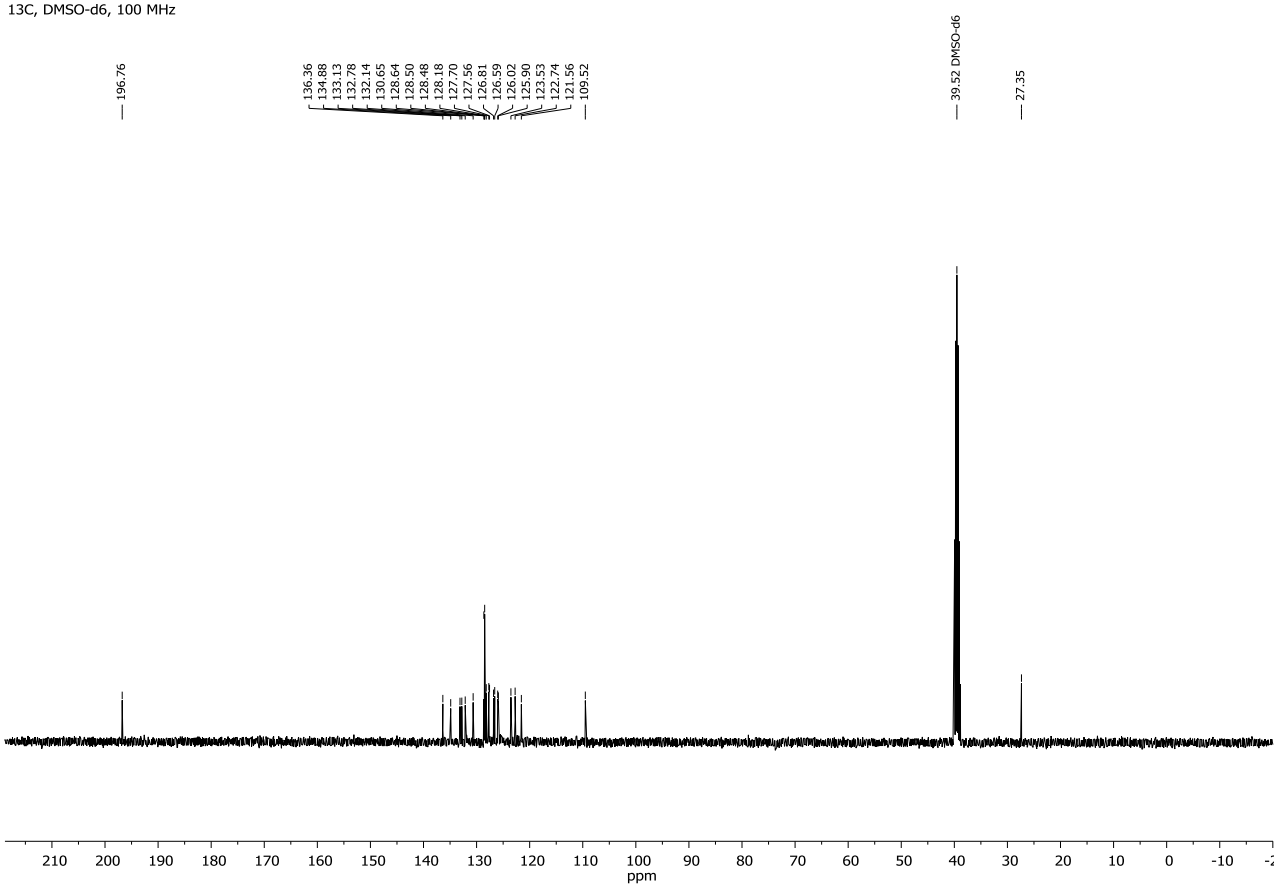
13C, DMSO-d6, 100 MHz



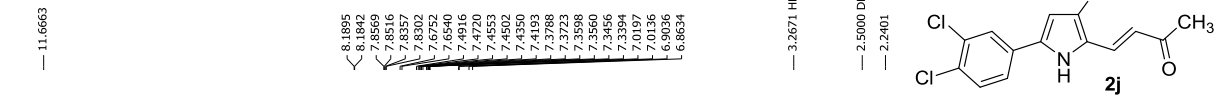
1H, DMSO-d6, 400 MHz



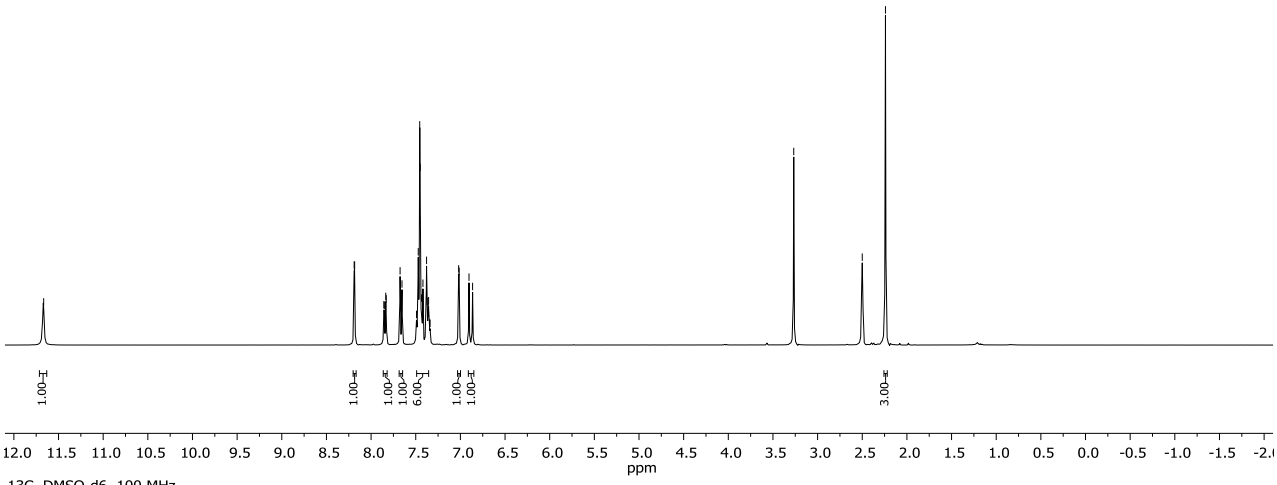
13C, DMSO-d6, 100 MHz



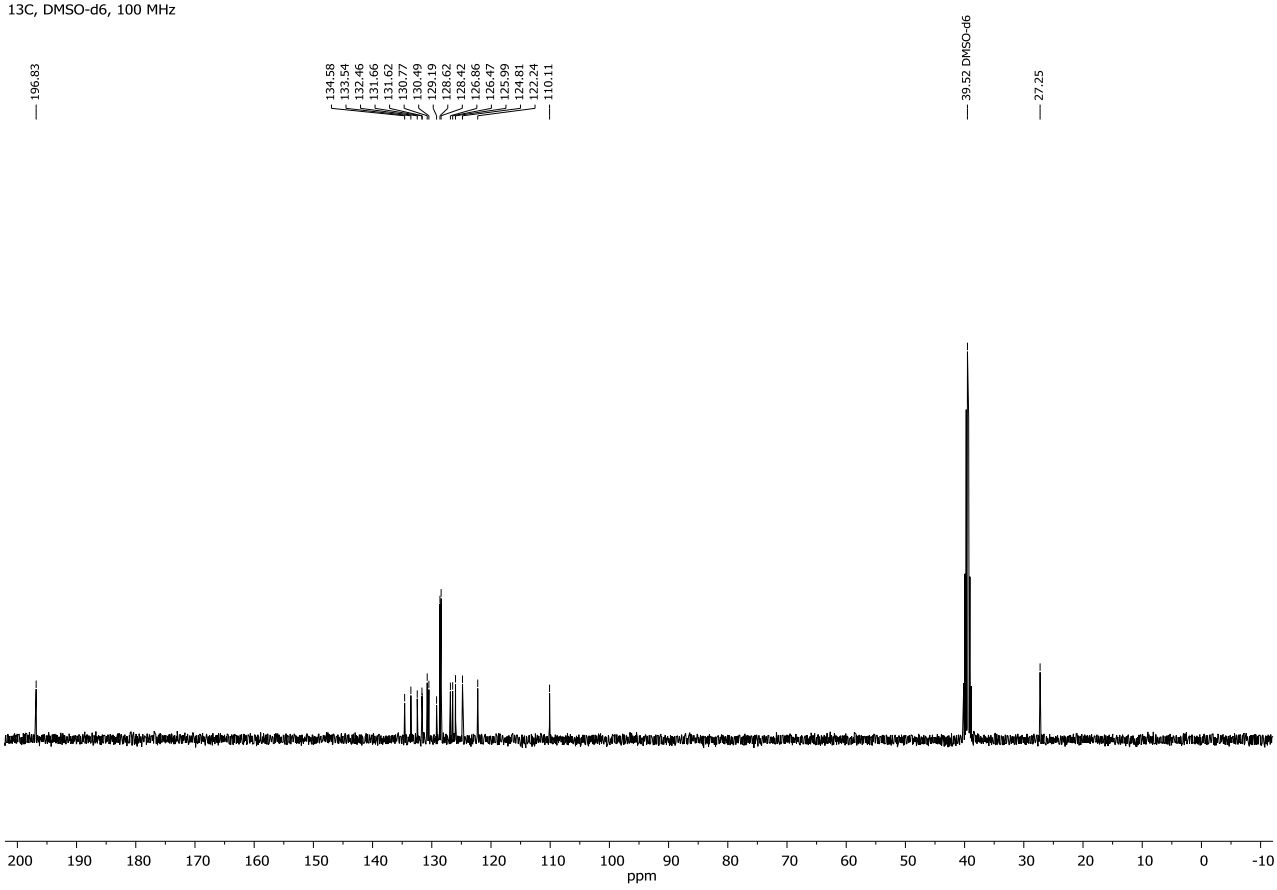
1H, DMSO-d6, 400 MHz



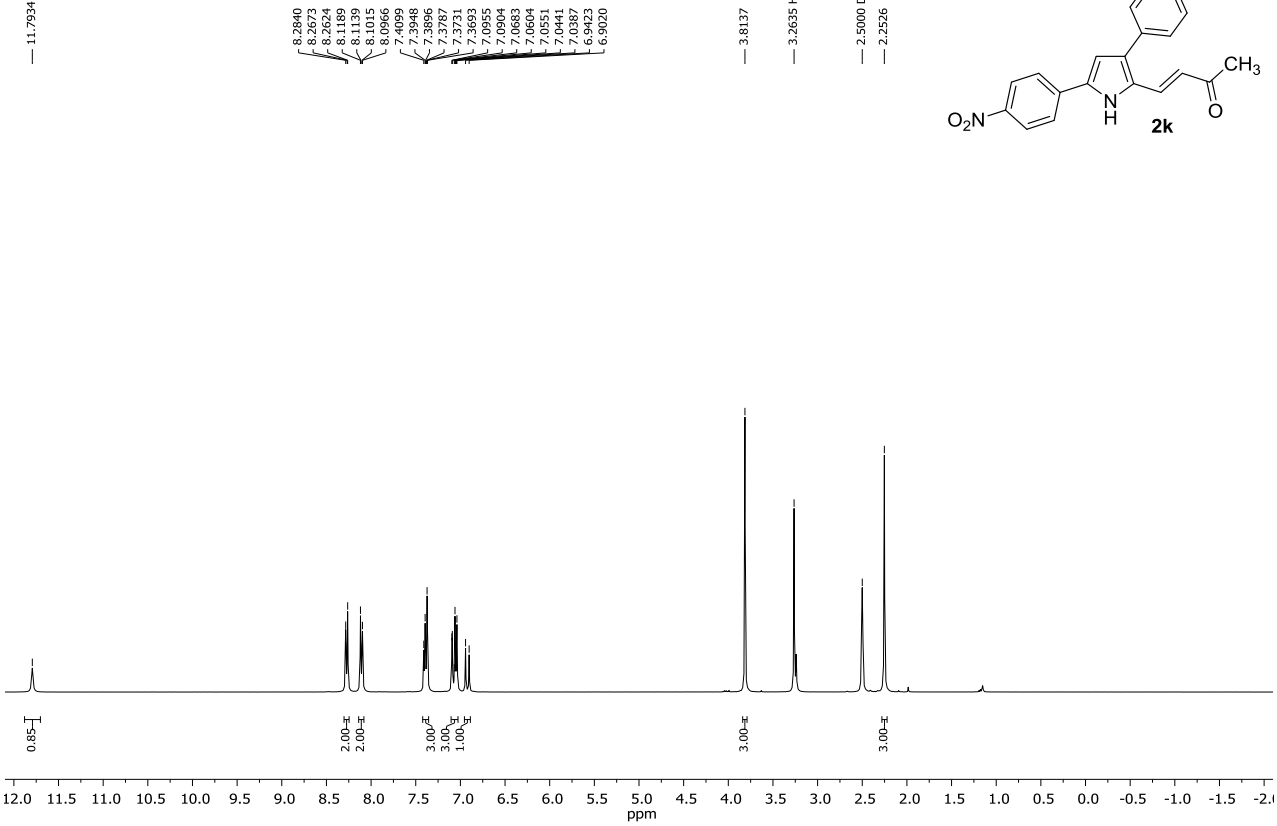
2j



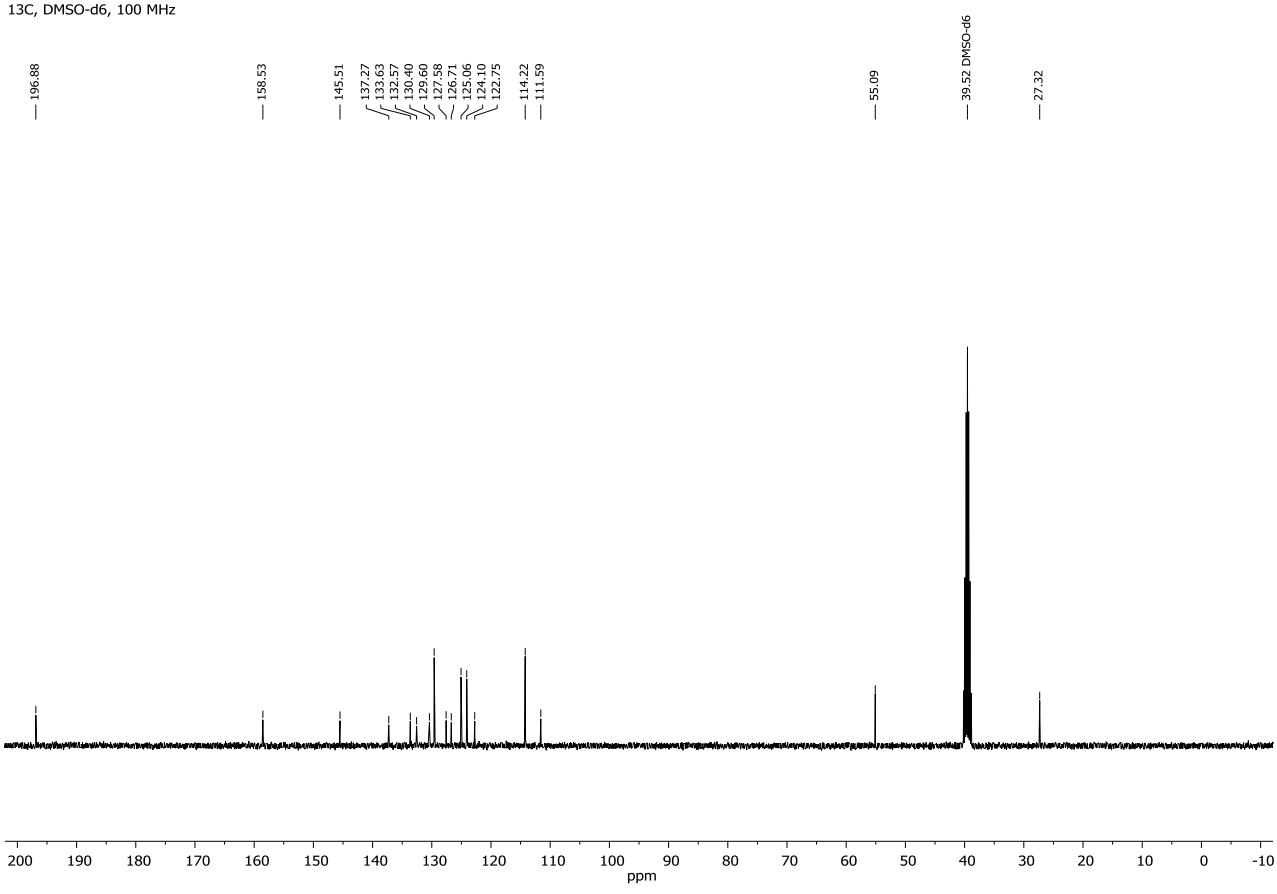
13C, DMSO-d6, 100 MHz



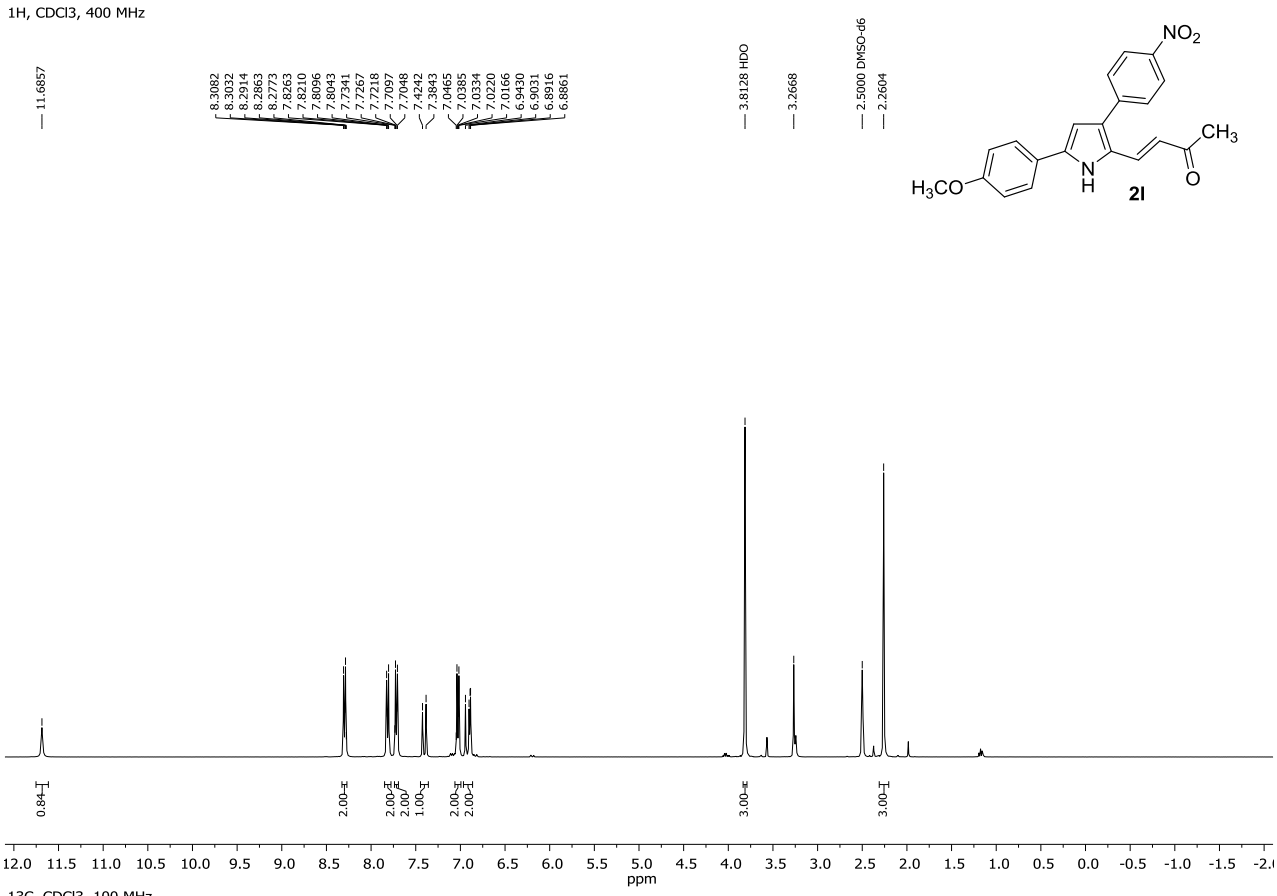
1H, DMSO-d6, 400 MHz



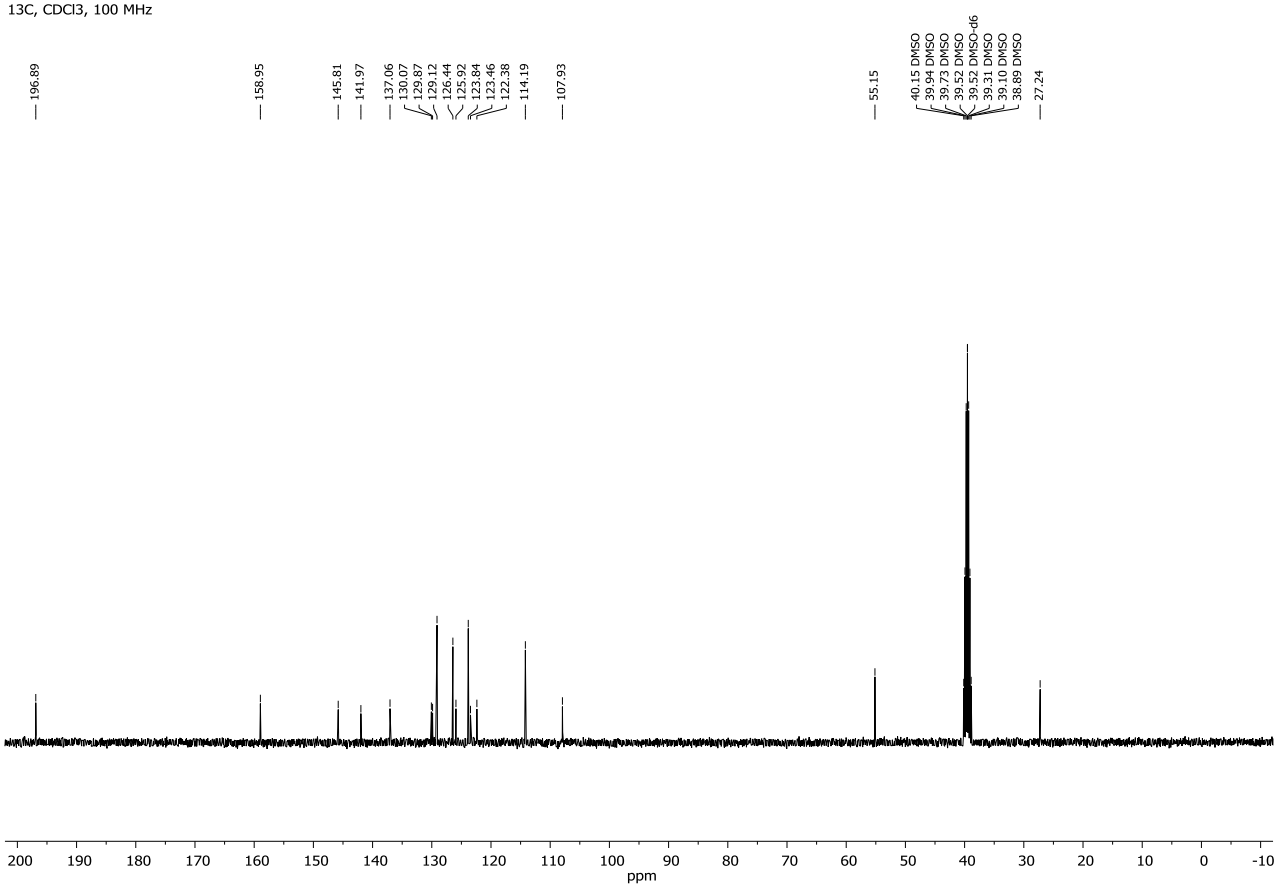
13C, DMSO-d6, 100 MHz



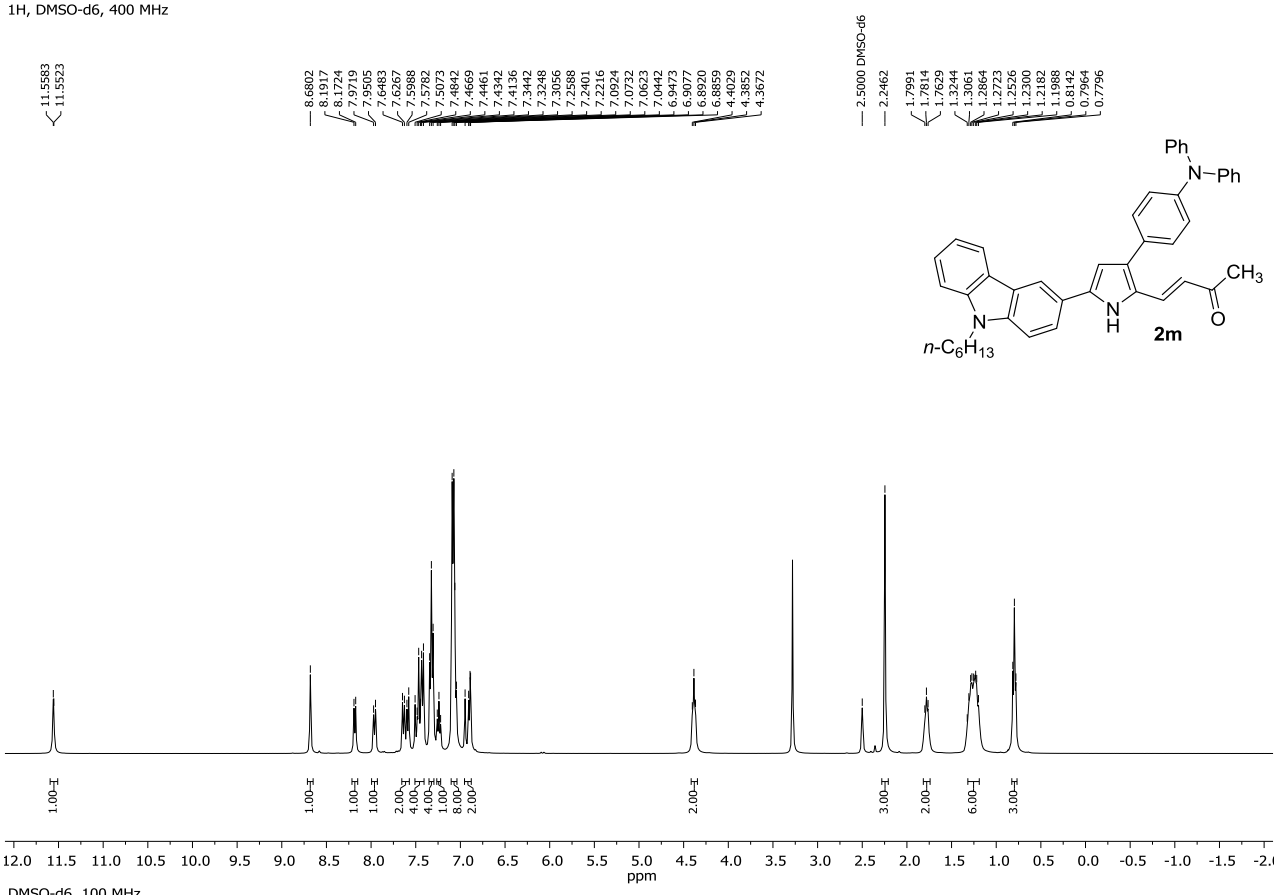
1H, CDCl3, 400 MHz



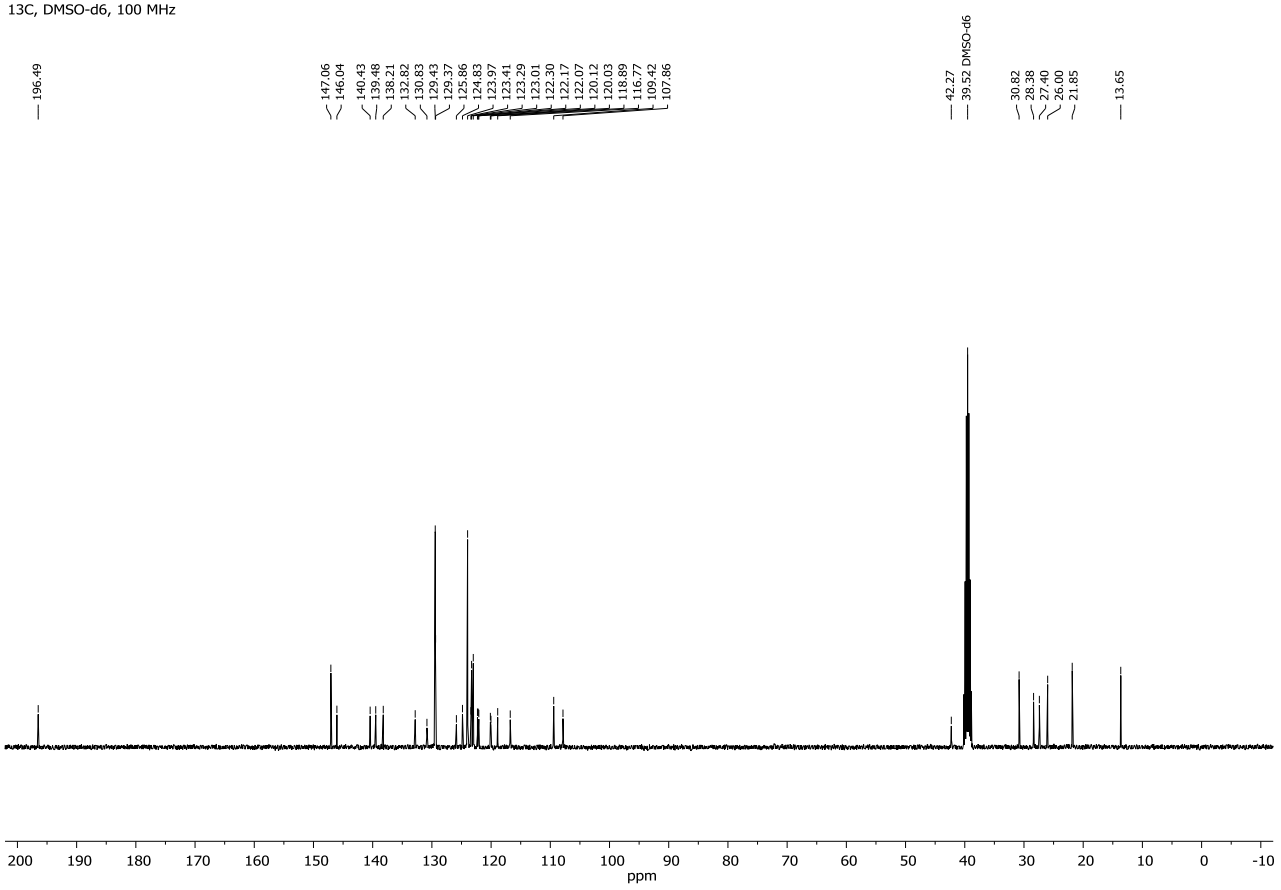
13C, CDCl3, 100 MHz



