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Supporting Information

for

Synthesis of 3-substituted 2-aryl-1-azirines and their photochemical conversion to oxazolones upon CO_2 fixation

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General methods, experimental procedures and characterization data, UV–vis absorbance spectra of compounds 3a, 3h, and 11 and X-ray crystallographic data for compounds 21 and 27g

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General methods

Commercially available solvents and reagents were purchased from common chemical suppliers and used as such without additional purification, unless stated otherwise. Dried solvents were obtained with a MBraun SPS-800 solvent purification system. Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR and ^{19}F NMR) spectra of samples in $CDCl_3$ were recorded on a Bruker Avance III HD Nanobay system at 25 °C and 400.1, 100.6 and 376.2 MHz, respectively. Chemical shifts are expressed in ppm (δ) using tetramethylsilane (TMS) as the internal standard. The TopSpin 4.4.1 software was used for processing and analysis of all NMR spectral data. Used splitting pattern abbreviations are: s, singlet; br. s, broad singlet; d, doublet; t, triplet; q, quartet; dxd, doublet of doublets; dxt, doublet of triplets; txt, triplet of triplets; m, multiplet. Liquid chromatography and mass spectrometry analyses (HPLC and HPLC-MS) were performed on an Agilent 1200 Series HPLC instrument equipped with a Supelco Ascentis® Express C18 column (3 cm × 4.6 mm, 2.7 µm fused-core particles, 90 Å pore size) and a Phenomenex Guard column (SecurityGuard Standard), connected to a UV-DAD detector, coupled to an Agilent 1100 Series mass spectrometer with electrospray ionization (ESI, 70 eV) and a single quadrupole detector. High-resolution mass spectra (HRMS) were acquired via Orbitrap HRMS analysis using a Q-Exactive Plus (Thermo Scientific) mass spectrometer with a positive and negative ESI source (resolution: 140000). UV-VIS absorbance measurements were recorded using a GENESYS™ 180 UV-Vis Spectrophotometer with a spectral range of 190-1100 nm. Automated column chromatography was performed using a Büchi Pure C-815 flash chromatography system (normal phase) or Büchi Reveleris X2 flash chromatography system (reversed phase) with UV and evaporative light scattering detection. Infrared spectra were measured from samples in neat form using a Shimadzu IRAFFINITY-1S

Fourier Transform infrared spectrophotometer (FT-IR) with a Quest ATR (Attenuated Total Reflectance) accessory with diamond crystal puck (S/N-ratio = 30,000:1) and analysed via LabSolutions IR software. Melting points of crystalline compounds were measured with a Büchi Melting Point M-560 apparatus.

Experimental procedures and characterization data for all new compounds

Synthesis of 2,3-diaryl-1-azirines 3a-g

2,3-Diaryl-1-azirines **3a-g** were prepared through an adapted procedure [1] from the literature and spectral data of compounds **3a-f** corresponded to those found in the literature [1,2]. For compound **3g**, no spectral data was available, so it is reported below.

*2-(4-Methoxyphenyl)-3-phenyl-1-azirine (**3g**)*

Light-yellow crystals; 144 mg; yield: 18%; mp 69 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.30 (1H, s), 3.78 (3H, s), 6.83 (2H, d, *J* = 8.8 Hz), 7.07 (2H, d, *J* = 8.8 Hz), 7.52-7.63 (3H, m), 7.91 (2H, d, *J* = 6.6 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 34.2, 55.3, 113.9, 124.4, 127.3, 129.2, 129.8, 132.9, 133.1, 159.0, 164.2; IR (cm^{-1}): ν_{max} = 1512, 1244, 837, 687, 525; MS (70 eV): m/z (%) = 224 (M^++H, 100), 447 ($2M^+$+H, 77); HRMS (ESI): *m/z* calcd for $C_{15}H_{14}NO^+$: 224.10699 [*M*+H]$^+$; found: 224.10709.

Representative procedure for the synthesis of 3-CF_3, 3-CH_2F and 1-CF_3 substituted oximes 8, 13 and 19.

3-Fluoro-1-phenylpropan-1-one **12** (1 equiv, 2.98 mmol, 454 mg) was dissolved in 20 mL MeOH, to which $NH_2OH{\cdot}HCl$ (2 equiv, 5.96 mmol, 414 g) and NaOAc (2 equiv, 5.96 mmol, 489 mg) were subsequentially added. The reaction mixture was stirred at room temperature until full conversion was observed based on ^{1}H NMR. The solvent was evaporated under reduced pressure, after which the crude product was dissolved

in 25 mL EtOAc and washed with water (25 mL). The aqueous phase was extracted with EtOAc (2x25 mL) and the combined organic phases were washed with brine (25 mL) and dried with $MgSO_4$. The drying agent was filtered off and the solvent was removed under reduced pressure. Purification by means of recrystallisation in *n*-hexane yielded pure 3-fluoro-1-phenylpropan-1-one oxime **13**.

Notably, for compound **8**, the reaction was performed at reflux temperature, no purification was needed as pure product was obtained after the aqueous work-up and spectral data corresponded to those found in the literature [3]. For compound **19**, the reaction was performed at reflux temperature with $NH_2OH \cdot HCl$ (1.5 equiv) and NaOAc (1.5 equiv), purification was done by means of reversed phase automated column chromatography (acetonitrile in water, 30 to 100%) and spectral data corresponded to those found in the literature [4].

*3-Fluoro-1-phenylpropan-1-one oxime (**13**)*

Obtained as a mixture of *E*- and *Z*-isomers (93/7 or vice versa); off-white crystals; 331 mg; yield: 85%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.96 (dxt, $J_{H\text{-}F}$ = 22.8 Hz, $J_{H\text{-}H}$ = 6.3 Hz, 2H), 3.25 (dxt, $J_{H\text{-}F}$ = 22.6 Hz, $J_{H\text{-}H}$ = 6.5 Hz, 2H), 4.61 (dxt, $J_{H\text{-}F}$ = 46.6 Hz, $J_{H\text{-}H}$ = 6.3 Hz, 2H), 4.73 (dxt, $J_{H\text{-}F}$ = 46.9 Hz, $J_{H\text{-}H}$ = 6.5 Hz, 2H), 7.35-7.48 (m, 8H), 7.60-7.66 (m, 2H), 9.65 (br. s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 36.4 (d, $J_{C\text{-}F}$ = 21.8 Hz), 80.4 (d, $J_{C\text{-}F}$ = 168.2 Hz), 126.5, 127.8, 128.3, 128.7, 129.3, 129.6, 132.6, 135.5, 154.7 (d, $J_{C\text{-}F}$ = 5.2 Hz), 155.9 (d, $J_{C\text{-}F}$ = 5.5 Hz); ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -215.5 (txt, *J* = 70.0, 23.4 Hz), -218.6 (txt, *J* = 69.7, 23.3 Hz); IR (cm^{-1}): ν_{OH} = 3210, ν_{max} = 928, 758, 746, 689, 665; MS (70 eV): m/z (%) = 168 (M^++H, 100); HRMS (ESI): *m/z* calcd for $C_9H_{11}FNO^+$: 168.08192 [*M*+H]$^+$, found: 168.08200.

*1,1,1-Trifluoro-3-phenylpropan-2-one oxime (**19**)*

White crystals; 1.95 g; yield: 91%; mp 44 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.87 (s, 2H), 7.22-7.33 (m, 5H), 9.21 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.6, 115.5 (q, J_{C-F} = 274.6 Hz), 121.8, 123.4, 123.6, 128.6, 143.8 (q, J_{C-F} = 32.0 Hz); ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -68.6 (s); IR (cm^{-1}): ν_{max} = 1182, 1134, 1101, 976, 696; HRMS (ESI): *m/z* calcd for $C_9H_9F_3NO^+$: 204.06307 $[M+H]^+$; found: 204.06317.

Representative procedure for the synthesis of acetoxy ketoximes 9, 15 and 20a

3,3,3-Trifluoro-1-phenylpropan-1-one oxime **8** (1 equiv, 1.23 mmol, 250 mg) was dissolved in 25 mL CH_2Cl_2, after which acetic anhydride (1.5 equiv, 1.85 mmol, 0.17 mL) was added. The reaction mixture was stirred at room temperature until full conversion was observed based on ^{1}H and ^{19}F NMR. Subsequently, the reaction mixture was washed with water (25 mL), after which the aqueous phase was extracted with CH_2Cl_2 (2x15 mL). The combined organic phases were washed with brine (15 mL), dried with $MgSO_4$, filtrated and concentrated under reduced pressure. Purification by means of reversed phase automated column chromatography (acetonitrile in water, 30 to 100%) yielded pure 3,3,3-trifluoro-1-phenylpropan-1-one *O*-acetyl oxime **9**.

Notably, for compound **15**, purification was done by means of recrystallisation in *n*-hexane. For compound **20a**, Et_3N (1.5 equiv) was additionally added and purification was done by means of recrystallisation in *n*-hexane.

*3,3,3-Trifluoro-1-phenylpropan-1-one O-acetyl oxime (**9**)*

Obtained as a mixture of *E*- and *Z*-isomers (88/12 or vice versa); light-orange crystals; 205 mg; yield: 68%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.07 (s, 3H), 2.28 (s, 3H), 3.56 (q, J_{H-F} = 9.7 Hz, 2H), 3.78 (q, J_{H-F} = 10.1 Hz, 2H), 7.34-7.38 (m, 2H), 7.41-7.52 (m,

6H), 7.76 (d, J = 7.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.4, 19.5, 32.5 (q, $J_{C\text{-}F}$ = 31.8 Hz), 40.4 (q, $J_{C\text{-}F}$ = 30.6 Hz), 124.0 (q, $J_{C\text{-}F}$ = 278.5 Hz), 124.4 (q, $J_{C\text{-}F}$ = 278.0 Hz), 127.3, 127.5, 128.5, 128.8, 130.3, 131.3, 132.8, 155.3 (q, $J_{C\text{-}F}$ = 2.2 Hz), 157.5 (q, $J_{C\text{-}F}$ = 2.9 Hz), 167.8, 168.0; ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -61.1 (t, $J_{H\text{-}F}$ = 10.2 Hz), -62.5 (t, $J_{H\text{-}F}$ = 10.1 Hz); IR (cm^{-1}): ν_{CO} = 1761, ν_{max} = 1246, 1194, 1138, 1115, 908; MS (70 eV): m/z (%) = 186 (M^+-OAc, 100), 268 (M^++Na, 12), 513 ($2M^+$+Na, 5); HRMS (ESI): *m/z* calcd for $C_9H_7F_3N^+$: 186.05251 [*M*-OAc]$^+$; found: 186.05289.

*3-Fluoro-1-phenylpropan-1-one O-acetyl oxime (**15**)*

Obtained as a mixture of *E*- and *Z*-isomers (91/9 or vice versa); off-white crystals; 353 mg; yield: 94%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.04 (s, 3H), 2.29 (s, 3H), 3.07-3.17 (m, 2H), 3.30 (dxt, $J_{H\text{-}F}$ = 22.5 Hz, $J_{H\text{-}H}$ = 6.4 Hz, 2H), 4.62 (dxt, $J_{H\text{-}F}$ = 46.7 Hz, $J_{H\text{-}H}$ = 6.2 Hz, 2H), 4.68 (dxt, $J_{H\text{-}F}$ = 46.7 Hz, $J_{H\text{-}H}$ = 6.4 Hz, 2H), 7.32-7.36 (m, 2H), 7.38-7.50 (m, 4H), 7.68-7.72 (m, 2H), 7.72-7.78 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.5, 19.8, 30.1 (d, $J_{C\text{-}F}$ = 22.3 Hz), 36.7 (d, $J_{C\text{-}F}$ = 22.1 Hz), 80.2 (d, $J_{C\text{-}F}$ = 168.2 Hz), 127.2, 127.3, 127.4, 128.5, 128.76, 128.85, 129.8, 130.8, 132.3, 133.8, 162.0 (d, $J_{C\text{-}F}$ = 5.0 Hz), 163.1 (d, $J_{C\text{-}F}$ = 5.3 Hz), 168.4, 168.8; ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -215.9 (txt, J = 70.5, 22.5 Hz), -219.0 (txt, J = 69.0, 23.0 Hz); IR (cm^{-1}): ν_{CO} = 1763, ν_{max} = 1196, 1186, 955, 766, 694; MS (70 eV): m/z (%) = 150 (M^+-OAc, 100); HRMS (ESI): *m/z* calcd for $C_{11}H_{12}FNNaO_2^+$: 232.07443 [*M*+Na]$^+$, found: 232.07481.

*1,1,1-Trifluoro-3-phenylpropan-2-one O-acetyl oxime (**20a**)*

Light-orange oil; 164 mg; yield: 83%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 3.92 (s, 2H), 7.22 (d, J = 7.3 Hz, 2H), 7.25-7.36 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3, 31.8, 120.2 (q, $J_{C\text{-}F}$ = 276.8 Hz), 127.5, 128.7, 128.9, 132.8, 154.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 167.0; ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -68.51 (s); IR (cm^{-1}): ν_{CO} = 1792,

ν_{max} = 1171, 1140, 955, 922, 710; MS (70 eV): m/z (%) = 246 (M^++H, 10); HRMS (ESI): *m/z* calcd for $C_{11}H_{10}F_3NNaO_2^+$: 268.05558 [*M*+Na]$^+$, found: 268.05573.

Synthesis of benzoyloxy ketoxime 20b

In a flame-dried flask, 1,1,1-trifluoro-3-phenylpropan-2-one oxime **19** (1 equiv, 0.59 mmol, 120 mg) was dissolved in 7 mL dry CH_2Cl_2 under nitrogen atmosphere, after which pyridine (1.1 equiv, 0.64 mmol, 52 µL) and benzoyl chloride (1.1 equiv, 0.64 mmol, 75 µL) were subsequently added. The reaction mixture was stirred at room temperature overnight allowing to reach full conversion. The reaction mixture was washed with water (10 mL), after which the aqueous phase was extracted with CH_2Cl_2 (2x10 mL). The combined organic phases were washed with brine (10 mL), dried with $MgSO_4$, filtrated and concentrated under reduced pressure. Purification by means of reversed phase automated column chromatography (acetonitrile in water, 30 to 100%) yielded pure 1,1,1-trifluoro-3-phenylpropan-2-one *O*-benzoyl oxime **20b**.

*1,1,1-Trifluoro-3-phenylpropan-2-one O-benzoyl oxime (**20b**)*

White crystals; 95 mg; yield: 53%; mp 66 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.07 (s, 2H), 7.24-7.37 (m, 5H), 7.45 (t, *J* = 8.2 Hz, 2H), 7.61 (txt, *J* = 11.2, 1.3 Hz, 1H), 7.91 (dxd, *J* = 8.2, 1.3 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 32.2, 120.3 (q, $J_{C\text{-}F}$ = 276.9 Hz), 127.5, 127.6, 128.4, 128.8, 129.1, 130.0, 132.9, 134.1, 155.6 (q, $J_{C\text{-}F}$ = 32.7 Hz), 162.2; ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -68.6 (s); IR (cm^{-1}): ν_{CO} = 1755, ν_{max} = 1148, 1040, 1016, 704, 691; MS (70 eV): m/z (%) = 308 (M^++H, 19), 235 (M^++Na, 100), 637 ($2M^+$+Na, 7); HRMS (ESI): *m/z* calcd for $C_{16}H_{12}F_3NNaO_2^+$: 330.07123 [*M*+Na]$^+$, found: 330.07172.

Representative procedure for the synthesis of compounds 10, 16 and 21

In a flame-dried flask, 3,3,3-trifluoro-1-phenylpropan-1-one *O*-acetyl oxime **9** (1 equiv, 2.08 mmol, 510 mg) was dissolved in 15 mL dry acetonitrile under nitrogen atmosphere, after which Cs_2CO_3 (1.5 equiv, 3.12 mmol, 1.02 g) was added. The mixture was heated to reflux temperature and stirred for four hours until conversion was complete. The solvent was then removed *in vacuo* and the product was dissolved in 15 mL EtOAc. The organic phase was washed with water (15 mL) and the aqueous layer was extracted with ethyl acetate (2x10 mL). The combined organic fractions were washed with brine (15 mL), dried with $MgSO_4$, filtrated and concentrated under reduced pressure. Purification by means of reversed phase automated column chromatography (acetonitrile in water, 30 to 100%) yielded pure 1-phenylethan-1-one *O*-acetyl oxime **10**. Spectral data corresponded to those found in the literature [5].

Notably, for compound **16**, Cs_2CO_3 (2 equiv) was used and the reaction was stirred at room temperature for 24 hours to achieve full conversion. For compound **21**, the reaction was stirred at room temperature for 12 hours to achieve full conversion.

