

## Supporting Information

### Multiple Neighboring Active Sites of Atomically Precise Copper Nanocluster Catalyst for Efficient Bond-Forming Reactions

Atanu Ghosh,<sup>a,#</sup> Arunachalam Sagadevan,<sup>a,#</sup> Kathiravan Murugesan<sup>a</sup>, Stefan Adrian F. Nastase,<sup>a</sup> Bholanath Maity,<sup>a</sup> Mohammad Bodiuzzaman,<sup>a</sup> Aleksander Shkurenko,<sup>b</sup> Mohamed Nejib Hedhili,<sup>c</sup> Jun Yin,<sup>d</sup> Omar F. Mohammed,<sup>b</sup> Mohamed Eddaoudi,<sup>b</sup> Luigi Cavallo,<sup>a</sup> Magnus Rueping,<sup>\*,a</sup> and Osman M. Bakr<sup>\*,a</sup>

<sup>a</sup>KAUST Catalysis Center (KCC), Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

<sup>b</sup>Advanced Membranes and Porous Materials Center (AMPMC), Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

<sup>c</sup>Core Labs, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia.

<sup>d</sup>Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, 999077, Hong Kong, China.

# contributed equally to this work

Email: [osman.bakr@kaust.edu.sa](mailto:osman.bakr@kaust.edu.sa) & [magnus.rueping@kaust.edu.sa](mailto:magnus.rueping@kaust.edu.sa)

#### Experimental section

**Chemicals:** Cuprous oxide ( $\text{Cu}_2\text{O}$ ,  $\geq 99.99\%$  trace metals basis, anhydrous), Tetrafluoroboric acid solution ( $\text{HBF}_4$ , 48 wt. % in water), *tert*-butylthiol ( $(\text{CH}_3)_3\text{CSH}$ ), Triphenylphosphine ( $(\text{C}_6\text{H}_5)_3\text{P}$ ), Sodium borohydride (powder,  $\geq 98.0\%$ ), Triethylamine ( $(\text{C}_2\text{H}_5)_3\text{N}$ ,  $\geq 99\%$ ) were purchased from Sigma-Aldrich and used without further purification. HPLC grade solvents (acetonitrile ( $\text{CH}_3\text{CN}$ ), chloroform ( $\text{CHCl}_3$ ), and ethanol ( $\text{EtOH}$ )) were purchased from Sigma-Aldrich and also used without further purification.

**Synthesis of  $[\text{Cu}_{29}(\text{StBu})_{13}\text{Cl}_5(\text{PPh}_3)_4\text{H}_{10}]\text{tBuSO}_3$  cluster ( $\text{Cu}_{29}\text{NC}$ ):** Initially  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  complex was synthesized by a reported method. The above prepared complex (312 mg) was dissolved in 15 mL of acetonitrile. Next, 180  $\mu\text{L}$  of *tert*-butyl thiol was added to the above solution before the drop-wise addition of 1 mL triethylamine. The color of the solution was changed from colorless to light yellow. After 2.5 hrs of stirring, 200 mg of solid triphenylphosphine was added to the above solution. The stirring continued for 30 minutes. Then the solvent was removed by rotary evaporator and the residue was dissolved in 15 mL chloroform.

Next, 17 mg of  $\text{NaBH}_4$  powder was dispersed in 7 mL Ethanol. 3 mL of the above prepared copper complex solution was taken in a 12 mL glass vial. After 5 minutes of stirring, the ethanolic solution of  $\text{NaBH}_4$  was added to this solution under stirring condition. After 4 hours of stirring, the orange

color precipitate was collected using centrifugation. The precipitate was washed two times with acetonitrile and further dissolved in 2.5 ml of Chloroform. 2ml of Ethanol was added to the above solution and kept for crystallization at ambient condition. After 10-12 days red color crystals of appropriate sizes were collected for the SCXRD measurement. The Cu<sub>29</sub> NC crystals were washed with acetonitrile few times and dried under vacuum. The dried material was used for further characterization.

**Synthesis of supported Cu<sub>29</sub> NC:** 4 mg of CuNC powder was taken in a 30 mL glass vial and 20 mL CHCl<sub>3</sub> was added to it which produced a red color solution. 300 mg of solid support was added to the above prepared solution under stirring conditions. After 12 hours of stirring the solid part was collected using centrifugation and washed two times with chloroform. After that the solid part was dried for 3-4 hours under vacuum at room temperature. This solid part was characterized with different analytical tools and used for catalysis reactions. We followed the same loading procedure for all the five supports, celite S, celite 545, alumina ( $\gamma$ ), CeO<sub>2</sub>, and carbon powder. We also tried to increase loading amount by increasing the input cluster amount. But any improvement in the loading was not observed.

### Characterization

**UV-vis absorption spectroscopy:** UV-vis measurement of Cu<sub>29</sub> NC was performed by using Cary 5000 UV-Vis-NIR spectrometer. Dilute chloroform solution of Cu<sub>29</sub> NC was for the UV-vis measurement.

**Electrospray ionization mass spectrometry (ESI-MS):** Bruker MicroTOF-II mass spectrometer was used for the mass spectrometry measurement. Dilute chloroform solution of Cu<sub>29</sub> NC was used for the ESI MS measurement. The spectrometer was operated in the mass range of m/z 20-10000. Details of the instrumental conditions are given below

Flow rate: 1200  $\mu$ L/h

Capillary voltage: 4.5 kV

Nebulizer: 0.4 bar

Dry gas flow: 4.0 L/h

Dry temperature: 180°C

**Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES):** To investigate the leaching of copper (Cu) during the reaction ICP-OES was employed. The ICP-OES analysis was conducted using an Agilent 5110 instrument. To prepare the samples, the final mixture of reaction products from each cycle was subjected to centrifugation, and the resulting supernatant was digested using a microwave-assisted acid digestion method. The digested samples were then diluted to 50 mL of Millipore water and agitated to ensure homogeneous mixing. The resulting solution was subjected to ICP-OES measurement. The ICP instrument was calibrated using standard solutions.

ICP-OES Agilent 5110 spectrometer equipped with a dual detector assembly covering a wavelength range from 165 to 782 nm was utilized. The flow rates for the plasma and

auxiliary argon (Ar) gas were set at 16.5 L min<sup>-1</sup> and 1.5 L min<sup>-1</sup>, respectively. The nebulizer Ar gas flow rate was maintained at 0.7 L min<sup>-1</sup>. The forward radio frequency (RF) power was set to 1.2 kW. Parameters such as the sample uptake rate, rinse time, pump rate, integration time, and replicate were set at 1 mL min<sup>-1</sup>, 35 s, 15 rpm, 30 s, and 3, respectively.

The microwave-assisted acid digestion of the samples was carried out using a polypropylene rotor equipped with 10 segments, each capable of holding Teflon vessels with a capacity of 15 mL. Prior to use, the vessels were thoroughly cleaned by washing with concentrated nitric acid (HNO<sub>3</sub>), followed by rinsing with Millipore water. Approximately 4 mL of HNO<sub>3</sub> and 1 mL of hydrofluoric acid (HF) were added to each sample. The vessels were then placed into the segments of the polypropylene rotor. The samples were subjected to microwave heating, reaching a temperature of 220 °C within 10 minutes (at 300 W) under a pressure of 180 bar, and held at this temperature for 20 minutes. Subsequently, the vessels were cooled to room temperature and transferred individually to a fume hood. The acid-digested samples were then transferred into 50 mL vials and diluted to 50 mL of Millipore water. Then the solutions were used for ICP-OES measurements.

#### **X-ray photoelectron spectroscopy (XPS):**

XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of  $\sim 10^{-9}$  mbar. All spectra were recorded using an aperture slot of 300  $\mu\text{m}$  x 700  $\mu\text{m}$ . Survey spectra were collected using a pass energy of 160 eV and a step size of 1 eV. A pass energy of 20 eV and a step size of 0.1 eV were used for the high-resolution spectra. Samples were mounted in floating mode in order to avoid differential charging. Charge neutralization was required for all the samples. Binding energies were referenced to the C 1s peak of (C-C, C-H) bond, which was set at 284.8 eV.

#### **Single-crystals X-ray diffraction (SCXRD):**

Single Crystal X-ray Diffraction data were collected using Bruker X8 PROSPECTOR APEX2 CCD diffractometer using CuK $\alpha$  radiation ( $\lambda = 1.54178$  Å). Indexing was performed using APEX3 v2018.7-2<sup>1</sup> (Difference Vectors method). Data integration and reduction were performed using SAINTplus 8.38A.<sup>2</sup> Absorption correction was performed by multi-scan method implemented in SADABS-2016/2<sup>3</sup> Space group was determined using XPREP implemented in APEX3<sup>1</sup> The structure was solved using Direct Methods (SHELXS-2008)<sup>4</sup> and refined using SHELXL-2018/3<sup>5</sup> (full-matrix least-squares on  $F^2$ ) contained OLEX2 program<sup>6</sup> package.

The structure reveals significant disorder; therefore, a large set of restraints and constraints was applied to make both geometry and ADPs of the atoms reasonable. Thus, ADPs of closely located Cl and S atoms were refined with the same ADPs (EADP). The geometry of the disordered <sup>t</sup>Bu was restrained by a set of DFIXes and the ADPs were restrained to be similar (SIMU). In the case of closely located pivot atoms of different parts, their ADPs were refined with the same ADPs (EADP). Geometries of disordered Ph<sub>3</sub>P were

constrained by AFIX 66 and restrained by a set of DFIXes, SADI and FLAT. The ADPs were restrained to be similar (SIMU). All the hydrogen atoms were located from the difference Fourier maps first and then placed at the calculated positions and refined using a riding model with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{sp}2})$  or  $1.5U_{\text{eq}}(\text{C}_{\text{sp}3})$ .

There are voids in the structure. The only residual electron density peaks which were arranged in an interpretable pattern were treated as disordered over 3 positions [ $^t\text{BuSO}_3$ ]<sup>-</sup> anions. The anions were refined isotropically with a set of restraints for the geometries and ADPs. The refined occupancies of two of them was fixed later and for the third one was arbitrary fixed at 25% results in similar ADPs as for two ones mentioned above. There are still a few electron density peaks located close either heavy Cu atoms or disordered [ $^t\text{BuSO}_3$ ]<sup>-</sup> and  $^t\text{BuS}^-$  moieties lower than  $0.96 \text{ e} \cdot \text{\AA}^{-3}$ . The uninterpretable electron density was masked from the refinement using SQUEEZE routine implemented in the program PLATON: the structure factors were augmented via reverse Fourier transform methods.<sup>7</sup> The resultant .FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original .HKL file in the further refinement. The .FAB file with details of the SQUEEZE results is appended to this .CIF file. The SQUEEZE procedure corrected for 286 electrons within the solvent accessible voids.

The X-ray crystallographic data for **Cu<sub>29</sub> NC** has been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number 2292096. These data can be obtained free of charge from the CCDC via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

## Computational Methods:

**Hydride fixing in Cu<sub>29</sub> nanocluster.** The molecular geometry of the Cu<sub>29</sub> nanocluster with ten hydrides was optimized by using the projector-augmented wave (PAW)<sup>8</sup> method as implemented in the Vienna Ab initio simulation package (VASP).<sup>9, 10</sup> The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE)<sup>11</sup> exchange-correlation functional was used. The  $\Gamma$ -point sampling was used and the plane-wave basis set cutoff of the wavefunctions was set at 450 eV. Starting from the experimental nanocluster structure, the initial coordinates of the ten hydrides were set according to the coordination behavior of hydrides observed in previously reported hydride-containing Cu clusters.<sup>12</sup> In this study, only the hydrides and Cu atoms were allowed to relax during the optimization in order to retain the crystal symmetry of the Cu<sub>29</sub> nanocluster.



**Geometry optimizations.** Copper hydride clusters have successfully been simulated previously<sup>12-14</sup> as follows: periodic DFT calculations were conducted using the Vienna Ab Initio Simulation Package (VASP)<sup>9, 10</sup>, the Perdew–Burke–Ernzerhof functional<sup>11</sup> with Grimme’s dispersion correction<sup>15</sup> (PBE-D3), and a plane-wave basis set of the projector-augmented-wave (PAW) method.<sup>8</sup> An energy cut-off of 450 eV was used for the expansion of the wave function in the plane wave basis set. A  $(1 \times 1 \times 1)$   $\gamma$ -centered k-point mesh was employed to sample the first Brillouin zone and Gaussian smearing with a width of 1 eV. All atoms were relaxed until electronic energies varied by  $< 1 \times 10^{-5}$  eV, and the forces on all atoms were  $< 0.01$  eV  $\text{\AA}^{-1}$ . The cluster was centered in a  $30 \times 30 \times 30$   $\text{\AA}^3$  cubic unit cell.

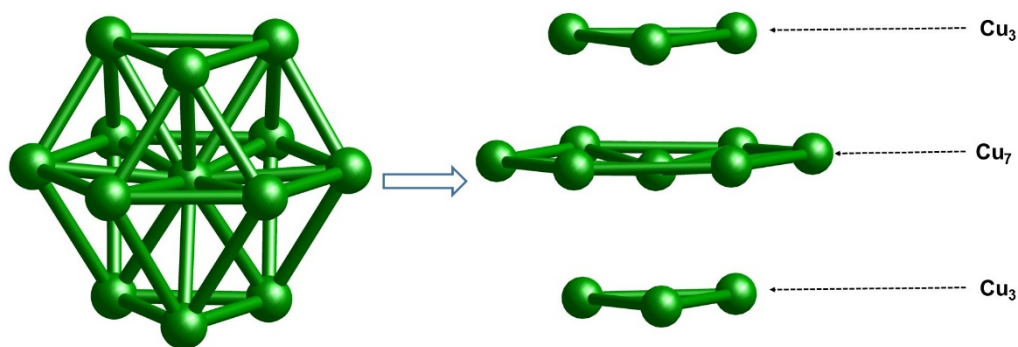
**Solvation effects.** Implicit solvation effects were included as implemented in the VASPSol module.<sup>16</sup> The solvent dielectric constant of acetonitrile used was 31.05.<sup>17</sup> The plane wave cutoff was increased to 600 eV to converge the cavitation energy. The cavity surface tension is set to zero to increase the numerical robustness, with default values applied with all other factors (width of dielectric cavity, cutoff charge density).