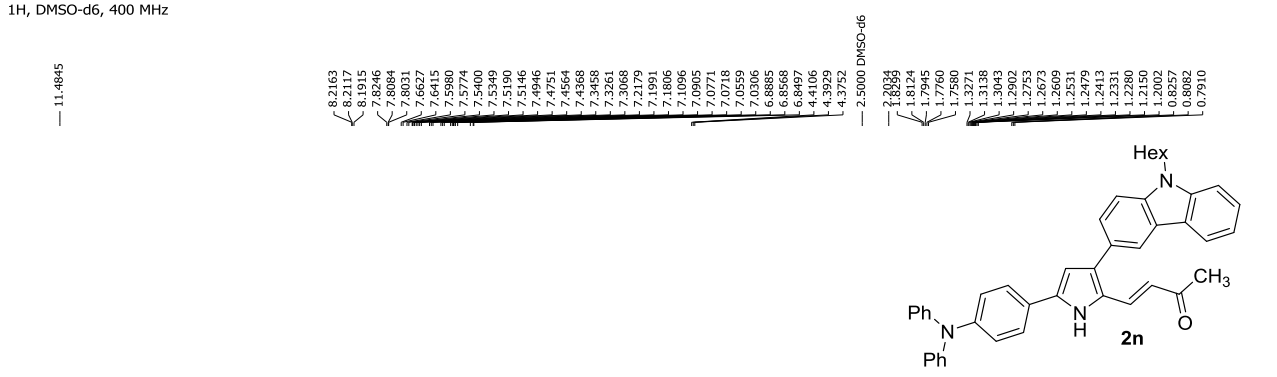
1H, DMSO-d6, 400 MHz



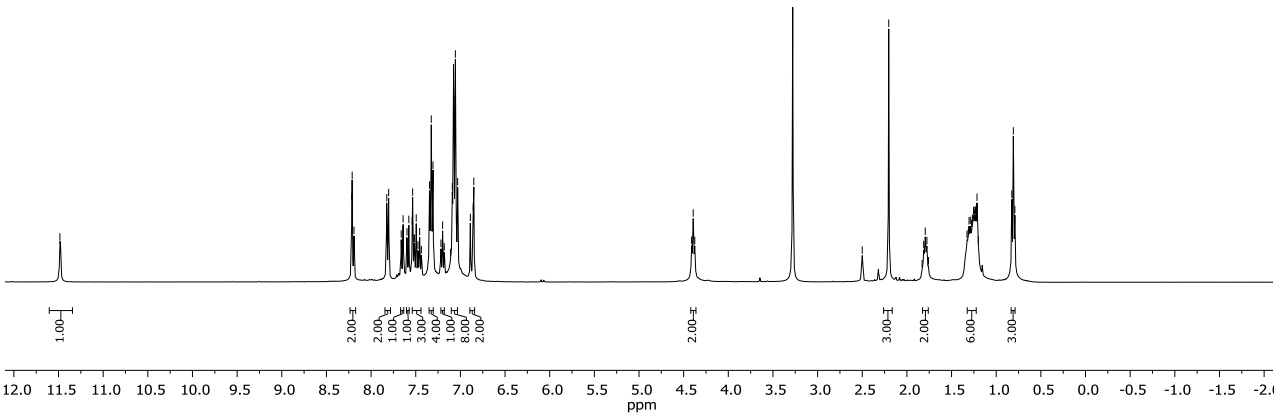
13C, DMSO-d6, 100 MHz



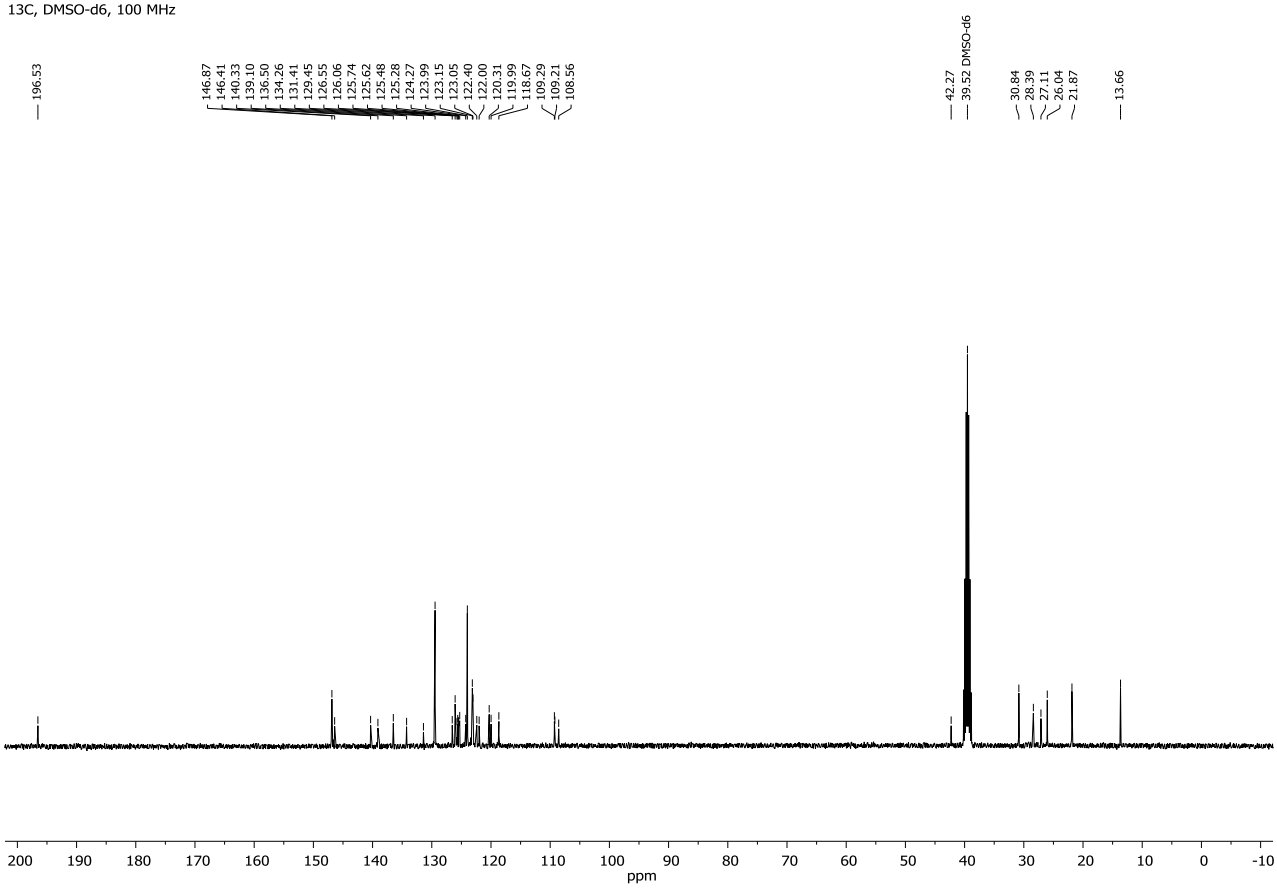
1H, DMSO-d6, 400 MHz



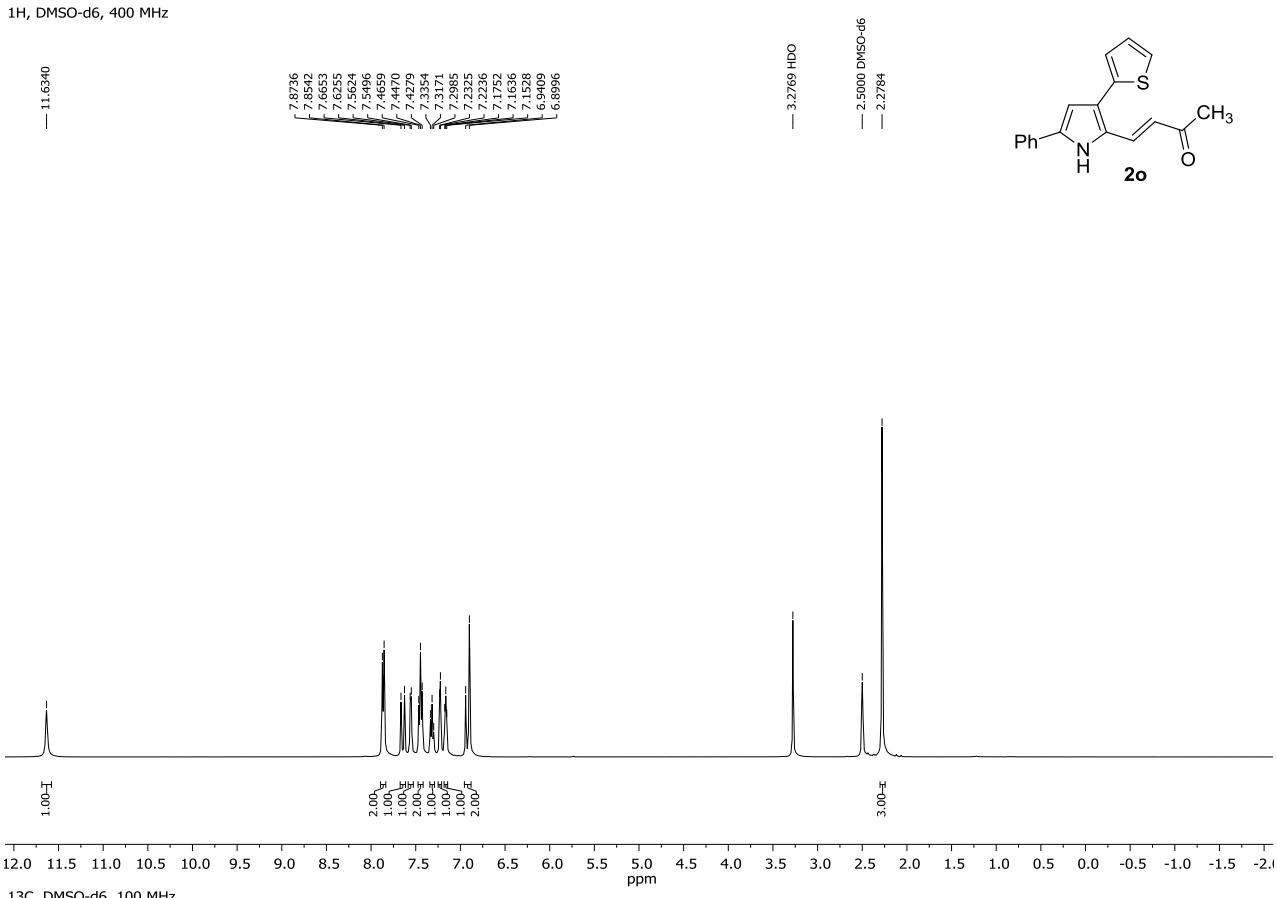
2n



13C, DMSO-d6, 100 MHz

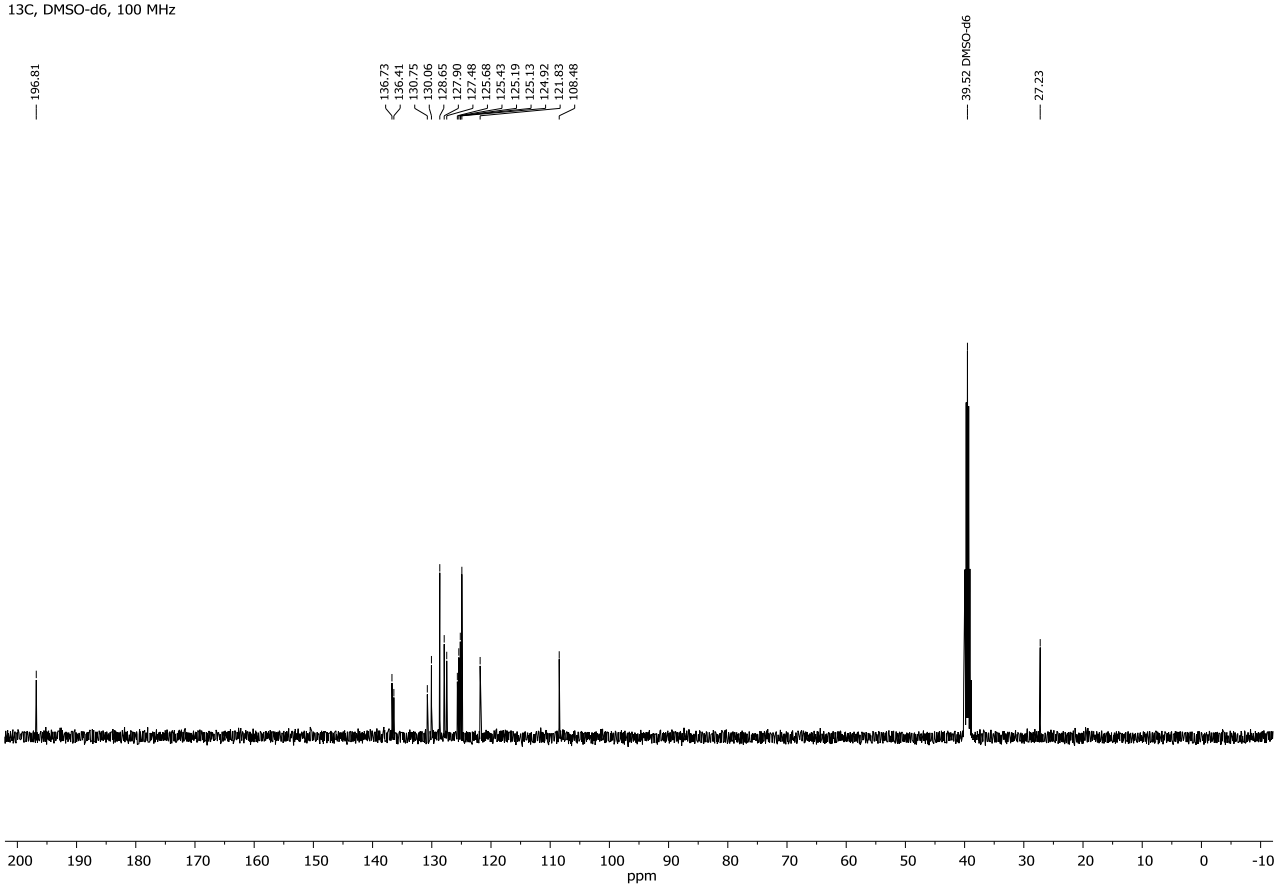


1H, DMSO-d6, 400 MHz

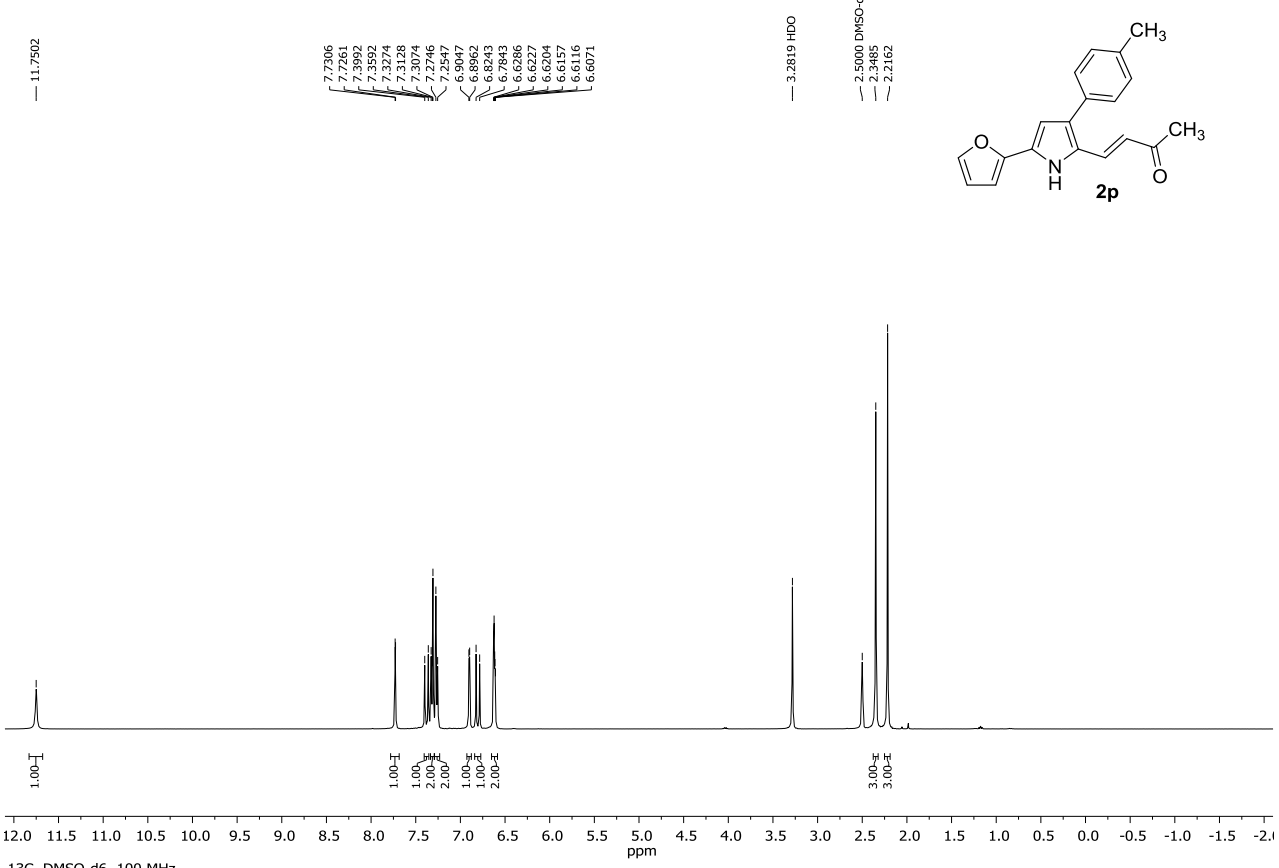


2o

13C, DMSO-d6, 100 MHz

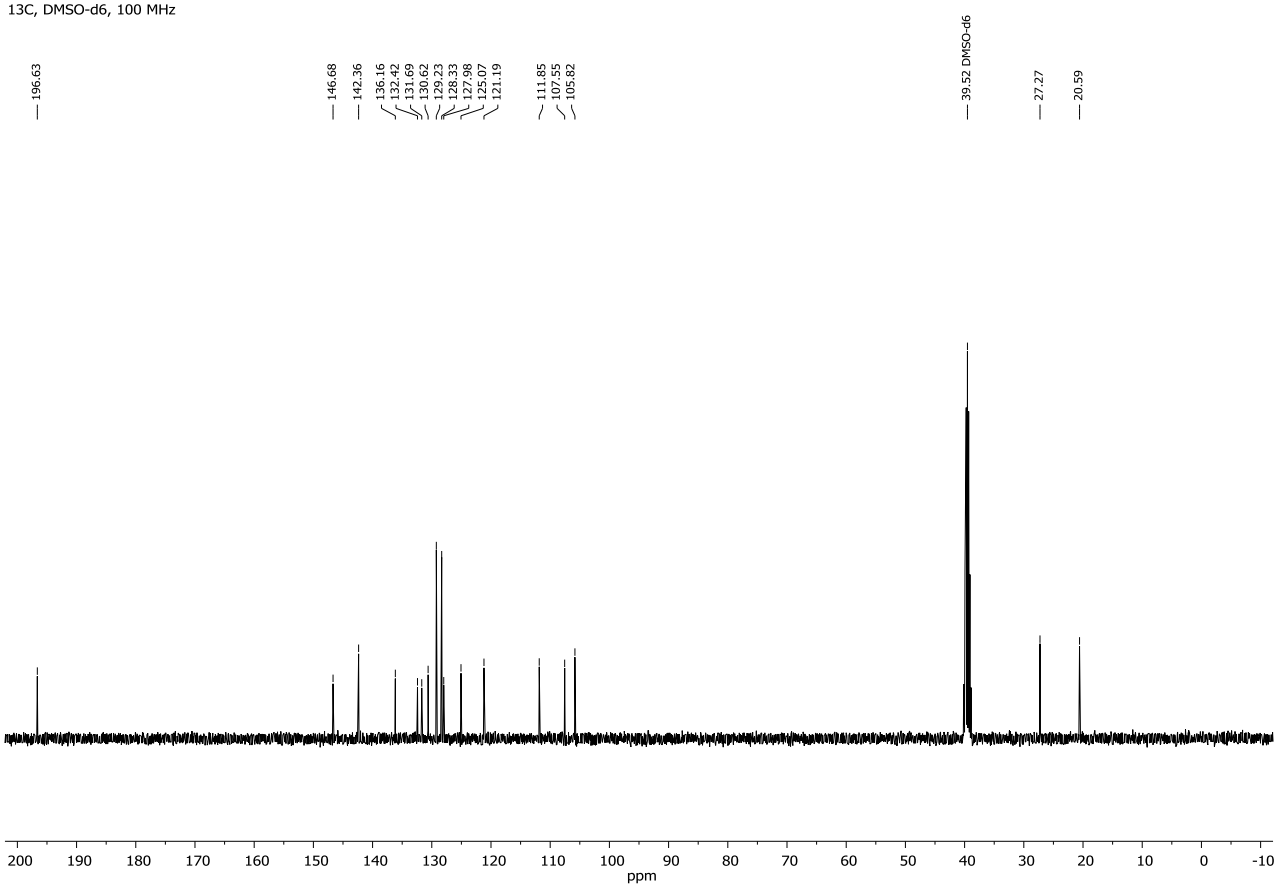


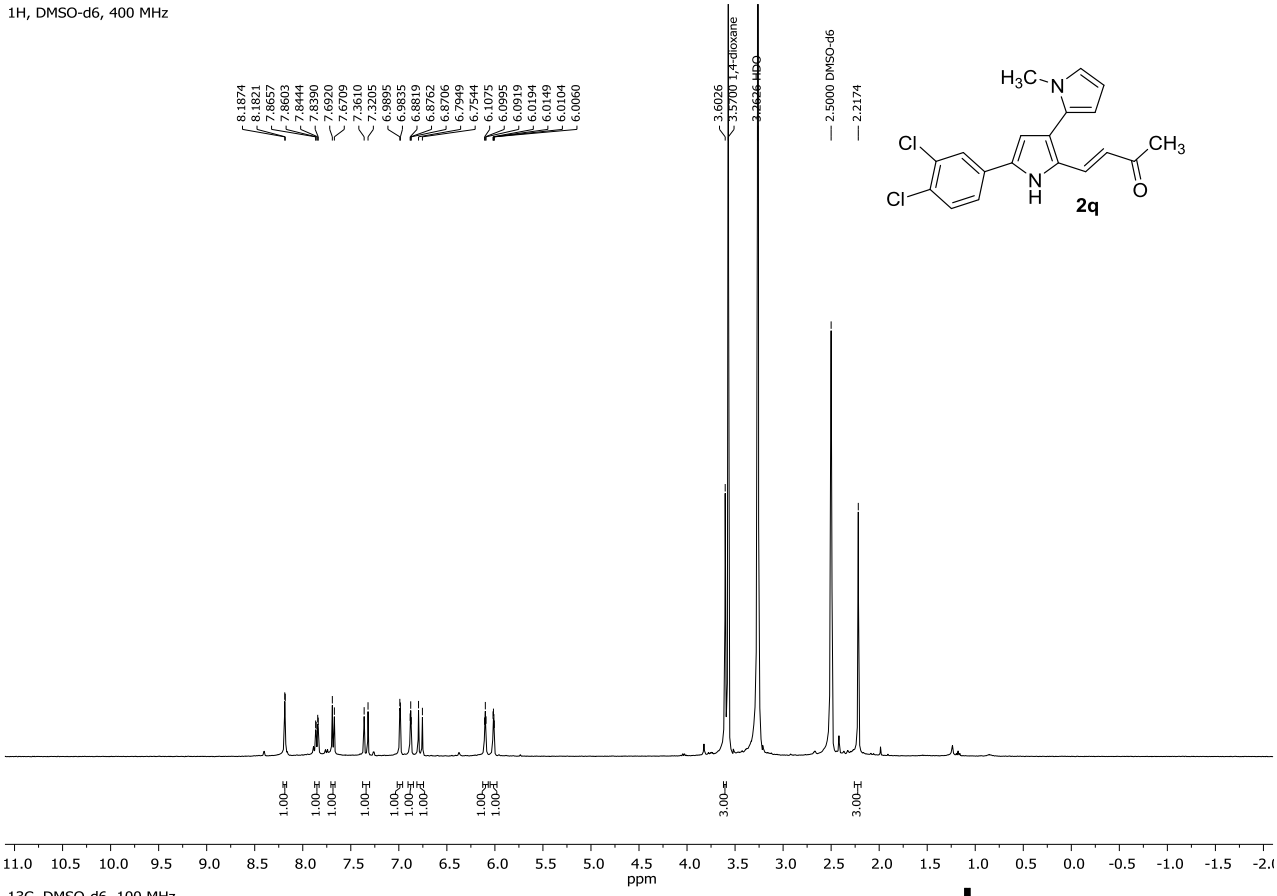
1H, DMSO-d6, 400 MHz



2p

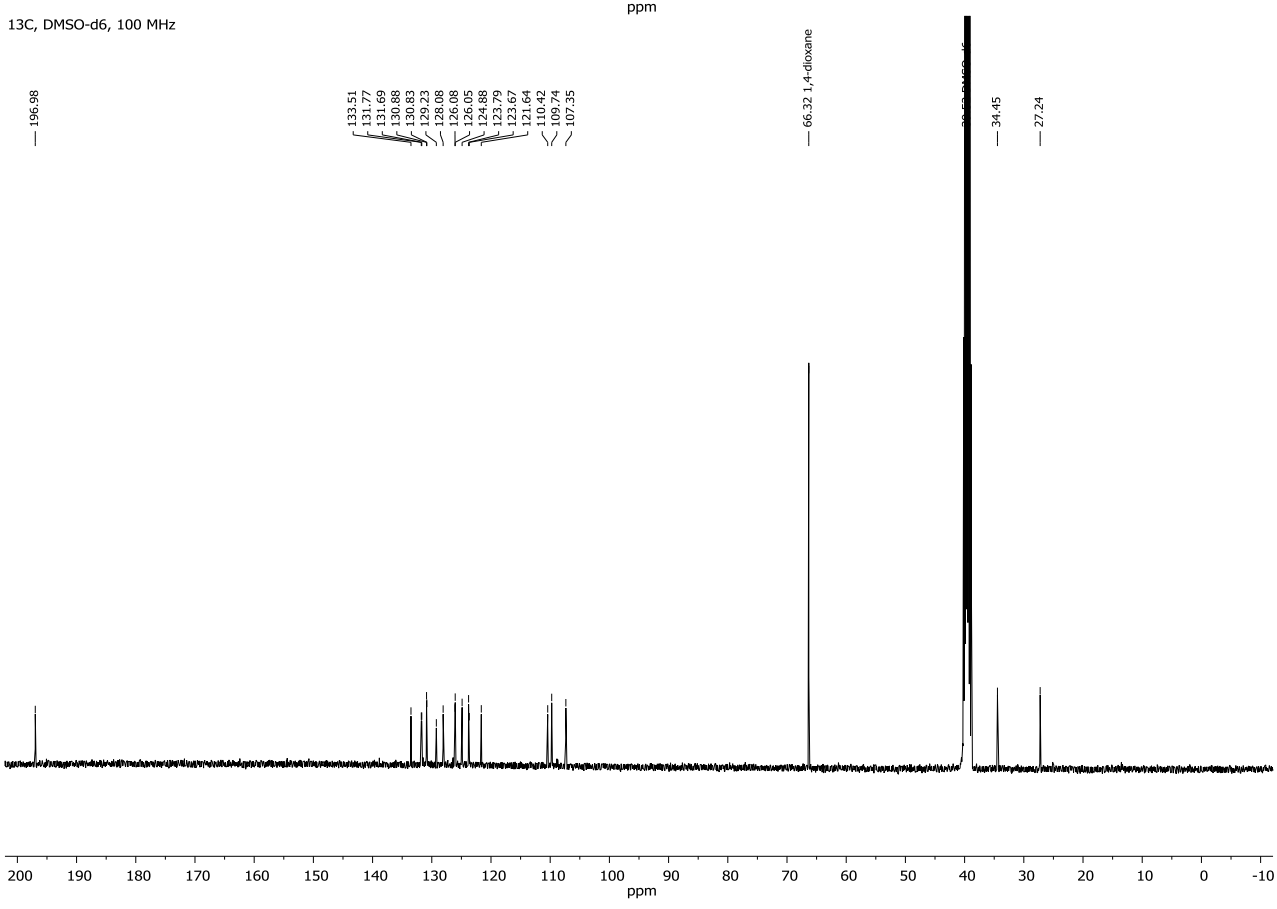
13C, DMSO-d6, 100 MHz



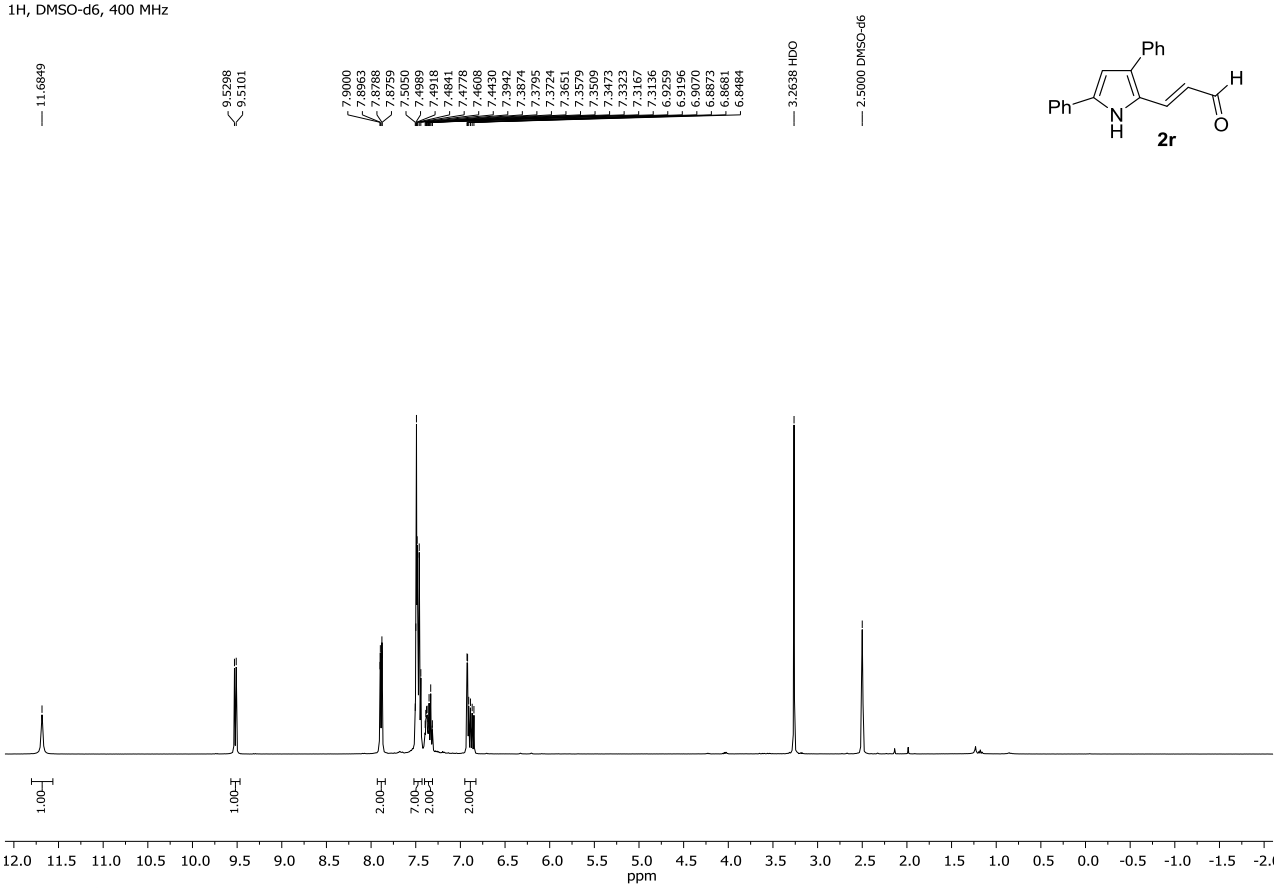