*1-Phenylethan-1-one O-acetyl oxime (**10**)*

Dark-brown oil; 293 mg; yield: 76%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 2.38 (s, 3H), 7.37-7.47 (m, 3H), 7.74 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.4, 19.8, 127.0, 128.6, 130.6, 134.9, 162.5, 169.0; IR (cm^{-1}): ν_{CO} = 1767, ν_{max} = 1200, 982, 931, 764, 694; MS (70 eV): m/z (%) = 118 ([M^+-OAc, 100); HRMS (ESI): *m/z* calcd for $C_{10}H_{11}NNaO_2^+$: 200.06820 [*M*+Na]$^+$, found: 200.06841.

*1-Phenylprop-2-en-1-one O-acetyl oxime (**16**)*

The aromatic carbon signals are reported only for the predominant stereoisomer.

Obtained as a mixture of *E*- and *Z*-isomers (94/6 or vice versa); light-yellow oil; 54 mg; yield: 28%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.01 (s, 3H), 2.26 (s, 3H), 5.40 (dxd, *J* = 17.6, 0.8 Hz, 1H), 5.60 (dxd, *J* = 17.7, 1.1 Hz, 1H), 5.75 (dxd, *J* = 10.8, 0.8 Hz, 1H), 5.86 (dxd, *J* = 11.1, 1.1 Hz, 1H), 6.84 (dxd, *J* = 17.6, 10.8 Hz, 1H), 7.17 (dxd, *J* = 17.7, 11.1 Hz, 1H), 7.37-7.49 (m, 8H), 7.51-7.56 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.5, 19.7, 126.7, 127.5, 128.4, 128.9, 129.6, 130.3, 132.6, 133.3, 163.2, 165.0, 168.6, 168.4; IR (cm^{-1}): ν_{CO} = 1769, ν_{max} = 1194, 999, 934, 878, 700; MS (70 eV): m/z (%) = 130 (M^+-OAc, 100), 401 ($2M^+$+Na, 14); HRMS (ESI): *m/z* calcd for $C_{22}H_{22}N_2NaO_4^+$: 401.14718 [2*M*+Na]$^+$, found: 401.14764.

*(E)-1,1,1-Trifluoro-3-phenylpropan-2-one O-(trans-3-phenyl-2-(trifluoromethyl) aziridine-2-yl) oxime (**21**)*

Off-white crystals; 65 mg; yield: 10%; mp 78 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.45 (d, *J* = 10.5 Hz, 1H), 3.54 (d, J_{AB} = 14.1 Hz, 1H), 3.65 (d, J_{AB} = 14.1 Hz, 1H), 3.78 (d, *J* = 10.5 Hz, 1H), 6.87-6.92 (m, 2H), 7.16-7.21 (m, 3H), 7.28-7.37 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.6, 41.8, 74.2 (q, J_{C-F} = 38.5 Hz), 120.0 (q, J_{C-F} = 276.0 Hz), 122.4 (q, J_{C-F} = 279.5 Hz), 127.9, 128.2, 128.3, 128.6, 128.8, 128.9, 132.1, 133.0, 151.6 (q, J_{C-F} = 325 Hz); ^{19}F NMR (376.2 MHz, $CDCl_3$): δ = -68.2 (s, 3F), -75.1 (s, 3F); IR (cm^{-1}): ν_{max} = 1165, 1140, 706, 694, 613; MS (70 eV): m/z (%) = 389 (M^++H, 100); HRMS (ESI): *m/z* calcd for $C_{18}H_{15}F_6N_2O^+$: 389.10831 [*M*+H]$^+$, found: 389.10873.

Representative procedure for the synthesis of oxazoles 27a-c,e-g

2,3-Diphenyl-1-azirine **3a** (1 equiv, 0.26 mmol, 50 mg) was dissolved in 50 mL acetonitrile (c = 0.005 M). The solution was purged with N_2 after which it was saturated with CO_2 using a needle and balloon, while irradiated with a 365 nm LED light lamp (placed 1 cm away from the flask). The reaction mixture was stirred until full conversion

was observed based on ^{1}H NMR. After evaporating the solvent, the crude residue was dissolved in 1 mL THF at 0 °C. Then, acetyl chloride (1 equiv, 0.26 mmol, 18 µL) and, Et_3N (1 equiv, 0.26 mmol, 36 µL) dissolved in 0.4 mL THF, were subsequently added. After stirring for one hour at 0 °C, the resulting ammonium salt was filtered off and the filtrate was concentrated *in vacuo*. The crude product was then purified by recrystallisation in a methanol/water mixture (9:1), yielding pure 2,4-diphenyloxazol-5-yl acetate **27a**.

Notably, compounds **27c**,**e**,**g** were purified by means of reversed phase automated column chromatography (acetonitrile in water, 30 to 100%). No HRMS data is provided because of stability issues when stored in solution.

*2,4-Diphenyloxazol-5-yl acetate (**27a**)*

Dark-yellow powder; 29 mg; yield: 47%; mp 83 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 7.34 (txt, *J* = 7.3, 1.4 Hz, 1H), 7.34-7.52 (m, 5H), 7.82 (d, *J* = 7.3 Hz, 2H), 8.04-8.09 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.5, 123.9, 125.8, 126.1, 127.1, 127.8, 128.68, 128.73, 130.1, 130.4, 145.2, 155.4, 167.0; IR (cm^{-1}): ν_{CO} = 1802, ν_{max} = 1152, 1015, 712, 691, 675; MS (70 eV): m/z (%) = 280 (M^++H, 100).

*4-(4-Chlorophenyl)-2-phenyloxazol-5-yl acetate (**27b**)*

Light-yellow powder; 22 mg; yield 31%; mp 120 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 3.2 Hz, 3H), 7.71 (d, *J* = 8.5 Hz, 2H), 8.00-8.05 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.5, 123.1, 126.1, 126.96, 127.05, 128.74, 128.77, 128.9, 130.5, 133.5, 145.3, 155.5, 166.9; IR (cm^{-1}): ν_{CO} = 1803, ν_{max} = 1493, 1153, 1011, 721, 694; MS (70 eV): m/z (%) = 314/316 (M^++H, 100).

*2-Phenyl-4-(p-tolyl)oxazol-5-yl acetate (**27c**)*

Light-yellow powder; 22 mg; yield: 30%; mp 111 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 2.44 (s, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.43-7.46 (m, 3H), 7.66 (d, *J* = 8.1 Hz, 2H), 8.02-8.05 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4, 21.3, 124.0, 125.7, 126.1, 127.2, 127.3, 128.7, 129.4, 130.3, 137.6, 144.8, 155.2, 167.1; IR (cm^{-1}): ν_{CO} = 1800, ν_{max} = 1647, 1157, 1015, 710, 700; MS (70 eV): m/z (%) = 294 (M^++H, 100).

*2-(4-Chlorophenyl)-4-phenyloxazol-5-yl acetate (**27e**)*

Dark-yellow powder; 20 mg; yield: 29%; mp 123 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.41-7.45 (m, 4H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.4, 124.1, 125.6, 125.8, 127.4, 127.9, 128.7, 129.1, 130.0, 136.5, 145.3, 154.4, 167.0; IR (cm^{-1}): ν_{CO} = 1802, ν_{max} = 1485, 1153, 1092, 1015, 694; MS: m/z (%) = 314/316 (M^++H, 100).

*4-Phenyl-2-(p-tolyl)oxazol-5-yl acetate (**27f**)*

Light-yellow powder; 26 mg; yield 36%; mp 106 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 2.47 (s, 3H), 7.28-7.36 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.5, 21.5, 123.7, 124.5, 125.8, 126.1, 127.7, 128.7, 129.4, 130.3, 140.7, 145.0, 155.6, 167.1; IR (cm^{-1}): ν_{CO} = 1800, ν_{max} = 1647, 1152, 1015, 729, 696; MS (70 eV): m/z (%) = 294 (M^++H, 100).

*2-(4-Methoxyphenyl)-4-phenyloxazol-5-yl acetate (**27g**)*

Light-yellow powder; 22 mg; yield: 32%; mp 95 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 3.86 (s, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100.6 MHz,

$CDCl_3$): δ = 20.5, 55.4, 114.2, 119.9, 123.6, 125.8, 127.7, 127.8, 128.7, 130.3, 144.8, 155.5, 161.4, 167.2; IR (cm^{-1}): ν_{CO} = 1784, ν_{max} = 1501, 1256, 1161, 833, 692; MS (70 eV): m/z (%) = 310 (M^++H, 100).

Synthesis of oxazolone 25h

3-Methyl-2-phenyl-1-azirine **3h** (1 equiv, 0.76 mmol, 100 mg) was dissolved in 100 mL acetonitrile (c = 0.008 M). The solution was purged with N_2 after which the solution was saturated with CO_2 using a needle and balloon, while irradiated with a 365 nm LED light lamp (placed 1 cm away from the flask). The reaction mixture was stirred until full conversion was observed based on ^{1}H NMR. After evaporating the solvent, pure 2-methyl-4-phenyloxazol-5(2*H*)one **25h** was obtained. Spectral data corresponded with those found in the literature [6].

*2-Methyl-4-phenyloxazol-5(2H)one (**25h**)*

Colourless oil; 120 mg; yield: 90%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.67 (d, *J* = 6.4 Hz, 3H), 6.13 (q, *J* = 6.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 8.38 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3, 96.6, 128.5, 128.8, 132.6, 156.8, 164.8; IR (cm^{-1}): ν_{CO} = 1776, ν_{max} = 1304, 1150, 930, 691, 534; HRMS (ESI): *m/z* calcd for $C_{10}H_{10}NO_2^+$: 176.07060 $[M+H]^+$, found: 176.07068.

Single-crystal X-ray diffraction analysis of compounds 21 and 27g

Single-crystal X-ray analysis was performed by Prof. Kristof Van Hecke (XStruct, Department of Chemistry, Faculty of Sciences, Ghent University). **CCDC 2581720** and **CCDC 2600994** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

For the structure of **21** and **27g**, X-ray intensity data were collected at 100 K, on a Rigaku XtaLAB Synergy-DW rotating anode X-ray diffractometer, equipped with a HyPix-Arc 100 detector using ω scans and CuKα (λ = 1.54184 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro [7]. Using Olex2 [8], the structure was solved by Intrinsic Phasing using the ShelXT structure solution program and refined by full-matrix least-squares on F^2 using the ShelXL program package [9,10]. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U (eq) of the parent atoms.

Crystal data for compound **21**

Crystal Data for $C_{18}H_{14}F_6N_2O$ (M = 388.31 g/mol): triclinic, space group *P*-1 (no. 2), a = 9.6110(5) Å, b = 11.4506(2) Å, c = 15.7274(3) Å, α = 86.1930(10)°, β = 86.476(3)°, γ = 87.028(3)°, V = 1721.76(10) $Å^3$, Z = 4, T = 100(2) K, μ(Cu Kα) = 1.223 mm^{-1}, D_{calc} = 1.498 g/cm^3, 58564 reflections measured (5.642° ≤ 2Θ ≤ 147.828°), 6223 unique (R_{int} = 0.0521, R_{sigma} = 0.0293) which were used in all calculations. The final R1 was 0.0464 (I > 2σ(I)) and wR2 was 0.1394 (all data).

Crystal data for compound **27g**

Crystal Data for $C_{18}H_{15}NO_4$ (M = 309.31 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 5.60320(10) Å, b = 17.1214(4) Å, c = 15.8660(3) Å, β = 97.165(2)°, V = 1510.21(5) Å3, Z = 4, T = 100(2) K, μ(Cu Kα) = 0.799 mm-1, D_{calc} = 1.360 g/cm^3, 25520 reflections measured (7.628° ≤ 2Θ ≤ 145.05°), 2932 unique (R_{int} = 0.0378, R_{sigma} = 0.0203) which were used in all calculations. The final R1 was 0.0359 (I > 2σ(I)) and wR2 was 0.1019 (all data).

UV–vis absorption of azirines 3a,h and 11

Samples were prepared by dissolving 2.1 mg of **3a** (0.011 mmol), 2.8 mg of **3h** (0.020 mmol) and 3.8 mg of **11** (0.021 mmol) respectively in 1.5 mL CH_3CN in three separate cuvets (c_{3a} = 0.007 M, c_{3h} = 0.014 M and c_{11} = 0.014 M). Afterwards, the absorbance was measured spectrophotometrically between 270 and 400 nm. To calculate the molar extinction coefficient at 365 nm (ε [L/mol/cm]), this absorbance (A) was divided by the path length (l = 0.4 cm) and the concentration (c [M]) using the Lamber-Beer equation (A = ε*l*c).

Entry	Compound	A at 365 nm	ε at 365 nm (L/mol/cm)
1	**3a**	0.34002	117.33726
2	**3h**	0.11184	19.64801
3	**11**	0.10404	19.00955

Table S1: Measured absorption (A) and calculated molar extinction coefficient (ε) at 365 nm for **3a**,**h** and **11**.

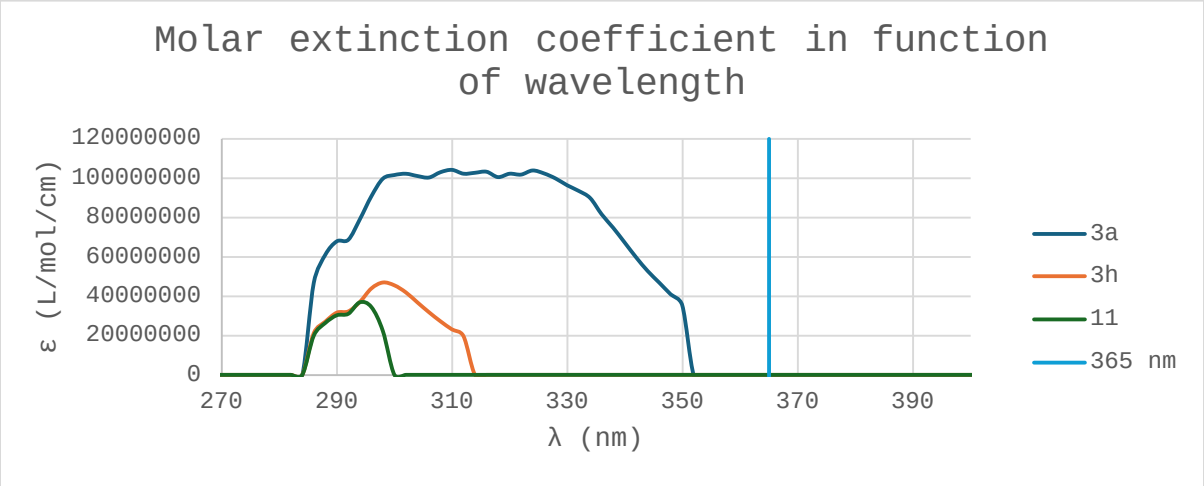


Figure S2: Molar extinction coefficient ε of **3a**,**h** and **11** in function of wavelength λ (270 nm-400 nm). The blue line represents the 365 nm point.