## Results

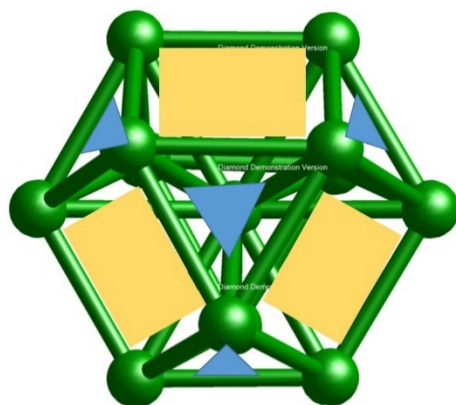
**Table S1.** Crystal data and structure of Cu<sub>29</sub> NC

Empirical formula	C <sub>129.23</sub> H <sub>188.77</sub> Cl <sub>4.69</sub> Cu <sub>29</sub> O <sub>3</sub> P <sub>4</sub> S <sub>14.31</sub>
Formula weight	4381.90
Crystal system, space group	Triclinic, <i>P</i> -1
Unit cell dimensions	$a = 20.0520(8) \text{ \AA}$ , $\alpha = 94.177(2)^\circ$ $b = 20.1859(8) \text{ \AA}$ , $\beta = 107.105(2)^\circ$ $c = 24.6290(9) \text{ \AA}$ , $\gamma = 103.932(2)^\circ$
Volume	9136.2(6) $\text{\AA}^3$
Z, calculated density	2, 1.593 Mg m <sup>-3</sup>
<i>F</i> (000)	4396
Temperature (K)	100.0(1)
Radiation type, $\lambda$	Cu <i>K</i> $\alpha$ , 1.54178 $\text{\AA}$
Absorption coefficient	6.29 mm <sup>-1</sup>
Absorption correction	Multi-scan
Max and min transmission	0.271 and 0.143
Crystal size	0.20 $\times$ 0.22 $\times$ 0.22 mm
Shape, colour	Prism, red
$\theta$ range for data collection	2.3–66.9°
Limiting indices	$-23 \leq h \leq 23$ , $-23 \leq k \leq 23$ , $-29 \leq l \leq 29$
Reflection collected / unique / observed with $I > 2\sigma(I)$	237138 / 31975 ( $R_{\text{int}} = 0.068$ ) / 26252
Completeness to $\theta_{\text{full}} = 66.9^\circ$	98.3 %
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	31975 / 1493 / 2214
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.055$ , $wR_2 = 0.158$
Final <i>R</i> indices (all data)	$R_1 = 0.064$ , $wR_2 = 0.170$
Weighting scheme	$[\sigma^2(F_o^2) + (0.1019P)^2 + 10.1178P]^{-1}$ *
Goodness-of-fit	1.05
Largest diff. peak and hole	0.96 and -0.70 e $\text{\AA}^{-3}$

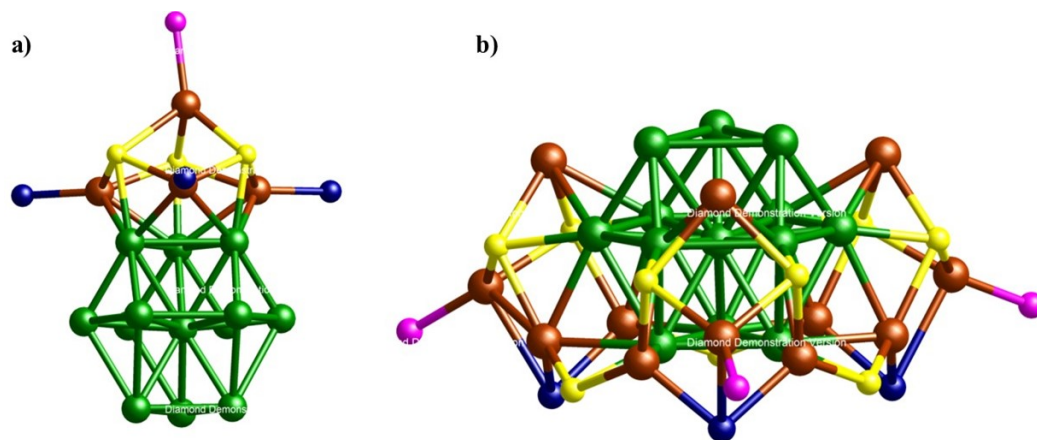
\* $P = (F_o^2 + 2F_c^2)/3$



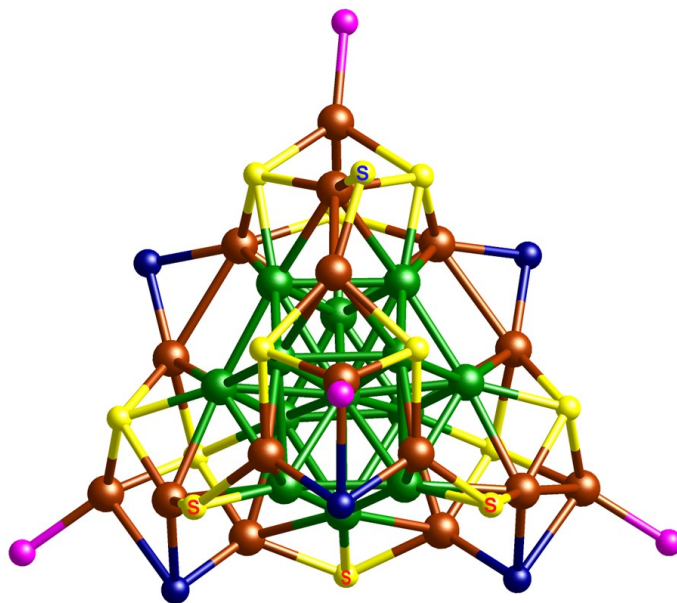
**Figure S1.** Construction of  $\text{Cu}_{13}$  core. The core can be viewed as it is composed of three layers,  $\text{Cu}_3$  triangle (top),  $\text{Cu}_7$  centered-hexagons (middle), and  $\text{Cu}_3$  triangle (bottom), respectively (Figure S1). Interestingly the Cu-Cu bond distances in the upper triangular layer are in the ranges of 2.65-2.71 Å whereas for the bottom triangular layer, the bond distances are comparatively shorter (2.50-2.51 Å). In the middle layer, the bond distances are in the ranges of 2.58-2.62 Å.



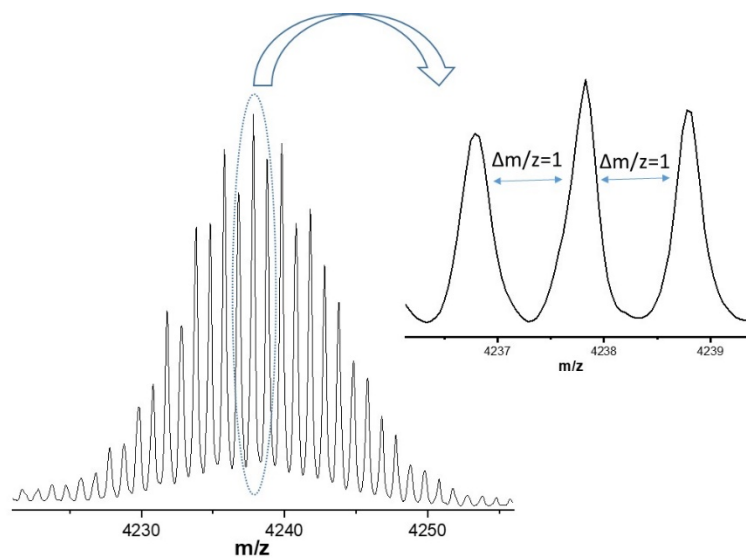
**Figure S2.** Top view of the core. Only half of the structure is visible. Four triangular and three square faces are highlighted with blue and light golden colors, respectively.



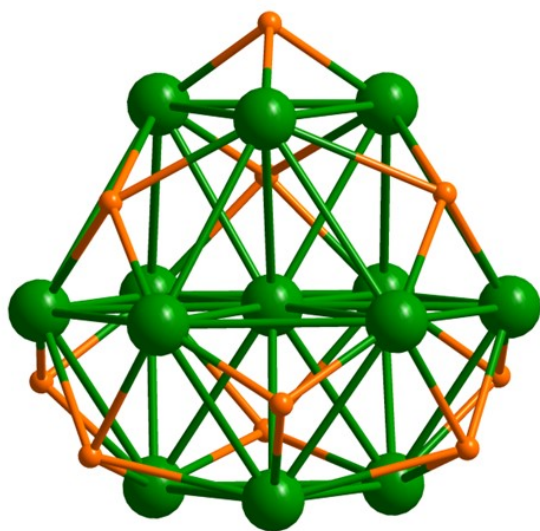
**Figure S3.** Bonding interactions between the core and motifs. a) **Motif 1** occupied the triangular face b) **Motifs 2 and 3** occupied square faces.



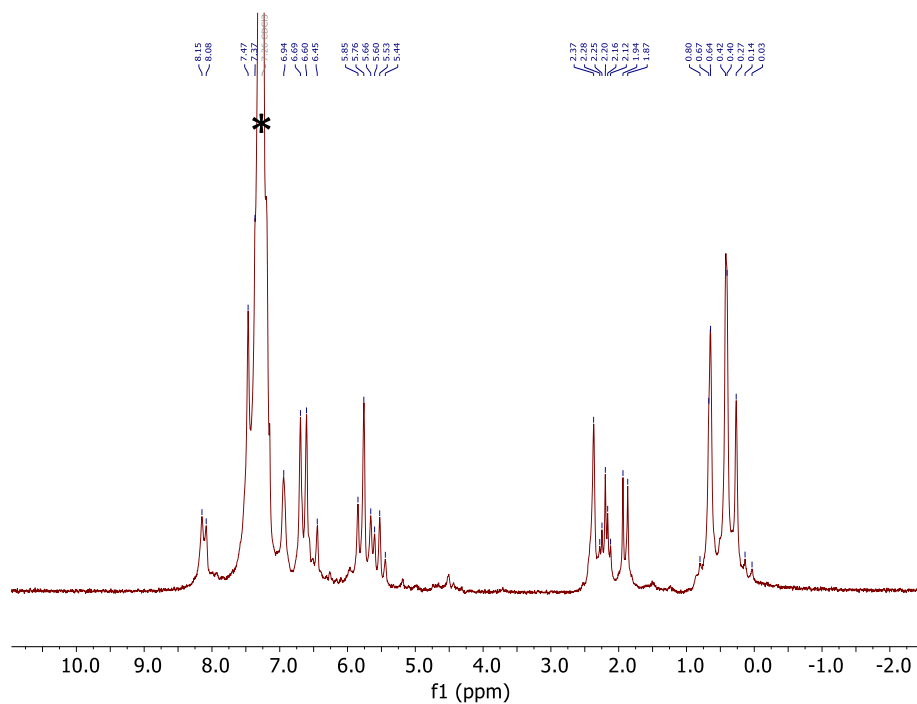
**Figure S4.** Bridging mode of the thirteen thiolate ligands. One thiolate bonded through  $\mu_2$  bridging mode (highlighted with blue 'S'). Three thiolate ligands are bonded through  $\mu_3$  bridging mode (highlighted with red 'S'). Remaining 9 thiolate ligands are connected through  $\mu_4$  bridging mode. Color legend: green, and brown, copper atoms of the  $\text{Cu}_{13}$  core, and shell, respectively; yellow, sulfur; pink, phosphine; and dark blue, chlorine.



**Figure S5.** An expanded view of the peak at  $m/z$  4237.8. Inset: the separation between two peaks is  $\Delta m/z = 1$  which confirms that the cluster has 1+ charge state.

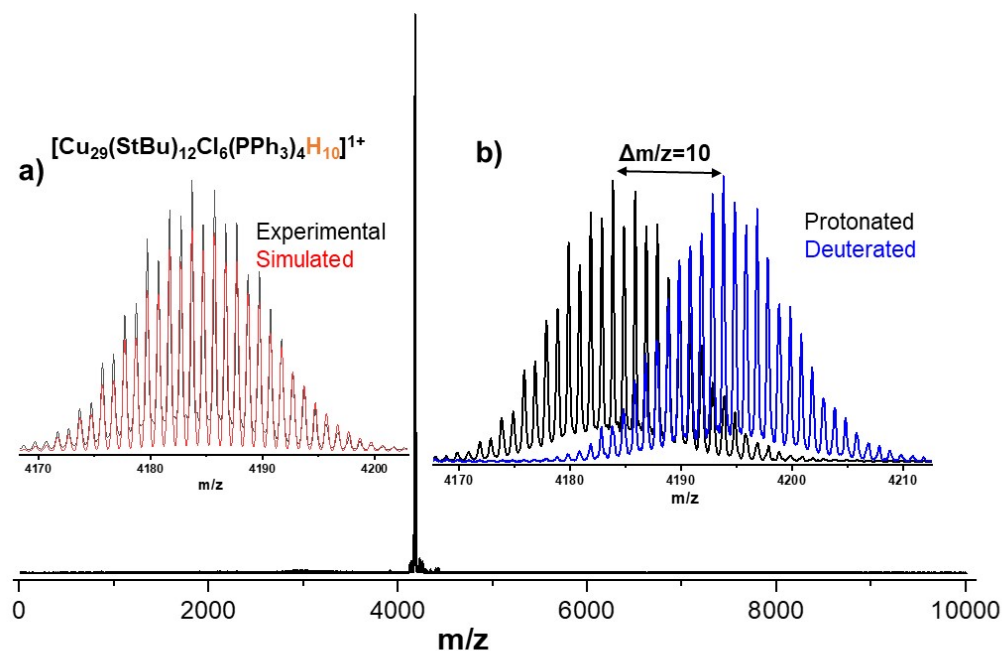


**Figure S6A.** DFT optimized positions of the hydrides. Color legend: green, copper atoms of  $\text{Cu}_{13}$  core; saffron, hydrides.

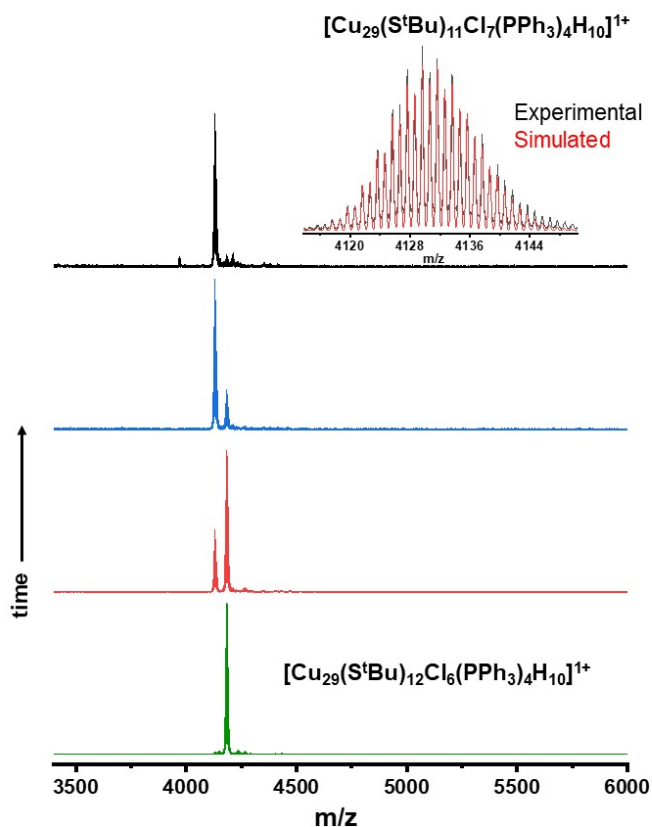


**Figure S6B.**  $^2\text{H}$  NMR of  $\text{Cu}_{29}\text{D}$  in  $\text{CHCl}_3$ . The peak marked in asterisk (\*) due to  $\text{CDCl}_3$  added for calibration of the chemical shift.