1H, DMSO-d6, 400 MHz
8.1874
8.1821
7.8657
7.8603
7.8444
7.8390
7.6920
7.6709
7.3610
7.3205
6.9895
6.9835
6.8819
6.8762
6.8706
6.7949
6.7544
6.1075
6.0995
6.0919
6.0194
6.0149
6.0104
6.0060
3.6026
3.5700 1,4-dioxane
3.2636 HDO
2.5000 DMSO-d6
2.2174
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
ppm

H3C
N
Cl
Cl
N
H
CH3
O

2q

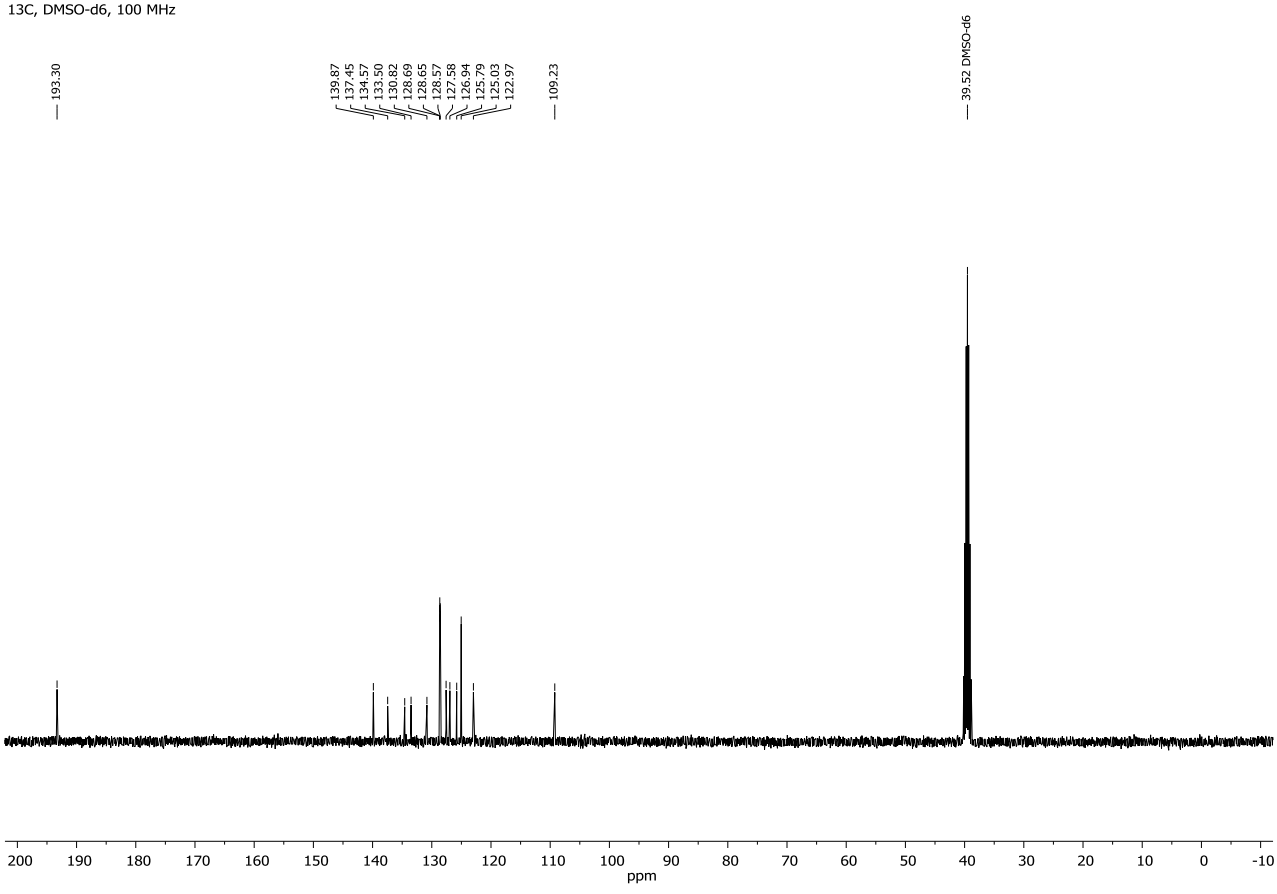

13C, DMSO-d6, 100 MHz
196.98
133.51
131.77
131.69
130.88
130.83
129.23
128.08
126.08
126.05
124.88
123.79
123.67
121.64
110.42
109.74
107.35
66.32 1,4-dioxane
39.53 DMSO-d6
34.45
27.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