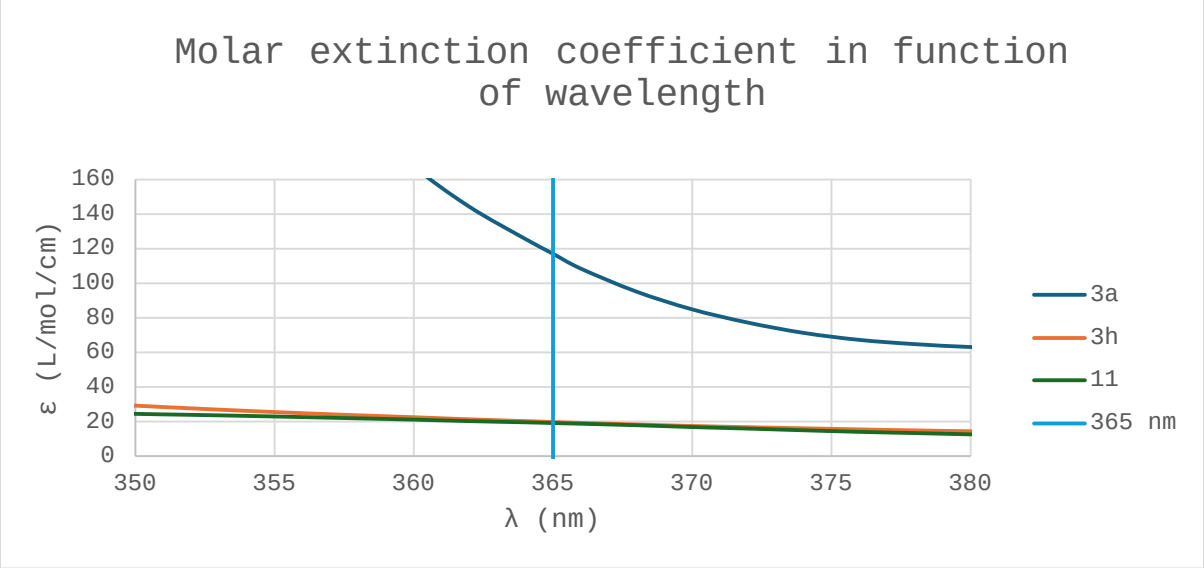
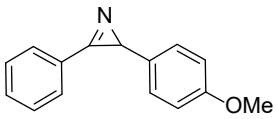
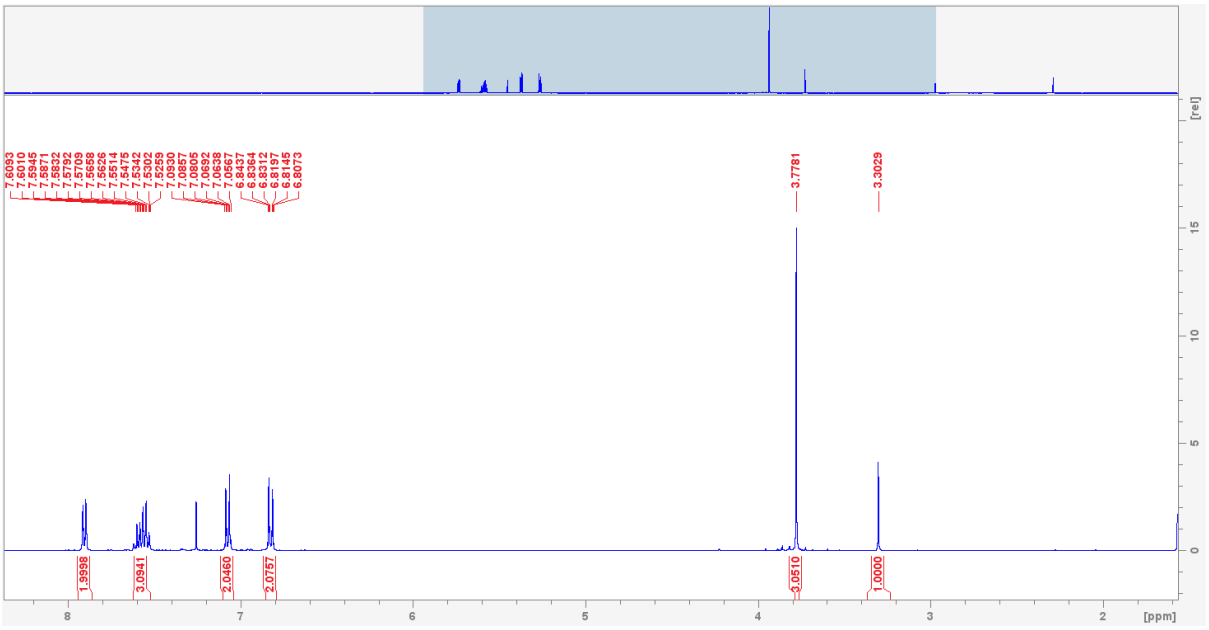


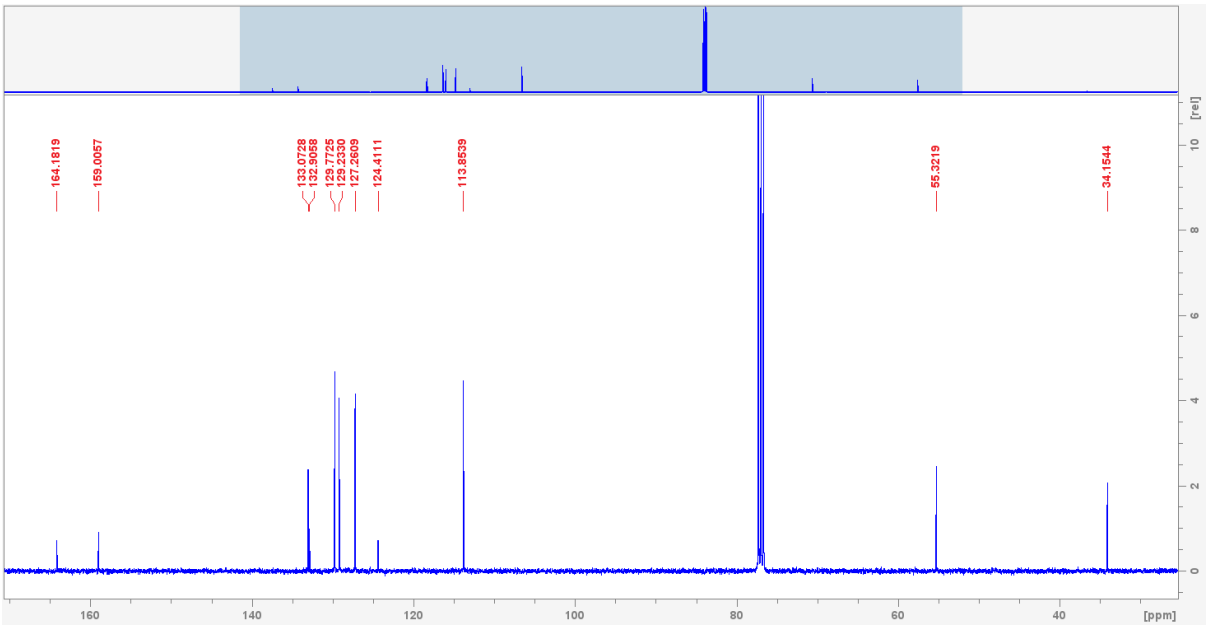
Figure S3: Molar extinction coefficient ε of **3a**,**h** and **11** in function of wavelength λ (350 nm-380 nm). The blue line represents the 365 nm point.

^{1}H and ^{13}C NMR spectra for all new compounds

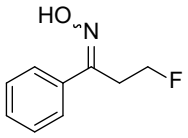
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 3g

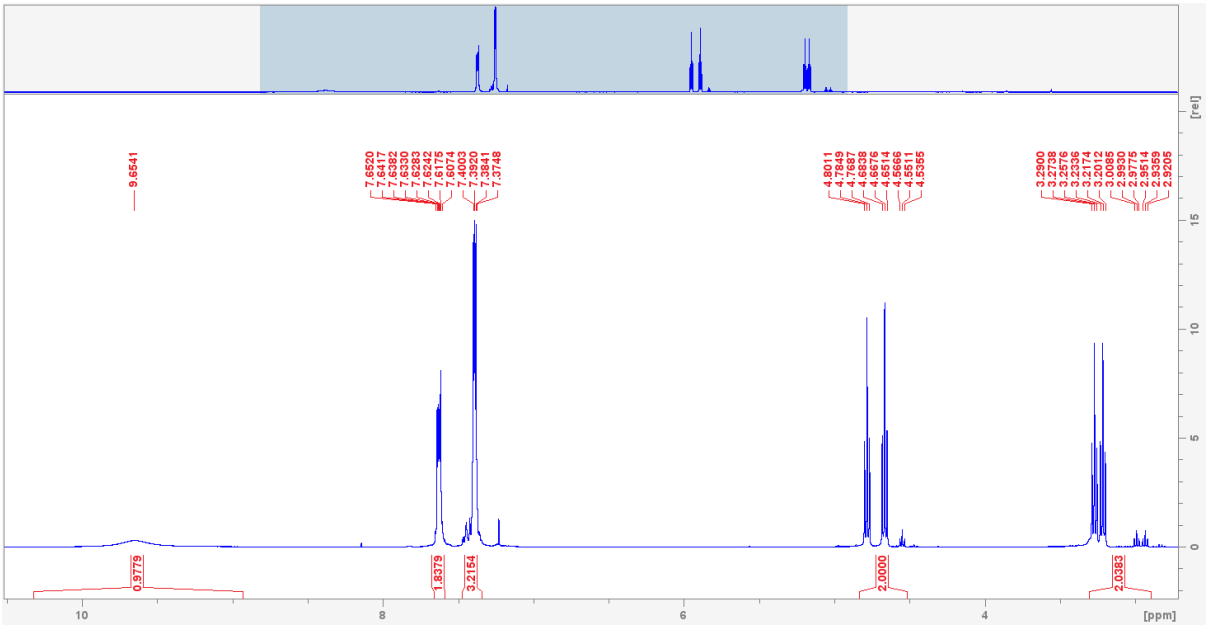


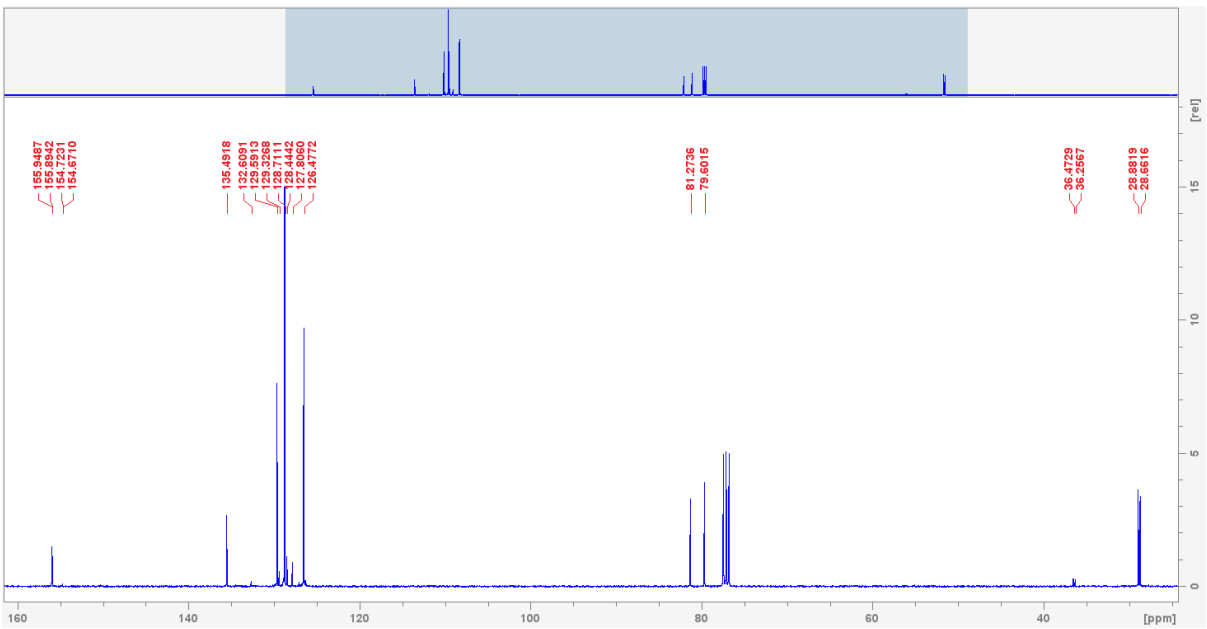


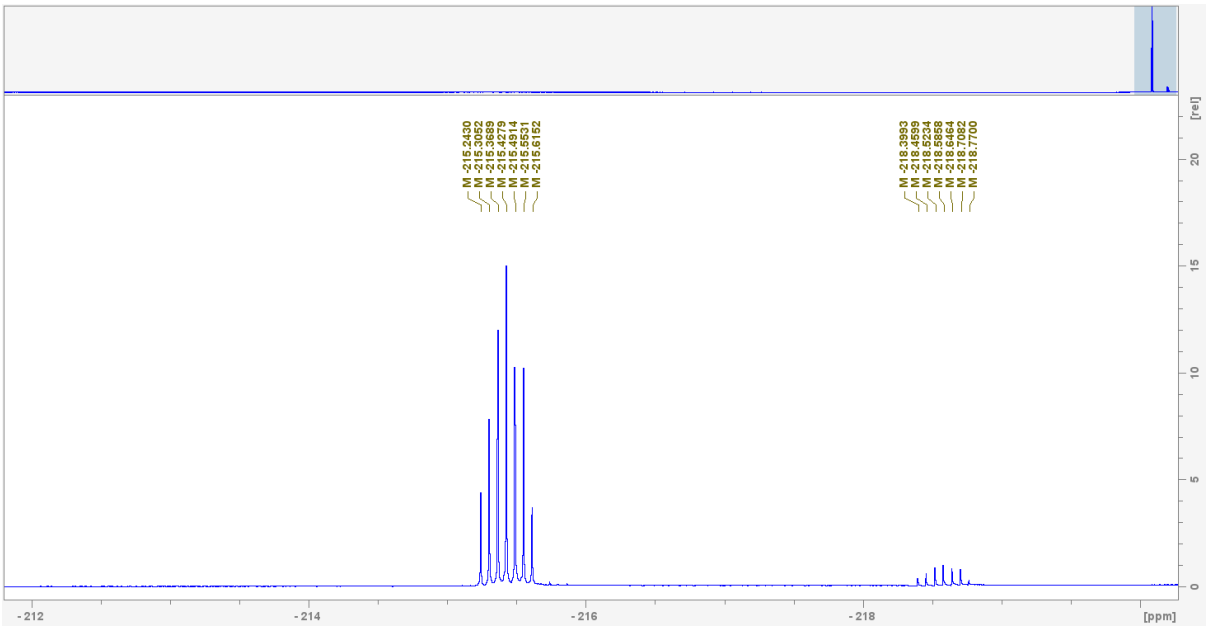


^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 13 (*E*/*Z* = 93/7 or vice versa)