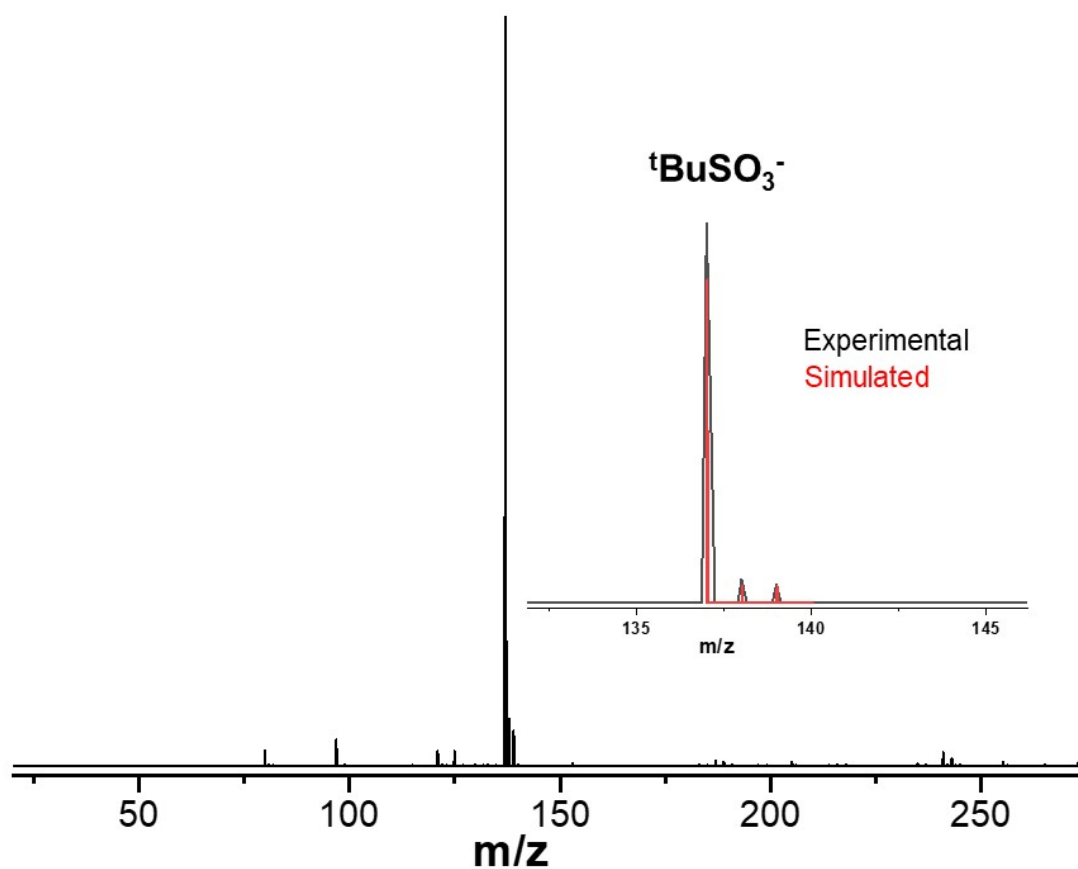




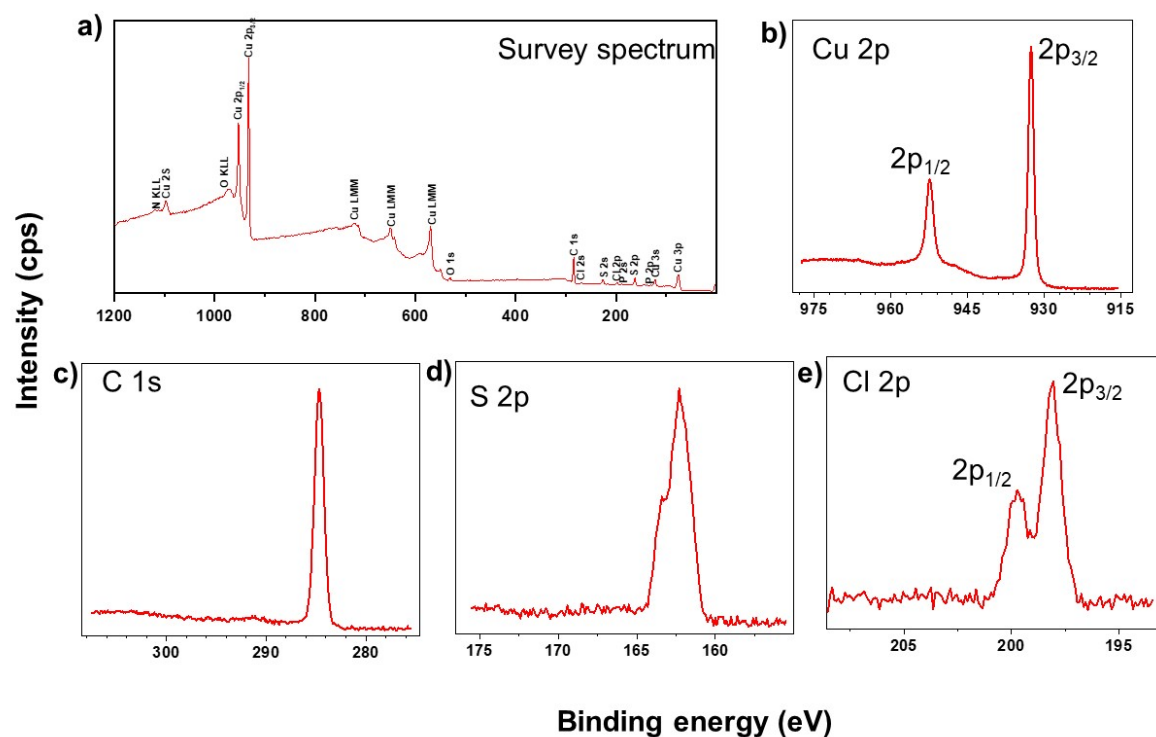
**Figure S7.** The chloroform solution of the pristine cluster,  $[\text{Cu}_{29}(\text{S}^t\text{Bu})_{13}\text{Cl}_5(\text{PPh}_3)_4\text{H}_{10}]^+$ , produced a single peak at  $m/z$  4183.8 on resting for 15 days at ambient conditions. Interestingly one of the thiolate ligands of the pristine cluster is replaced by the chloride ligand and converted to  $[\text{Cu}_{29}(\text{S}^t\text{Bu})_{12}\text{Cl}_6(\text{PPh}_3)_4\text{H}_{10}]^+$  (Figure S7). Positive mode ESI MS spectrum of  $[\text{Cu}_{29}(\text{S}^t\text{Bu})_{12}\text{Cl}_6(\text{PPh}_3)_4\text{H}_{10}]^+$  cluster. The peak at  $m/z$  4183.7 corresponds to the molecular ion peak. Insets: a) Exact matching of experimental (black trace) and simulated (red trace) isotopic distributions confirm the assigned compositions. b) Comparison of protonated,  $[\text{Cu}_{29}(\text{S}^t\text{Bu})_{12}\text{Cl}_6(\text{PPh}_3)_4\text{H}_{10}]^+$ , and deuterated,  $[\text{Cu}_{29}(\text{S}^t\text{Bu})_{12}\text{Cl}_6(\text{PPh}_3)_4\text{D}_{10}]^+$ , molecular ion peaks.



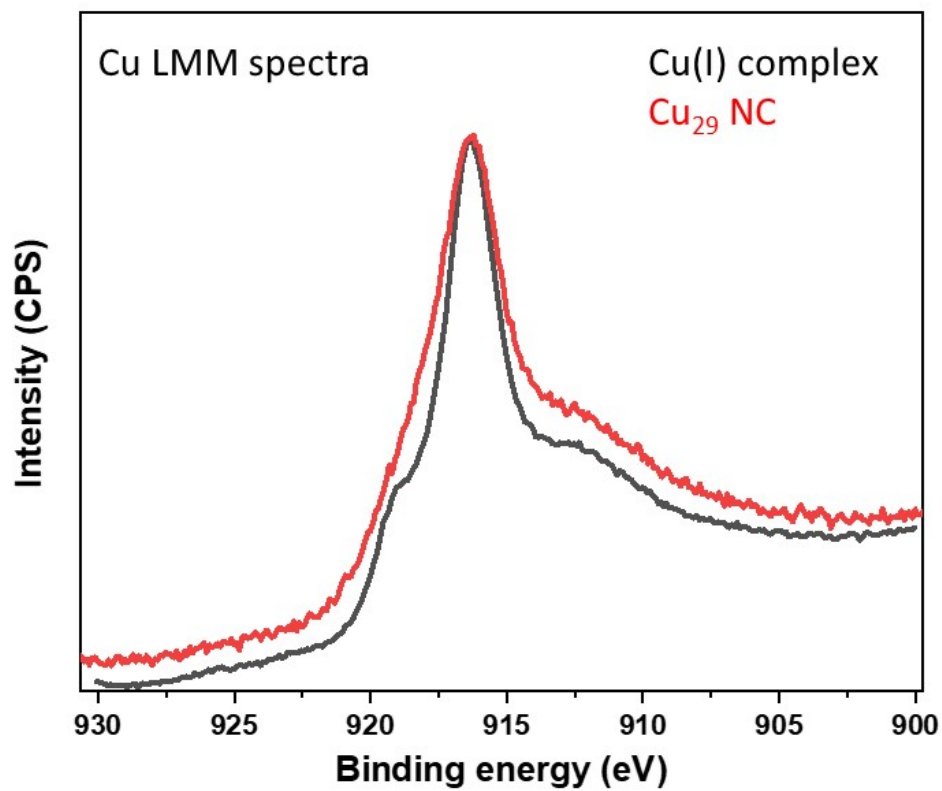
**Figure S8.** Conversion of  $[\text{Cu}_{29}(\text{StBu})_{12}\text{Cl}_6(\text{PPh}_3)_4\text{H}_{10}]^{1+}$  to  $[\text{Cu}_{29}(\text{StBu})_{11}\text{Cl}_7(\text{PPh}_3)_4\text{H}_{10}]^{1+}$ . The ligand exchanged product,  $[\text{Cu}_{29}(\text{St}^t\text{Bu})_{12}\text{Cl}_6(\text{PPh}_3)_4\text{H}_{10}]^+$  (Figure S6), on treatment with tetraphenylphosphonium chloride (acts as a chloride source) again underwent ligand exchange reactions and produced chloride-rich cluster,  $[\text{Cu}_{29}(\text{St}^t\text{Bu})_{11}\text{Cl}_7(\text{PPh}_3)_4\text{H}_{10}]^+$  (Figure S8). Such bulky thiolate to single atom (chloride) exchange reactions have not been observed before for the nanocluster family. It is worth mentioning that recently copper nanocluster consisting of 29 atoms have been reported in the literature. The reported cluster is protected with three chloride and fifteen bulky adamantane thiolate ligands. During ESI MS measurement, the cluster was found to be unstable, resulting in a series of fragmented peaks.<sup>18</sup> In contrast, for our  $\text{Cu}_{29}$  nanocluster, the presence of five chlorides along with thirteen less bulky tert-butyl thiolate ligands produces only the molecular ion peak during ESI MS measurement, which allowed us to study the unique ligand exchanged reactions (as discussed before). Inset: Exact matching of experimental (black trace) and simulated (red trace) isotopic distributions confirm the assigned compositions,  $[\text{Cu}_{29}(\text{St}^t\text{Bu})_{11}\text{Cl}_7(\text{PPh}_3)_4\text{H}_{10}]^{1+}$ .



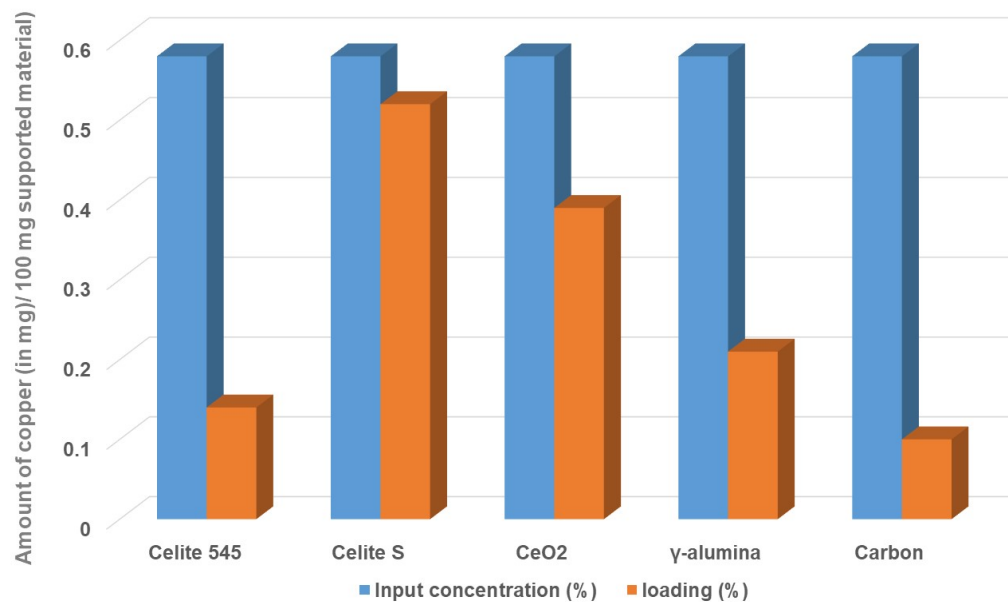
**Figure S9.** Negative mode ESI MS spectrum of  $\text{Cu}_{29}$  NC. Inset: Exact matching of experimental (black trace) and simulated (red trace) isotopic distribution confirms the presence of  ${}^t\text{BuSO}_3^-$  as the counter ion.



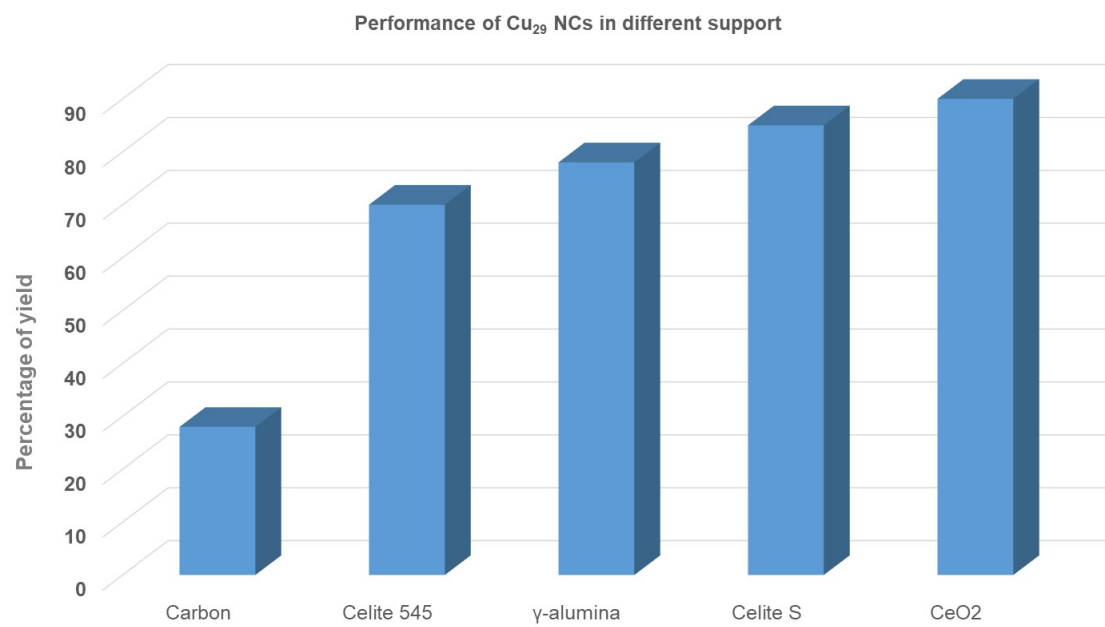
**Figure S10** XPS spectra of  $\text{Cu}_{29}$  NC cluster. a) Survey spectrum of the cluster confirms the presence of all the expected elements (Cu, S, C, and Cl). (b-e) High resolution spectra of the Cu 2p, C 1s, S 2p and Cl 2p core levels.