1H, DMSO-d6, 400 MHz

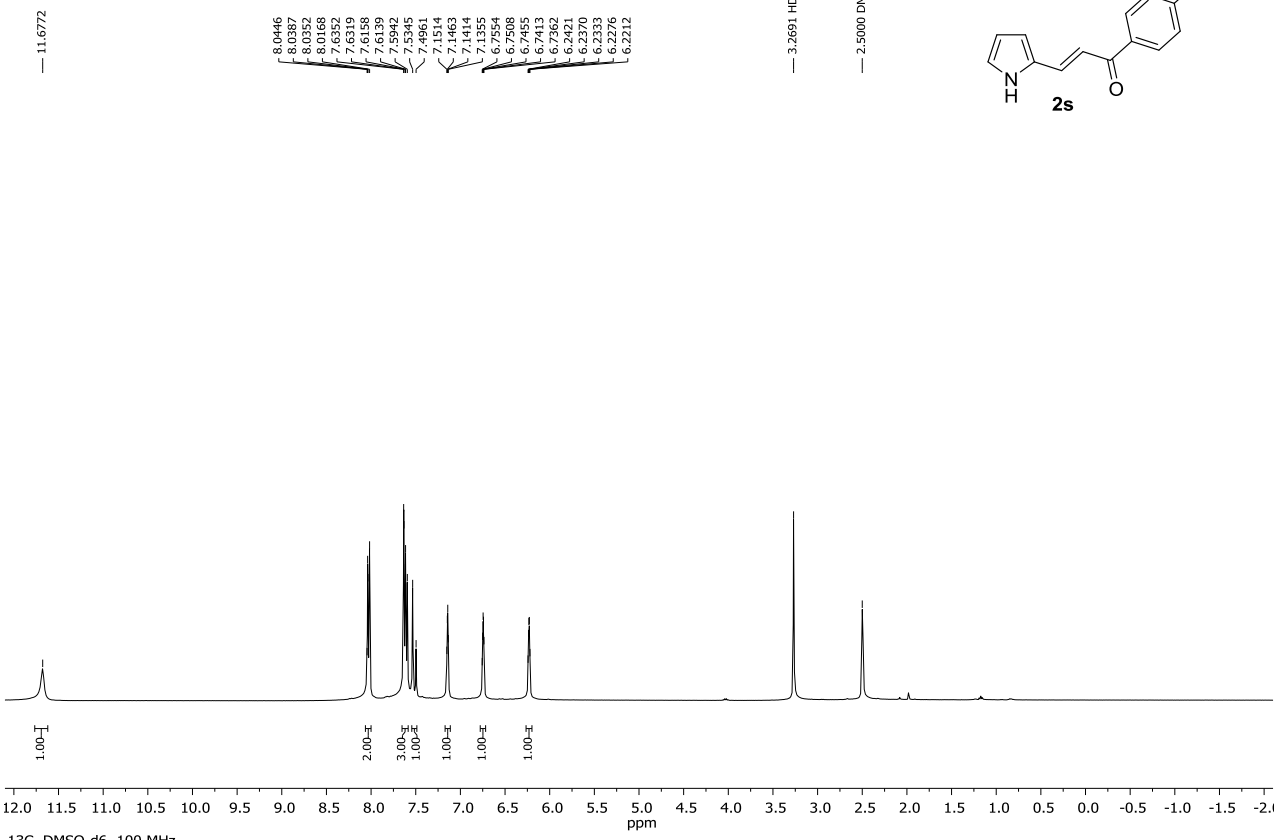


2r

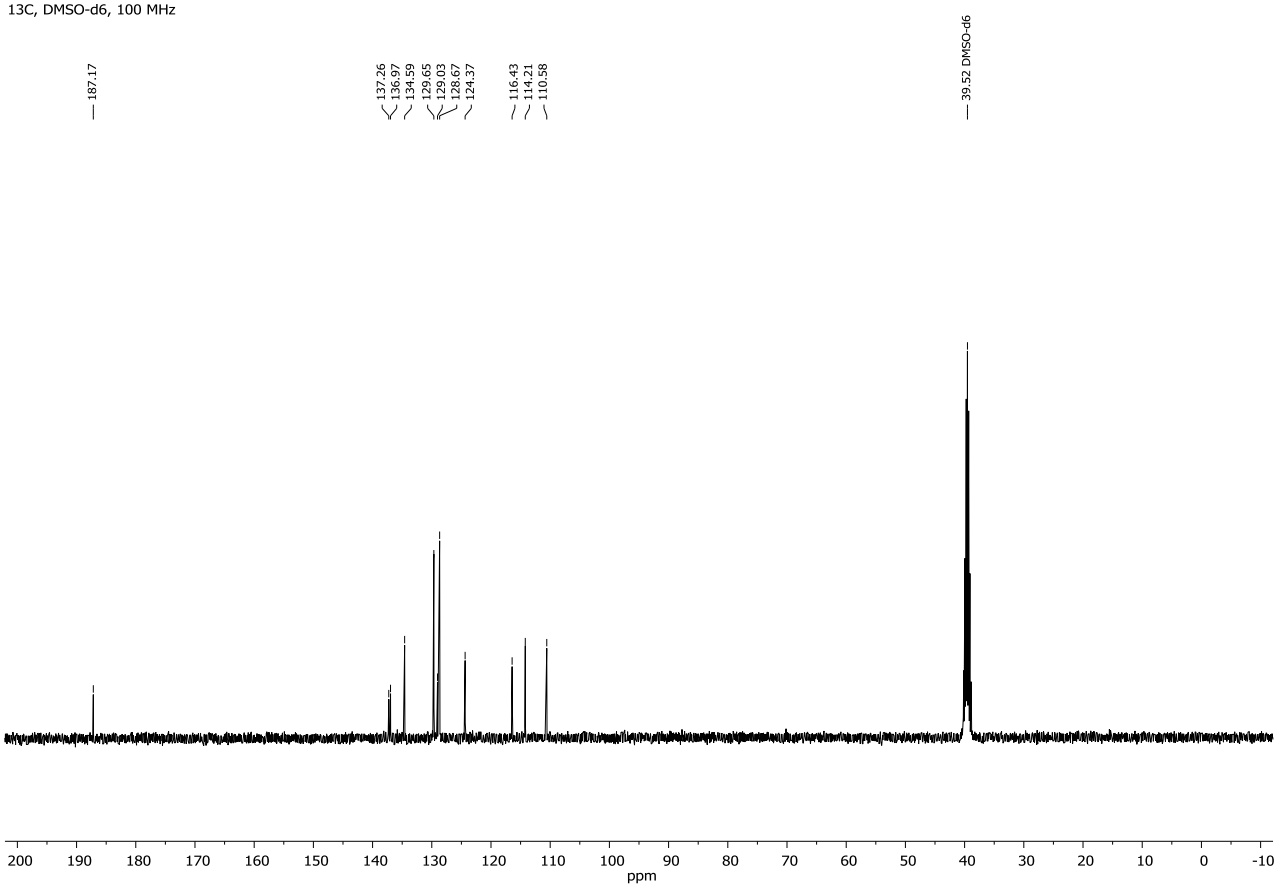
13C, DMSO-d6, 100 MHz



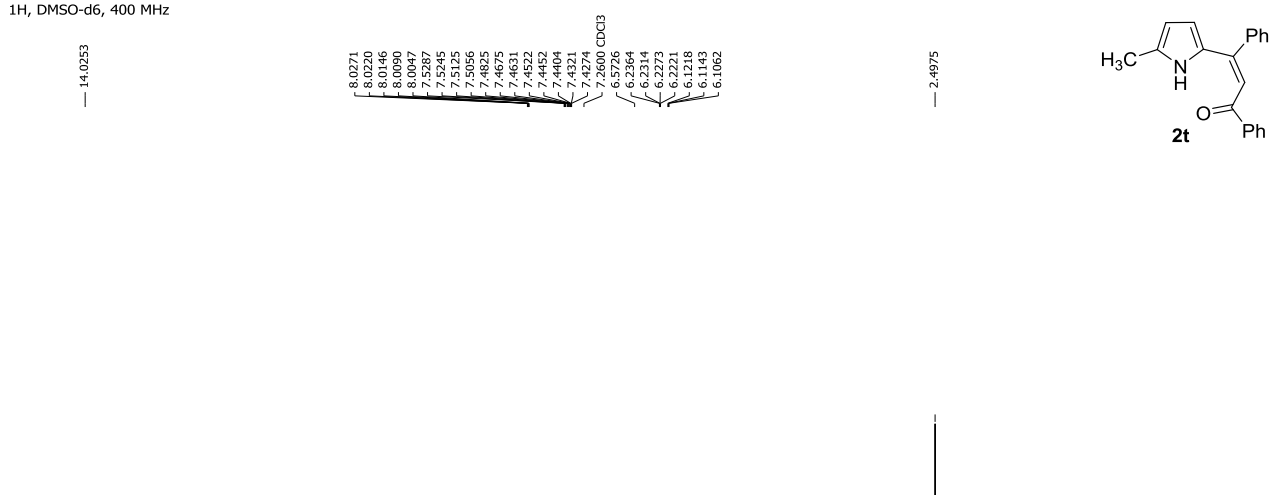
1H, DMSO-d6, 400 MHz



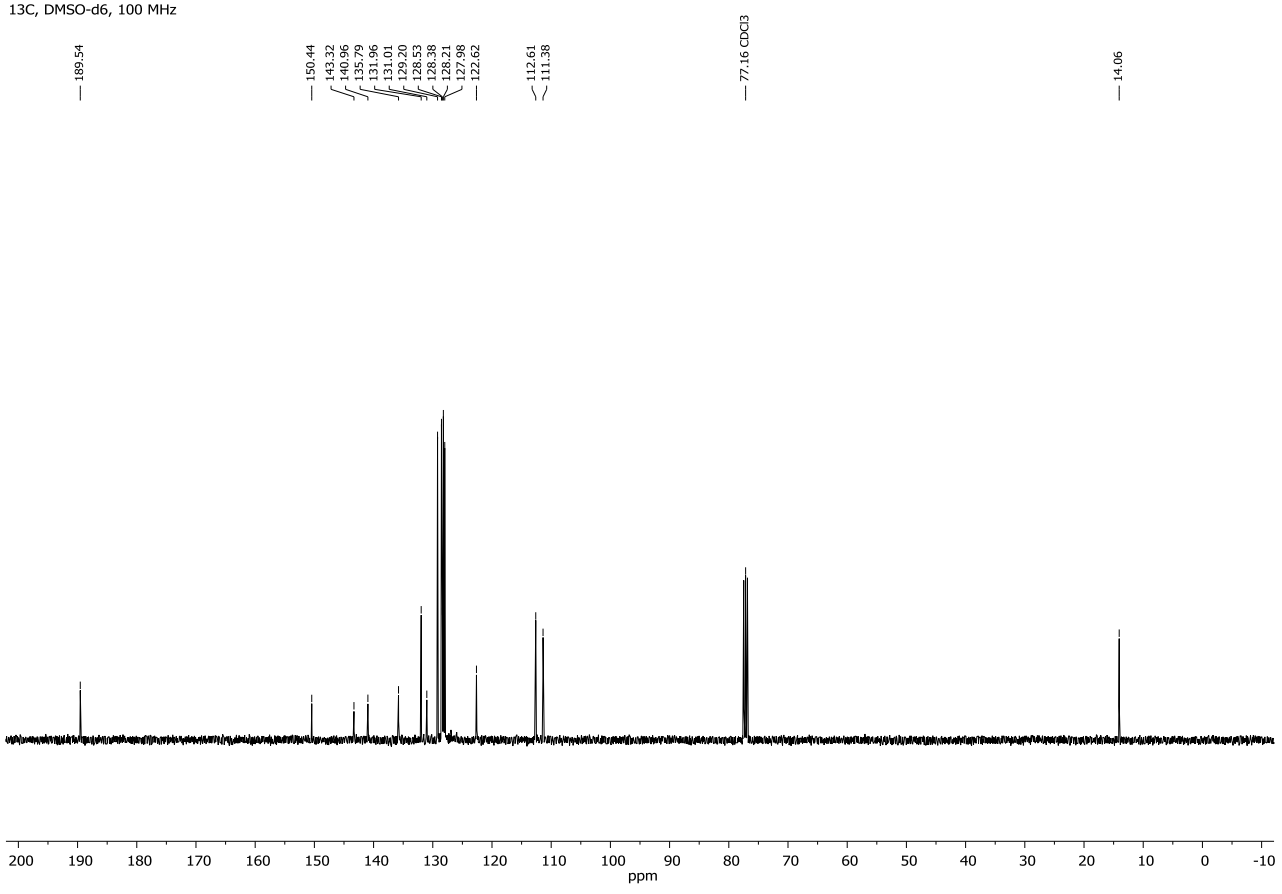
13C, DMSO-d6, 100 MHz



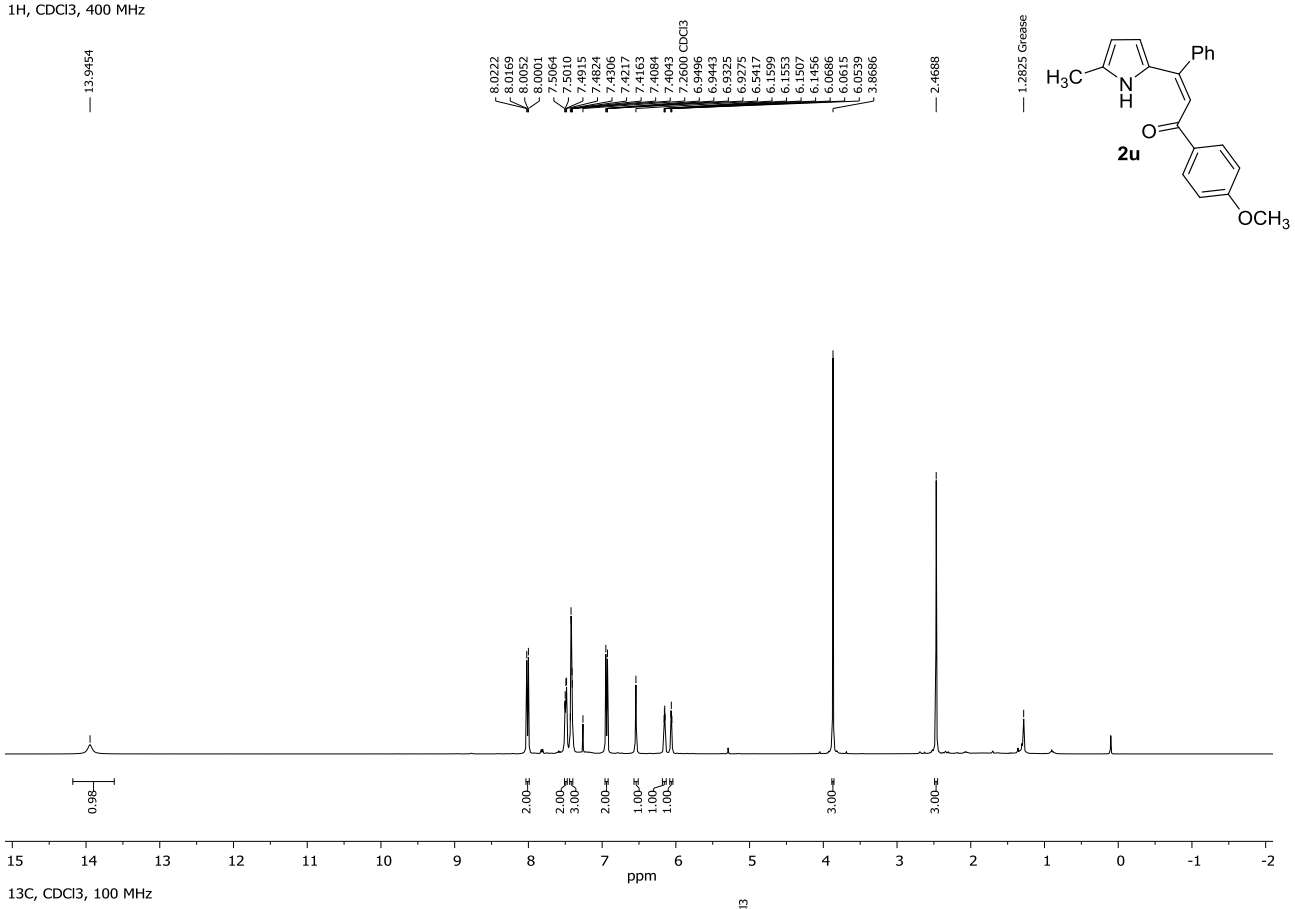
1H, DMSO-d6, 400 MHz



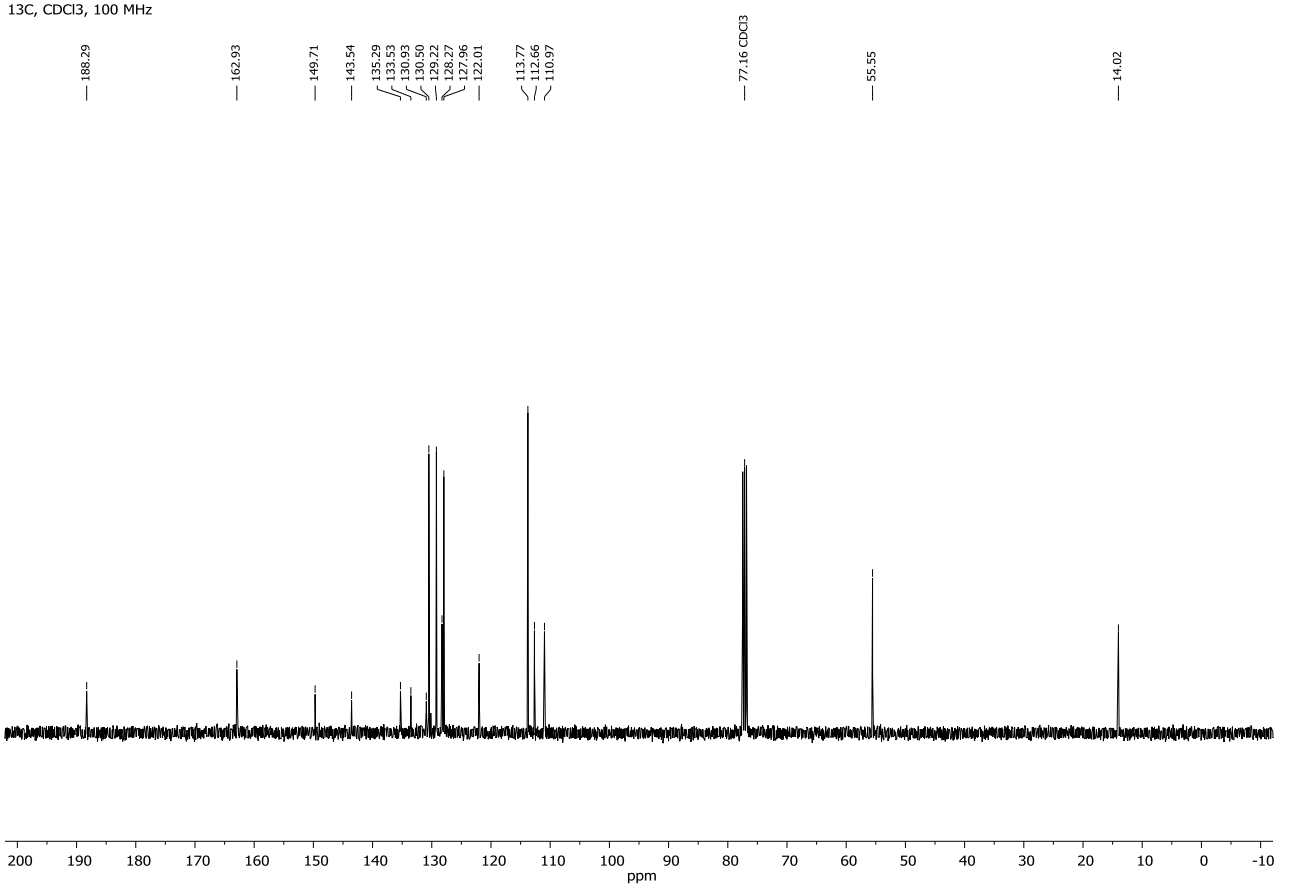
13C, DMSO-d6, 100 MHz



1H, CDCl3, 400 MHz

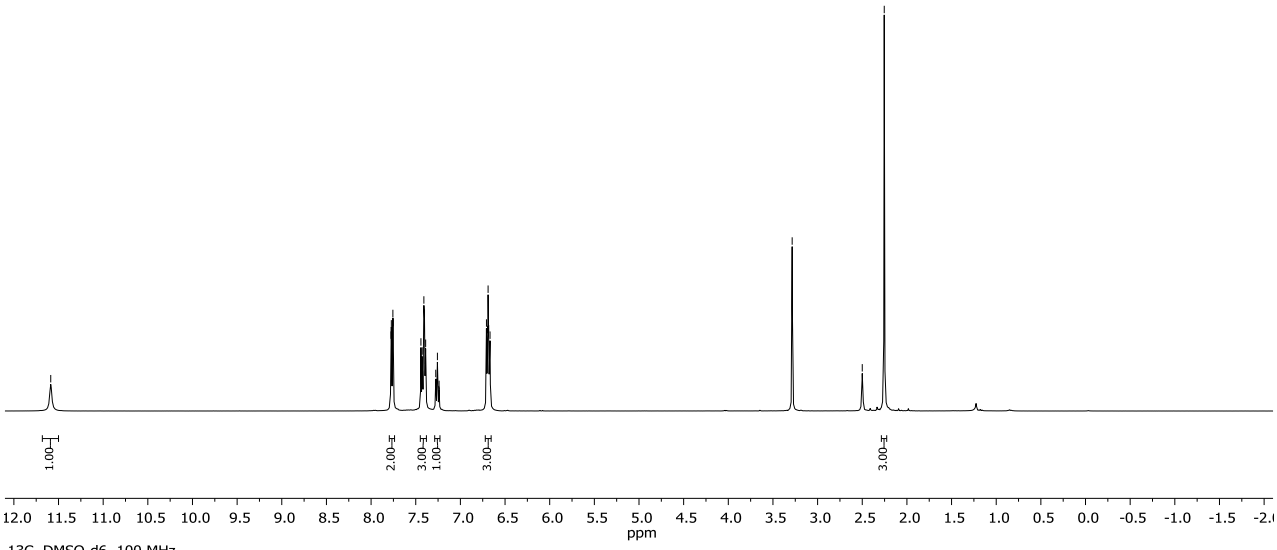


13C, CDCl3, 100 MHz

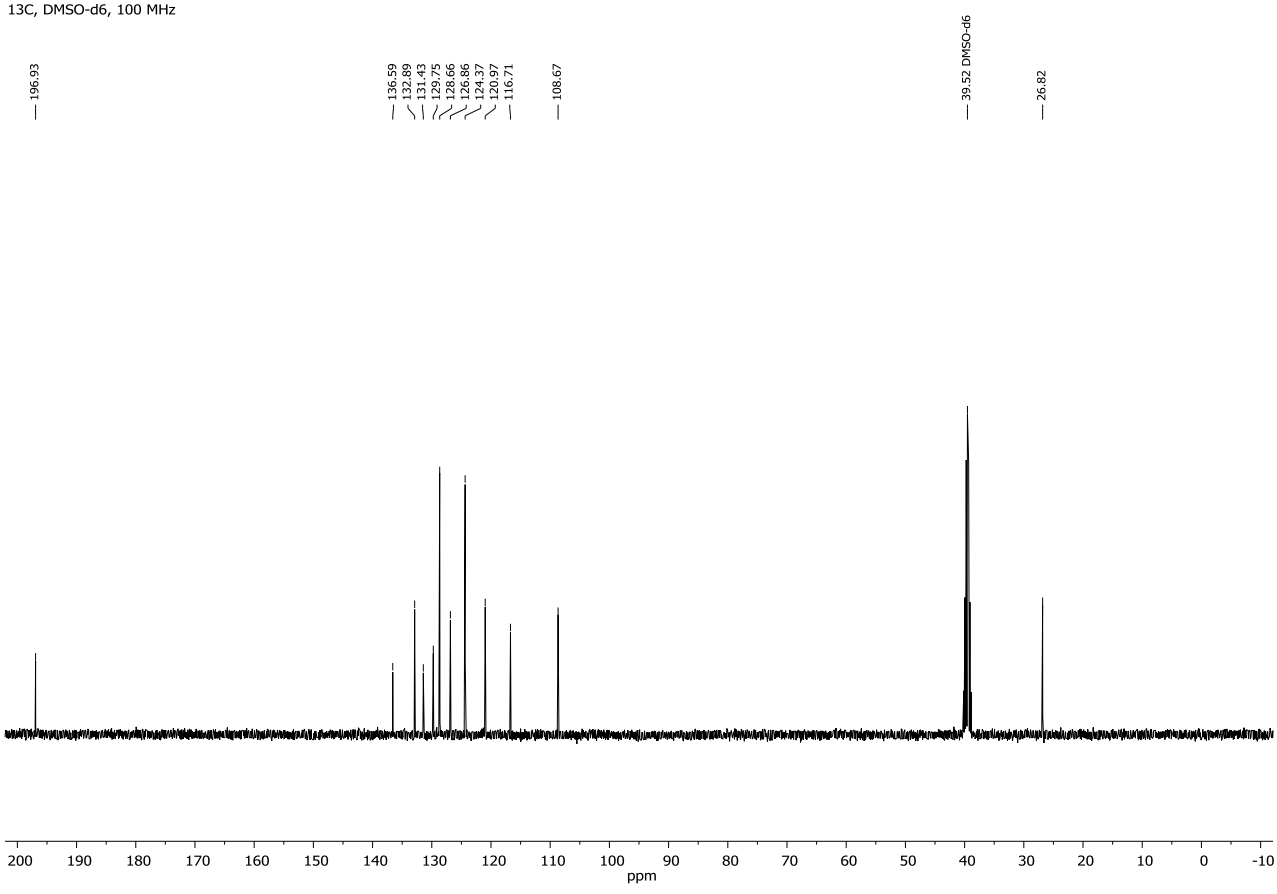


1H, DMSO-d6, 400 MHz

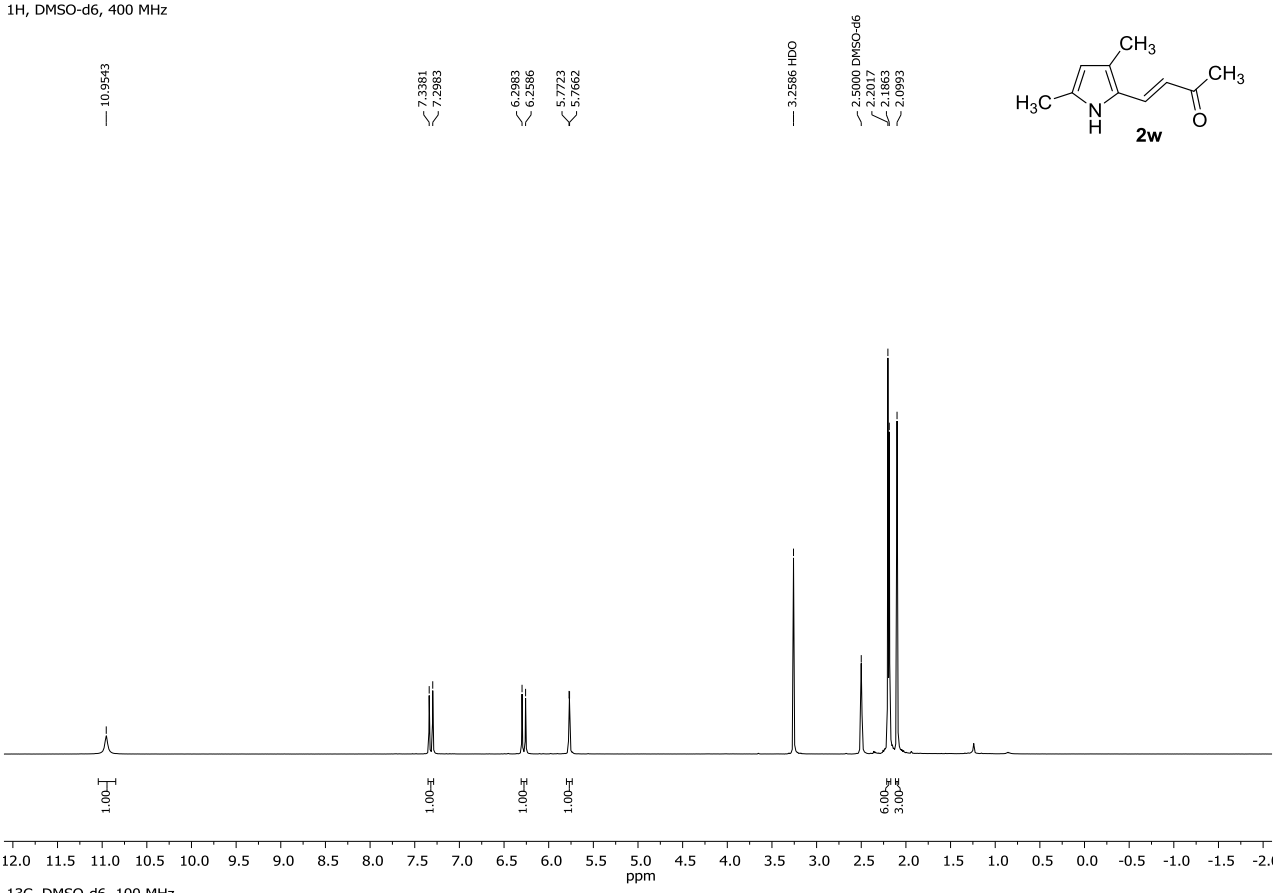