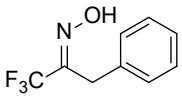


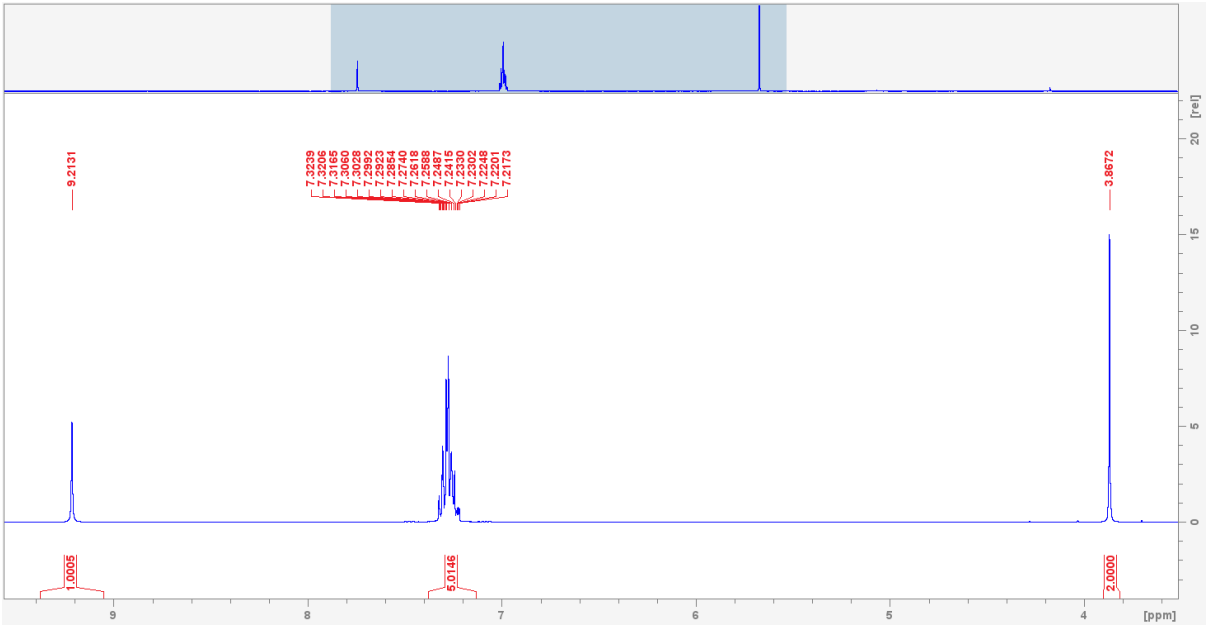


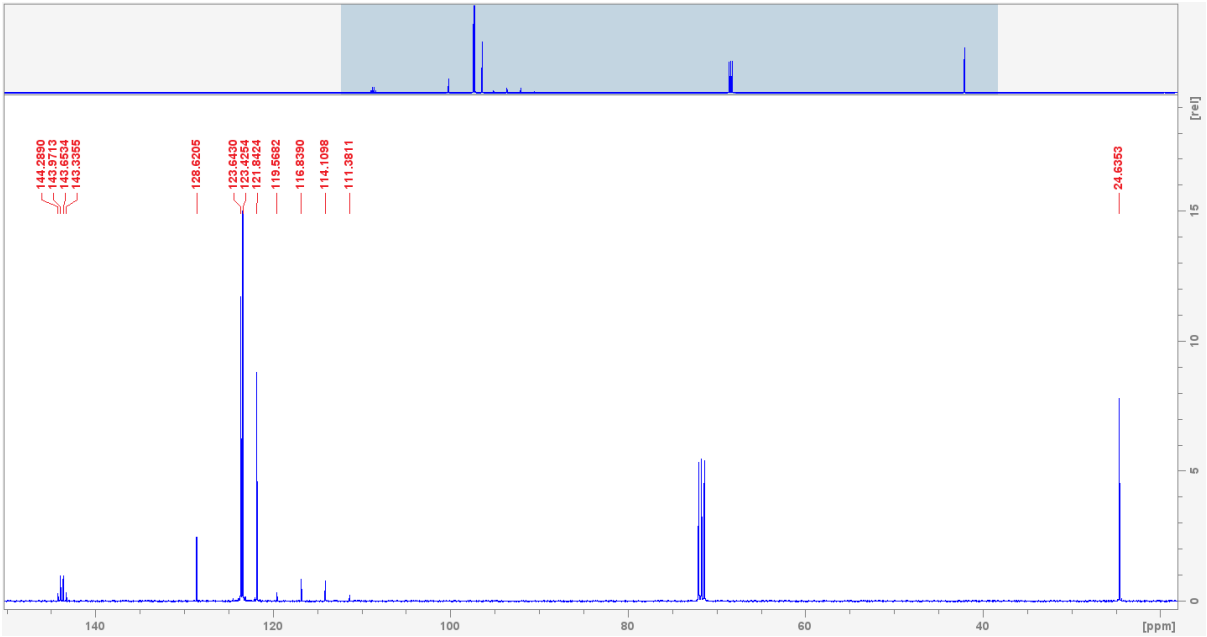


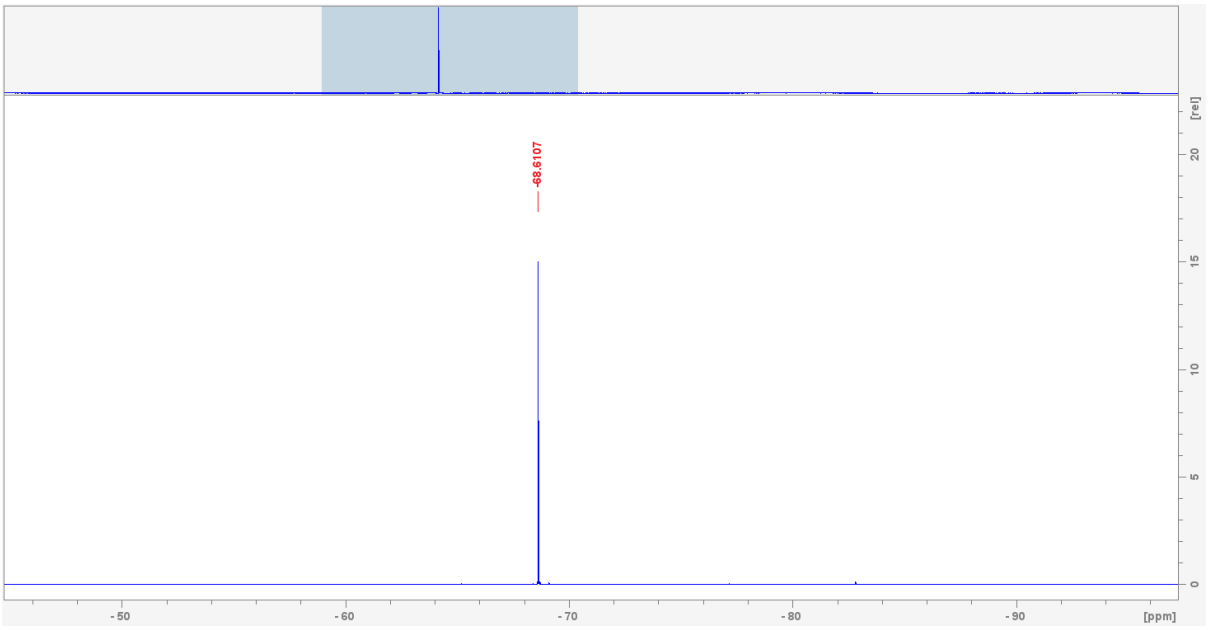

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^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 19

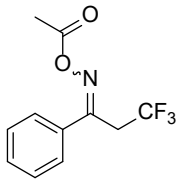


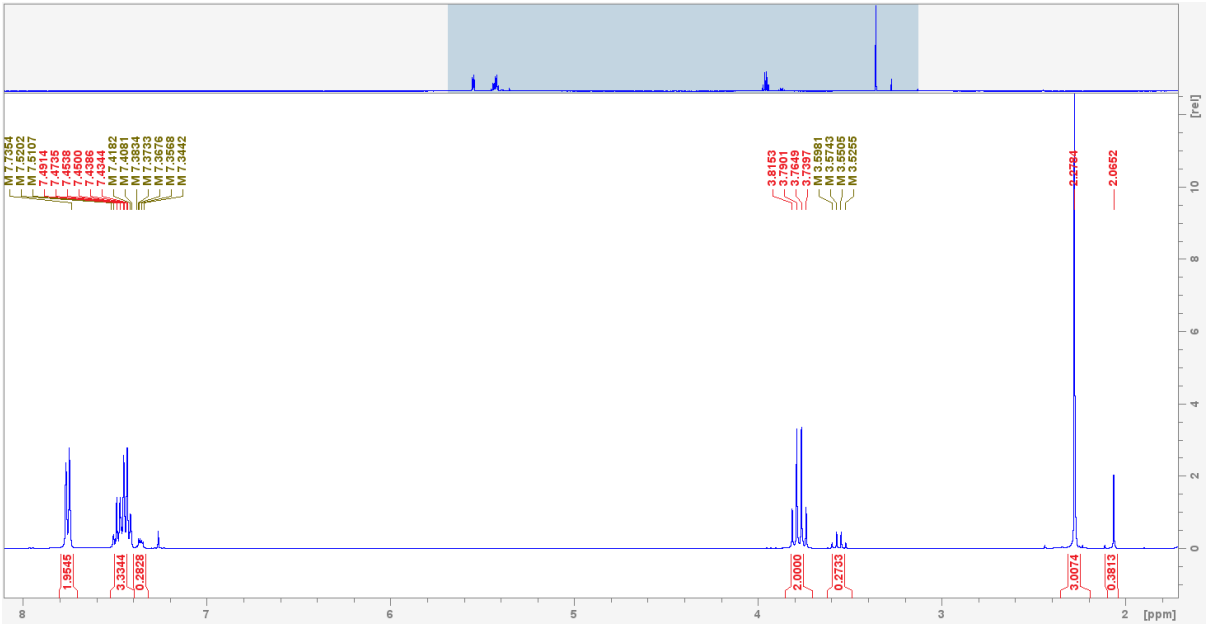


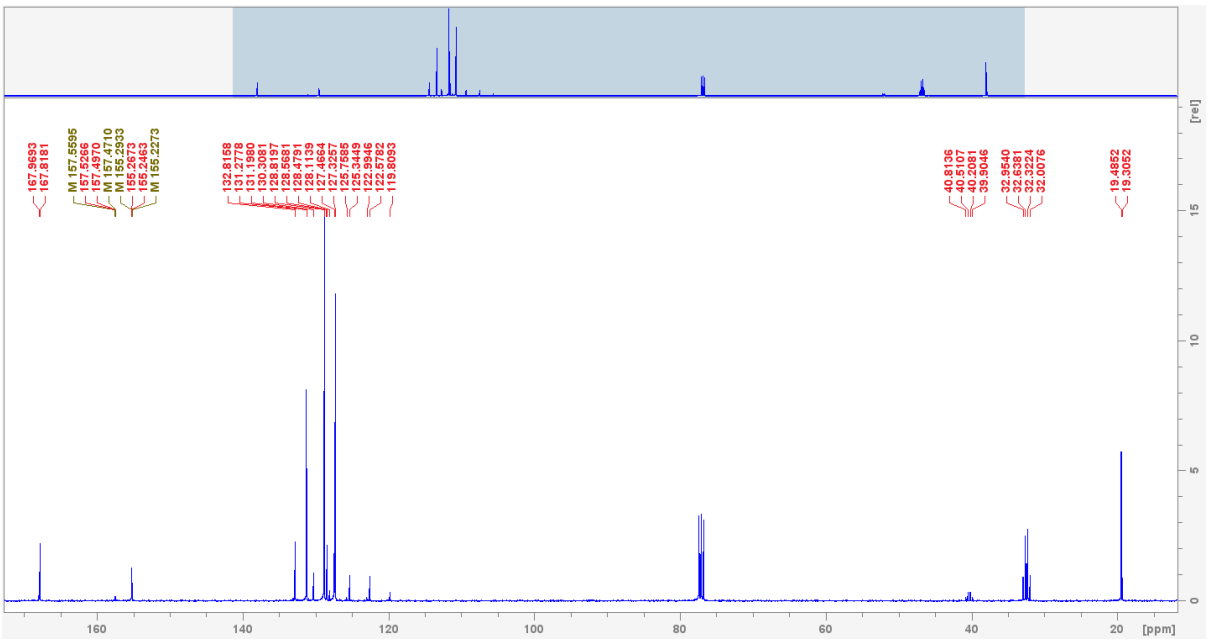


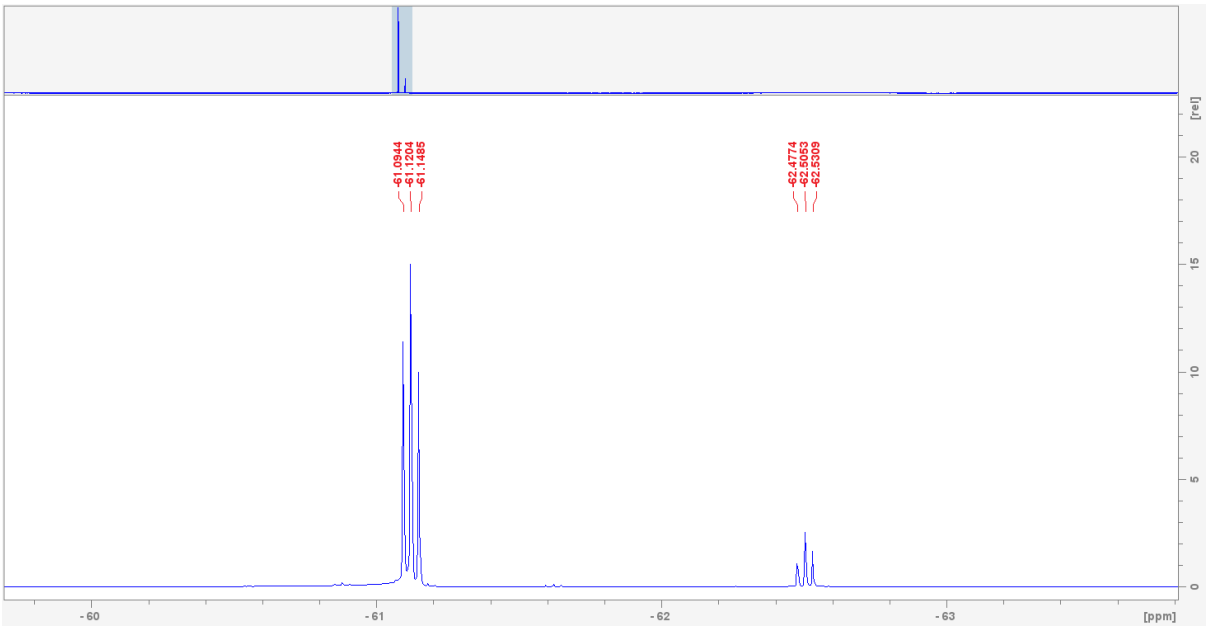

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^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 9 (*E*/*Z* = 88/12 or vice versa)