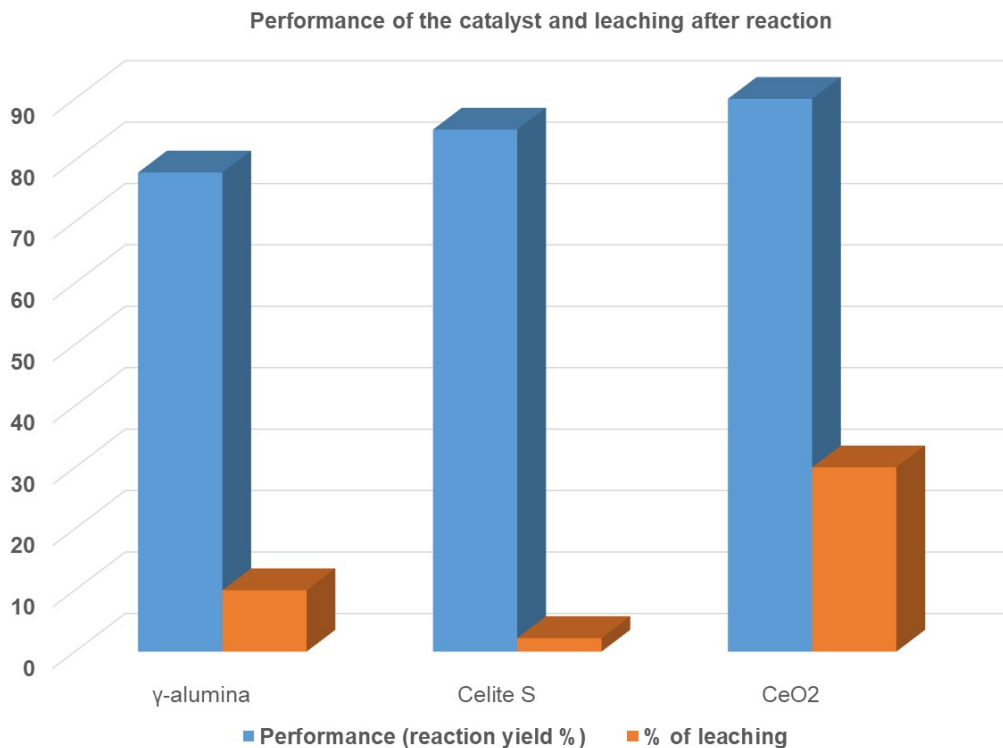
**Figure S11.** Comparison of Cu LMM Auger spectra of Cu(I)–S<sup>t</sup>Bu thiolate (black trace) and Cu<sub>29</sub> NC (red trace).



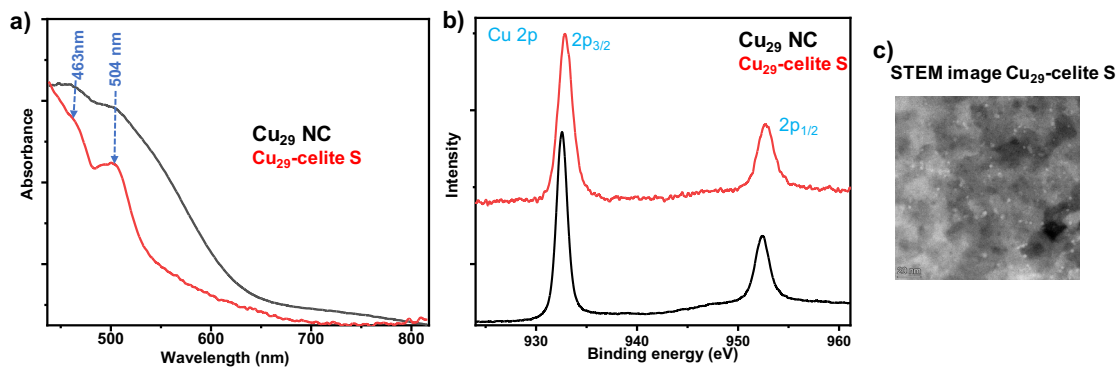
**Figure S12.** Cu<sub>29</sub> NC loading (in terms of copper amount) for different supports. Copper amounts were obtained from ICP-OES measurements.



**Figure S13.** Performance of the Cu<sub>29</sub> NC in different supports.



**Figure 14.** Performance and copper leaching for different supports. Least amount of leaching was observed for Cu<sub>29</sub>-celite S, Cu<sub>29</sub>-alumina ( $\gamma$ ), Cu<sub>29</sub>-CeO<sub>2</sub>.



**Figure S15.** Characterization of heterogeneous catalyst, Cu<sub>29</sub>-celite S. a) Diffuse reflectance optical spectrum of pure Cu<sub>29</sub> (black trace) and Cu<sub>29</sub>-celite S (red trace). b) Comparison of Cu 2p XPS spectra of Cu<sub>29</sub> (black trace) and Cu<sub>29</sub>-celite S (red trace). c) STEM image of Cu<sub>29</sub>-celite S. Scale bar in panel c: 20 nm



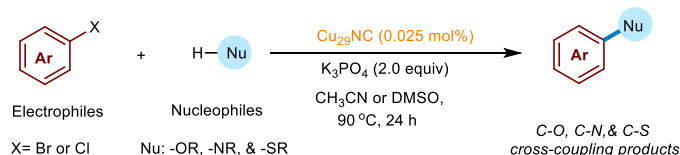
## Cu<sub>2</sub>-Catalyzed Cross-Couplings.

**Experimental section:** All reactions were conducted under an argon/nitrogen atmosphere in glassware. All chemical reactions were conducted at ~90 °C. Solvents of anhydrous quality were purchased and used as received. Starting materials were commercially available (Sigma–Aldrich or Alfa–Aesar) and used as received. For brevity, all the reported yields refer to the isolated compounds. Column chromatography was conducted using an Interchim PuriFlash®215 or Biotage Selekt automatic flash chromatography purification system. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

All isolated compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy, and gas chromatography-mass spectroscopy (GC-MS). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on 400 or 500-MHz Bruker NMR spectrometers. Signal positions were recorded in δ ppm and measured from the center of the signal, excluding multiples, which are given as a range. Splitting patterns are reported using the abbreviations s, br. s, d, t, q, quin, sept, and m (or combinations thereof) denoting singlet, broad singlet, doublet, triplet, quartet, quintet, septet, and multiplet respectively. The abbreviation “app” refers to “apparent”. All <sup>1</sup>H NMR and <sup>13</sup>C chemical shifts were referenced to the residual solvent peak of CDCl<sub>3</sub> (<sup>1</sup>H referenced to 7.26 ppm and <sup>13</sup>C referenced to 77.16 ppm). All coupling constants, J, are quoted in Hz and reported to the nearest 0.1 Hz as observed in the spectra. Thin-layer chromatography (TLC) was performed on commercially available pre-coated Merck aluminum TLC sheets (silica gel 60 F254). Gradient elution using 100% hexane and EtOAc/hexane was performed using the TLC. Visualization of spots on TLC plates was achieved under UV light at 254 nm. All GC analyses (calibrated GC yields) were performed on an Agilent 7890A GC system with an FID detector using a J & W HP–5ms column (10 m, 0.1 mm I.D.), and mesitylene was used as an internal standard. All GCMS analyses were performed using an Agilent 7890A GC system with a J & W DB–5ms column (30 m, 0.1 mm I.D.) connected to a 5975C inert XL EI/CI MSD (with triple-axis detector).

## Details of Catalytic Procedure

**Scheme S1**



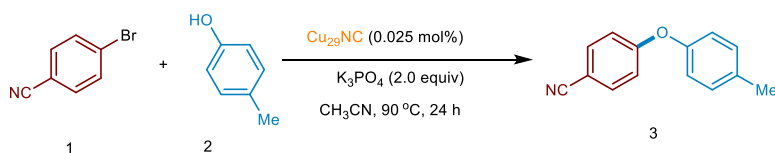
**C-O cross-coupling:** A 10 mL microwave vial was charged with a magnetic stirrer bar, (**Cu**<sub>29</sub>, (0.000075 mmol, 0.025 mol%, ~0.5mg), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv, 0.6 mmol, 127 mg) and aryl halides (X=Br/Cl) (0.3 mmol, 1.0 equiv), alcohol nucleophiles (0.375 mmol, 1.25 equiv), (if aryl halides or alcohols is solid or higher boiling liquid then added at this point before sealing the vial). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Acetonitrile (ACN) (1 mL), (if aryl halides or alcohols are lower boiling liquid then added last via syringe) was added via syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to collect the expected C-O coupling products.

**C-N cross-coupling:** A 10 mL microwave vial was charged with a magnetic stirrer bar, (**Cu**<sub>29</sub>, (0.000075 mmol, 0.025 mol%, ~0.5mg), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv, 0.6 mmol, 127 mg) and aryl halides (X=Br/Cl) (0.3 mmol, 1.0 equiv), amine nucleophiles (0.375 mmol, 1.25 equiv), (if aryl halides or amines is solid or higher boiling liquid then added at this point before sealing the vial). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Dimethylsulfoxide (DMSO) (1 mL), (if aryl halides or amines are lower boiling liquid then added last via syringe) was added via syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to collect the expected C-N coupling products.

**C-S cross-coupling:** A 10 mL microwave vial was charged with a magnetic stirrer bar, (**Cu**<sub>29</sub>, (0.000075 mmol, 0.025 mol%, ~0.5mg), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv, 0.6 mmol, 127 mg) and

aryl halides (X=Br/Cl) (0.3 mmol, 1.0 equiv), sulfur nucleophiles (0.375 mmol, 1.25 equiv), (if aryl halides or sulfur is solid or higher boiling liquid then added at this point before sealing the vial). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Dimethylsulfoxide (DMSO) (1 mL), (if aryl halides or sulfur is lower boiling liquid then added last via syringe) was added via syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to collect the expected C-S coupling products.

**Table S2. Reaction Optimization for C-O coupling reactions<sup>a</sup>**

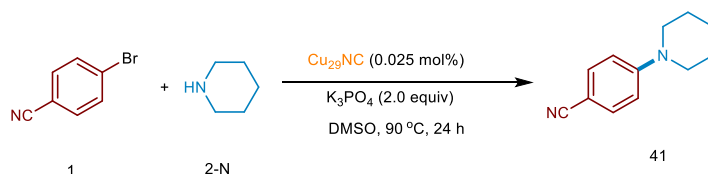


Entry	Variation from initial conditions	Yield (%) <sup>b</sup>
1	None (0.05mol% of Cu <sub>29</sub> )	86
2	None (0.025mol% of Cu <sub>29</sub> )	88 (86)
3	reaction at 70 °C	78
4	reaction at 40 °C	<20
5	K <sub>2</sub> CO <sub>3</sub>	82
6	DMSO, DMA or DMF	70-84
7	THF, dioxane, toluene, or DCE as solvent	<40
8	Cu <sub>61</sub> NC instead of Cu <sub>29</sub> NC	58
9	Cu <sub>28</sub> NC instead of Cu <sub>29</sub> NC	63
10	CuX (X= Cl, Br or I) instead of Cu <sub>29</sub> NC	<25 <sup>c</sup>
11	CuS <sup>t</sup> BuPPh <sub>3</sub>	34
12	CuS <sup>t</sup> Bu	42
13	no catalyst	0
14	Cu <sub>29</sub> NC-celite S (Cu29-S)	90(90)
15	Cu <sub>29</sub> NC-CeO <sub>2</sub> (Cu29-Ce)	91(89)
16	Cu <sub>29</sub> NC-Al <sub>2</sub> O <sub>3</sub> (Cu29-Al)	84
17	no base	0

<sup>a</sup>Initial conditions: **1** (0.3 mmol), **2** (0.375 mmol), Cu<sub>29</sub>NC (0.025 mol%, 0.000075 mmol), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv), and acetonitrile (CH<sub>3</sub>CN) (1 mL). The mixture was stirred at 90 °C for 24 h. <sup>b</sup>Yield refers to GC yield using 1,3,5-trimethylbenzene (mesitylene) as the internal standard, except for those in brackets which are isolated yields. <sup>c</sup>5 mol-% CuX was used. DMF = dimethylformamide,

DMSO= dimethylsulfoxide, DMA= dimethylacetamide, THF=tetrahydrofuran, DCE = 1,2-dichloroethane.

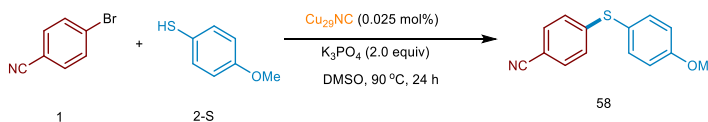
**Table S3. Reaction Optimization for C-N coupling reactions<sup>a</sup>**



Entry	Variation from initial conditions	Yield (%) <sup>b</sup>
1	None	84 (82)
2	K <sub>2</sub> CO <sub>3</sub>	74
3	ACN, DMA or DMF	64-78
4	THF, dioxane, toluene, or DCE as solvent	<44
5	Cu <sub>61</sub> NC instead of Cu <sub>29</sub> NC	63
6	CuX (X= Cl, Br or I) instead of Cu <sub>29</sub> NC	<28 <sup>c</sup>
7	CuS <sup>t</sup> BuPPh <sub>3</sub>	38
8	CuS <sup>t</sup> Bu	44
9	no catalyst	0
10	<i>Cu<sub>29</sub>NC-celite S (Cu29-S)</i>	86(85)
11	no base	0

<sup>a</sup>Initial conditions: **1** (0.3 mmol), **2-N** (0.375 mmol), Cu<sub>29</sub>NC (0.025 mol%, 0.000075 mmol), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv), and DMSO (1 mL). The mixture was stirred at 90 °C for 24 h. <sup>b</sup>Yield refers to GC yield using 1,3,5-trimethylbenzene (mesitylene) as the internal standard, except for those in brackets which are isolated yields. <sup>c</sup>5 mol-% CuX was used. DMF = dimethylformamide, DMSO= dimethylsulfoxide, DMA= dimethylacetamide, THF=tetrahydrofuran, DCE = 1,2-dichloroethane

**Table S4. Reaction Optimization for C-S coupling reactions<sup>a</sup>**



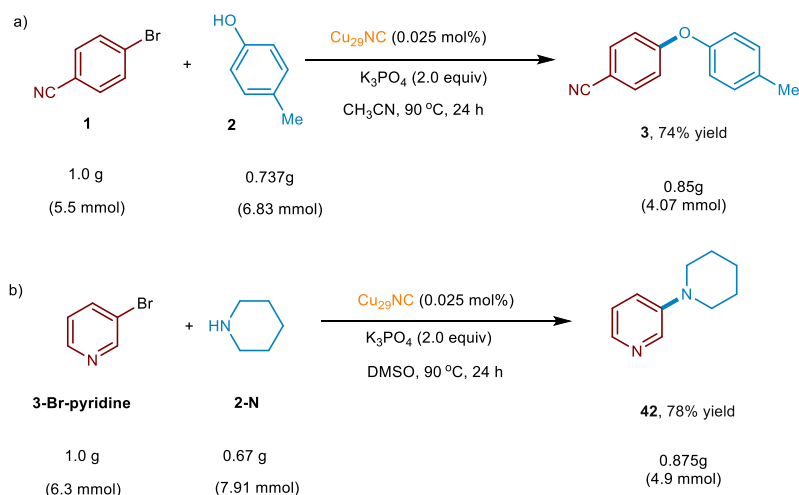
Entry	Variation from initial conditions	Yield (%) <sup>b</sup>
1	None	88 (85)
2	K <sub>2</sub> CO <sub>3</sub>	70
3	ACN, DMA or DMF	<74
4	CuCl instead of Cu <sub>29</sub> NC	<38 <sup>c</sup>

5	CuStBuPPh <sub>3</sub>	48
6	no catalyst	trace
7	Cu <sub>29</sub> NC-celite <i>S</i> (Cu29- <i>S</i> )	90(87)
8	no base	0

<sup>a</sup>Initial conditions: **1** (0.3 mmol), **2-S** (0.375 mmol), Cu<sub>29</sub>NC (0.025 mol%, 0.000075 mmol), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv), and DMSO (1 mL). The mixture was stirred at 90 °C for 24 h. <sup>b</sup>Yield refers to GC yield using 1,3,5-trimethylbenzene (mesitylene) as the internal standard, except for those in brackets which are isolated yields. <sup>c</sup>5 mol-% CuCl was used. DMF = dimethylformamide, DMSO = dimethylsulfoxide, DMA = dimethylacetamide.