2v



13C, DMSO-d6, 100 MHz

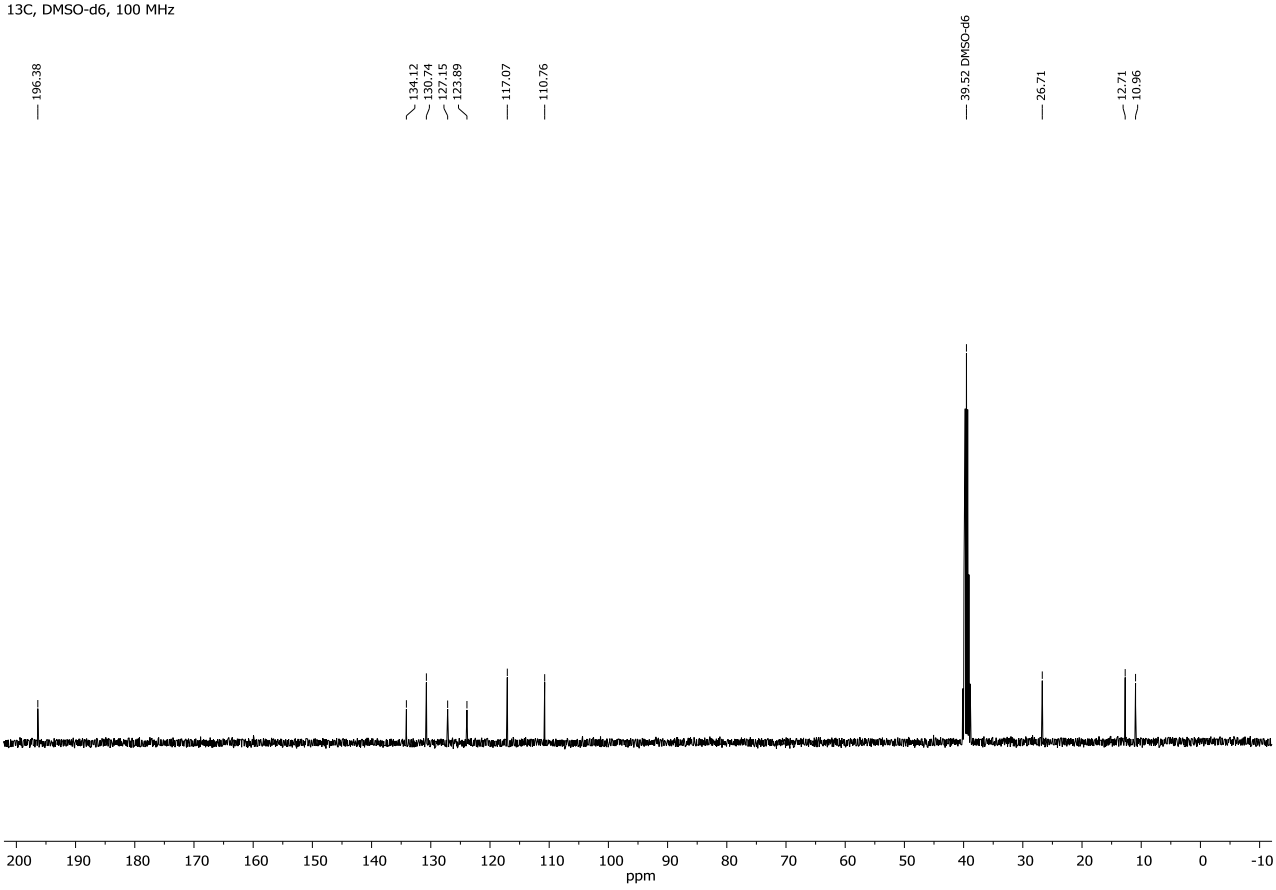


1H, DMSO-d6, 400 MHz

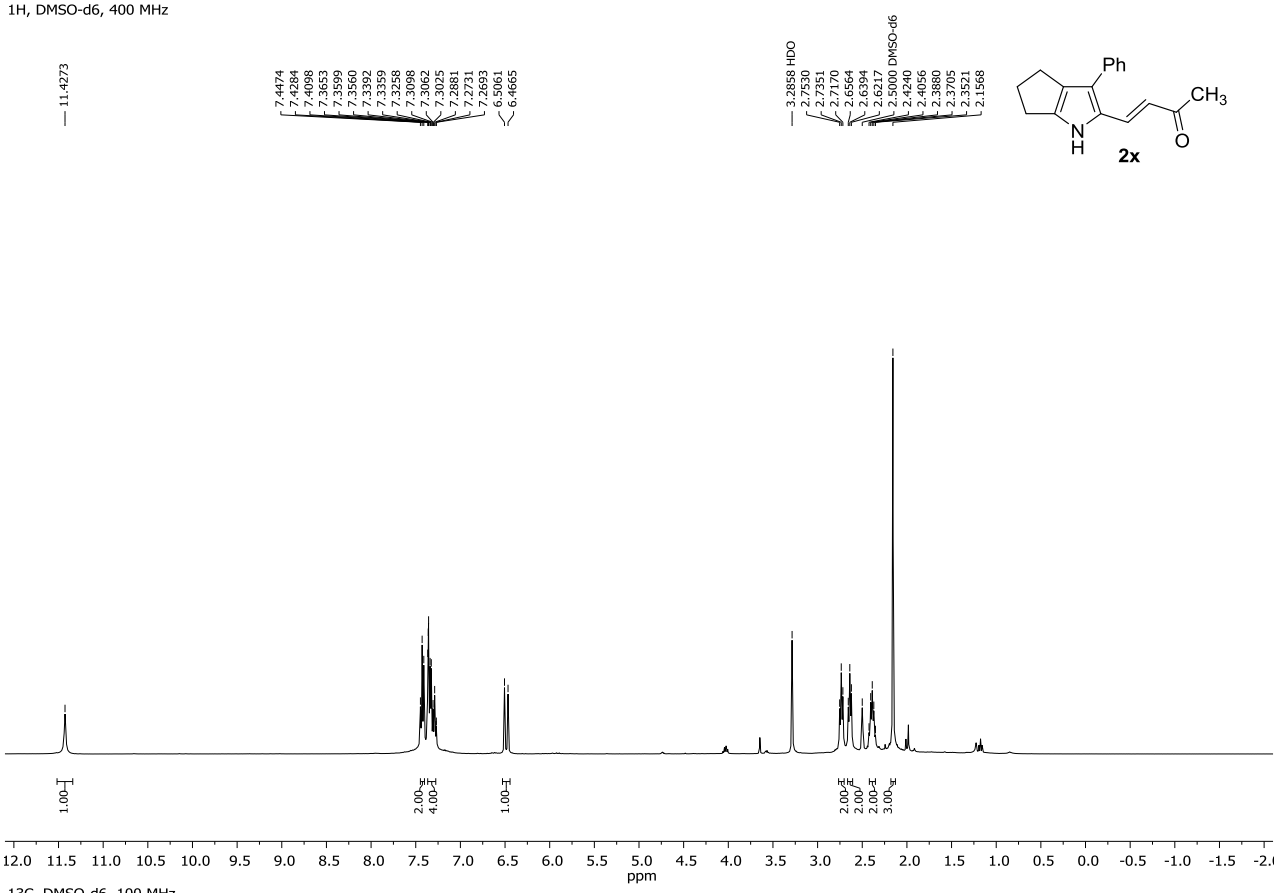


2w

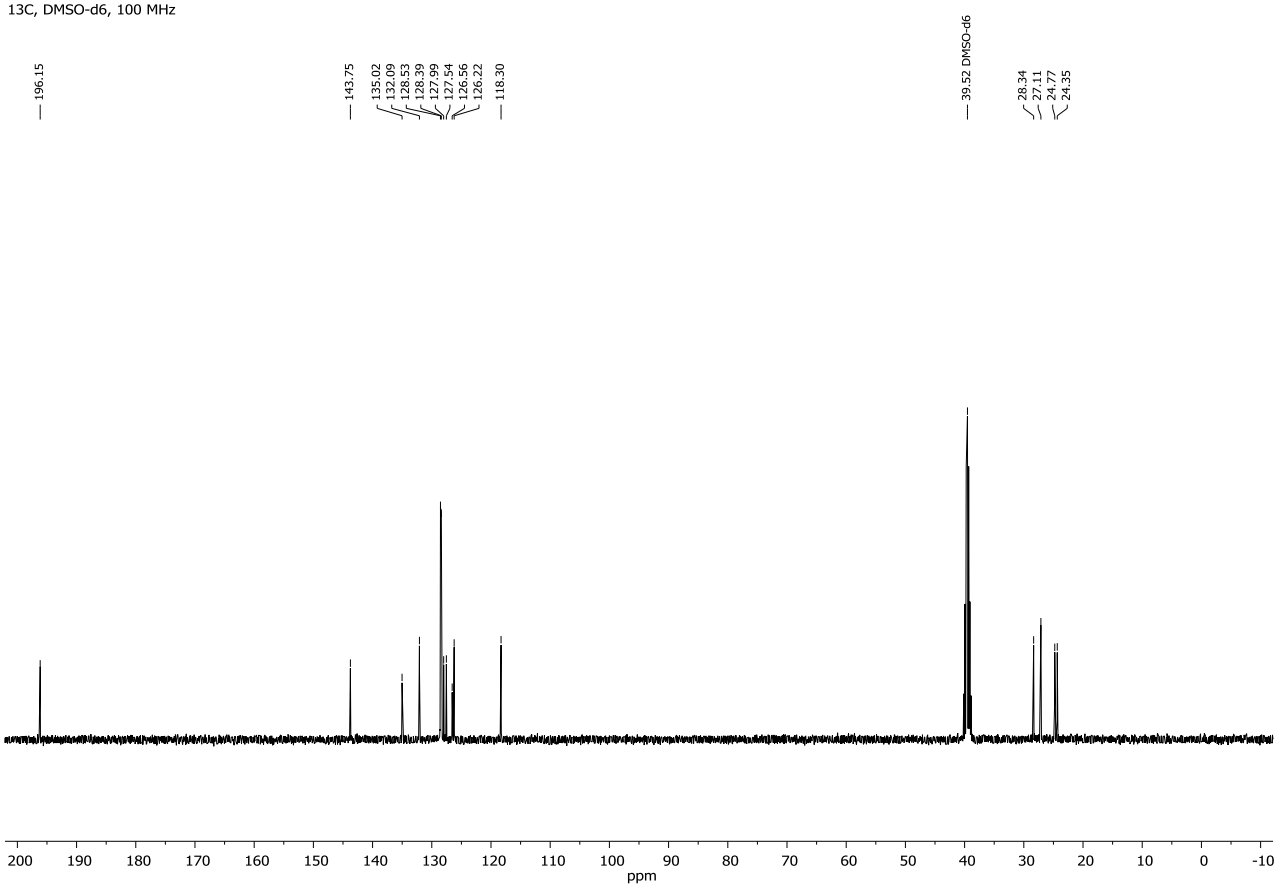
13C, DMSO-d6, 100 MHz



1H, DMSO-d6, 400 MHz

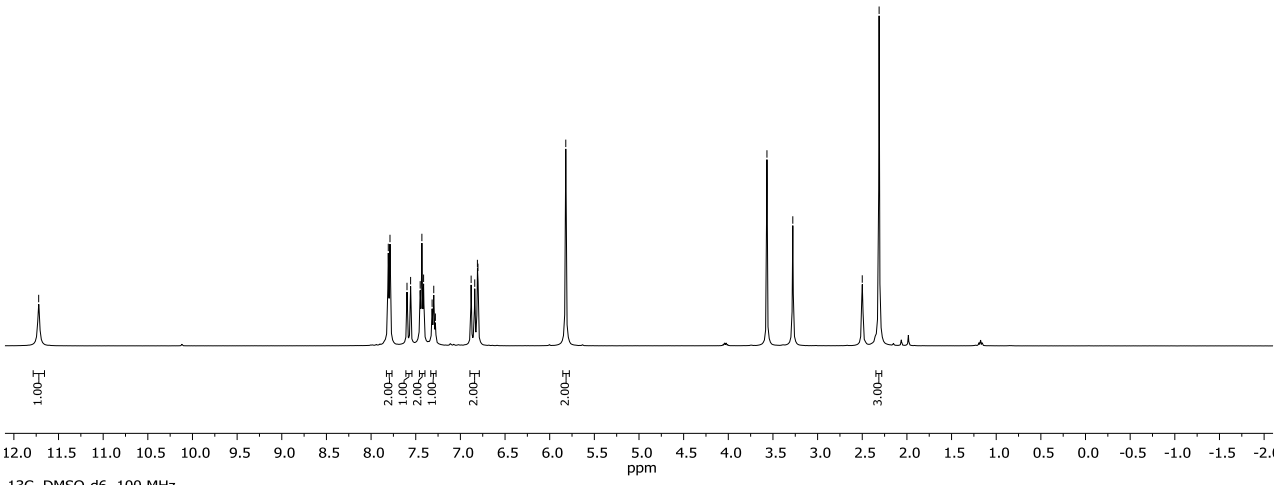


13C, DMSO-d6, 100 MHz

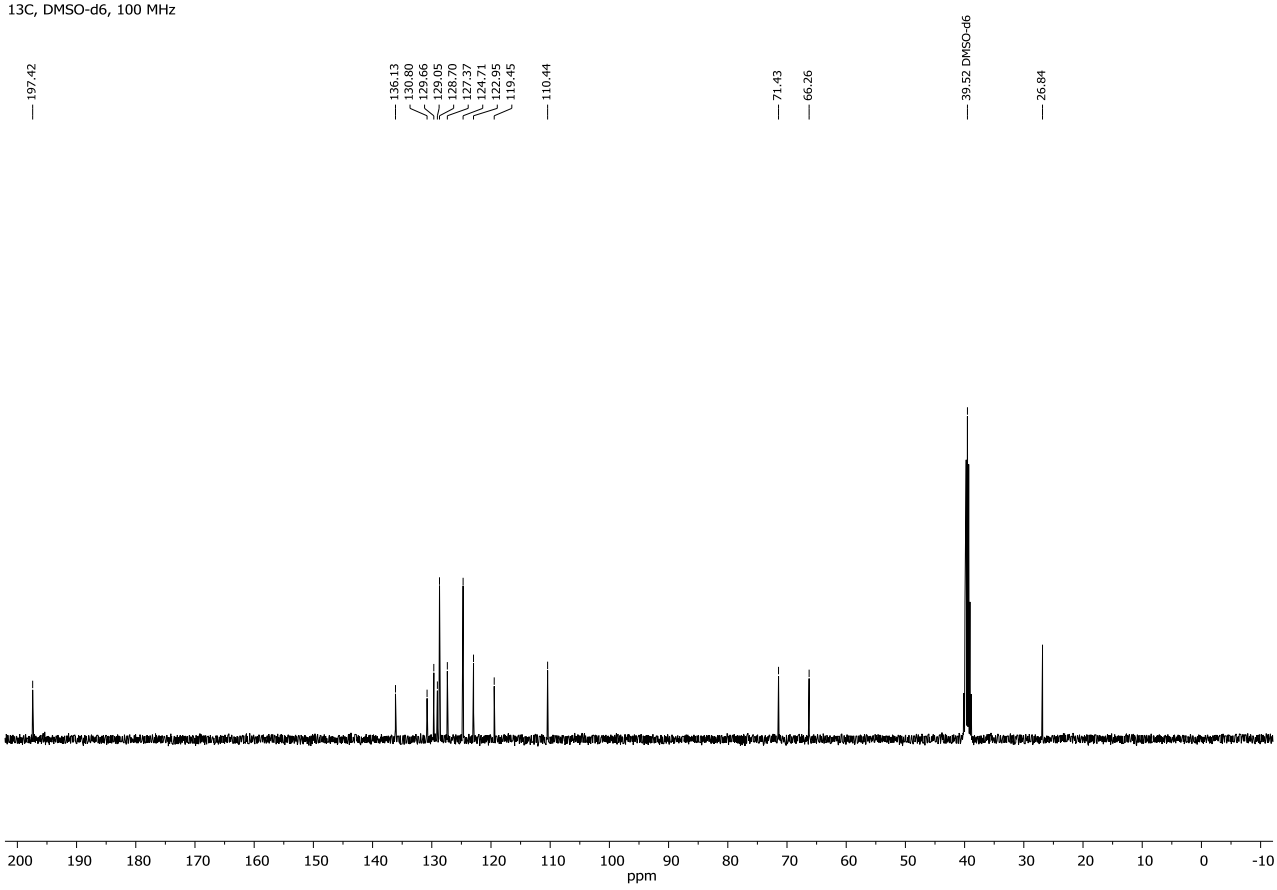


1H, DMSO-d6, 400 MHz

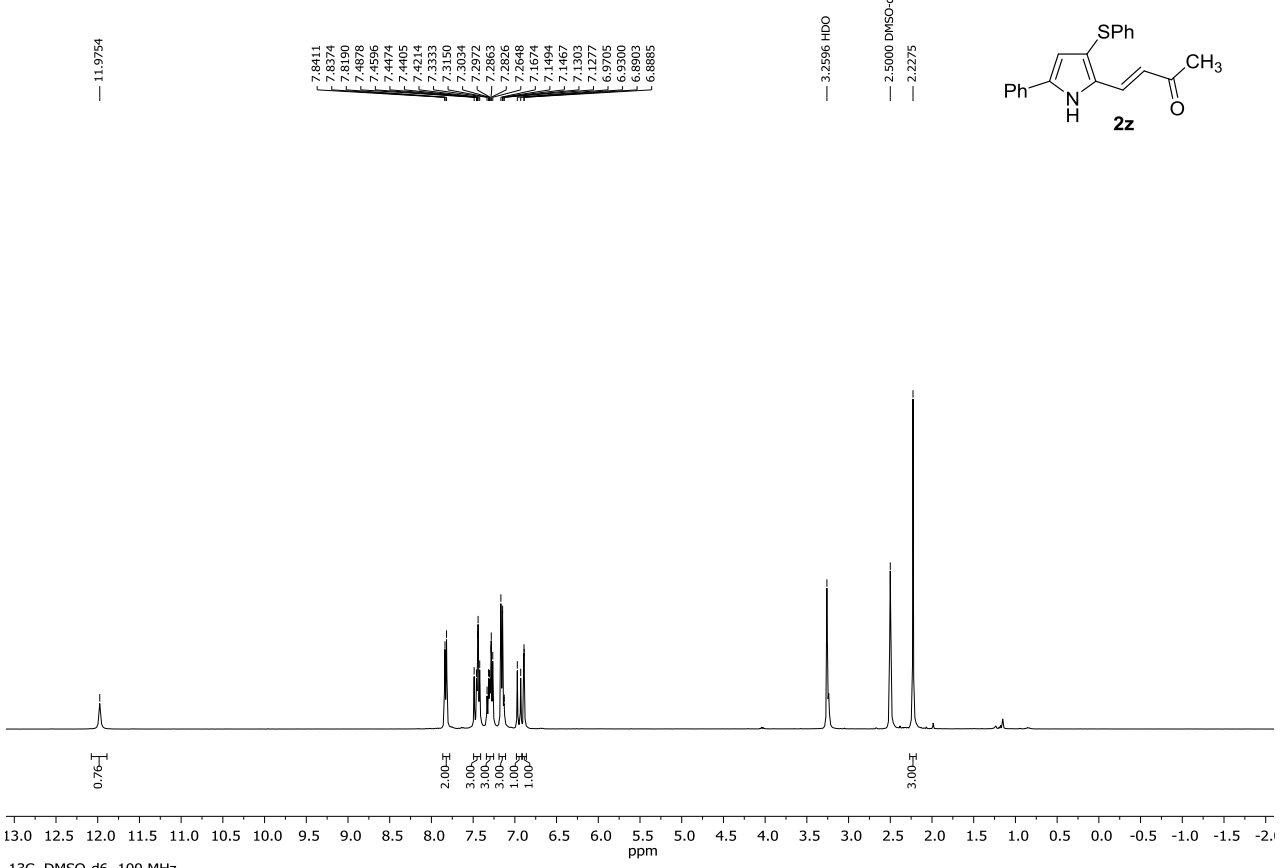
2y



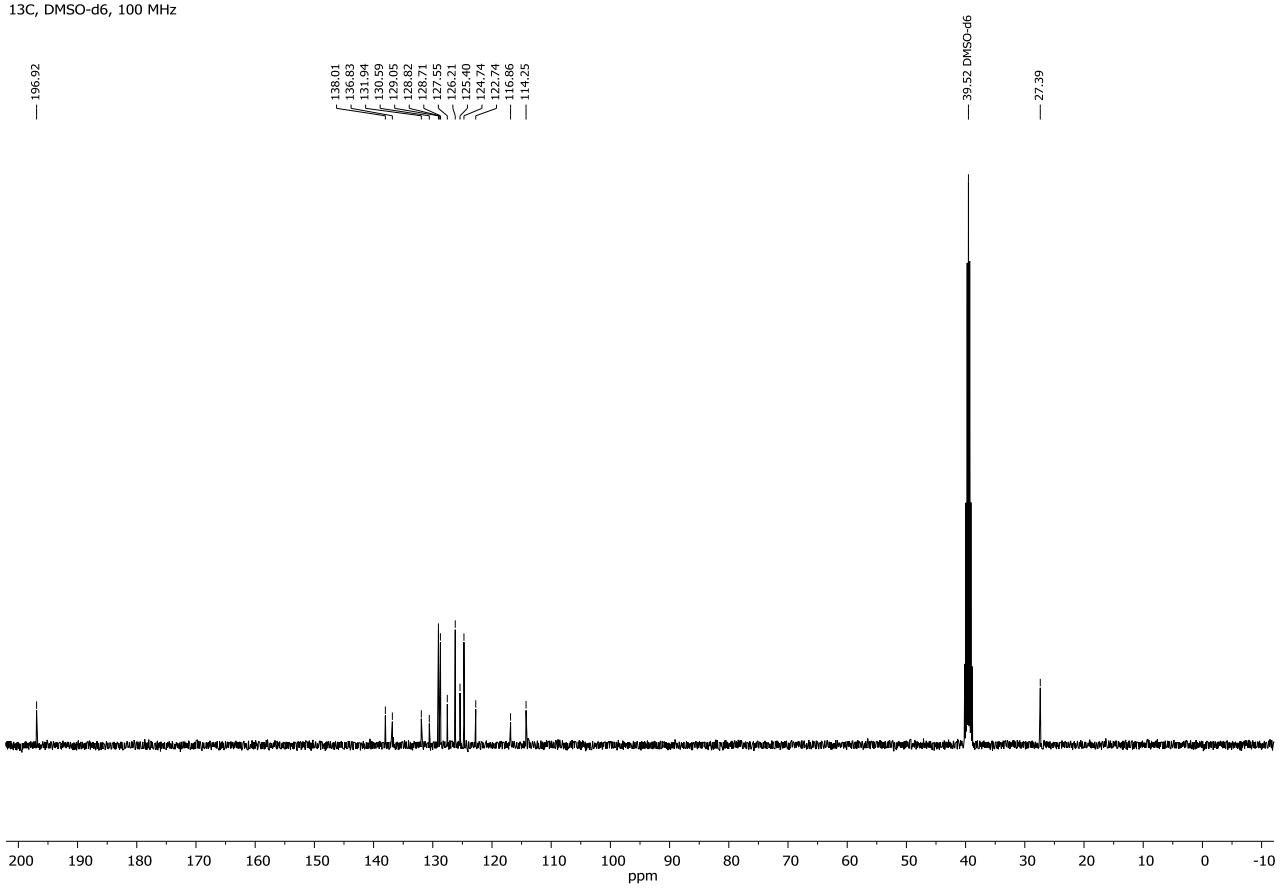
13C, DMSO-d6, 100 MHz



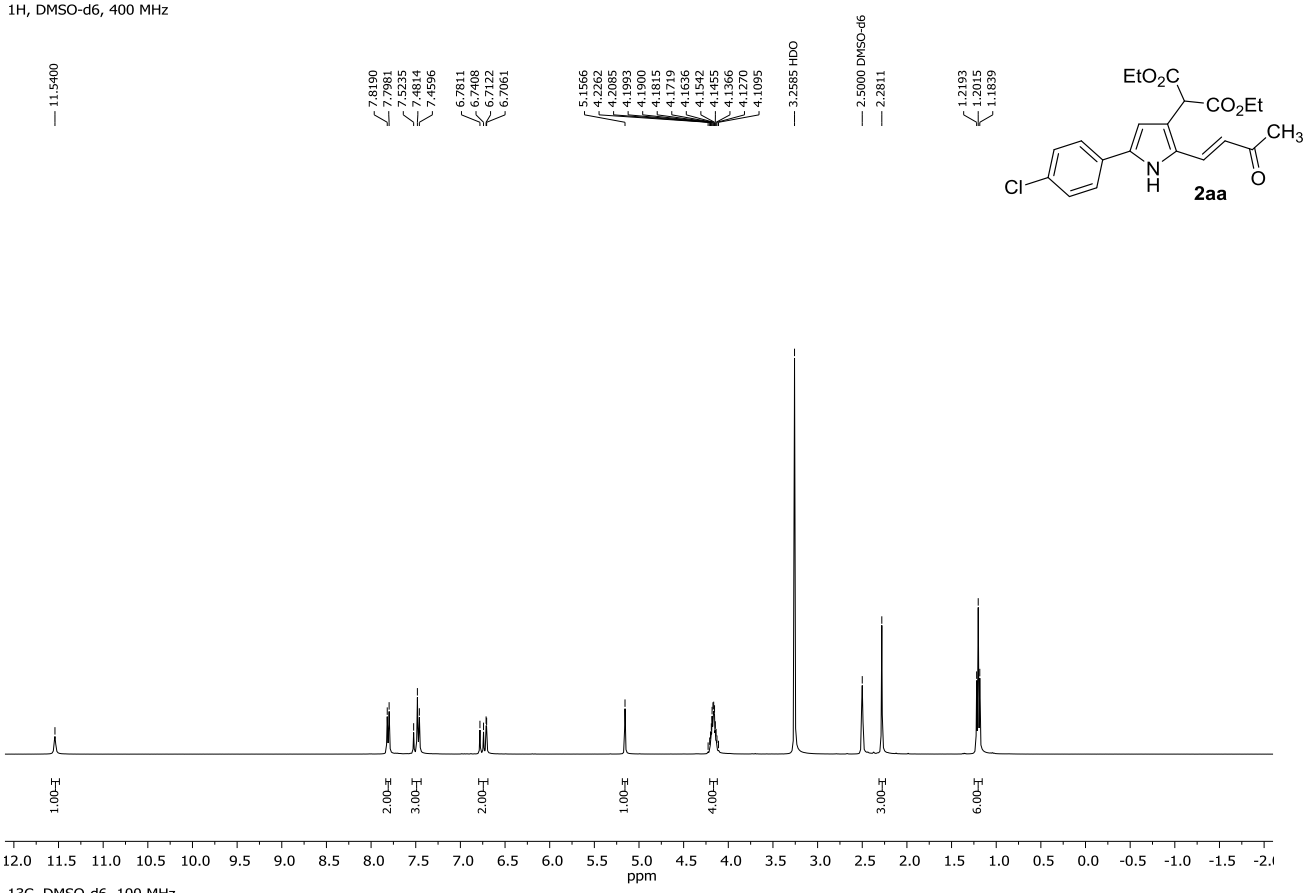
1H, DMSO-d6, 400 MHz



13C, DMSO-d6, 100 MHz

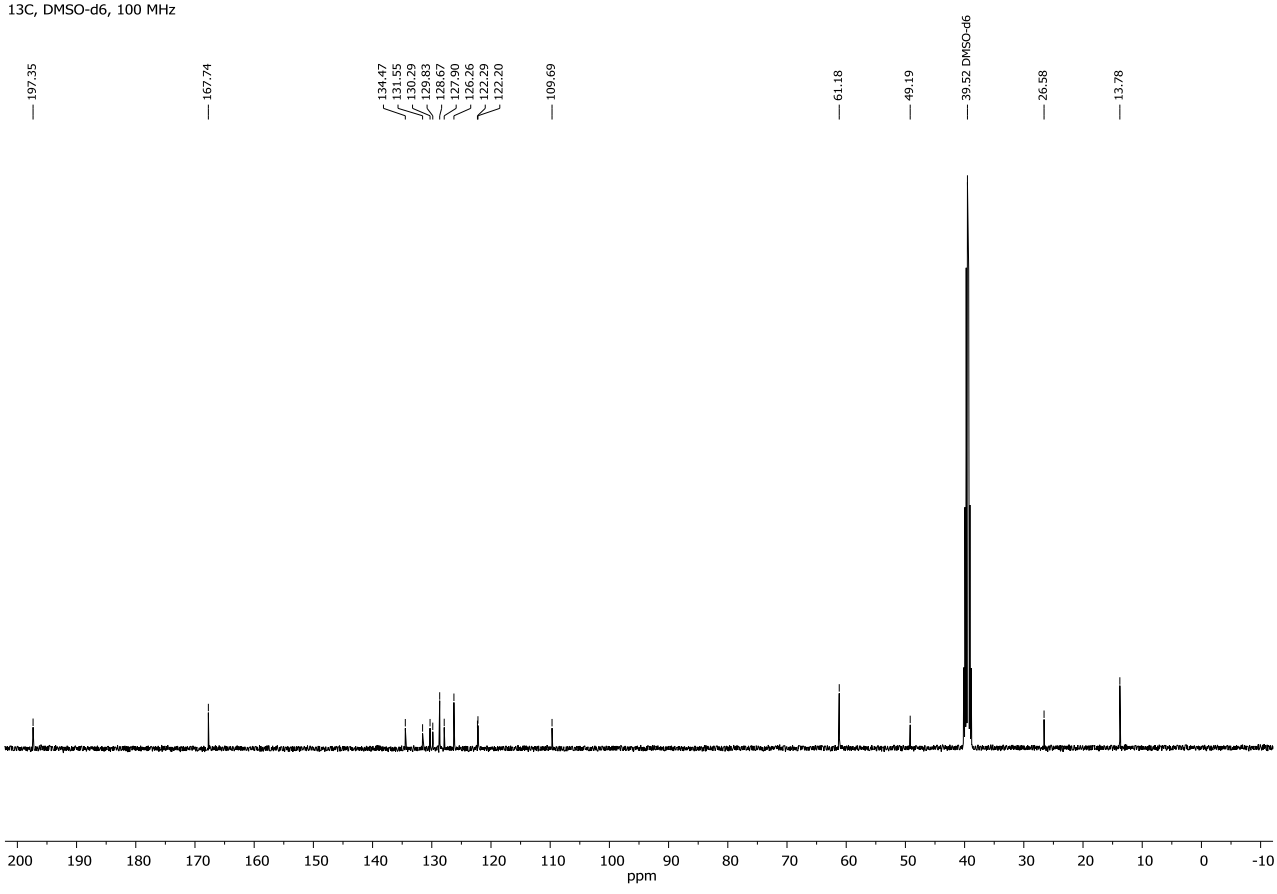