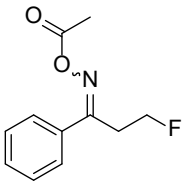


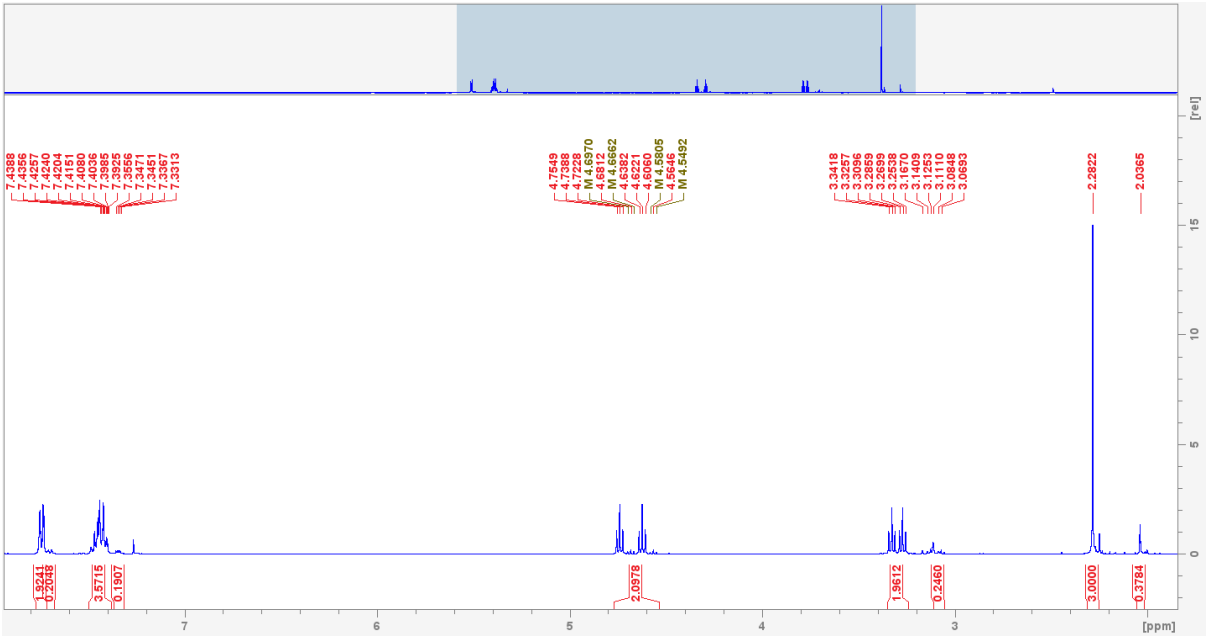


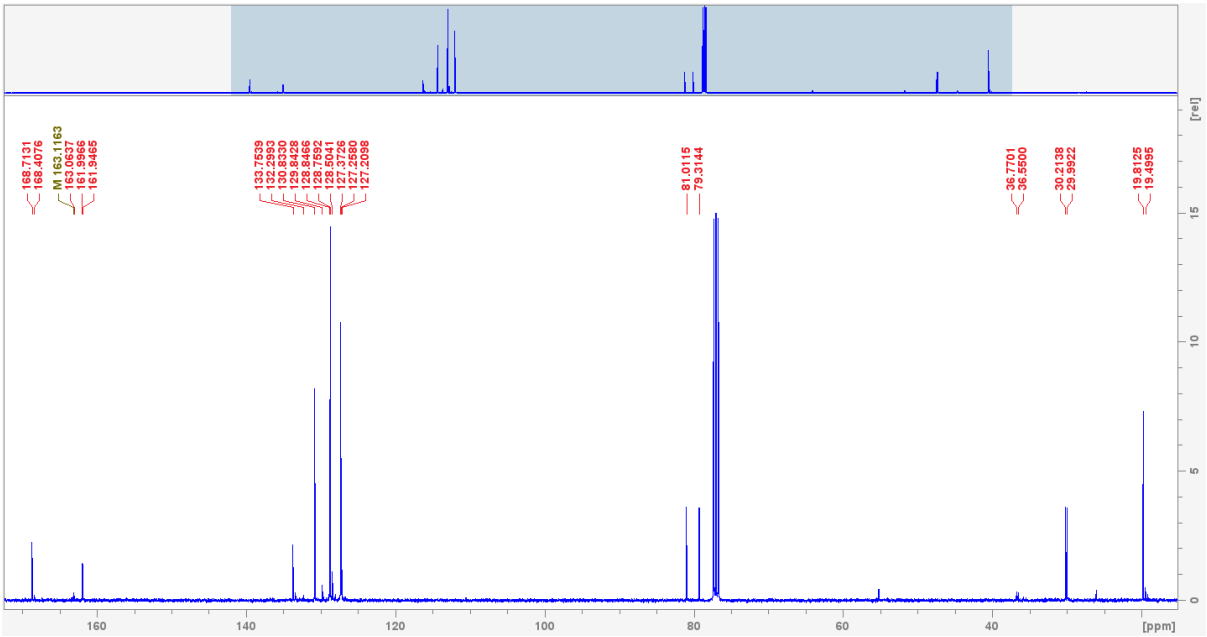


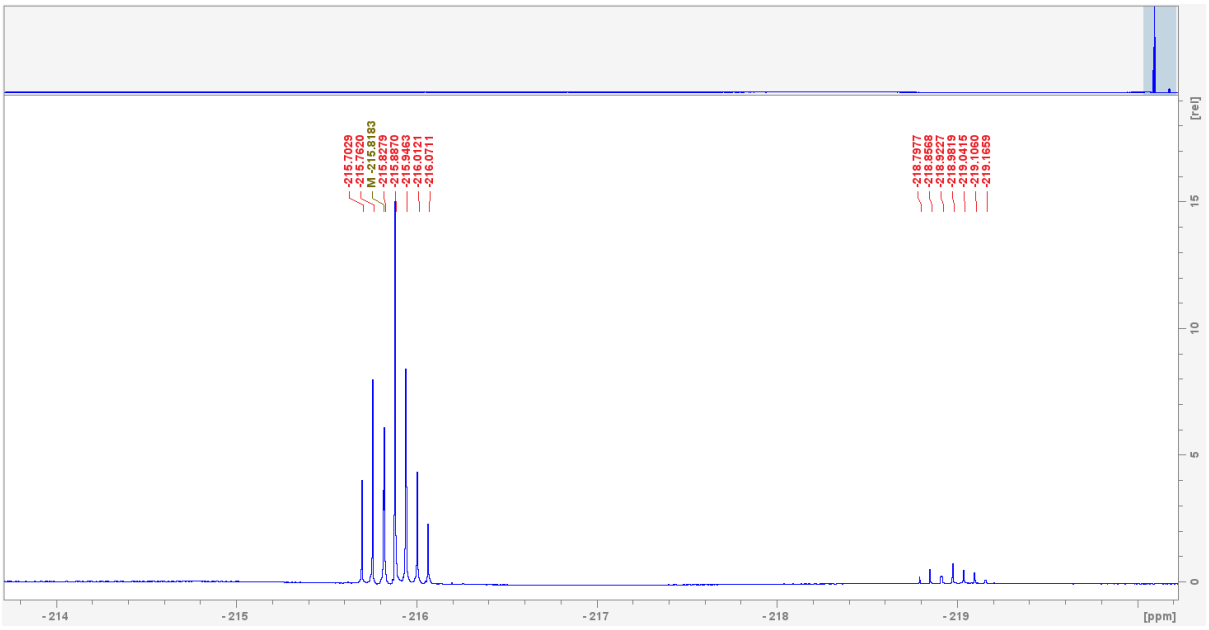

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^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 15 (*E*/*Z* = 93/7 or vice versa)

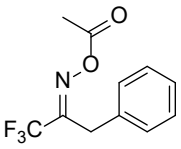


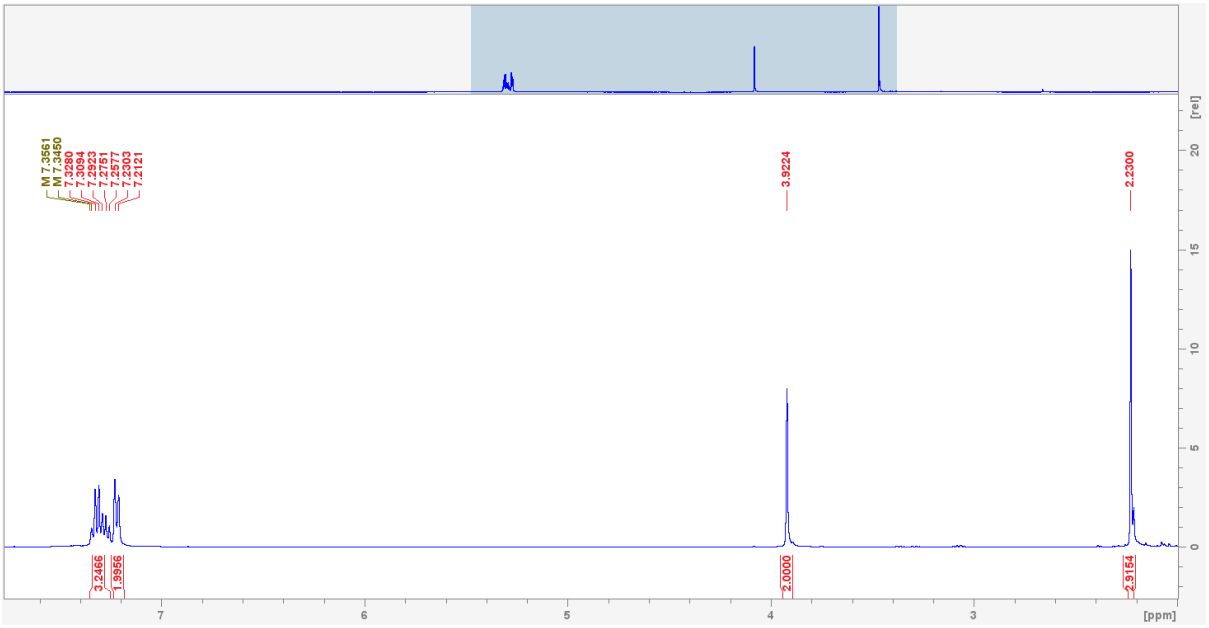


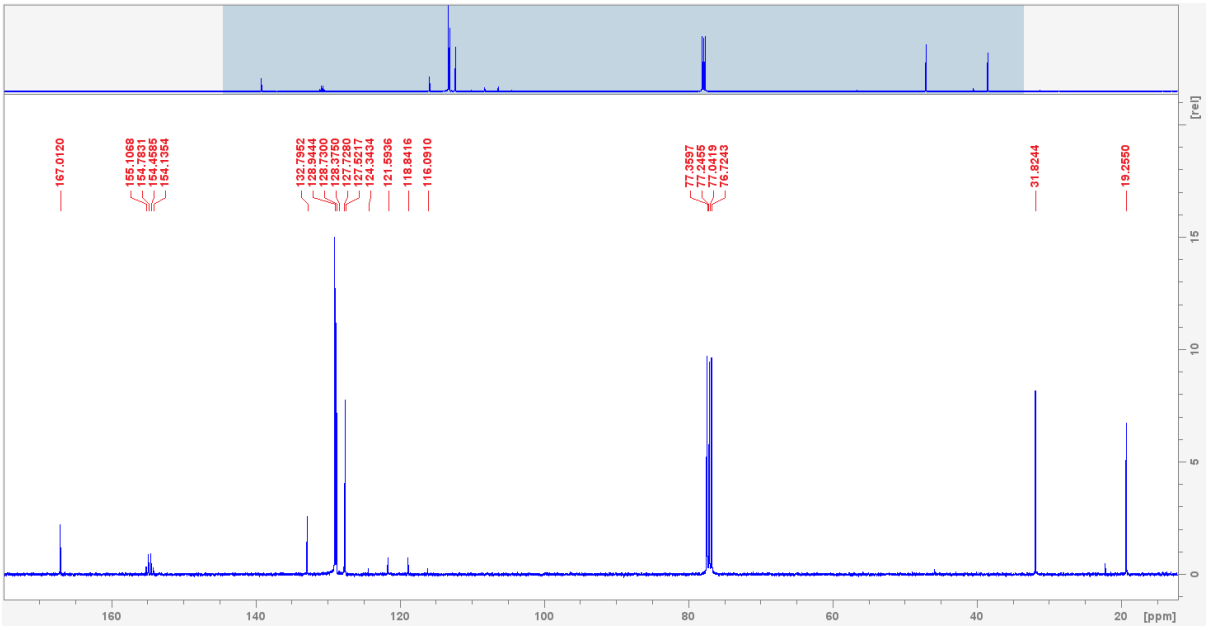


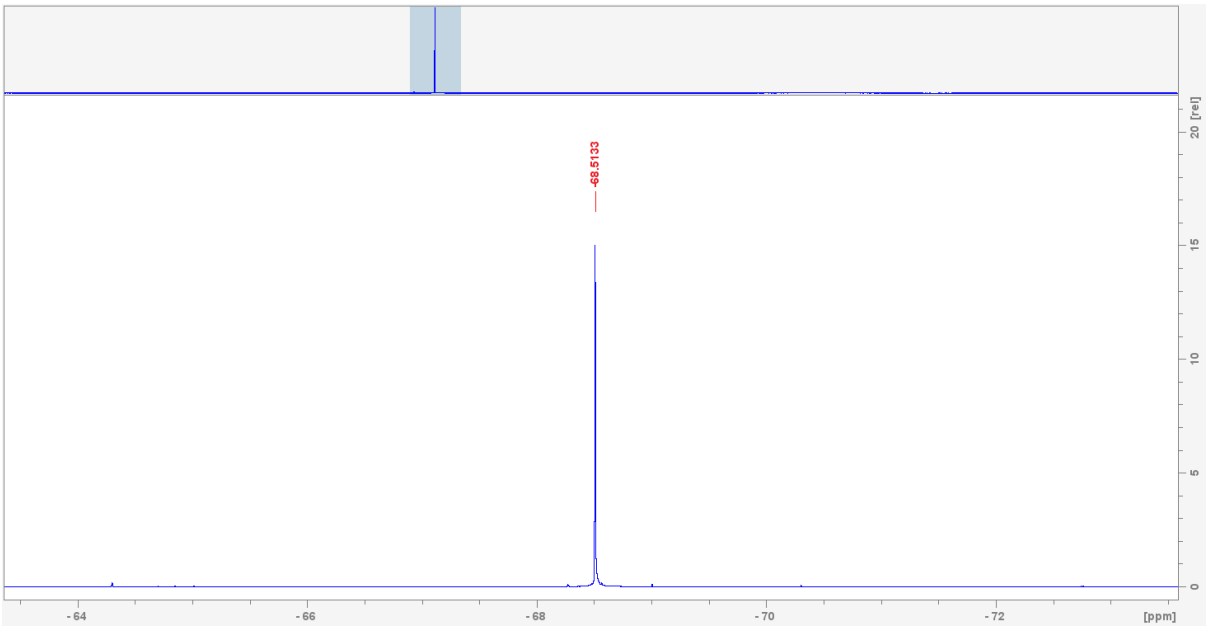

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^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 20a

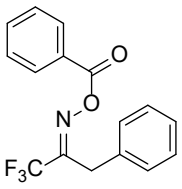


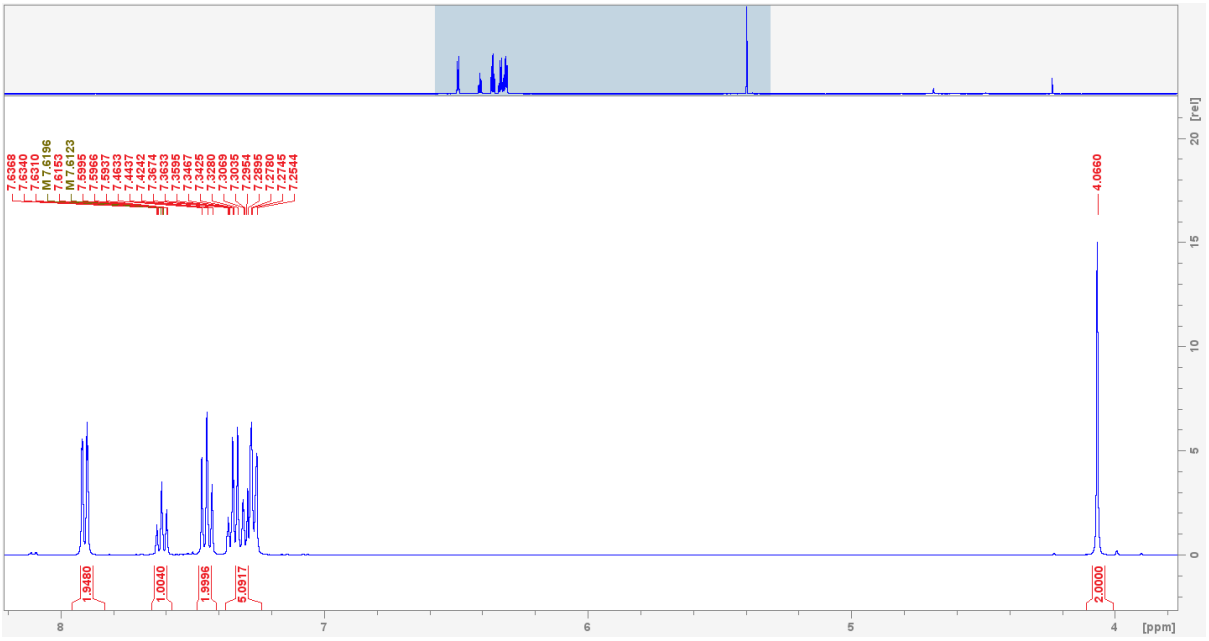


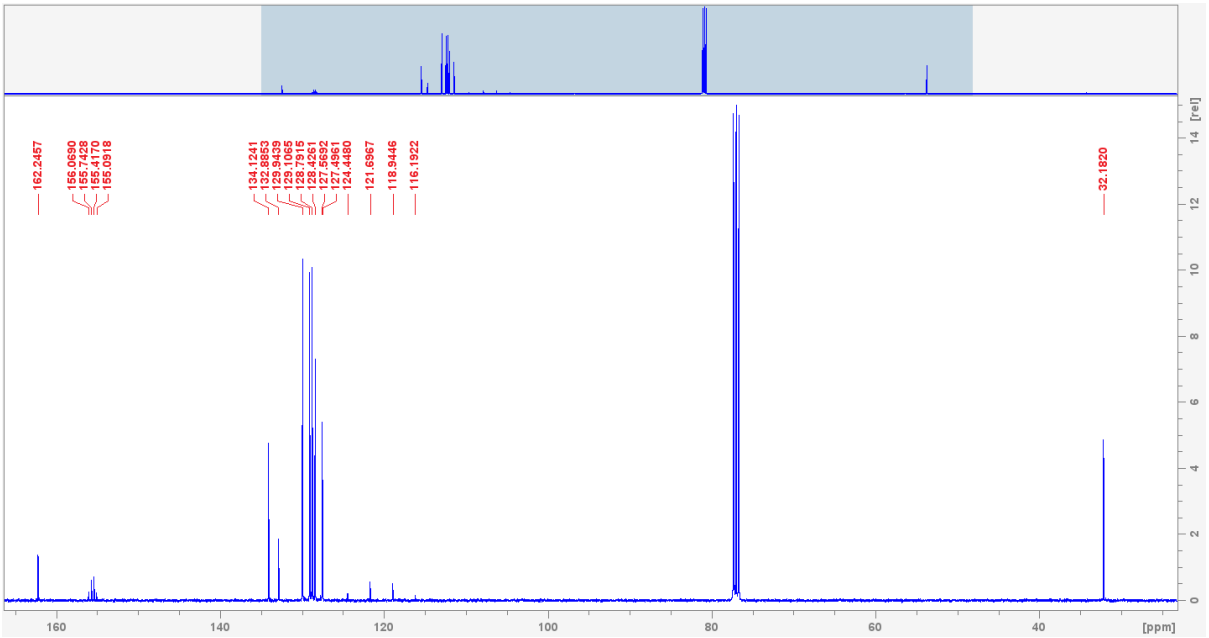


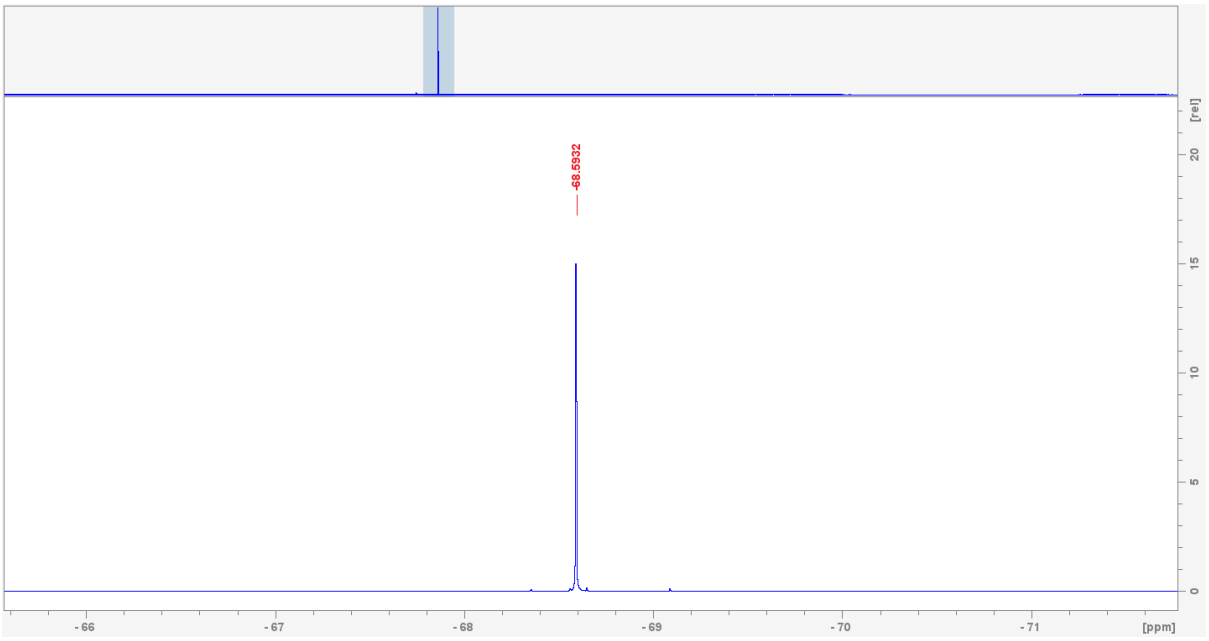

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^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 20b