## Preparative scale for *C-heteroatom* Cross-coupling:

### Scheme S2



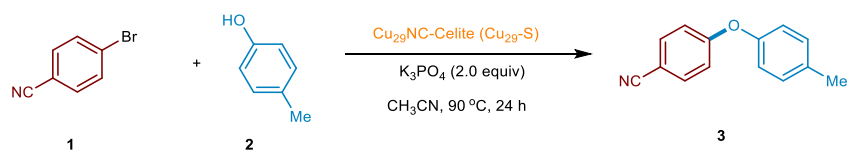
**a)** A 100 mL microwave vial was charged with a magnetic stirrer bar, (**Cu<sub>29</sub>**, (0.002 mmol, 0.025 mol%, 9.1 mg), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv, 11 mmol, 2.33g) and 4-bromobenzonitrile **1** (5.5 mmol, 1.0 equiv, 1.0g), *p*-cresol **2** (6.83 mmol, 1.25 equiv, 0.737g). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Acetonitrile (ACN) (20 mL) was added via syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to collect the expected *C-O coupling product* in 74% yield.

**b)** A 100 mL microwave vial was charged with a magnetic stirrer bar, (**Cu<sub>29</sub>**, (0.002 mmol, 0.025 mol%, 9.1 mg), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv, 11 mmol, 2.33g) and 3-Br-pyridine **1** (6.3 mmol,

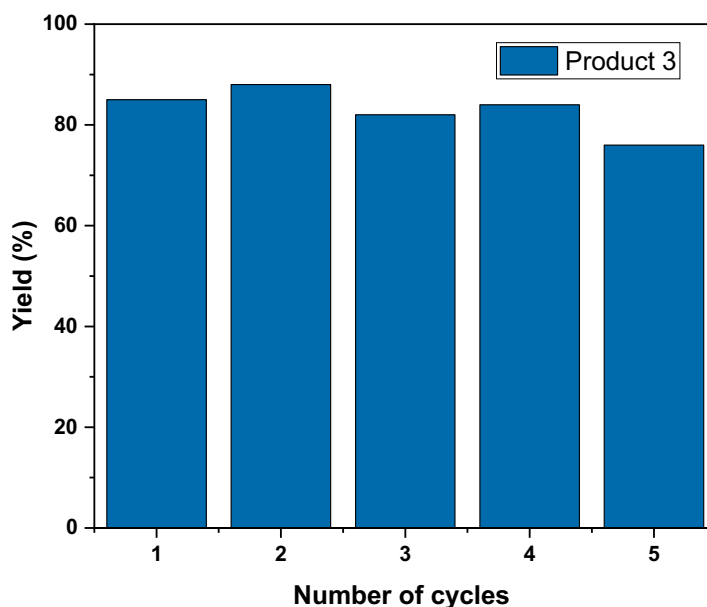
1.0 equiv, 1.0g), piperidine **2-N** (7.91 mmol, 1.25 equiv, 0.67g). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Dimethylsulfoxide (DMSO) (20 mL) was added via a syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to collect the expected *C-N coupling product* in 78 % yield.

## Catalyst Recycling experiments:

### Scheme S3



A 10 mL microwave vial was charged with a magnetic stirrer bar, (**Cu<sub>29</sub>S**, 240mg),  $\text{K}_3\text{PO}_4$  (2.0 equiv, 2.4 mmol, 508 mg), 4-bromobenzonitrile **1** (1.2 mmol, 1.0 equiv, 218mg), *p*-cresol **2** (1.5 mmol, 1.25 equiv, 162mg). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Acetonitrile (ACN) (4 mL) was added via syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. Then the reaction mixture was diluted with 12 mL of ACN and allowed to centrifugation process (6000 RPM for 7 min), followed by washing with 12 mL of distilled water. The recovered **Cu<sub>29</sub>S** catalyst was finally dried by high vacuum and 225 mg of recycled **Cu<sub>29</sub>S** catalyst was obtained. The resulting **Cu<sub>29</sub>S** catalyst was used in the next cycle followed by the **Cu<sub>29</sub>S** catalyst was recovered by centrifugation process, and further allowed for another three catalytic cycles (total 5-cycle). In each catalytic cycle, the product yield was calculated by GC-FID (mesitylene as internal std) (see below Figure S16). *Note: We detected negligible amounts of the copper in the solution which shows that there is no considerable cluster decomposition during the catalytic reactions.*

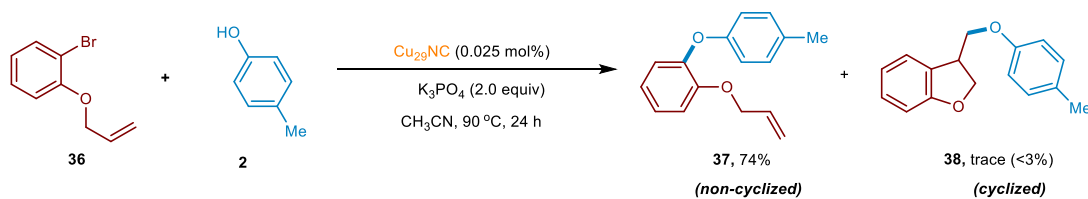


**Figure S16.** Recycling experiments for Cu<sub>29</sub>-S catalyzed C-O cross-coupling

## Mechanistic Control Experiments

Radical clock experiment:

### Scheme S4

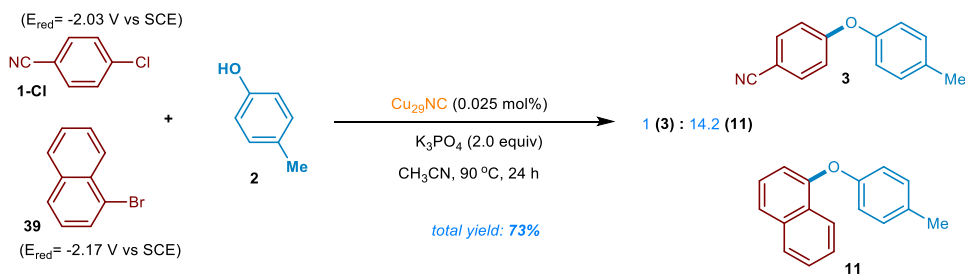


A 10 mL microwave vial was charged with a magnetic stirrer bar, (Cu<sub>29</sub>, (0.000075 mmol, 0.025 mol%), K<sub>3</sub>PO<sub>4</sub> (2.0 equiv, 0.6 mmol, 127 mg) and 1-(allyloxy)-2-bromobenzene **36** (0.3 mmol, 1.0 equiv), *p*-cresol **2** (0.375 mmol, 1.25 equiv). The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Acetonitrile (ACN) (1 mL) were added via syringe through the septum. The reaction mixture was then stirred at ~90 °C under N<sub>2</sub> (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to

collect C-O coupling product in the form of non-cyclized product **37** predominating over the cyclized product **38**. *Explanation: These control experiments indicate that the reaction does not proceed through radical formation. The above results also suggest that the oxidative addition of Ar-X is operated by a concerted mechanism instead of a single electron transfer (SET).*

## Competitive experiment:

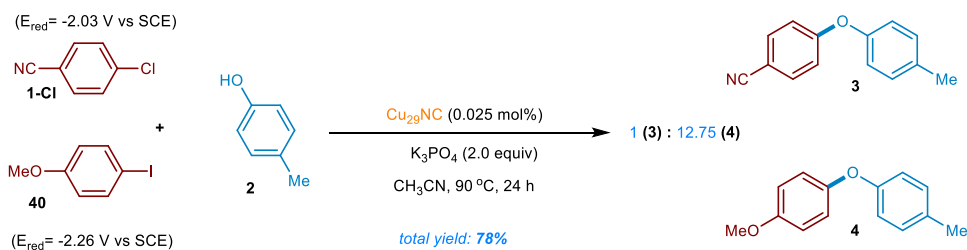
### Scheme S5a



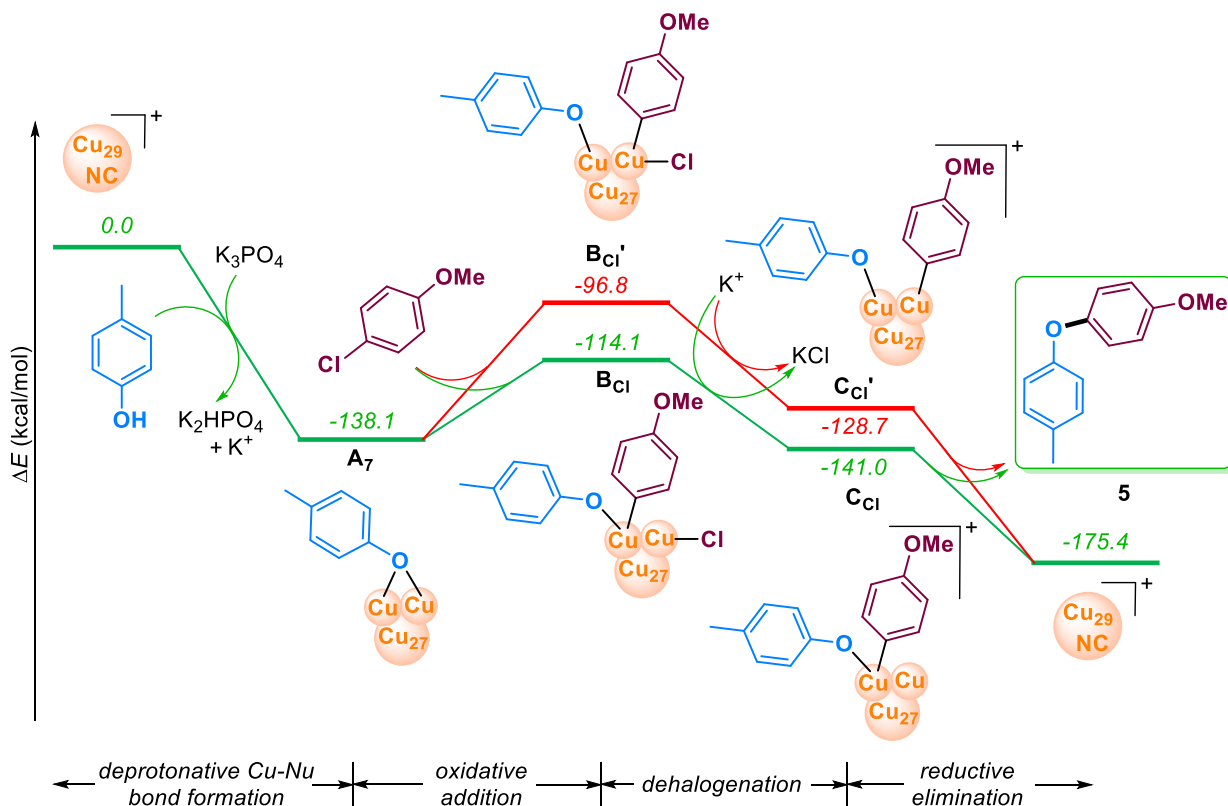
A 10 mL microwave vial was charged with a magnetic stirrer bar, (**Cu<sub>29</sub>**, (0.000075 mmol, 0.025 mol%),  $K_3PO_4$  (2.0 equiv, 0.6 mmol, 127 mg), *p*-cresol **2** (0.3 mmol, 1.0 equiv), 4-chlorobenzonitrile **1-Cl** (0.9 mmol, 3.0 equiv) and 1-bromonaphthalene **39** (0.9 mmol, 3.0 equiv), , The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Acetonitrile (ACN) (2 mL) were added via syringe through the septum. The reaction mixture was then stirred at  $\sim 90^\circ C$  under  $N_2$  (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to afford a 1:14.2 mixture of C-O coupled products **3** and **11** respectively. The ratio of the products was determined by GC using 1,3,5-trimethylbenzene (mesitylene) as an internal standard. *Explanation: Despite its lower reduction potential of 1-Cl, 39 reacts faster, which can be related to the weaker C-Br bond compared to C-Cl. Overall, these results indicate that conventional two-electron oxidative addition is operative instead of a radical pathway via SET.*

### Scheme S5b

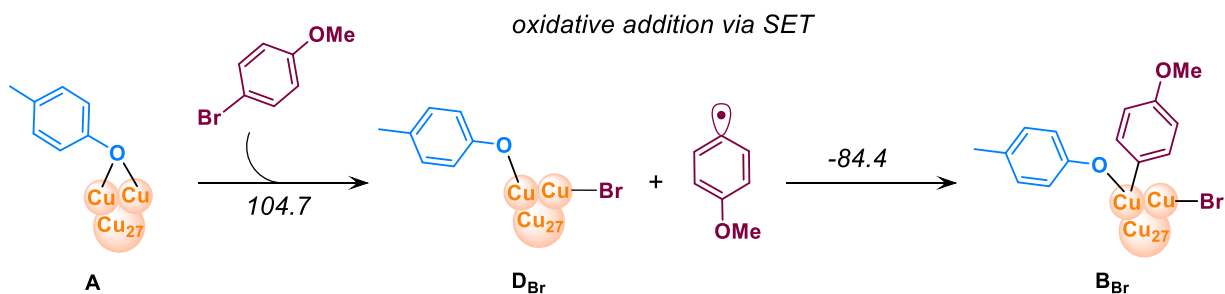




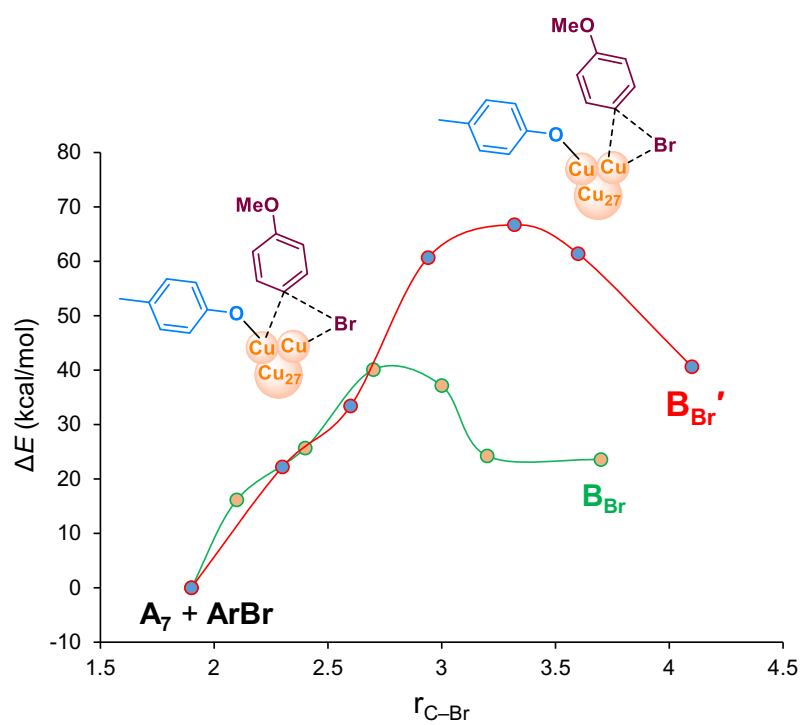
A 10 mL microwave vial was charged with a magnetic stirrer bar, (**Cu<sub>29</sub>**, (0.000075 mmol, 0.025 mol%),  $\text{K}_3\text{PO}_4$  (2.0 equiv, 0.6 mmol, 127 mg), *p*-cresol **2** (0.3 mmol, 1.0 equiv), 4-chlorobenzonitrile **1-Cl** (0.9 mmol, 3.0 equiv) and 4-iodoanisole **40** (0.9 mmol, 3.0 equiv), . The vial was then sealed and evacuated under vacuum for 10-15 minutes and backfilled with nitrogen five times. Acetonitrile (ACN) (2 mL) were added via syringe through the septum. The reaction mixture was then stirred at  $\sim 90^\circ\text{C}$  under  $\text{N}_2$  (1 atm) for 24 hrs. The mixture was filtered through celite and silica gel pads and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel to afford a 1:12.75 mixture of C-O coupled products **3** and **4** respectively. The ratio of the products was determined by GC using 1,3,5-trimethylbenzene (mesitylene) as an internal standard. *Explanation: these results indicate that current reaction is more predominant with concerted oxidative addition rather than SET process, as 4-iodoanisole more favors with oxidative cleavage of C-I than 4-chlorobenzonitrile C-Cl bond. Overall, the above controlled experiments indicate that conventional two-electron oxidative addition is operative instead of a radical pathway via SET.*



**Figure S17.** Computed energy profile of Cu<sub>29</sub>-NC catalyzed C-O coupling reaction of p-cresol using 4-chloroanisole. For energy convention, refer to Figure S16.