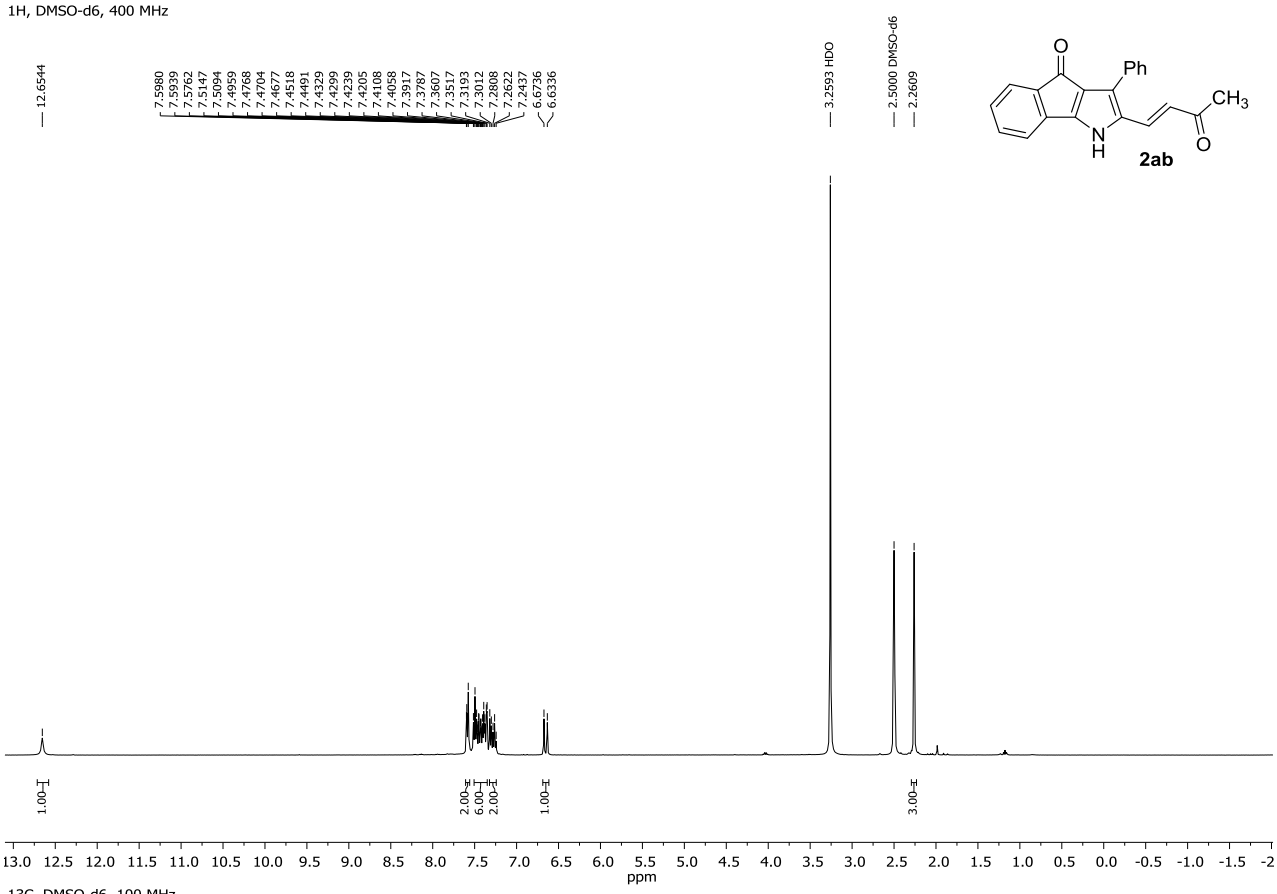
1H, DMSO-d6, 400 MHz

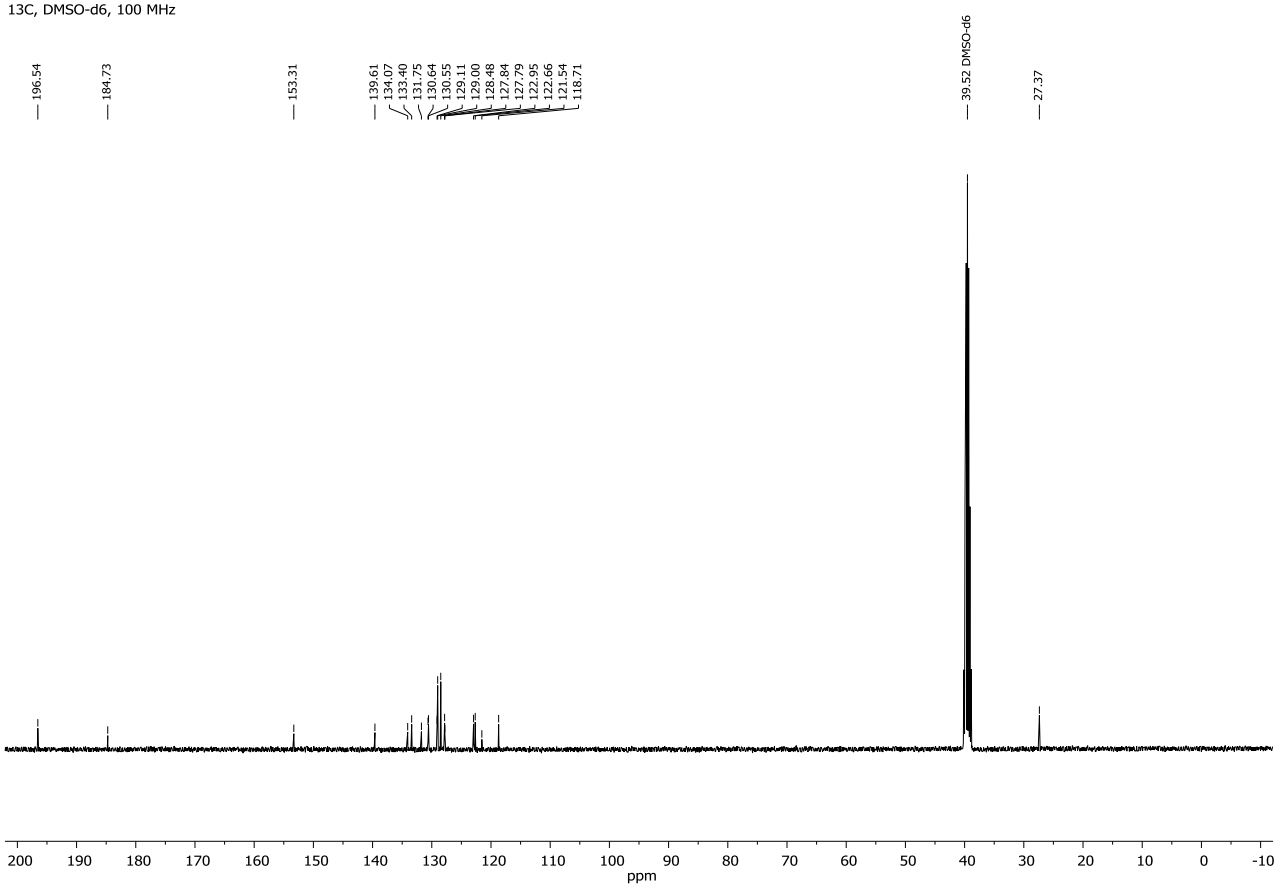


2aa

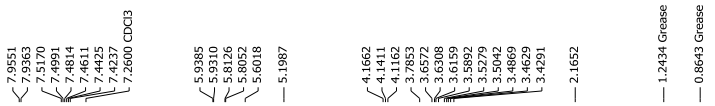
13C, DMSO-d6, 100 MHz

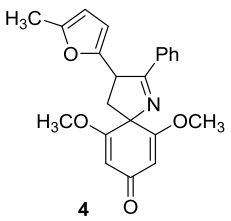


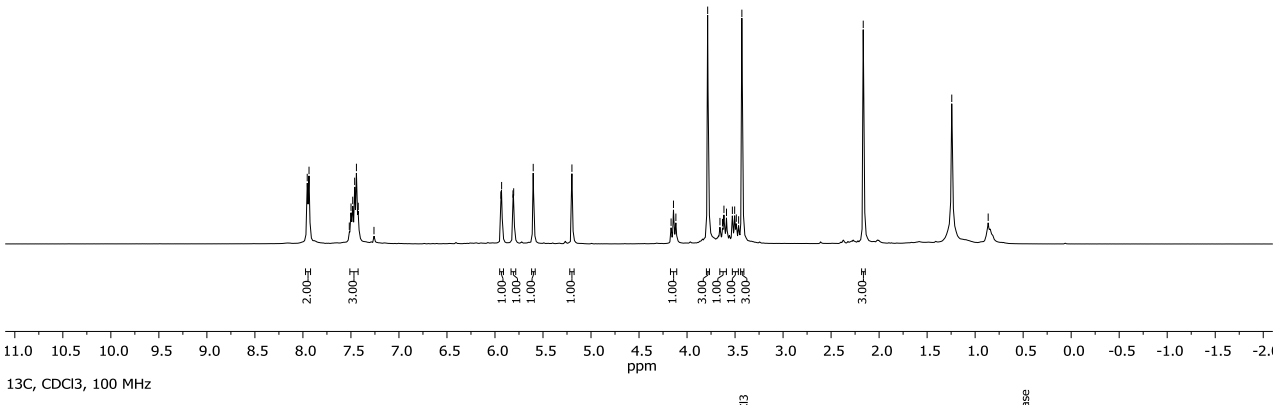

1H, DMSO-d6, 400 MHz
12.6544
7.5980
7.5939
7.5762
7.5147
7.5094
7.4959
7.4768
7.4704
7.4677
7.4518
7.4491
7.4329
7.4299
7.4239
7.4205
7.4108
7.4058
7.3917
7.3787
7.3607
7.3517
7.3193
7.3012
7.2808
7.2622
7.2437
6.6736
6.6336
3.2593 HDO
2.5000 DMSO-d6
2.2609
O
Ph
CH3
N
H
O
2ab
1.00
2.00
6.00
2.00
1.00
3.00
ppm