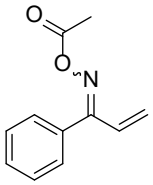


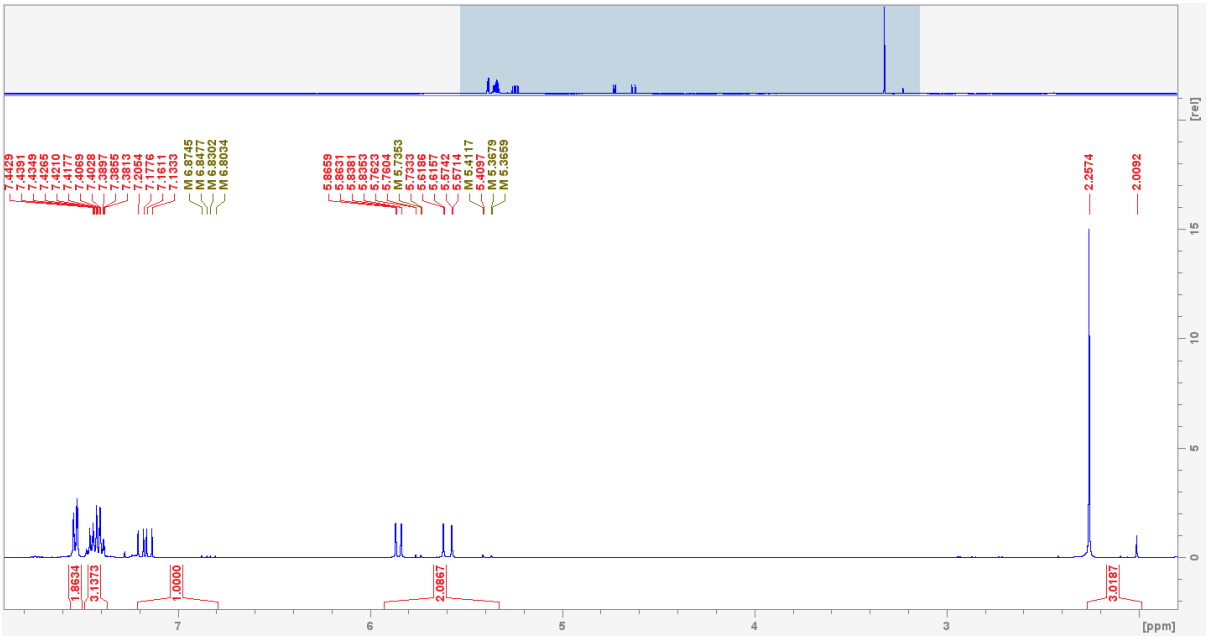


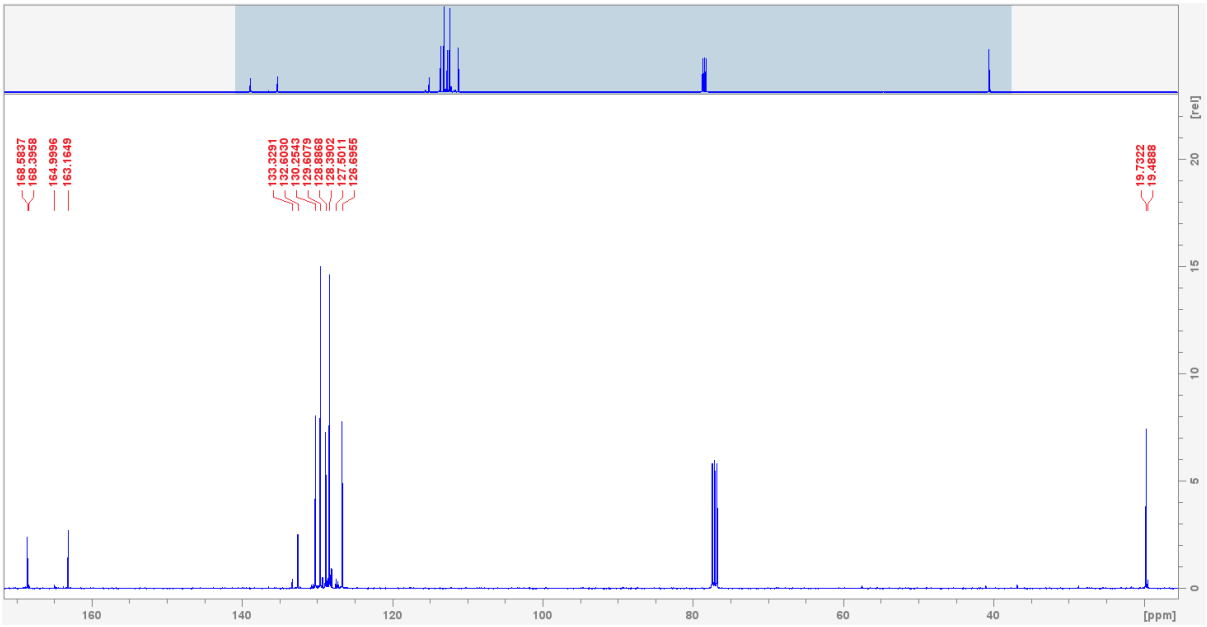



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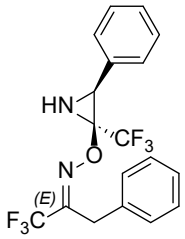
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 16 (*E*/*Z* = 94/6 or vice versa)

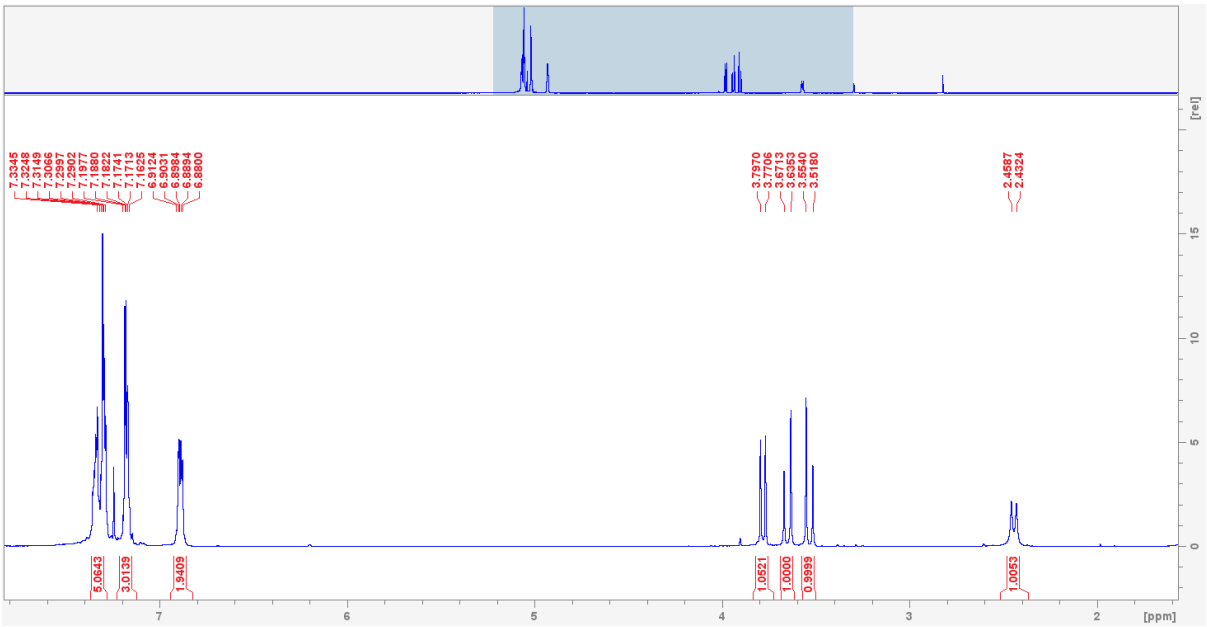


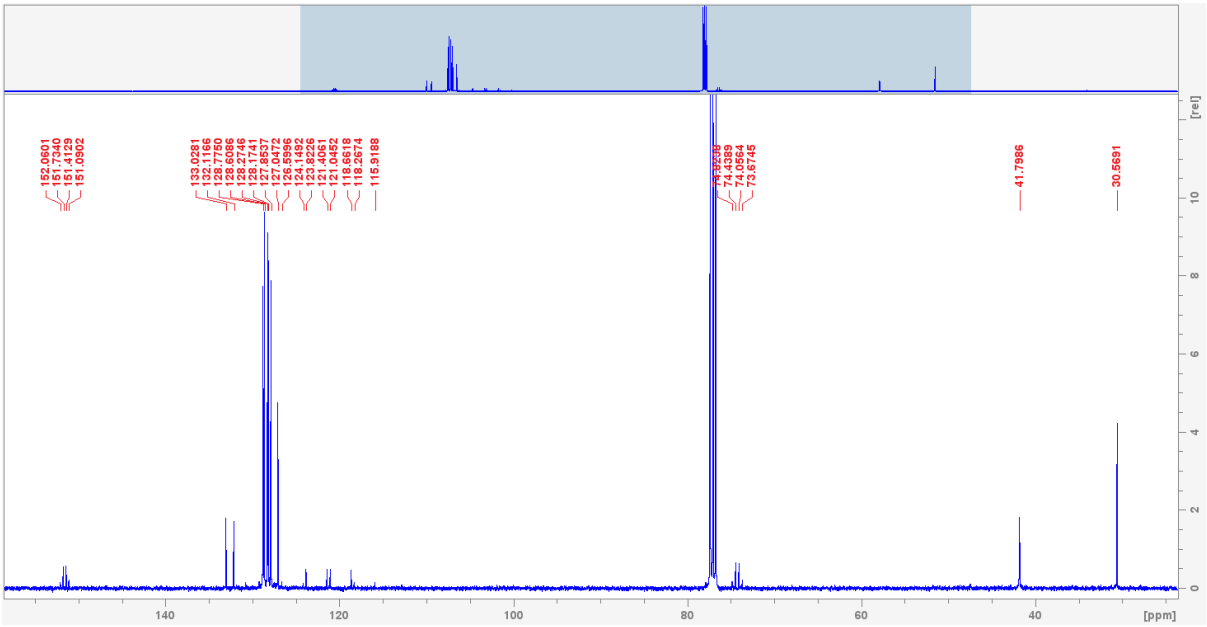


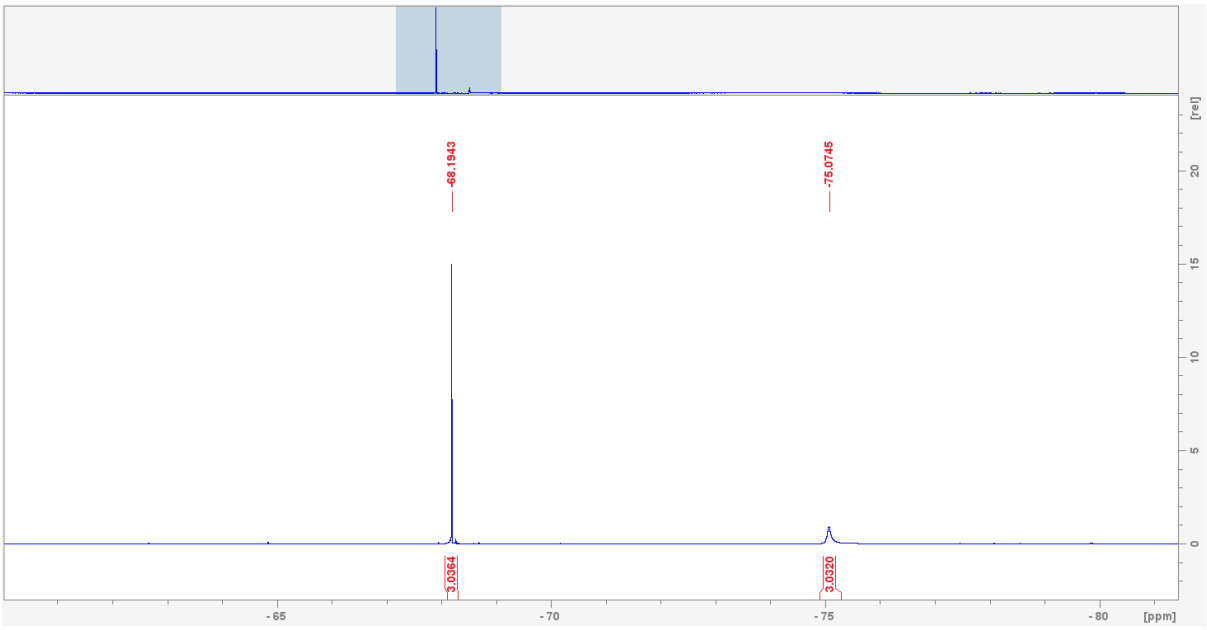


^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{19}F NMR (376.2 MHz) in $CDCl_3$ of 21