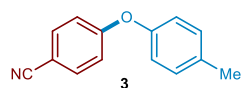
**Figure S18.** Thermochemistry of oxidative addition via SET pathway. Energy values are at the PBE-D3 level of theory using implicit solvation model in acetonitrile.



**Figure S19.** Computed potential energy surface (PES) of oxidative addition of Ar-Br to form  $B_{Br}$  and  $B_{Br}'$ .

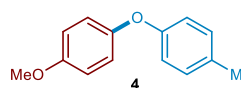
## Spectroscopic Data

### 4-(p-tolyloxy)benzonitrile (3)



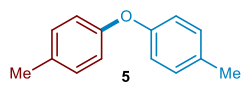
Yellow viscous oil, 90% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J = 8.8, 2.1$  Hz, 2H), 7.20 (d,  $J = 8.0$  Hz, 2H), 7.01 – 6.93 (m, 3H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.11, 152.41, 134.96, 134.11, 130.77, 120.42, 118.96, 117.59, 105.49, 20.86. GCMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{NO}$  [ $\text{M}^+$ ] 209.1, found 209.1. The data are in accordance with those reported in the literature.<sup>19</sup>

### 1-methoxy-4-(p-tolyloxy)benzene (4)



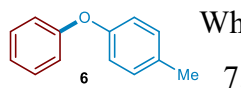
Brown oil, 76% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 (d,  $J = 8.4$  Hz, 2H), 6.98 (d,  $J = 9.0$  Hz, 2H), 6.92 – 6.84 (m, 4H), 3.81 (s, 3H), 2.33 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.21, 155.74, 150.87, 132.13, 130.21, 120.45, 117.93, 114.90, 55.76, 20.73. GCMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2$  [ $\text{M}^+$ ] 214.1, found 214.2. The data are in accordance with those reported in the literature.<sup>19</sup>

### 4,4'-oxybis(methylbenzene) (5)



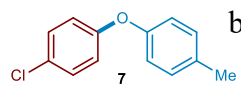
off-white oil, 78% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (d,  $J = 8.2$  Hz, 2H), 6.90 (d,  $J = 8.2$  Hz, 2H), 2.34 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.45, 132.58, 130.28, 118.73, 20.80. GCMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{14}\text{O}$  [ $\text{M}^+$ ] 198.1, found 198.2. The data are in accordance with those reported in the literature.<sup>19</sup>

### 1-methyl-4-phenoxybenzene (6)



White solid, 83% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.29 (m, 2H), 7.15 (d,  $J = 8.1$  Hz, 2H), 7.08 (t,  $J = 7.4$  Hz, 1H), 7.00 (d,  $J = 7.5$  Hz, 2H), 6.94 (d,  $J = 8.4$  Hz, 2H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.96, 154.85, 133.03, 130.37, 129.78, 122.93, 119.26, 118.48, 20.84. GCMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$  [ $\text{M}^+$ ] 184.1, found 184.2. The data are in accordance with those reported in the literature.<sup>19</sup>

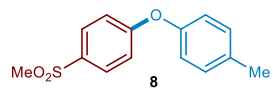
### 1-chloro-4-(p-tolyloxy)benzene (7)



brown oil, 80% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (d,  $J = 8.5$  Hz, 2H), 7.16 (d,  $J = 8.1$  Hz, 2H), 6.92 (d,  $J = 8.3$  Hz, 4H), 2.35 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.67, 154.49, 133.49, 130.49, 129.73, 127.86, 119.61,

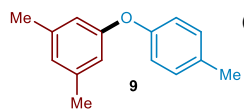
119.28, 20.84. **GCMS (EI)**  $m/z$  calcd for  $C_{13}H_{11}ClO$   $[M^+]$  218.0, found 218.1. The data are in accordance with those reported in the literature.<sup>19</sup>

### 1-methyl-4-(4-(methylsulfonyl)phenoxy)benzene (8)



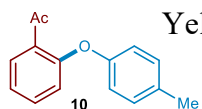
Off-White solid, 77% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.85 (d,  $J$  = 8.8 Hz, 2H), 7.20 (d,  $J$  = 8.2 Hz, 2H), 7.03 (d,  $J$  = 8.8 Hz, 2H), 6.95 (d,  $J$  = 8.4 Hz, 2H), 3.03 (s, 3H), 2.36 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  162.93, 152.51, 134.98, 133.78, 130.78, 129.66, 120.41, 117.39, 44.80, 20.87. **GCMS (EI)**  $m/z$  calcd for  $C_{14}H_{14}O_3S$   $[M^+]$  262.1, found 262.2. The data are in accordance with those reported in the literature.<sup>20</sup>

### 1,3-dimethyl-5-(p-tolyloxy)benzene (9)



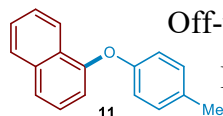
Colourless oil, 73% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.17 (d,  $J$  = 8.0 Hz, 2H), 6.95 (d,  $J$  = 8.6 Hz, 2H), 6.76 (s, 1H), 6.65 (s, 2H), 2.38 (s, 3H), 2.31 (s, 6H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  157.88, 155.02, 139.59, 132.75, 130.28, 124.70, 119.23, 116.19, 21.43, 20.83. **GCMS (EI)**  $m/z$  calcd for  $C_{15}H_{16}O$   $[M^+]$  212.1, found 212.2. The data are in accordance with those reported in the literature.<sup>21, 22</sup>

### 1-(2-(p-tolyloxy)phenyl)ethan-1-one (10)



Yellow pasty solid, 84% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.84 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 7.40 (ddd,  $J$  = 8.1, 7.2, 1.8 Hz, 1H), 7.21 – 7.10 (m, 3H), 6.93 (d,  $J$  = 8.5 Hz, 2H), 6.88 (d,  $J$  = 8.3 Hz, 1H), 2.66 (s, 3H), 2.35 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  199.23, 157.08, 154.07, 133.68, 130.62, 130.55, 130.24, 123.14, 119.11, 118.84, 31.72, 20.80. **GCMS (EI)**  $m/z$  calcd for  $C_{15}H_{14}O_2$   $[M^+]$  226.1, found 226.2. The data are in accordance with those reported in the literature.<sup>19</sup>

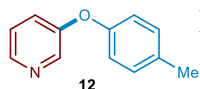
### 1-(p-tolyloxy)naphthalene (11)



Off-white solid, 69% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.36 (d,  $J$  = 7.8 Hz, 1H), 7.94 (d,  $J$  = 7.4 Hz, 1H), 7.66 (d,  $J$  = 8.3 Hz, 1H), 7.64 – 7.53 (m, 2H), 7.43 (t,  $J$  = 7.9 Hz, 1H), 7.22 (d,  $J$  = 8.2 Hz, 2H), 7.05 (d,  $J$  = 8.5 Hz, 2H), 6.98 (d,  $J$  = 7.6 Hz, 1H), 2.42 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  155.48, 153.77, 135.02, 132.91, 130.41, 127.83, 126.86, 126.67, 125.95, 125.91, 123.00, 122.26,

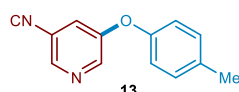
118.94, 112.72, 20.83. **GCMS (EI)**  $m/z$  calcd for  $C_{17}H_{14}O$   $[M^+]$  234.1, found 234.1. The data are in accordance with those reported in the literature.<sup>23</sup>

### 3-(p-tolyloxy)pyridine (12)



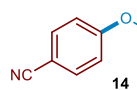
Pale yellow liquid, 85% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.38 (s, 1H), 8.32 (s, 1H), 7.27 – 7.19 (m, 2H), 7.15 (d,  $J$  = 8.2 Hz, 2H), 6.92 (d,  $J$  = 8.4 Hz, 2H), 2.34 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  154.53, 153.88, 143.96, 141.04, 133.94, 130.59, 124.89, 124.09, 119.25, 20.80. **GCMS (EI)**  $m/z$  calcd for  $C_{12}H_{11}NO$   $[M^+]$  185.1, found 185.2. The data are in accordance with those reported in the literature.<sup>19</sup>

### 5-(p-tolyloxy)nicotinonitrile (13)



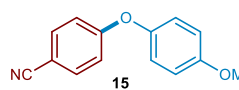
Yellow pasty solid, 82% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.57 (d,  $J$  = 12.4 Hz, 2H), 7.39 (s, 1H), 7.24 (d,  $J$  = 8.1 Hz, 2H), 6.96 (d,  $J$  = 8.0 Hz, 2H), 2.38 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  154.79, 152.17, 145.75, 144.24, 135.68, 131.16, 125.97, 120.02, 116.21, 110.33, 20.95. **GCMS (EI)**  $m/z$  calcd for  $C_{13}H_{10}N_2O$   $[M^+]$  210.1, found 210.1. The data are in accordance with those reported in the literature.<sup>19, 23</sup>

### 4-(4-(tert-butyl)phenoxy)benzonitrile (14)



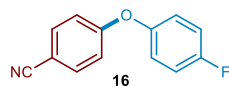
Off-white solid, 90% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.61 – 7.55 (m, 2H), 7.42 (d,  $J$  = 8.8 Hz, 2H), 7.03 – 6.95 (m, 4H), 1.34 (s, 9H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  162.09, 152.38, 148.30, 134.18, 127.16, 120.03, 119.06, 117.80, 105.60, 34.61, 31.55. **GCMS (EI)**  $m/z$  calcd for  $C_{17}H_{17}NO$   $[M^+]$  251.1, found 251.3. The data are in accordance with those reported in the literature.<sup>24</sup>

### 4-(4-methoxyphenoxy)benzonitrile (15)



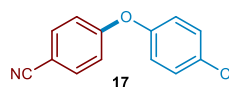
Off-white solid, 89% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.57 (s, 2H), 7.00 (d,  $J$  = 9.1 Hz, 2H), 6.96 – 6.91 (m, 4H), 3.82 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  162.59, 157.10, 147.94, 134.16, 121.90, 119.04, 117.23, 115.32, 105.34, 55.75. **GCMS (EI)**  $m/z$  calcd for  $C_{14}H_{11}NO_2$   $[M^+]$  225.1, found 225.2. The data are in accordance with those reported in the literature.<sup>24</sup>

### 4-(4-fluorophenoxy)benzonitrile (16)



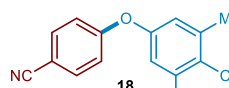
Yellow solid, 93% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.56 (m, 2H), 7.10 (dd,  $J$  = 9.2, 7.9 Hz, 2H), 7.04 (dd,  $J$  = 9.1, 4.5 Hz, 2H), 7.00 – 6.94 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.89, 160.88, 158.94, 150.65, 150.63, 134.29, 122.18, 122.11, 118.85, 117.64, 117.11, 116.92, 106.04. GCMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{FNO}$  [ $\text{M}^+$ ] 213.1, found 213.2. The data are in accordance with those reported in the literature.<sup>25</sup>

#### 4-(4-chlorophenoxy)benzonitrile (17)



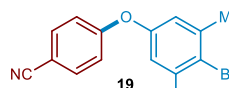
White solid, 84% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J$  = 8.9 Hz, 2H), 7.36 (d,  $J$  = 8.9 Hz, 2H), 7.04 – 6.97 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.29, 153.54, 134.32, 130.44, 130.37, 121.75, 118.74, 118.10, 106.43. GCMS (EI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_8\text{ClNO}$  [ $\text{M}^+$ ] 229.0, found 229.1. The data are in accordance with those reported in the literature.<sup>26</sup>

#### 4-(4-chloro-3,5-dimethylphenoxy)benzonitrile (18)



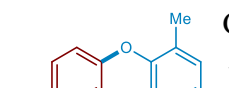
Off-white solid, 77% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J$  = 8.9 Hz, 2H), 7.25 (d,  $J$  = 8.9 Hz, 2H), 7.06 (s, 2H), 2.63 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.62, 152.51, 138.40, 134.20, 130.91, 120.24, 118.84, 117.90, 105.95, 20.94. GCMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{12}\text{ClNO}$  [ $\text{M}^+$ ] 257.1, found 257.2. The data are in accordance with those reported in the literature.<sup>27</sup>

#### 4-(4-bromo-3,5-dimethylphenoxy)benzonitrile (19)



Brown solid, 71% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J$  = 8.9 Hz, 2H), 7.25 (d,  $J$  = 8.9 Hz, 2H), 7.05 (s, 2H), 2.66 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.52, 153.30, 140.50, 134.25, 123.25, 120.06, 118.86, 118.00, 106.05, 24.10. GCMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{12}\text{BrNO}$  [ $\text{M}^+$ ] 302.0, found 301.1, 302.1 & 303.1. The data are in accordance with those reported in the literature.<sup>27</sup>

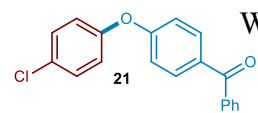
#### 4-(o-tolyloxy)benzonitrile (20)



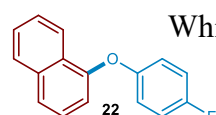
Colourless oil, 87% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J$  = 8.9 Hz, 2H), 7.30 (d,  $J$  = 6.9 Hz, 1H), 7.24 (t,  $J$  = 8.1 Hz, 1H), 7.17 (t,  $J$  = 7.5 Hz, 1H), 6.98 (d,  $J$  = 7.9 Hz, 1H), 6.91 (d,  $J$  = 10.1 Hz, 2H), 2.17 (s, 3H).  $^{13}\text{C}$

**NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  161.85, 152.49, 134.27, 132.02, 130.65, 127.75, 125.80, 121.19, 119.05, 116.87, 105.34, 16.11. **GCMS (EI)**  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>NO [M<sup>+</sup>] 209.1, found 209.2. The data are in accordance with those reported in the literature.<sup>28</sup>

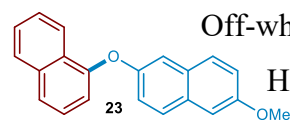
**(4-(4-chlorophenoxy)phenyl)(phenyl)methanone (21)**

 White solid, 77% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.83 (d,  $J$  = 8.7 Hz, 2H), 7.78 (d,  $J$  = 6.8 Hz, 2H), 7.58 (t,  $J$  = 7.4 Hz, 1H), 7.48 (t,  $J$  = 7.7 Hz, 2H), 7.35 (d,  $J$  = 8.8 Hz, 2H), 7.03 (dd,  $J$  = 8.9, 3.0 Hz, 4H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  195.49, 161.22, 154.34, 137.91, 132.62, 132.44, 132.35, 130.19, 129.93, 129.80, 128.39, 121.46, 117.37. **GCMS (EI)**  $m/z$  calcd for C<sub>19</sub>H<sub>13</sub>ClO<sub>2</sub> [M<sup>+</sup>] 308.1, found 308.1. The data are in accordance with those reported in the literature.<sup>29</sup>