13C, DMSO-d6, 100 MHz
196.54
184.73
153.31
139.61
134.07
133.40
131.75
130.64
130.55
129.11
129.00
128.48
127.84
127.79
122.95
122.66
121.54
118.71
39.52 DMSO-d6
27.37
ppm

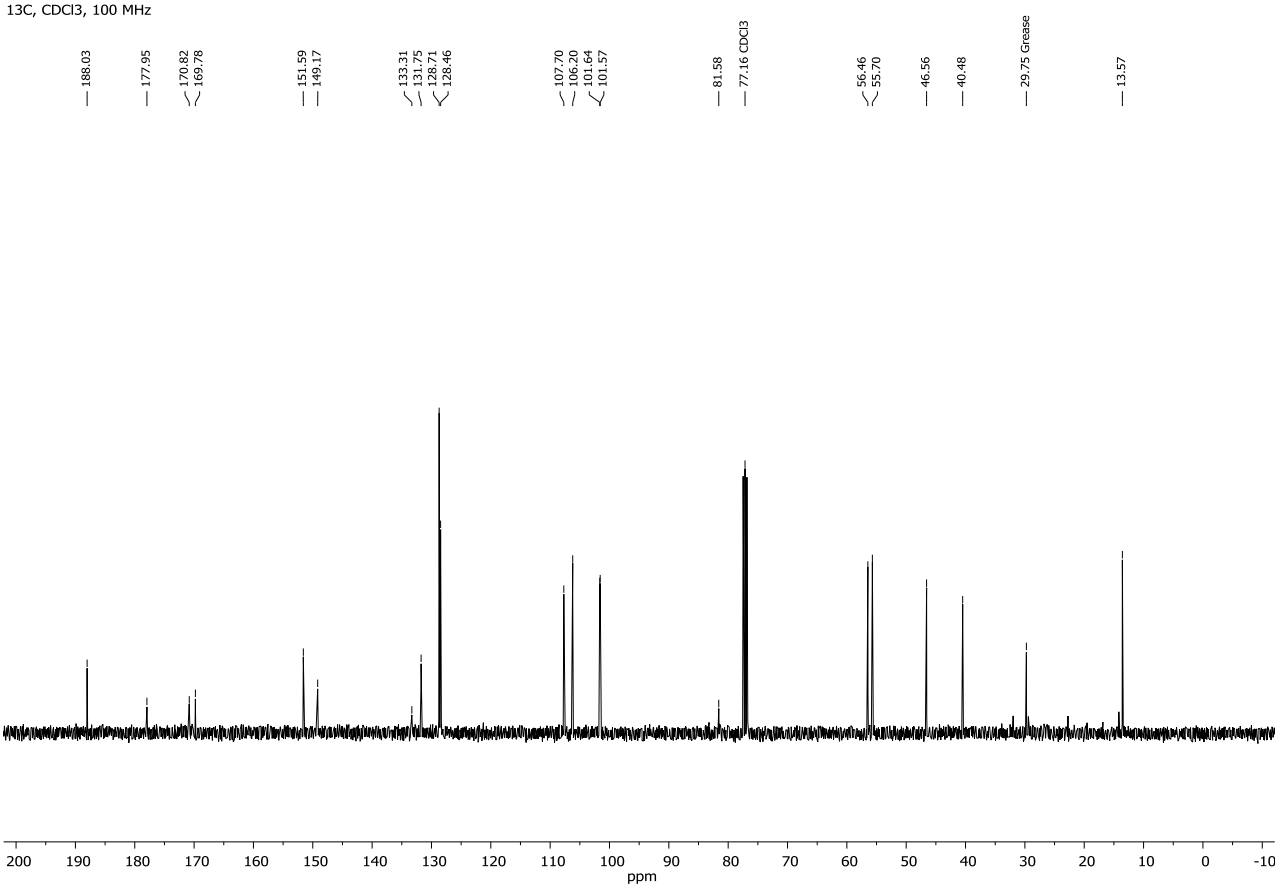
1H, CDCl3, 400 MHz



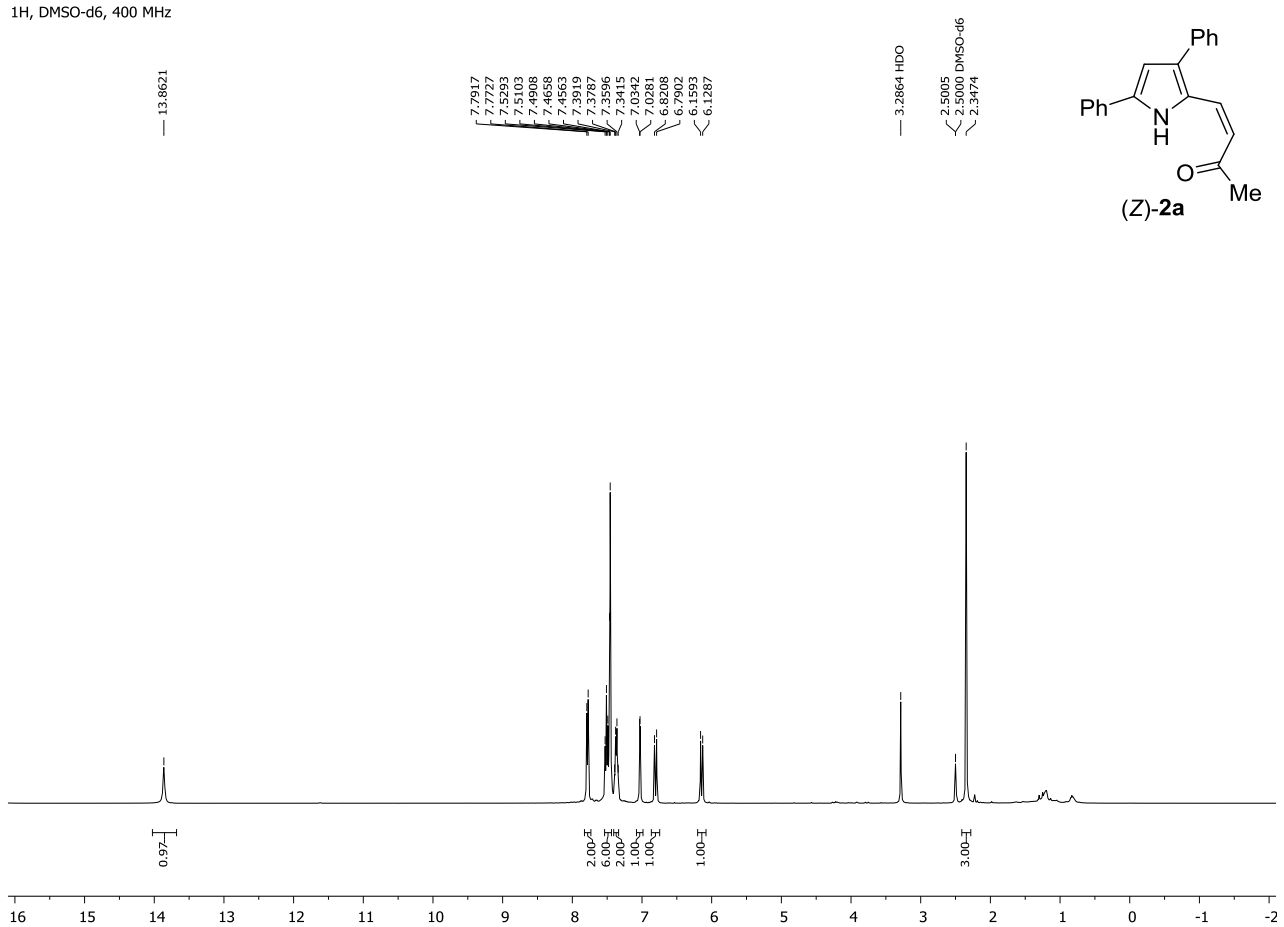




13C, CDCl3, 100 MHz

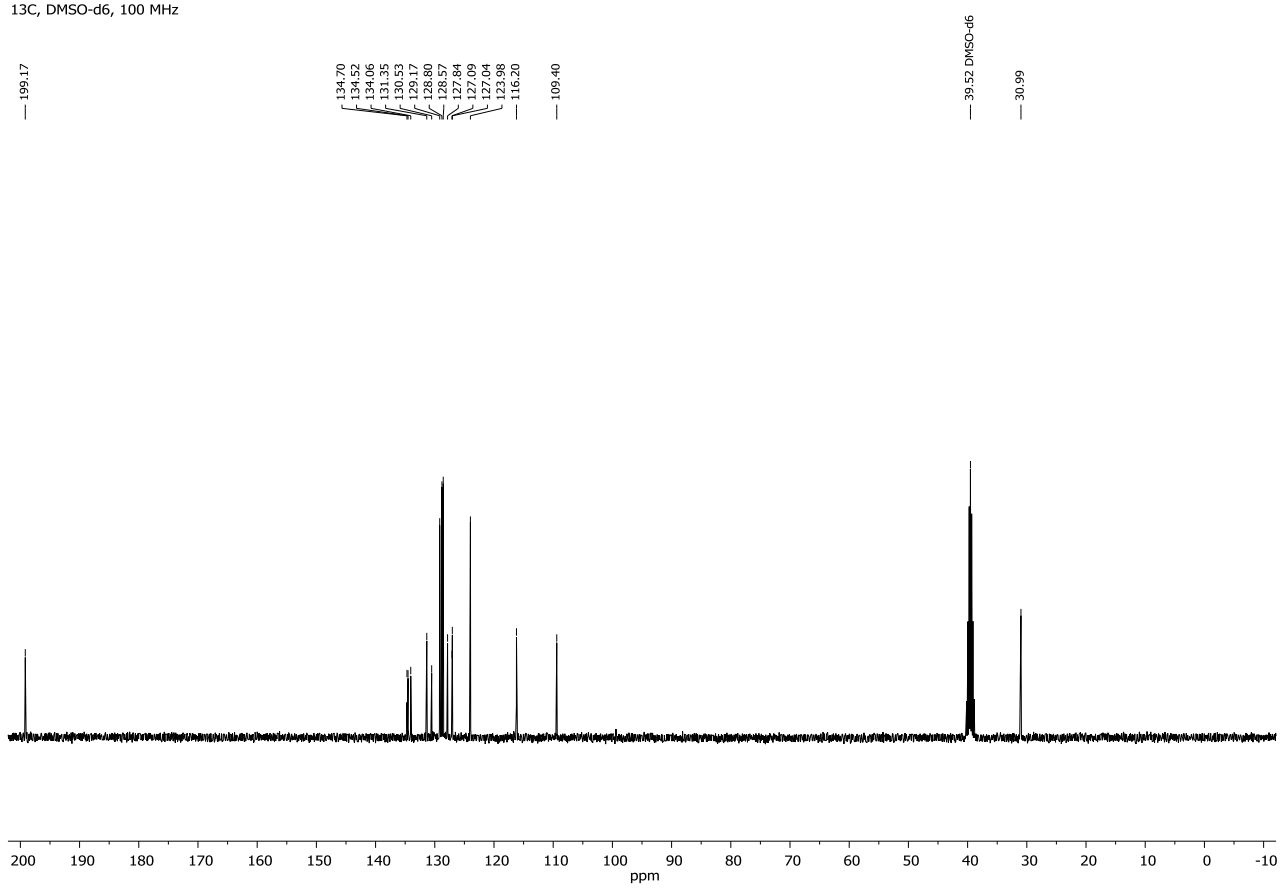


1H, DMSO-d6, 400 MHz

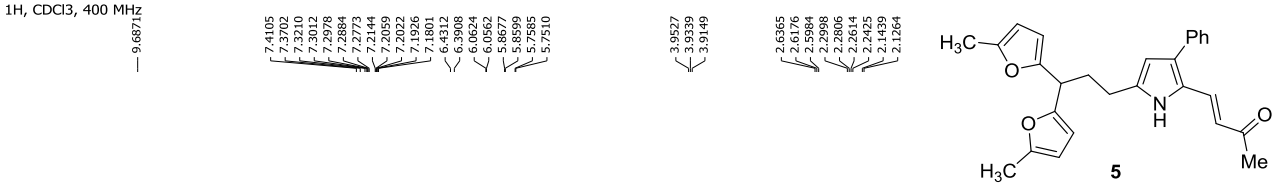


(*Z*)-**2a**

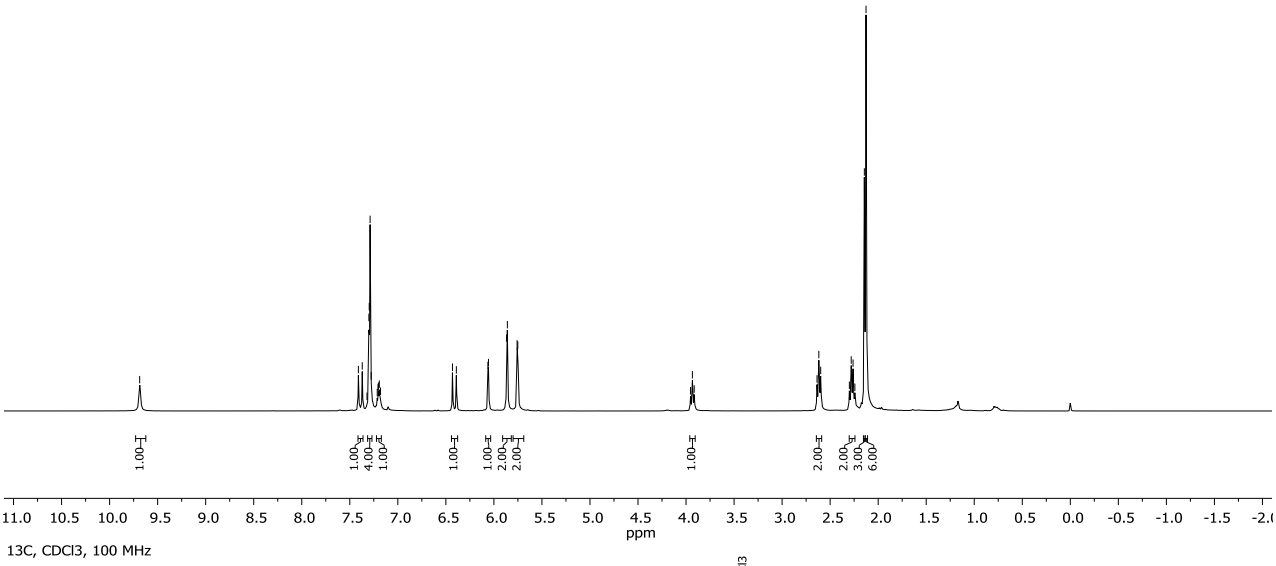
13C, DMSO-d6, 100 MHz



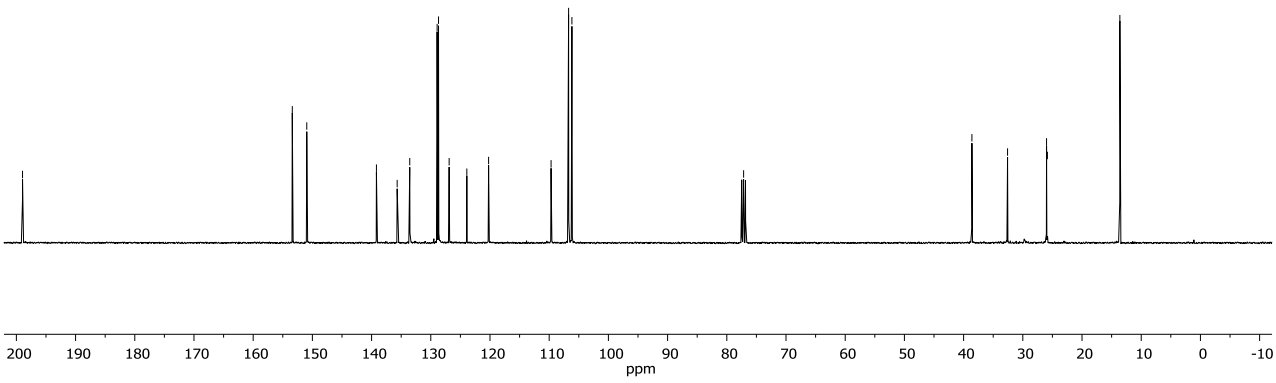
1H, CDCl3, 400 MHz



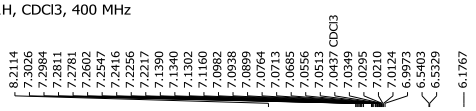
5

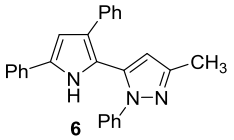


13C, CDCl3, 100 MHz

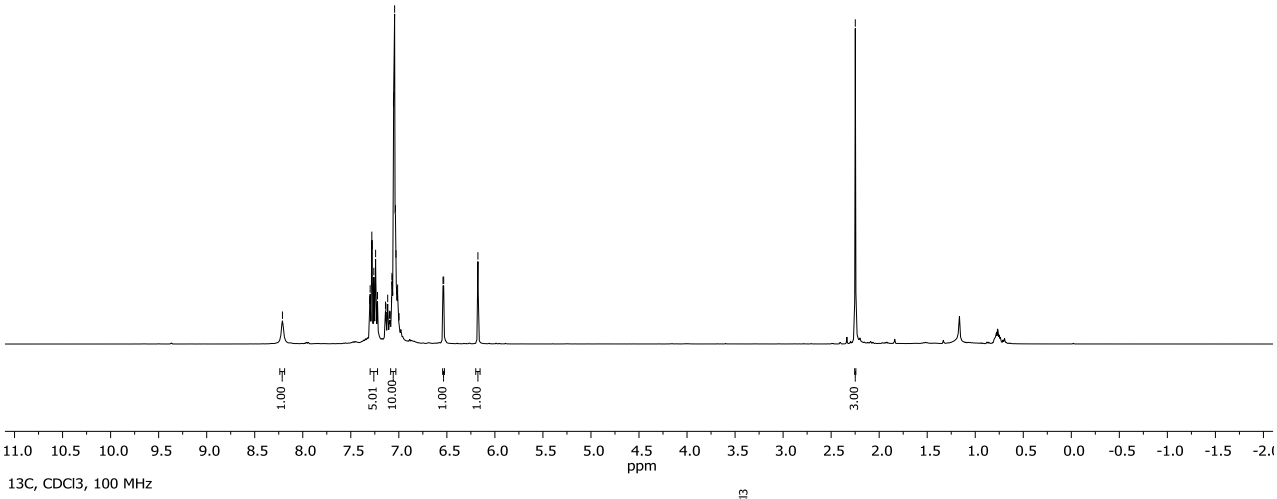


1H, CDCl3, 400 MHz

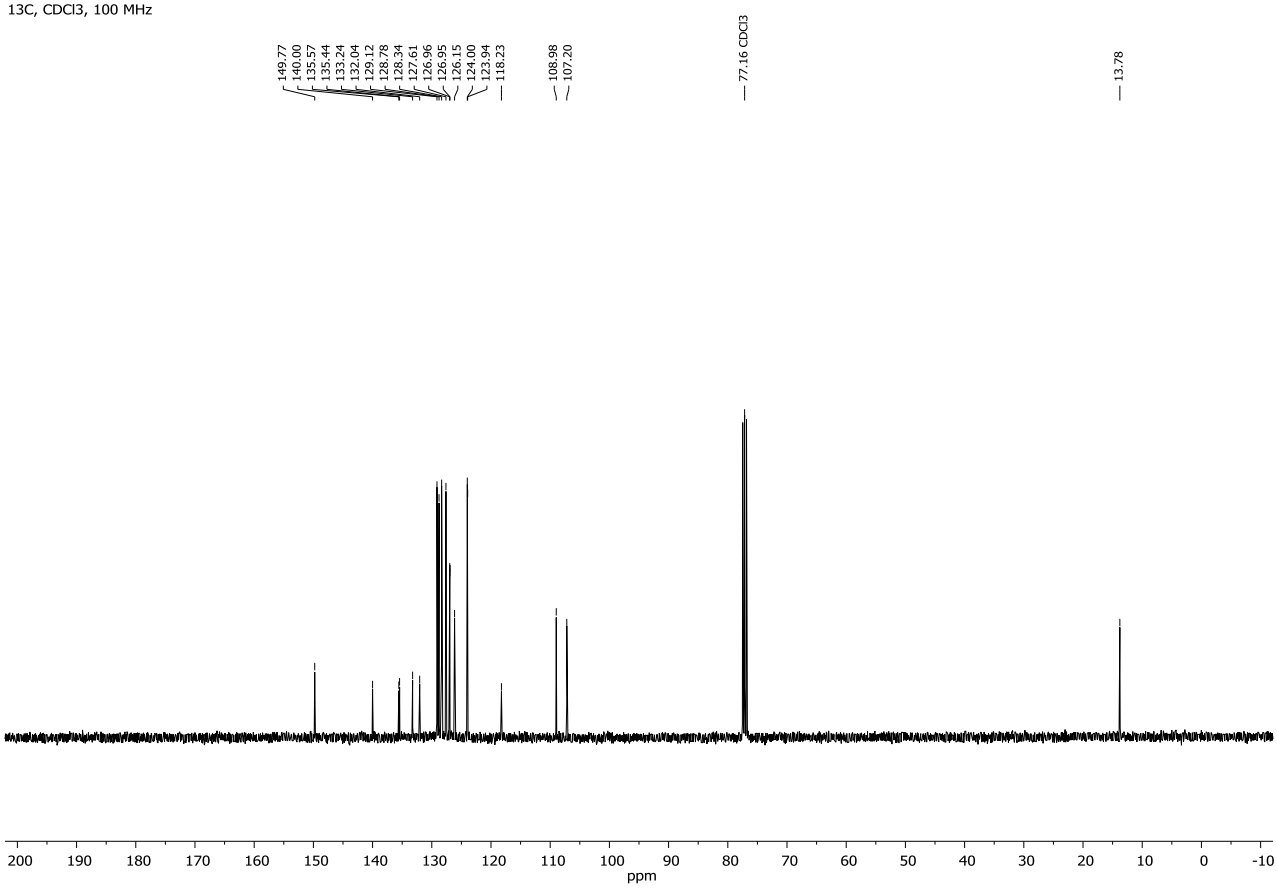




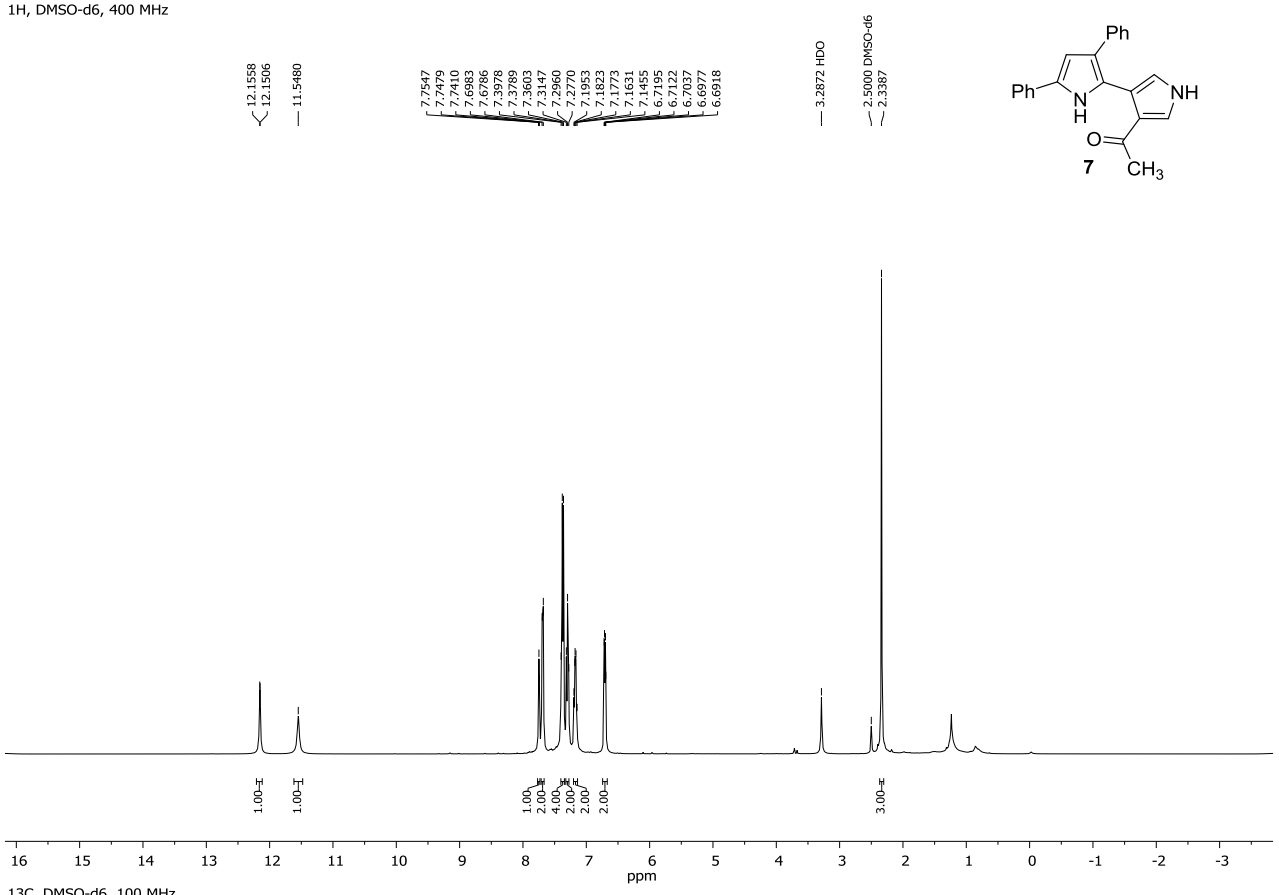
6