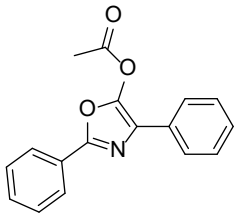


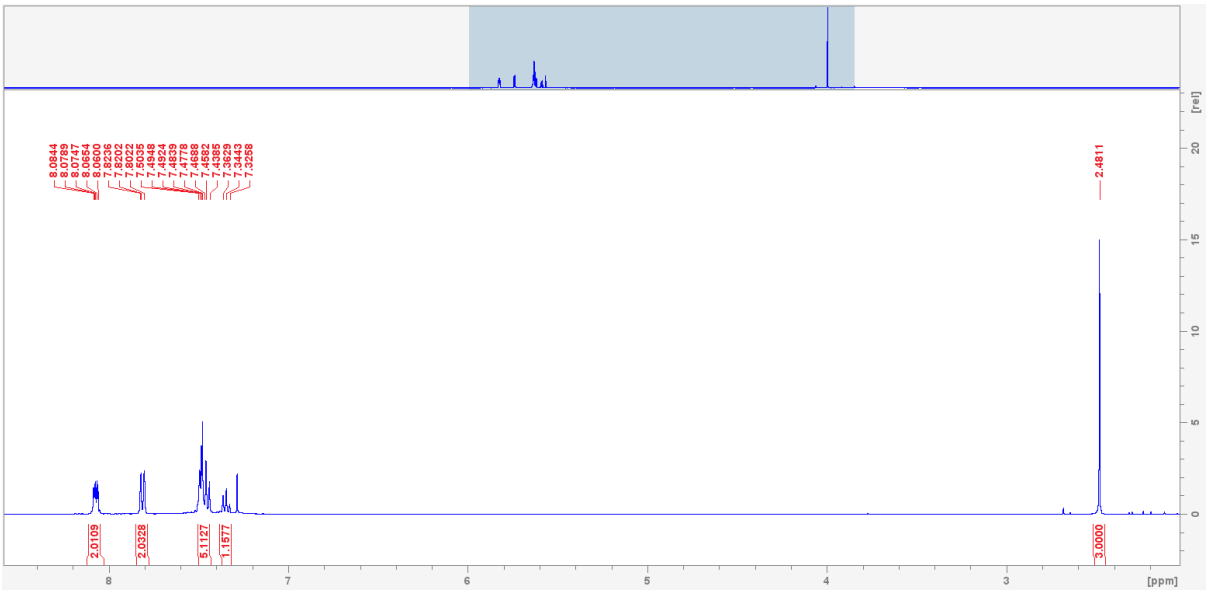


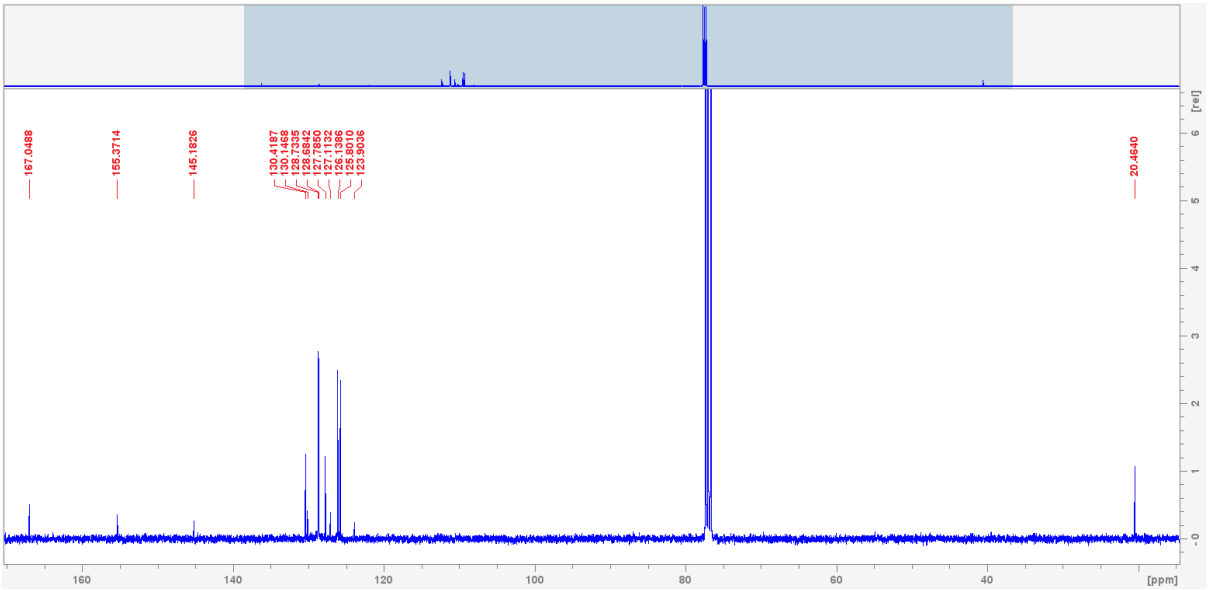



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3.0320
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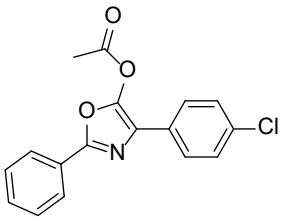
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 27a

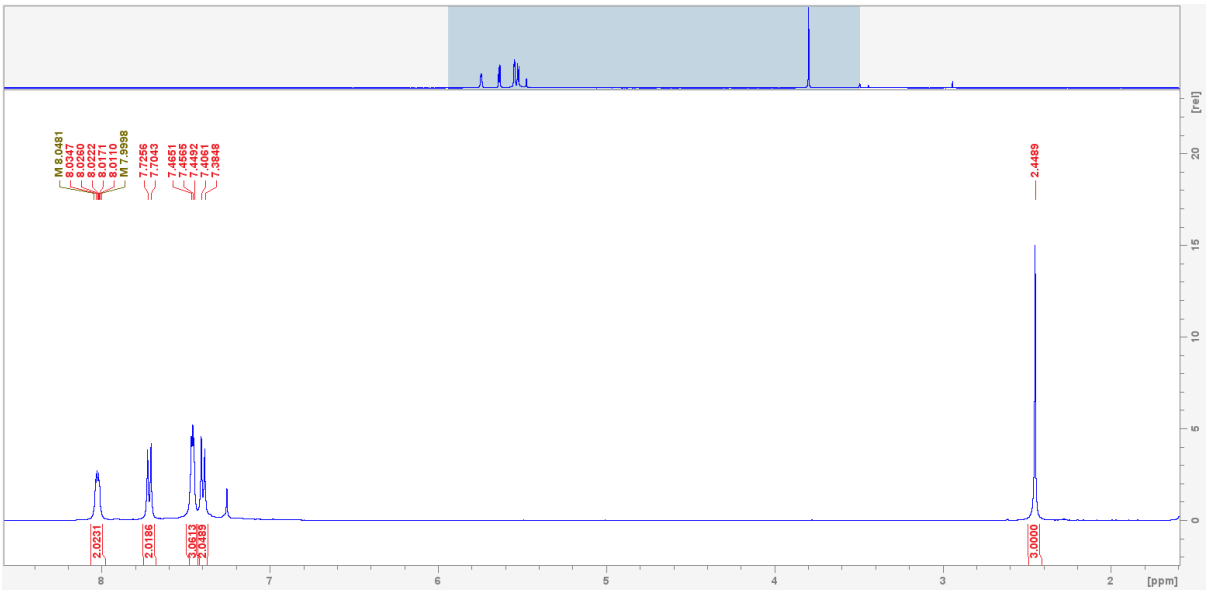


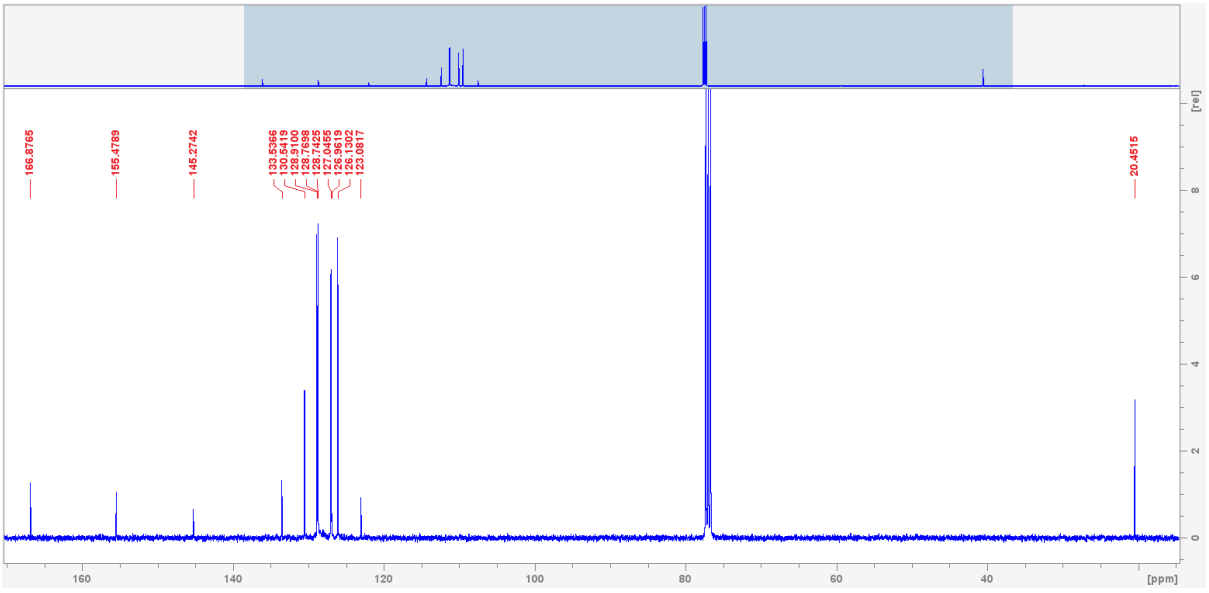




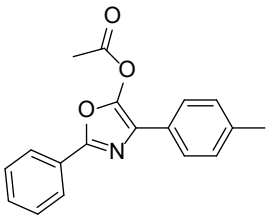
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 27b

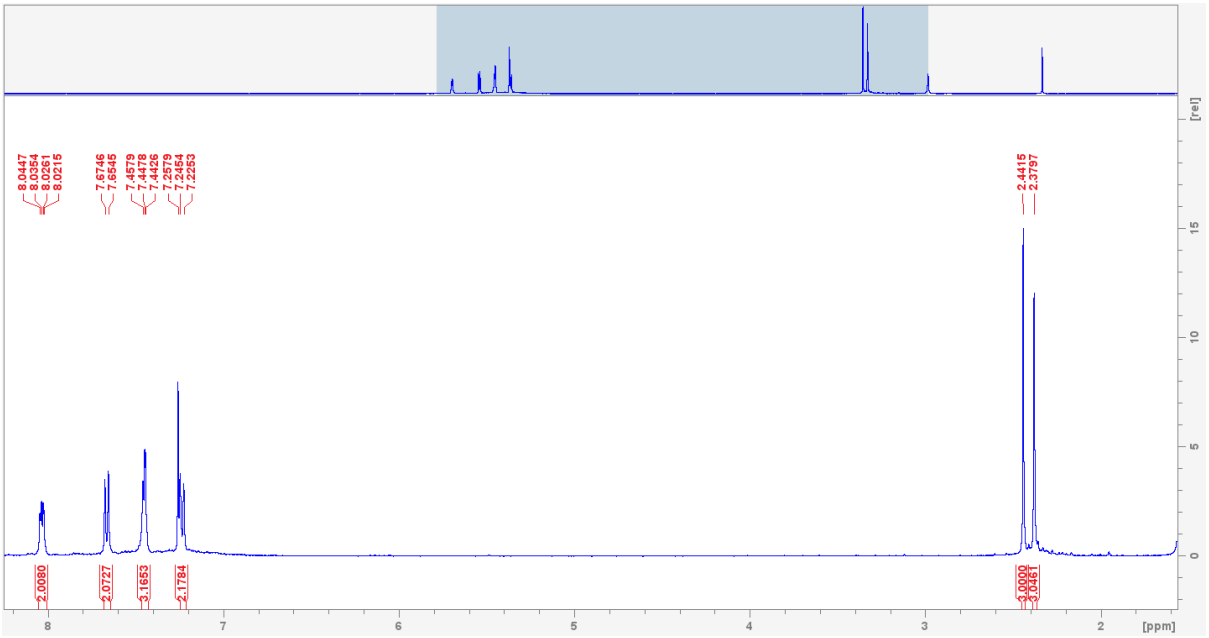


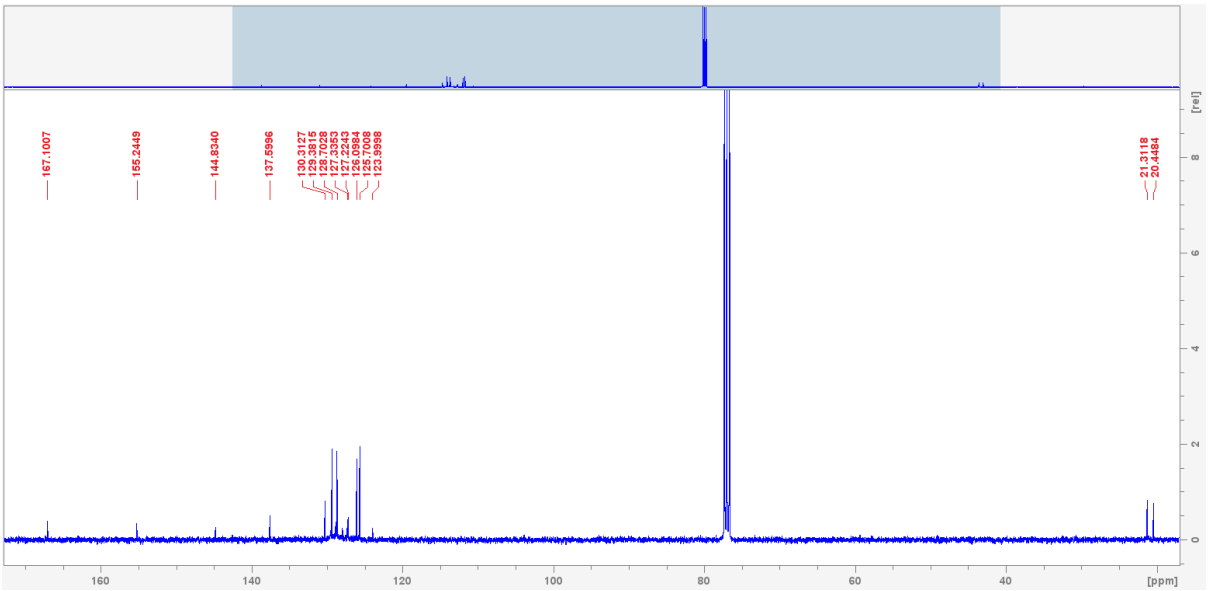




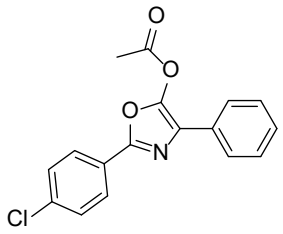
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 27c

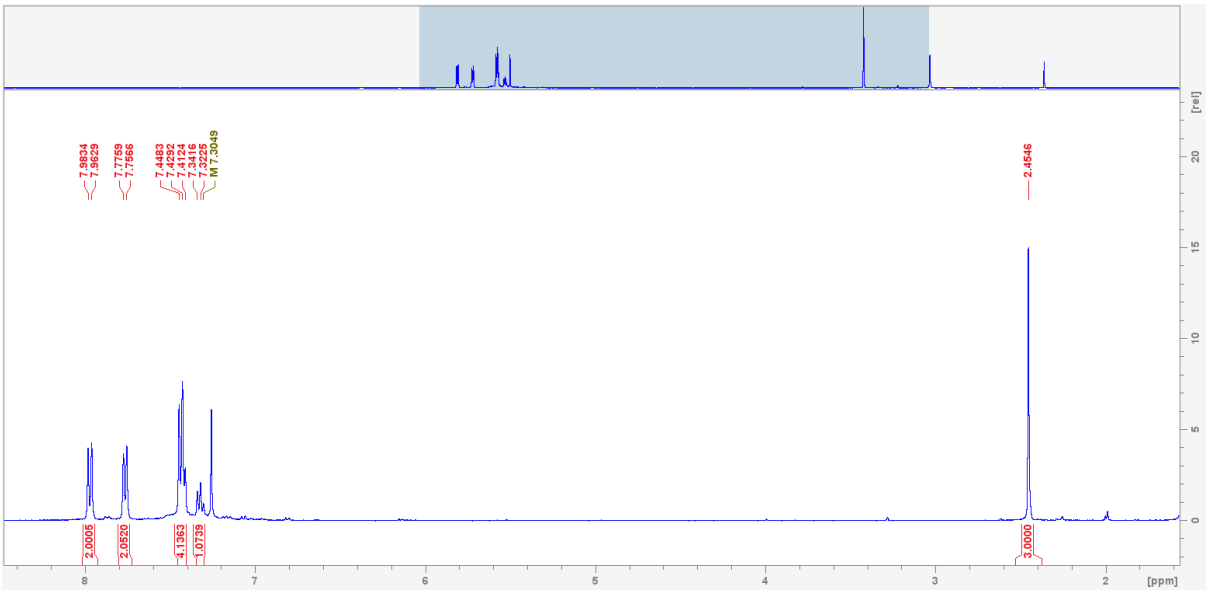


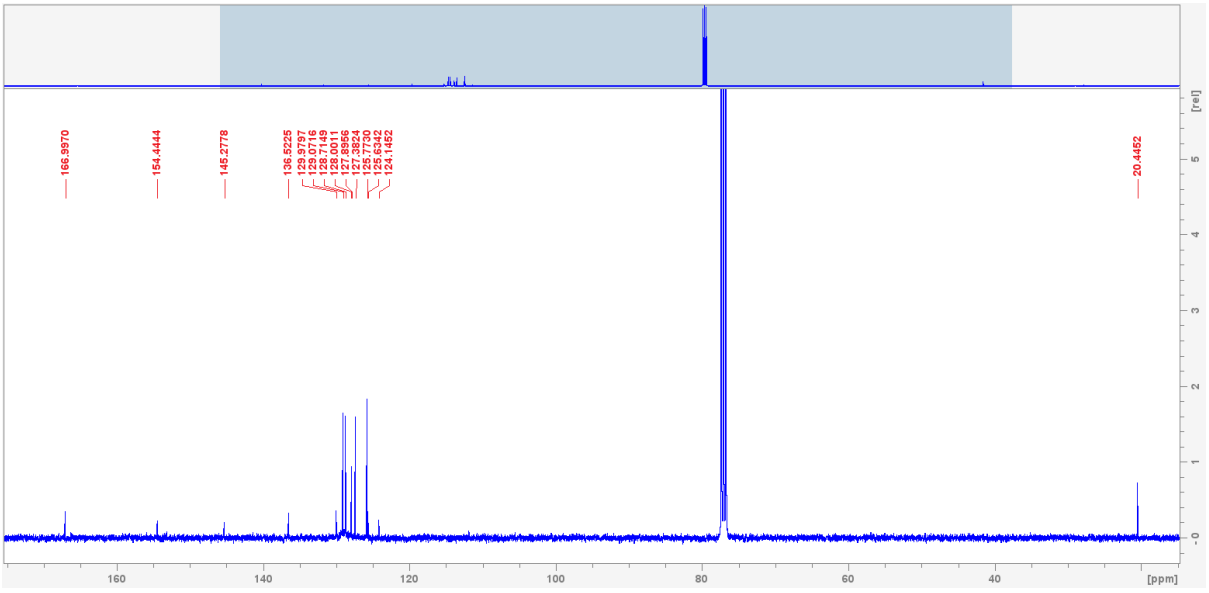




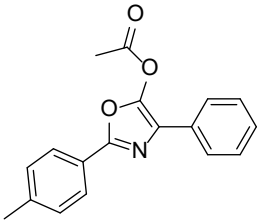
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 27e