**1-(4-fluorophenoxy)naphthalene (22)**

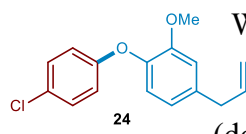
 White solid, 89% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.24 (d,  $J$  = 7.4 Hz, 1H), 7.89 (d,  $J$  = 7.2 Hz, 1H), 7.62 (d,  $J$  = 8.2 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.38 (t,  $J$  = 7.9 Hz, 1H), 7.10 – 7.00 (m, 4H), 6.88 (d,  $J$  = 7.6 Hz, 1H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  159.90, 157.98, 153.67, 153.60, 153.58, 135.06, 127.91, 126.82, 126.69, 126.12, 125.88, 123.36, 122.09, 120.37 (d,  $J$  = 8.2 Hz), 116.58, 116.39, 112.67. **GCMS (EI)**  $m/z$  calcd for C<sub>16</sub>H<sub>11</sub>FO [M<sup>+</sup>] 238.1, found 238.1. The data are in accordance with those reported in the literature.<sup>30</sup>

**2-methoxy-6-(naphthalen-1-yloxy)naphthalene (23)**

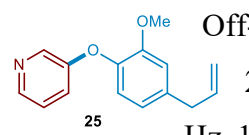
 Off-white solid, 84% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.28 (d,  $J$  = 8.5 Hz, 1H), 7.89 (d,  $J$  = 7.8 Hz, 1H), 7.76 (d,  $J$  = 8.6 Hz, 1H), 7.63 (d,  $J$  = 8.2 Hz, 1H), 7.59 (d,  $J$  = 8.8 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.38 (t,  $J$  = 7.9 Hz, 1H), 7.31 (d,  $J$  = 8.6 Hz, 2H), 7.19 – 7.10 (m, 2H), 6.96 (d,  $J$  = 7.6 Hz, 1H), 3.92 (s, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  157.08, 153.95, 153.65, 135.10, 131.37, 129.79, 128.73, 127.91, 126.91, 126.76, 126.07, 125.97, 123.30, 122.30, 120.50, 119.46, 114.63, 113.25, 106.07, 55.50. **GCMS (EI)**  $m/z$  calcd for C<sub>21</sub>H<sub>16</sub>O<sub>2</sub> [M<sup>+</sup>] 300.1, found 300.1. The data are in accordance with those reported in the literature.<sup>30</sup>



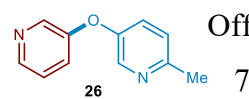
#### 4-allyl-1-(4-chlorophenoxy)-2-methoxybenzene (24)

 White solid, 84% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 9.0$  Hz, 2H), 6.94 (d,  $J = 8.1$  Hz, 1H), 6.86 (dd,  $J = 9.5, 2.5$  Hz, 3H), 6.78 (dd,  $J = 8.1, 2.1$  Hz, 1H), 6.01 (ddt,  $J = 16.8, 10.1, 6.7$  Hz, 1H), 5.19 – 5.12 (m, 1H), 5.12 (s, 1H), 3.81 (s, 3H), 3.41 (d,  $J = 6.8$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.06, 151.41, 142.61, 137.63, 137.21, 129.41, 127.06, 121.47, 121.12, 117.96, 116.20, 113.28, 55.92, 40.08. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{ClO}_2$  [ $\text{M}^+$ ] 274.1, found 274.1. The data are in accordance with those reported in the literature.<sup>31</sup>

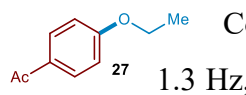
#### 3-(4-allyl-2-methoxyphenoxy)pyridine (25)

 Off-white solid, 84% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (dd,  $J = 21.1, 3.6$  Hz, 2H), 7.19 (ddd,  $J = 5.6, 3.5, 1.2$  Hz, 2H), 6.95 (d,  $J = 8.1$  Hz, 1H), 6.83 (d,  $J = 1.9$  Hz, 1H), 6.78 (dd,  $J = 8.1, 2.0$  Hz, 1H), 5.98 (ddt,  $J = 16.9, 10.2, 6.7$  Hz, 1H), 5.16 – 5.07 (m, 2H), 3.78 (s, 3H), 3.39 (d,  $J = 6.7$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.98, 151.37, 143.13, 141.90, 139.34, 138.27, 137.15, 124.02, 123.58, 121.61, 121.27, 116.34, 113.34, 55.95, 40.13. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_2$  [ $\text{M}^+$ ] 241.1, found 241.3. The data are in accordance with those reported in the literature.<sup>19, 25, 31</sup>

#### 2-methyl-5-(pyridin-3-yloxy)pyridine (26)

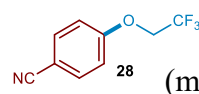
 Off-white solid, 77% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (dd,  $J = 7.1, 4.0$  Hz, 2H), 8.16 (d,  $J = 2.9$  Hz, 1H), 7.17 – 7.08 (m, 3H), 7.04 (d,  $J = 8.5$  Hz, 1H), 2.41 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  154.01, 153.52, 150.42, 144.47, 140.61, 140.50, 126.67, 124.85, 124.08, 123.83, 23.42. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$  [ $\text{M}^+$ ] 186.1, found 186.2. The data are in accordance with those reported in the literature.<sup>19</sup>

#### 1-(4-ethoxyphenyl)ethan-1-one (27)

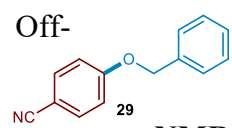
 Colourless liquid, 70% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 1.3$  Hz, 2H), 6.89 (d,  $J = 1.2$  Hz, 2H), 4.08 (qd,  $J = 7.0, 1.4$  Hz, 2H), 2.53 (s,

3H), 1.41 (d,  $J = 8.2$  Hz, 3H).  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  196.87, 163.01, 130.67, 130.24, 114.19, 63.83, 26.39, 14.75. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_2$  [ $\text{M}^+$ ] 164.1, found 164.2. The data are in accordance with those reported in the literature.<sup>32</sup>

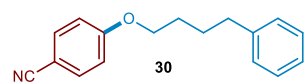
#### 4-(2,2,2-trifluoroethoxy)benzonitrile (28)

 Colourless liquid, 84% yield;  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.67 – 7.60 (m, 2H), 7.05 – 6.98 (m, 2H), 4.41 (q,  $J = 7.9$  Hz, 2H).  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  160.36, 134.36, 126.31, 124.10, 121.89, 119.68, 118.67, 115.63, 106.27, 65.66 (q,  $J = 36.3$  Hz). **GCMS (EI)**  $m/z$  calcd for  $\text{C}_9\text{H}_6\text{F}_3\text{NO}$  [ $\text{M}^+$ ] 201.1, found 201.1. The data are in accordance with those reported in the literature.<sup>19, 32</sup>

#### 4-(benzyloxy)benzonitrile (29)

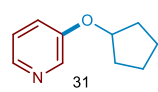
Off- white solid, 83% yield;  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.59 (d,  $J = 8.8$  Hz, 2H), 7.44 – 7.32 (m, 5H), 7.05 – 6.99 (m, 2H), 5.12 (s, 2H).  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  162.10, 135.83, 134.16, 128.91, 128.56, 127.61, 119.30, 115.73, 104.38, 70.42. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{NO}$  [ $\text{M}^+$ ] 209.1, found 209.2. The data are in accordance with those reported in the literature.<sup>19</sup>

#### 4-(4-phenylbutoxy)benzonitrile (30)

 White solid, 89% yield;  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.57 (d,  $J = 8.9$  Hz, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 6.92 (d,  $J = 8.9$  Hz, 2H), 4.01 (t,  $J = 5.9$  Hz, 2H), 2.70 (t,  $J = 7.1$  Hz, 2H), 1.82 (dtd,  $J = 10.4, 5.2, 2.9$  Hz, 4H).  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  162.49, 142.04, 134.09, 128.52, 126.04, 119.43, 115.29, 103.86, 68.29, 35.62, 28.67, 27.81. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{NO}$  [ $\text{M}^+$ ] 251.1, found 251.1. The data are in accordance with those reported in the literature.<sup>19,</sup>

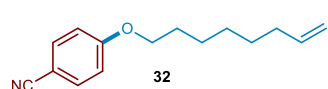
33

#### 3-(cyclopentyloxy)pyridine (31)

 Brown oil, 77% yield;  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  8.29 (s, 1H), 8.20 (s, 1H), 7.26 – 7.16 (m, 2H), 4.79 (dt,  $J = 5.9, 3.1$  Hz, 1H), 2.01 – 1.74 (m, 6H), 1.66 – 1.58 (m, 2H).  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  154.67, 141.07, 138.28, 124.20,

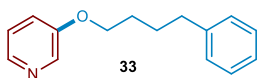
122.84, 80.04, 32.88, 24.12. **GCMS (EI)**  $m/z$  calcd for  $C_{10}H_{13}NO$   $[M^+]$  163.1, found 163.1. The data are in accordance with those reported in the literature.<sup>19</sup>

#### 4-(oct-7-en-1-yloxy)benzonitrile (32)



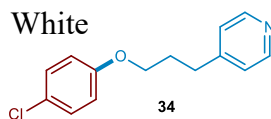
Brown oil, 79% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.57 (d,  $J = 8.8$  Hz, 2H), 6.93 (d,  $J = 8.8$  Hz, 2H), 5.81 (ddt,  $J = 16.9$ , 10.2, 6.7 Hz, 1H), 5.04 – 4.91 (m, 2H), 3.99 (t,  $J = 6.5$  Hz, 2H), 2.10 – 2.02 (m, 2H), 1.85 – 1.75 (m, 2H), 1.51 – 1.32 (m, 6H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  162.58, 139.04, 134.10, 119.47, 115.31, 114.52, 103.80, 68.49, 33.79, 29.06, 28.89, 25.92. **GCMS (EI)**  $m/z$  calcd for  $C_{15}H_{19}NO$   $[M^+]$  229.1, found 229.1. The data are in accordance with those reported in the literature.<sup>19, 25, 34</sup>

#### 3-(4-phenylbutoxy)pyridine (33)



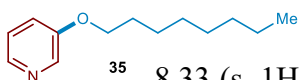
Off-white solid, 81% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.30 (d,  $J = 2.9$  Hz, 1H), 8.21 (d,  $J = 2.9$  Hz, 1H), 7.32 – 7.25 (m, 2H), 7.21 (t,  $J = 8.5$  Hz, 5H), 4.01 (t,  $J = 5.9$  Hz, 2H), 2.69 (t,  $J = 7.0$  Hz, 2H), 1.89 – 1.76 (m, 4H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  155.43, 142.05, 141.45, 137.41, 128.48, 128.45, 125.96, 124.10, 121.78, 68.29, 35.59, 28.77, 27.77. **GCMS (EI)**  $m/z$  calcd for  $C_{15}H_{17}NO$   $[M^+]$  227.1, found 227.3. The data are in accordance with those reported in the literature.<sup>35</sup>

#### 4-(3-(4-chlorophenoxy)propyl)pyridine (34)



White solid, 77% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.51 (s, 2H), 7.22 (d,  $J = 8.9$  Hz, 2H), 7.15 (d,  $J = 5.7$  Hz, 2H), 6.79 (d,  $J = 8.9$  Hz, 2H), 3.92 (t,  $J = 6.1$  Hz, 2H), 2.81 (dd,  $J = 8.5$ , 6.8 Hz, 2H), 2.15 – 2.06 (m, 2H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  157.49, 150.86, 149.62, 129.48, 125.80, 124.19, 115.83, 66.89, 31.69, 29.76. **GCMS (EI)**  $m/z$  calcd for  $C_{14}H_{14}ClNO$   $[M^+]$  247.1, found 247.2. The data are in accordance with those reported in the literature.<sup>35</sup>

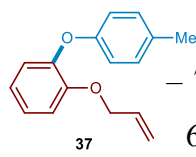
#### 3-(octyloxy)pyridine (35)



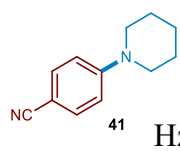
Yellow pasty solid, 81% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.33 (s, 1H), 8.22 (s, 0H), 7.22 (qd,  $J = 7.7$ , 6.8, 3.6 Hz, 2H), 4.00 (t,  $J = 6.5$  Hz, 2H), 1.84 – 1.75 (m, 2H), 1.40 – 1.22 (m, 7H), 0.89 (t,  $J = 6.9$  Hz, 2H).  **$^{13}C$  NMR (126**

**MHz, CDCl<sub>3</sub>**)  $\delta$  155.83, 140.83, 136.82, 124.45, 122.51, 69.76, 31.92, 29.42, 29.34, 29.23, 26.06, 22.78, 14.23. **GCMS (EI)**  $m/z$  calcd for C<sub>13</sub>H<sub>21</sub>NO [M<sup>+</sup>] 207.2, found 207.2. The data are in accordance with those reported in the literature.<sup>36</sup>

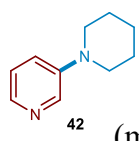
### 1-(allyloxy)-2-(p-tolyloxy)benzene (37)

 off-white viscous liquid, 74% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.13 – 7.04 (m, 3H), 6.99 (ddd,  $J$  = 13.4, 8.1, 1.7 Hz, 2H), 6.95 – 6.90 (m, 1H), 6.87 (d,  $J$  = 8.5 Hz, 2H), 5.97 (ddt,  $J$  = 17.2, 10.4, 5.1 Hz, 1H), 5.30 (dd,  $J$  = 17.3, 1.7 Hz, 1H), 5.21 (dd,  $J$  = 10.6, 1.5 Hz, 1H), 4.59 (dt,  $J$  = 5.2, 1.6 Hz, 2H), 2.32 (s, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  155.87, 150.40, 146.24, 133.33, 131.97, 130.05, 124.42, 121.63, 121.08, 117.52, 117.42, 115.19, 69.96, 20.75. **GCMS (EI)**  $m/z$  calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> [M<sup>+</sup>] 240.2, found 240.2. The data are in accordance with those reported in the literature.<sup>37</sup>

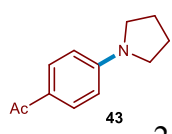
### 4-(piperidin-1-yl)benzonitrile (41)

 brown solid, 85% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.44 (d,  $J$  = 8.9 Hz, 2H), 6.82 (d,  $J$  = 9.0 Hz, 2H), 3.31 (t,  $J$  = 5.2 Hz, 4H), 1.65 (dd,  $J$  = 7.4, 3.6 Hz, 6H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  153.60, 133.50, 120.42, 114.11, 98.91, 48.47, 25.28, 24.27. **GCMS (EI)**  $m/z$  calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub> [M<sup>+</sup>] 187.1, found 187.2. The data are in accordance with those reported in the literature.<sup>38</sup>

### 3-(piperidin-1-yl)pyridine (42)

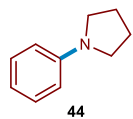
 Colourless oil, 90% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.16 (s, 2H), 7.17 (d,  $J$  = 7.5 Hz, 2H), 3.19 – 3.13 (m, 5H), 1.68 (p,  $J$  = 5.7 Hz, 4H), 1.61 – 1.54 (m, 2H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  148.45, 139.55, 138.59, 124.01, 122.65, 49.89, 25.57, 24.12. **GCMS (EI)**  $m/z$  calcd for C<sub>10</sub>H<sub>14</sub>N<sub>2</sub> [M<sup>+</sup>] 162.1, found 162.2. The data are in accordance with those reported in the literature.<sup>38, 39</sup>