13C, CDCl3, 100 MHz

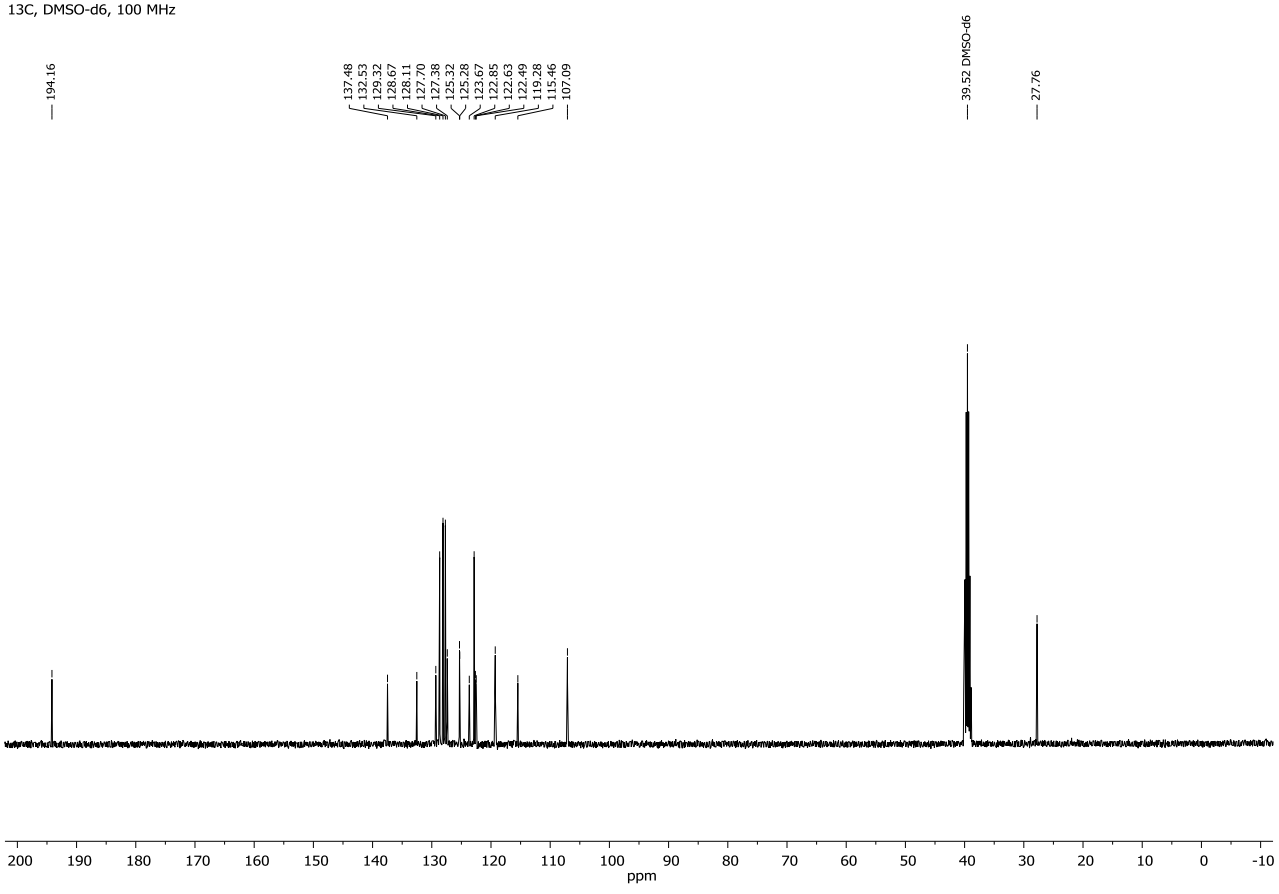


1H, DMSO-d6, 400 MHz

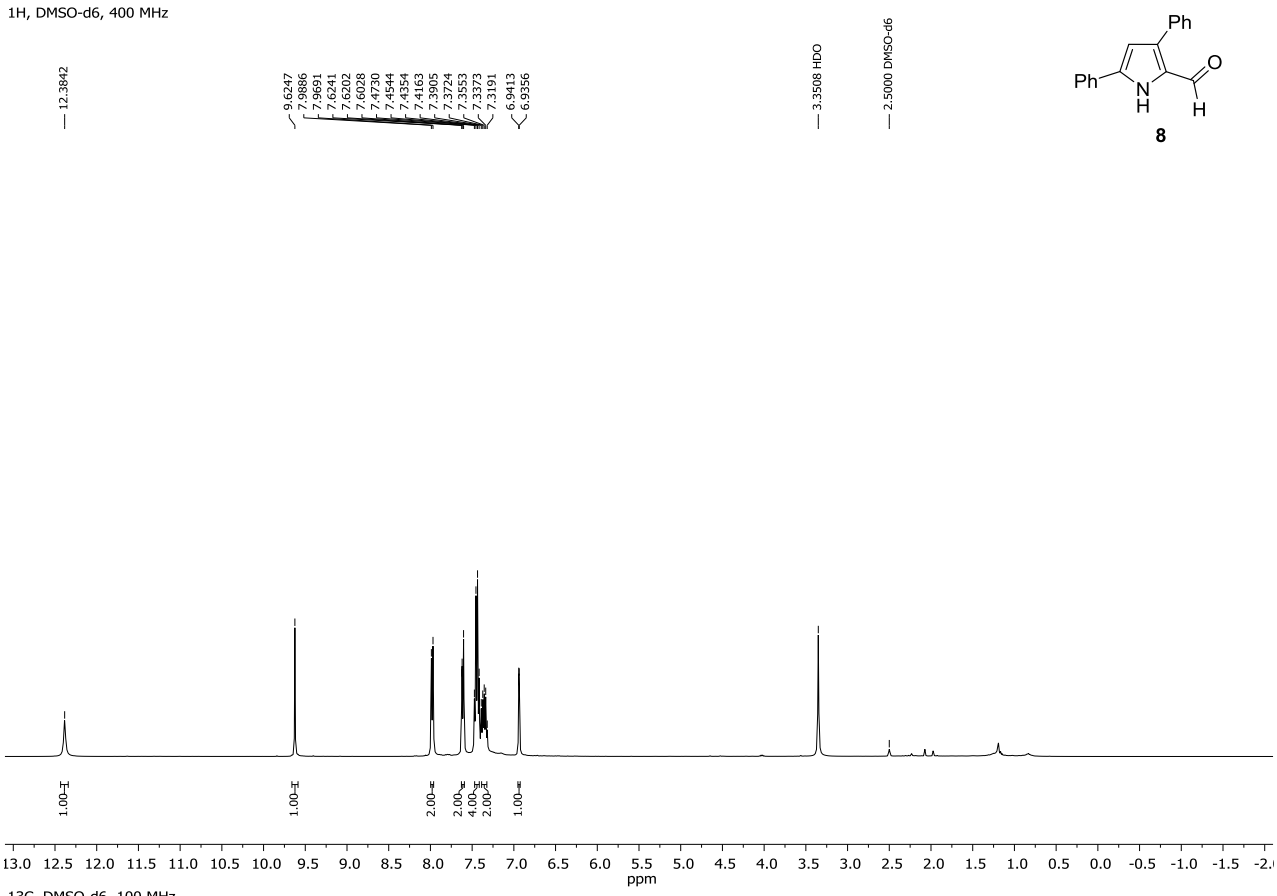


7

13C, DMSO-d6, 100 MHz

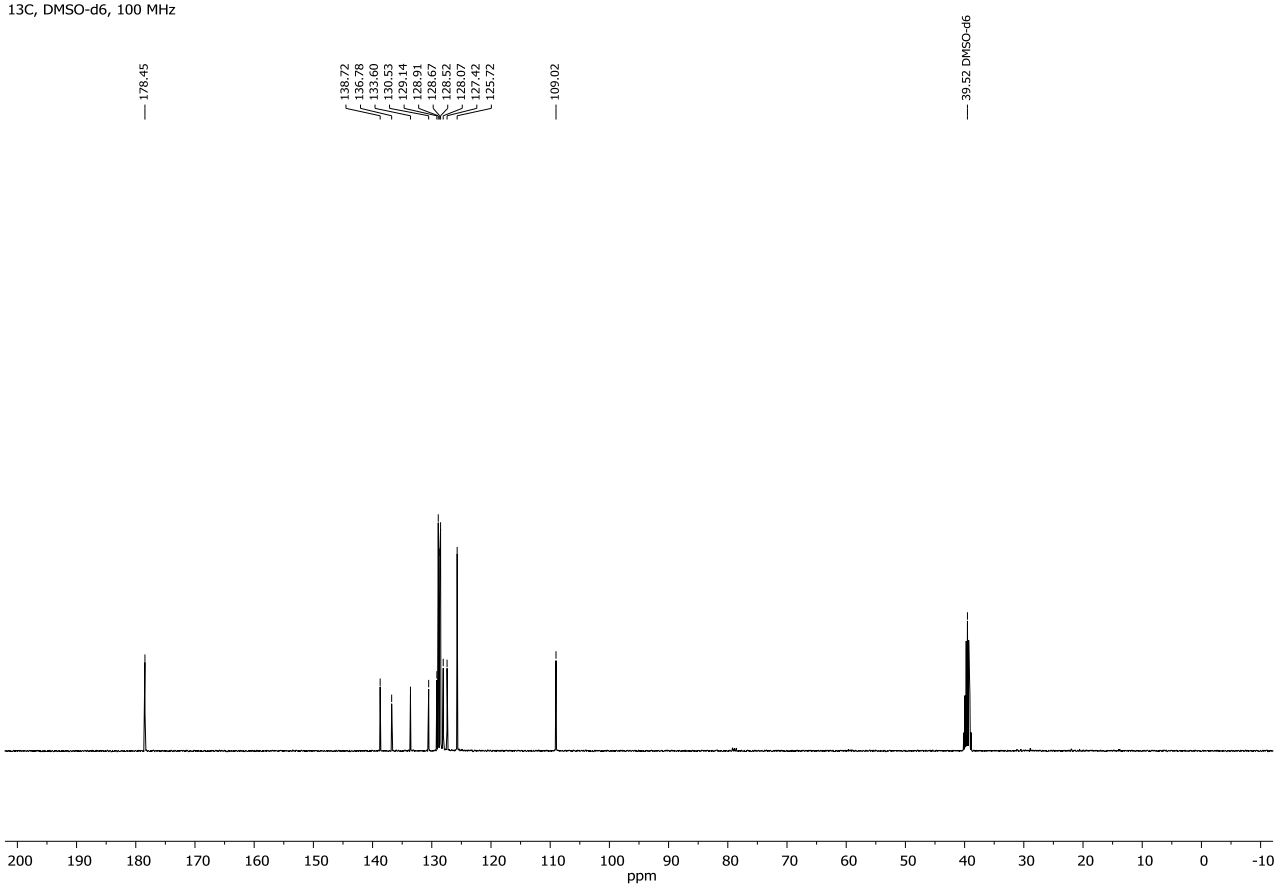


1H, DMSO-d6, 400 MHz



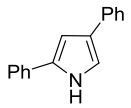
8

13C, DMSO-d6, 100 MHz

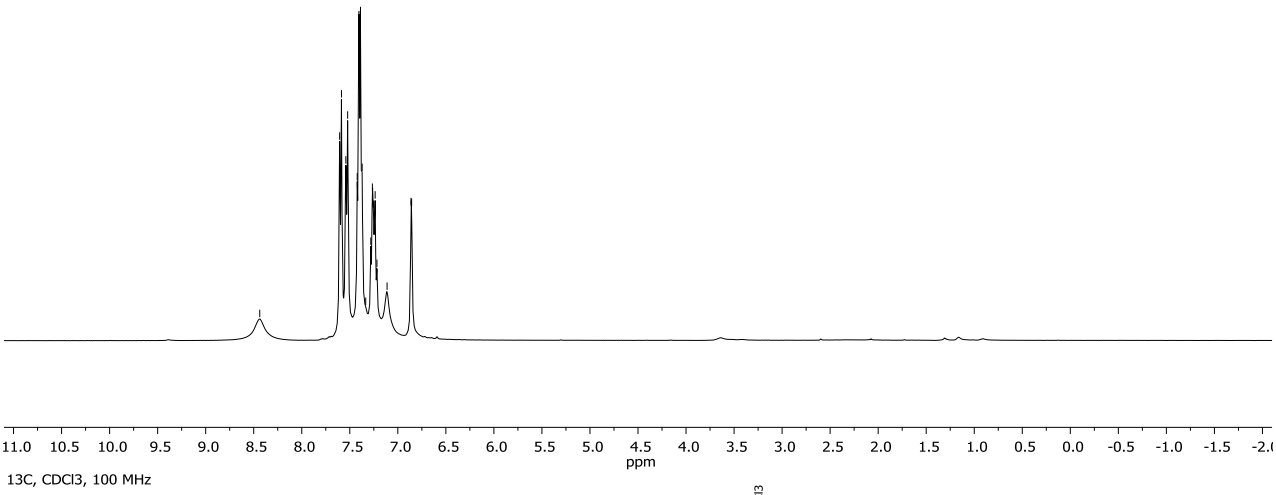


1H, CDCl3, 400 MHz

8.4373
7.6057
7.5866
7.5414
7.5222
7.4228
7.4055
7.3886
7.3711
7.3340 CDCl3
7.2815
7.2649
7.2541
7.2360
7.2173
7.1120
6.8628
6.8563

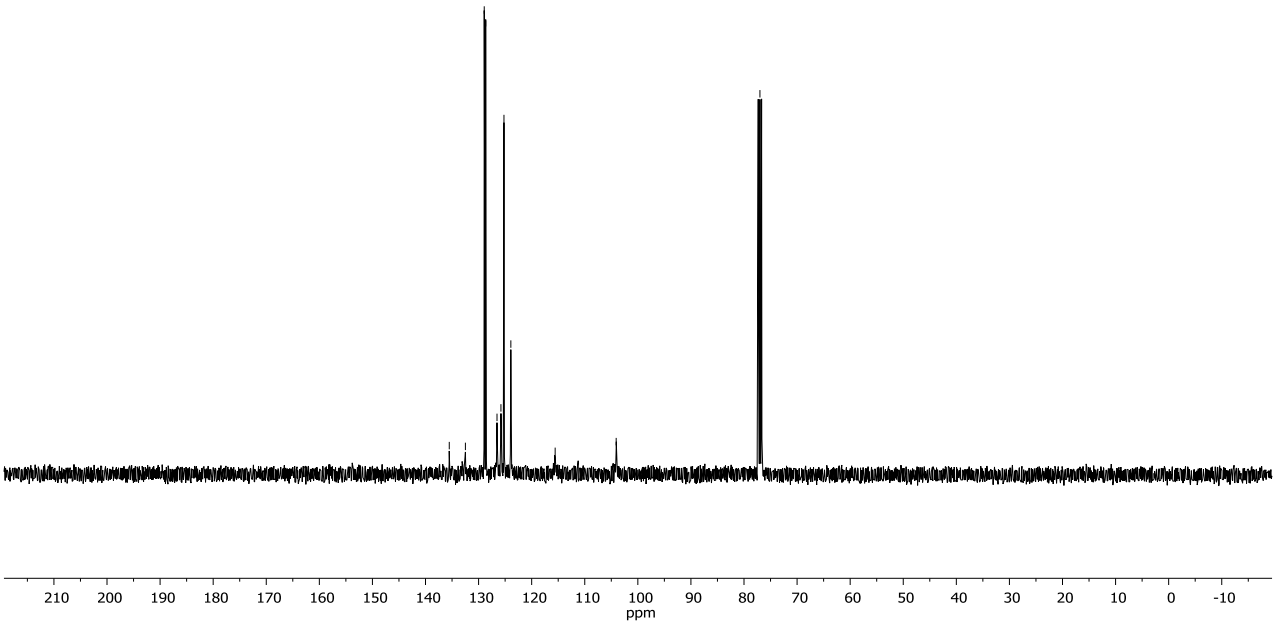


9

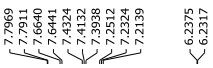


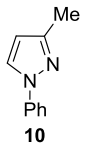
13C, CDCl3, 100 MHz

135.52
132.48
128.94
128.66
126.53
125.79
125.22
123.92
115.57
104.08
77.00 CDCl3

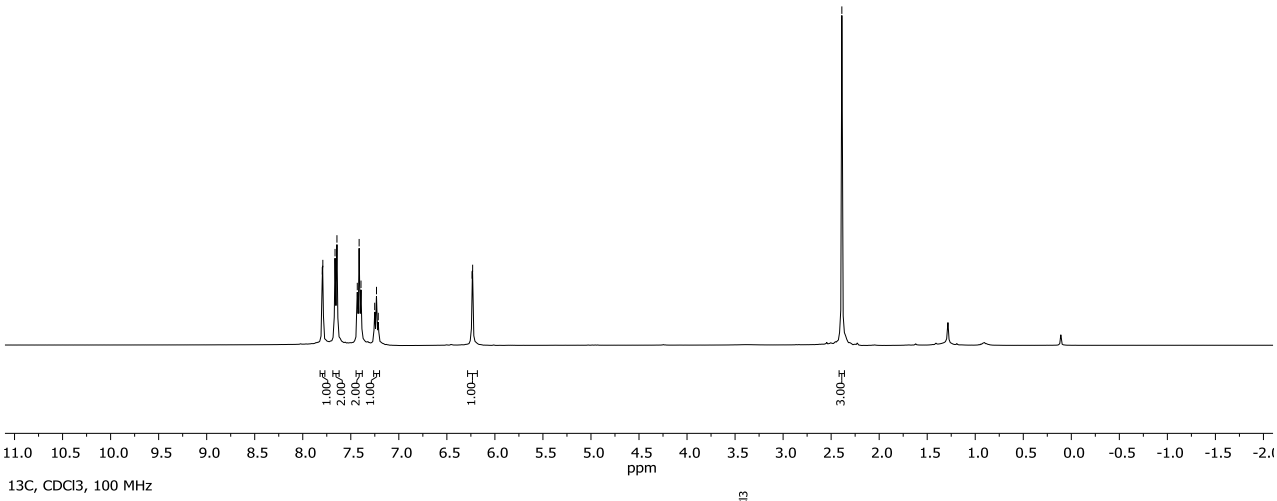


1H, CDCl3, 400 MHz





10



13C, CDCl3, 100 MHz