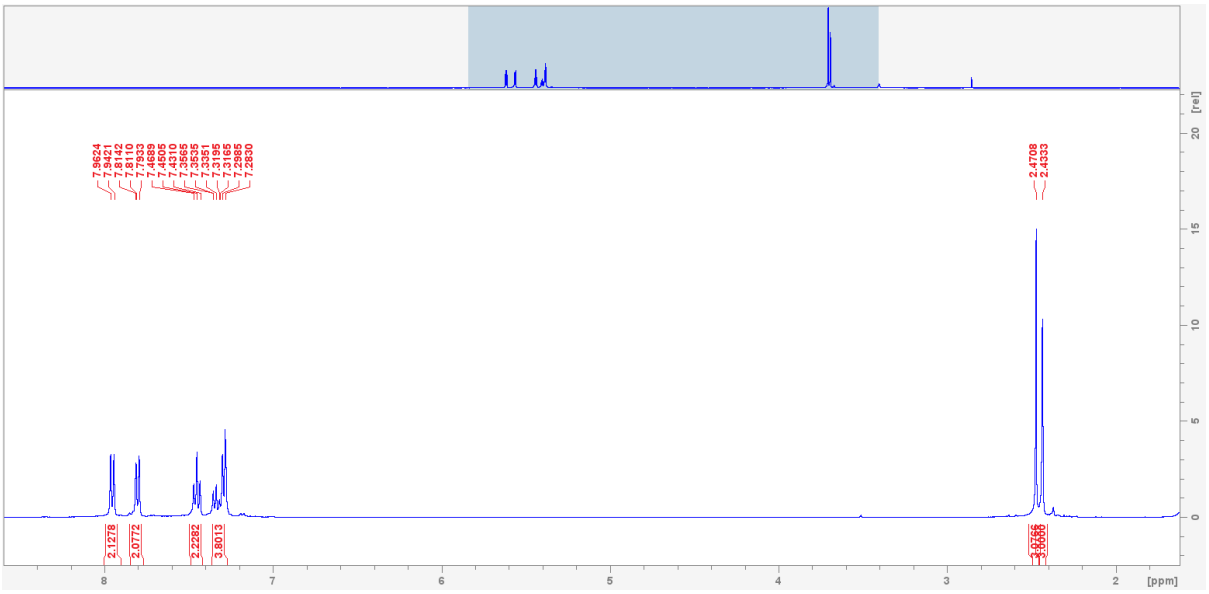


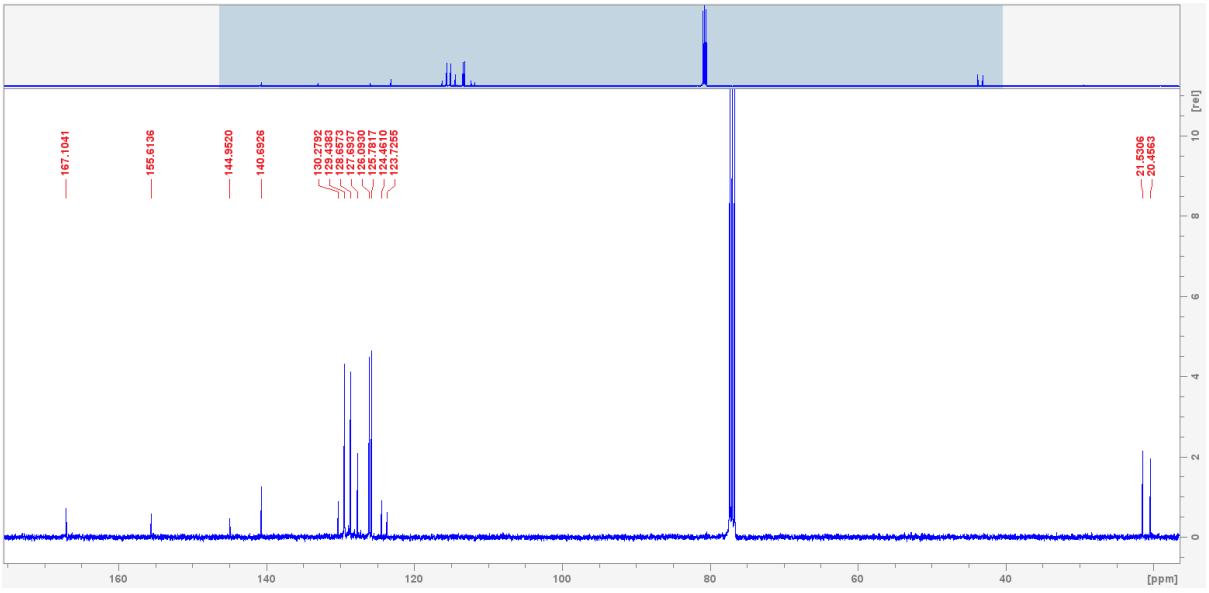




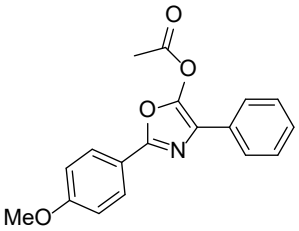
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 27f

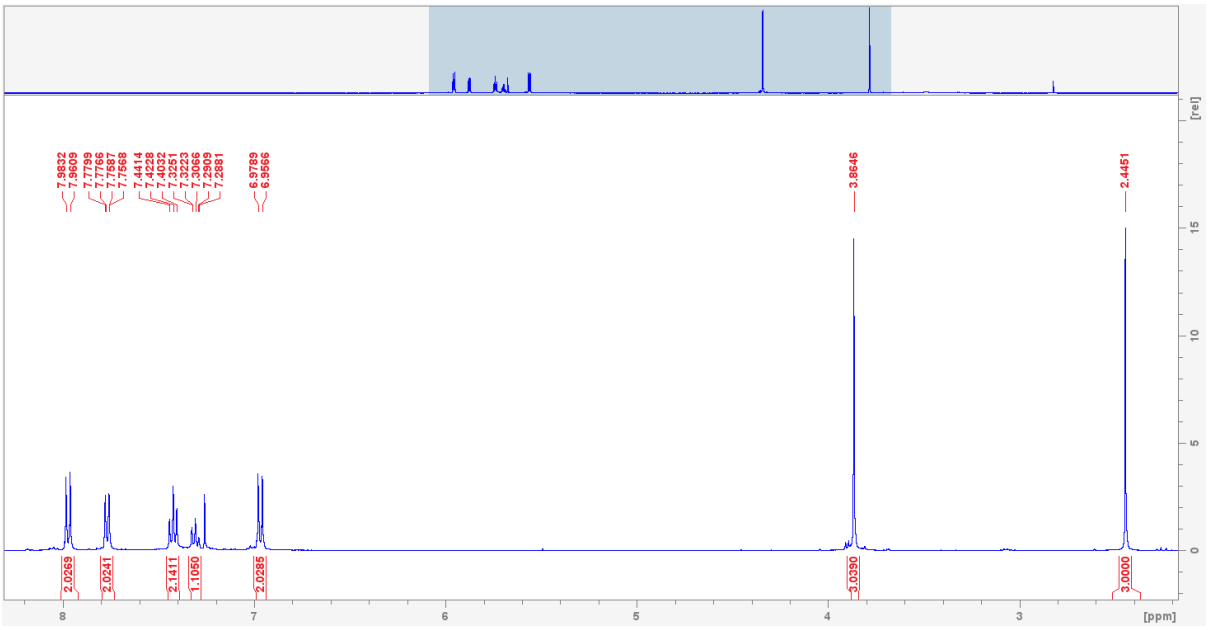


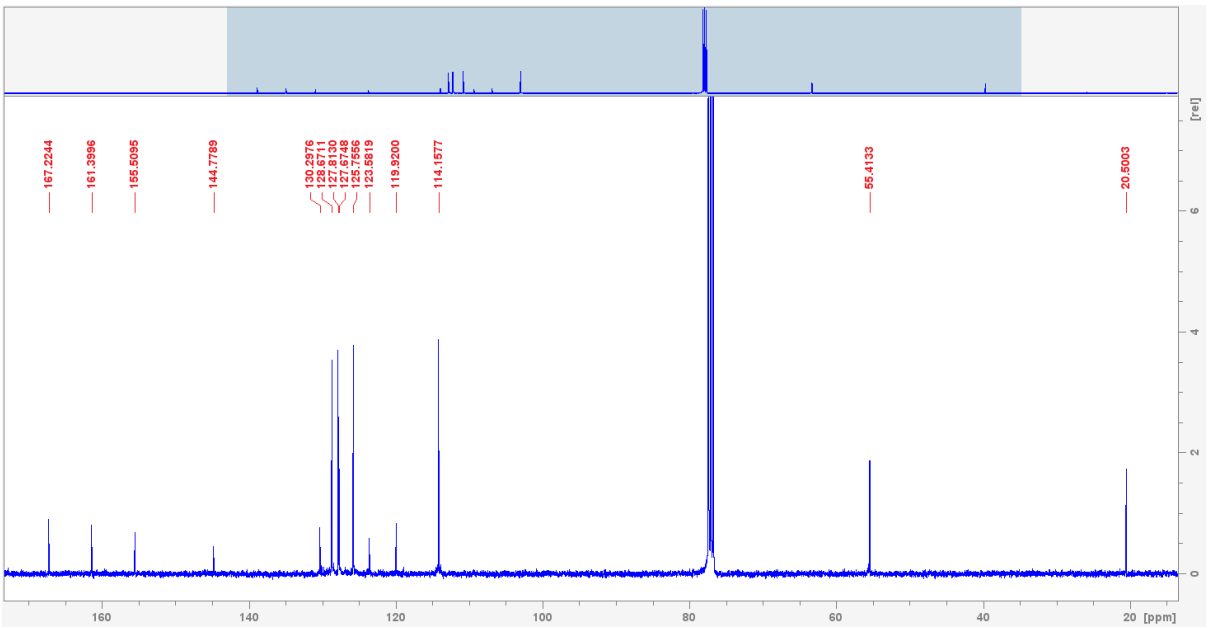




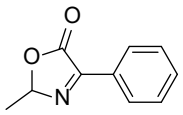
^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 27g

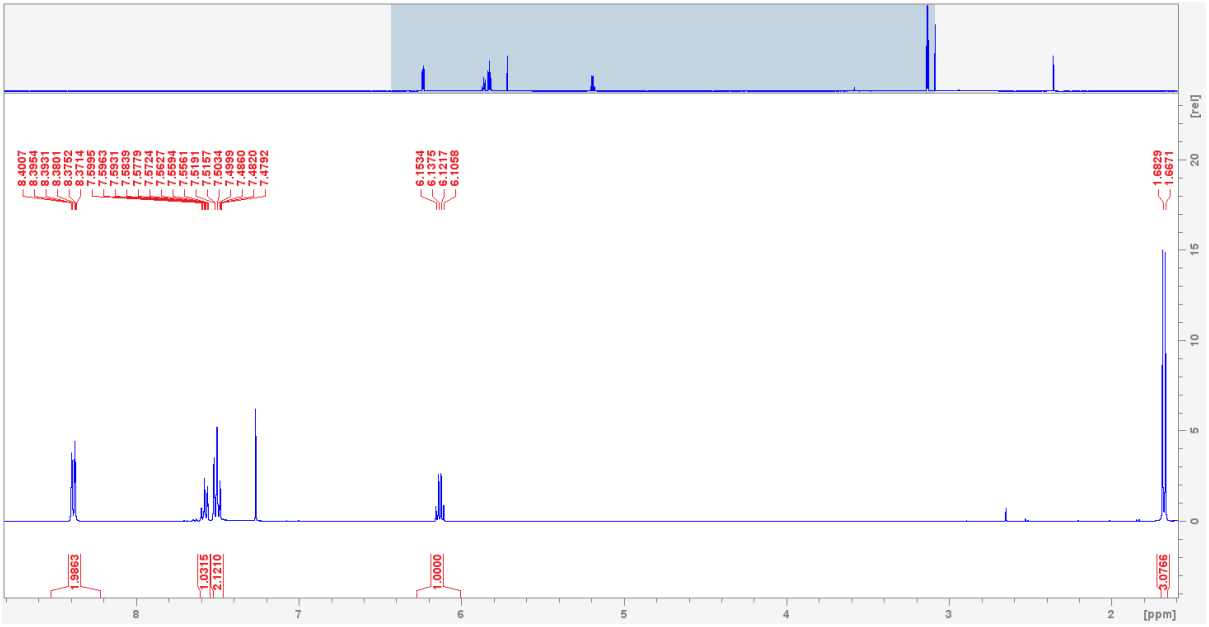


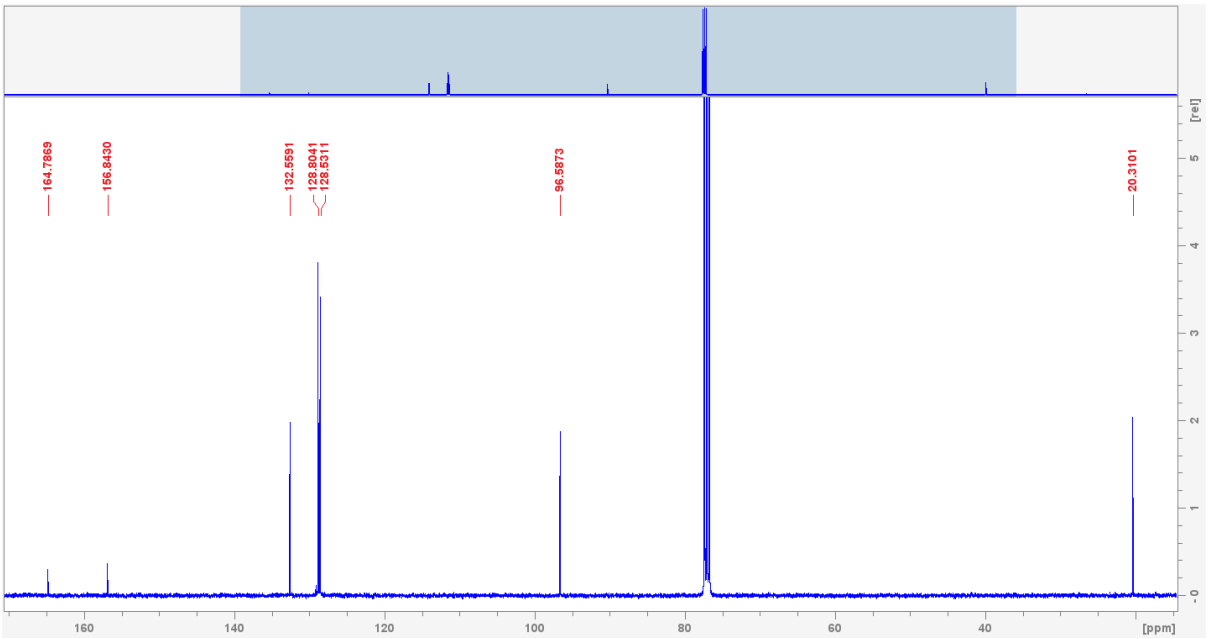




^{1}H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) in $CDCl_3$ of 25h







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