### 1-(4-(pyrrolidin-1-yl)phenyl)ethan-1-one (43)

 Yellow solid, 80% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.86 (d,  $J$  = 8.9 Hz, 2H), 6.50 (d,  $J$  = 8.9 Hz, 2H), 3.40 – 3.30 (m, 4H), 2.50 (s, 3H), 2.08 – 2.00 (m, 4H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  196.47, 151.10, 130.81, 125.00,

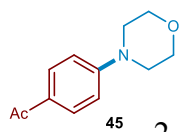
110.75, 47.66, 26.06, 25.56. **GCMS (EI)**  $m/z$  calcd for  $C_{12}H_{15}NO$   $[M^+]$  189.1, found 189.2. The data are in accordance with those reported in the literature.<sup>40</sup>

### 1-phenylpyrrolidine (44)



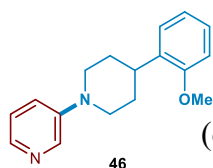
Yellow oil, 72% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.32 (t,  $J$  = 7.0 Hz, 2H), 6.75 (t,  $J$  = 7.3 Hz, 1H), 6.66 (d,  $J$  = 8.3 Hz, 2H), 3.36 (td,  $J$  = 6.5, 1.9 Hz, 4H), 2.08 (td,  $J$  = 6.6, 5.8, 2.3 Hz, 4H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  148.04, 129.20, 115.49, 111.76, 47.68, 25.54. **GCMS (EI)**  $m/z$  calcd for  $C_{10}H_{13}N$   $[M^+]$  147.1, found 147.2. The data are in accordance with those reported in the literature.<sup>41</sup>

### 1-(4-morpholinophenyl)ethan-1-one (45)



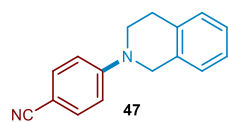
Brown solid, 82% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.89 (d,  $J$  = 9.0 Hz, 2H), 6.88 (d,  $J$  = 9.0 Hz, 2H), 3.89 – 3.83 (m, 4H), 3.33 – 3.28 (m, 4H), 2.52 (s, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  196.68, 154.23, 130.48, 128.43, 113.53, 66.65, 47.77, 26.28. **GCMS (EI)**  $m/z$  calcd for  $C_{12}H_{15}NO_2$   $[M^+]$  205.1, found 205.1. The data are in accordance with those reported in the literature.<sup>42</sup>

### 3-(4-(2-methoxyphenyl)piperidin-1-yl)pyridine (46)



Brown solid, 76% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.29 (s, 1H), 8.03 (s, 1H), 7.22 – 7.09 (m, 2H), 7.02 – 6.69 (m, 4H), 3.81 (s, 3H), 3.33 (dq,  $J$  = 5.4, 2.6 Hz, 4H), 3.16 (dq,  $J$  = 8.2, 2.9 Hz, 4H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  152.17, 147.03, 140.77, 140.15, 138.05, 123.54, 123.25, 122.46, 120.94, 118.14, 111.25, 55.34, 50.36, 48.58. **GCMS (EI)**  $m/z$  calcd for  $C_{17}H_{20}N_2O$   $[M^+]$  268.2, found 268.2. The data are in accordance with those reported in the literature.<sup>42</sup>

### 4-(3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (47)



White solid, 73% yield; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.50 (d,  $J$  = 9.0 Hz, 2H), 7.29 – 7.10 (m, 4H), 6.85 (d,  $J$  = 9.1 Hz, 2H), 4.49 (s, 2H), 3.62 (t,  $J$  = 5.9 Hz, 2H), 2.99 (t,  $J$  = 6.0 Hz, 2H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  152.20, 134.93, 133.55, 133.41, 128.20, 126.97, 126.55, 126.50, 120.49, 112.66, 98.54, 48.75, 44.60, 28.94. **GCMS (EI)**  $m/z$  calcd for  $C_{16}H_{14}N_2$   $[M^+]$  234.1, found 234.2. The data are in accordance with those reported in the literature.<sup>43</sup>

#### 4-(9H-carbazol-9-yl)benzonitrile (48)

Off-white solid, 84% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.34 (ddd, *J* = 8.0, 6.3, 1.8 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 142.24, 140.05, 134.08, 127.27, 126.52, 124.15, 121.14, 120.73, 118.51, 110.63, 109.67. GCMS (EI) *m/z* calcd for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub> [M<sup>+</sup>] 268.1, found 268.1. The data are in accordance with those reported in the literature.<sup>44</sup>

#### 9-(pyridin-3-yl)-9H-carbazole (49)

Yellow solid, 88% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.92 (d, *J* = 2.5 Hz, 1H), 8.74 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.17 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.92 (ddd, *J* = 8.1, 2.6, 1.4 Hz, 1H), 7.57 (dt, *J* = 7.9, 3.1 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.47, 148.33, 140.66, 134.75, 134.69, 126.37, 124.58, 123.79, 120.69, 120.60, 109.38. GCMS (EI) *m/z* calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub> [M<sup>+</sup>] 244.1, found 244.1. The data are in accordance with those reported in the literature.<sup>44</sup>

#### 1-(naphthalen-1-yl)-1H-indole (50)

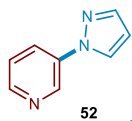
White solid, 75% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 3.1 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 3.2 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 138.14, 136.20, 134.61, 130.72, 129.94, 128.61, 128.59, 128.39, 127.09, 126.79, 125.65, 125.29, 123.55, 122.27, 121.05, 120.25, 110.97, 103.04. GCMS (EI) *m/z* calcd for C<sub>18</sub>H<sub>13</sub>N [M<sup>+</sup>] 243.1, found 243.1. The data are in accordance with those reported in the literature.<sup>44</sup>

#### 1-(3,5-dimethylphenyl)-1H-pyrazole (51)

Colourless oil, 77% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.32 (s, 2H), 6.93 (s, 1H), 6.44 (t, *J* = 2.1 Hz, 1H), 2.38 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.88, 140.21, 139.39,

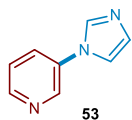
128.29, 126.96, 117.26, 107.42, 21.49. **GCMS (EI)**  $m/z$  calcd for  $C_{11}H_{12}N_2$   $[M^+]$  172.1, found 172.2. The data are in accordance with those reported in the literature.<sup>45</sup>

### 3-(1H-pyrazol-1-yl)pyridine (52)



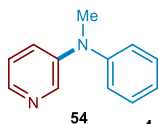
Yellow oil, 88% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.87 (d,  $J = 2.8$  Hz, 1H), 8.39 (d,  $J = 5.3$  Hz, 1H), 7.92 (d,  $J = 8.3$  Hz, 1H), 7.88 (d,  $J = 2.6$  Hz, 1H), 7.62 (s, 1H), 7.30 – 7.24 (m, 1H), 6.38 (t,  $J = 2.2$  Hz, 1H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  147.20, 141.71, 140.26, 136.35, 126.78, 126.26, 123.80, 108.25. **GCMS (EI)**  $m/z$  calcd for  $C_8H_7N_3$   $[M^+]$  145.1, found 145.1. The data are in accordance with those reported in the literature.<sup>46</sup>

### 3-(1H-imidazol-1-yl)pyridine (53)



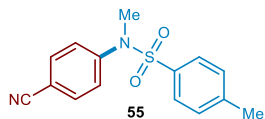
Brown oil, 86% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.49 (d,  $J = 3.0$  Hz, 1H), 8.34 (d,  $J = 5.0$  Hz, 1H), 7.69 (s, 1H), 7.57 – 7.51 (m, 1H), 7.24 – 7.17 (m, 1H), 7.12 (t,  $J = 1.6$  Hz, 1H), 6.96 (s, 1H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  148.07, 142.06, 135.00, 133.31, 130.33, 128.30, 123.91, 117.5. **GCMS (EI)**  $m/z$  calcd for  $C_8H_7N_3$   $[M^+]$  145.1, found 145.2. The data are in accordance with those reported in the literature.<sup>47</sup>

### N-methyl-N-phenylpyridin-3-amine (54)



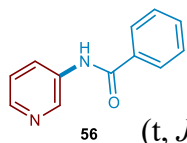
Brown pasty solid, 76% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  8.28 (s, 1H), 8.12 (s, 1H), 7.34 (t,  $J = 7.9$  Hz, 2H), 7.27 – 7.22 (m, 1H), 7.18 (dd,  $J = 8.6$ , 4.6 Hz, 1H), 7.14 – 7.07 (m, 3H), 3.34 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  147.57, 145.59, 139.62, 138.78, 129.89, 125.10, 124.03, 123.99, 123.02, 40.16. **GCMS (EI)**  $m/z$  calcd for  $C_{12}H_{12}N_2$   $[M^+]$  184.1, found 184.1. The data are in accordance with those reported in the literature.<sup>48</sup>

### N-(4-cyanophenyl)-N,4-dimethylbenzenesulfonamide (55)



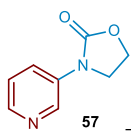
Yellow solid, 73% yield;  **$^1H$  NMR (500 MHz,  $CDCl_3$ )**  $\delta$  7.59 (d,  $J = 8.6$  Hz, 2H), 7.40 (d,  $J = 8.1$  Hz, 2H), 7.29 – 7.23 (m, 4H), 3.18 (s, 3H), 2.42 (s, 3H).  **$^{13}C$  NMR (126 MHz,  $CDCl_3$ )**  $\delta$  145.81, 144.44, 133.10, 132.90, 129.79, 127.75, 126.16, 118.41, 110.35, 37.51, 21.69. **GCMS (EI)**  $m/z$  calcd for  $C_{15}H_{14}N_2O_2S$   $[M^+]$  286.1, found 286.2. The data are in accordance with those reported in the literature.<sup>49</sup>

### N-(pyridin-3-yl)benzamide (56)



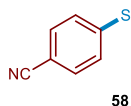
Off-white solid, 68% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.48 (s, 1H), 8.75 (d,  $J = 2.7$  Hz, 1H), 8.26 – 8.19 (m, 1H), 7.86 (d,  $J = 7.5$  Hz, 2H), 7.46 (t,  $J = 7.4$  Hz, 1H), 7.36 (t,  $J = 7.7$  Hz, 2H), 7.20 (dd,  $J = 8.3, 4.8$  Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.90, 144.89, 141.97, 135.64, 134.42, 131.96, 128.54, 128.04, 127.57, 123.64. GCMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$  [ $\text{M}^+$ ] 198.1, found 198.0. The data are in accordance with those reported in the literature.<sup>50</sup>

### 3-(pyridin-3-yl)oxazolidin-2-one (57)



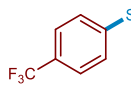
White solid, 71% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (q,  $J = 2.6$  Hz, 1H), 8.29 (t,  $J = 4.7$  Hz, 1H), 8.04 (ddt,  $J = 6.4, 3.7, 1.7$  Hz, 1H), 7.24 (ddd,  $J = 8.6, 4.7, 1.6$  Hz, 1H), 4.49 – 4.41 (m, 2H), 4.03 (t,  $J = 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.07, 144.85, 138.93, 134.99, 125.38, 123.50, 61.65, 44.35. GCMS (EI)  $m/z$  calcd for  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$  [ $\text{M}^+$ ] 164.1, found 164.1. The data are in accordance with those reported in the literature.<sup>51</sup>

### 4-((4-methoxyphenyl)thio)benzonitrile (58)



Yellow viscous oil, 87% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.6$  Hz, 2H), 7.45 (d,  $J = 7.1$  Hz, 2H), 7.08 (d,  $J = 6.9$  Hz, 2H), 6.98 (d,  $J = 7.0$  Hz, 2H), 3.87 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.99, 147.38, 137.10, 132.25, 126.07, 120.36, 118.97, 115.60, 108.01, 55.47. GCMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{NOS}$  [ $\text{M}^+$ ] 241.1, found 241.2. The data are in accordance with those reported in the literature.<sup>52</sup>

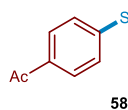
### (4-methoxyphenyl)(4-(trifluoromethyl)phenyl)sulfane (59)



Pale yellow viscous oil, 89% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.41 (m, 4H), 7.17 (d,  $J = 8.2$  Hz, 2H), 6.99 (d,  $J = 6.8$  Hz, 1H), 3.88 (s, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.67, 144.89, 136.74, 127.20 (q,  $J = 32.6$  Hz), 126.41, 125.64 (q,  $J = 3.8$  Hz), 124.22 (q,  $J = 271.7$  Hz), 121.67, 115.40, 55.40.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.34. GCMS (EI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{F}_3\text{OS}$  [ $\text{M}^+$ ] 284.0, found 284.1. The data are in accordance with those reported in the literature.<sup>52</sup>

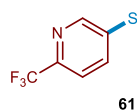
### 1-(4-((4-methoxyphenyl)thio)phenyl)ethan-1-one (60)





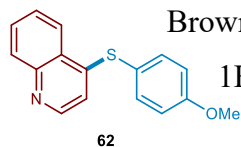
Yellow viscous oil, 88% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 6.8$  Hz, 2H), 7.47 (d,  $J = 7.1$  Hz, 2H), 7.09 (d,  $J = 6.7$  Hz, 2H), 6.96 (d,  $J = 7.1$  Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.08, 160.68, 146.88, 136.82, 133.87, 128.81, 125.80, 121.35, 115.40, 55.42, 26.43. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$  [ $\text{M}^+$ ] 258.1.0, found 258.0. The data are in accordance with those reported in the literature.<sup>52</sup>

#### 5-((4-methoxyphenyl)thio)-2-(trifluoromethyl)pyridine (61)



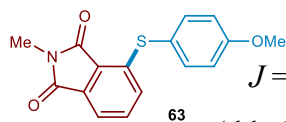
Yellow pasty solid, 84% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 (s, 1H), 7.49 – 7.42 (m, 3H), 7.42 – 7.37 (m, 1H), 6.95 (d,  $J = 7.1$  Hz, 2H), 3.83 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.12, 147.25, 144.48 (q,  $J = 34.8$  Hz), 141.47, 136.87, 134.33, 125.00, 122.82, 120.65, 120.41 (q,  $J = 2.8$  Hz), 119.92, 118.47, 115.76, 55.49. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{13}\text{H}_{10}\text{F}_3\text{NOS}$  [ $\text{M}^+$ ] 285.0, found 285.2. The data are in accordance with those reported in the literature.<sup>53</sup>

#### 4-((4-methoxyphenyl)thio)quinoline (62)



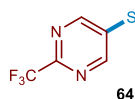
Brown solid, 84% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (d,  $J = 4.8$  Hz, 1H), 8.19 (dd,  $J = 8.4, 1.4$  Hz, 1H), 8.10 – 8.03 (m, 1H), 7.71 (ddd,  $J = 8.4, 6.9, 1.4$  Hz, 1H), 7.60 – 7.52 (m, 1H), 7.50 (s, 2H), 7.00 (d,  $J = 8.7$  Hz, 2H), 6.64 (d,  $J = 4.8$  Hz, 1H), 3.85 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.21, 150.27, 149.50, 147.53, 137.67, 129.98, 129.84, 126.42, 125.76, 123.39, 119.25, 116.79, 115.79, 55.53. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{NOS}$  [ $\text{M}^+$ ] 267.1, found 267.2. The data are in accordance with those reported in the literature.<sup>53</sup>

#### 4-((4-methoxyphenyl)thio)-2-methylisoindoline-1,3-dione (63)



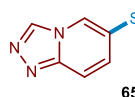
Yellow solid, 87% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 7.8$  Hz, 1H), 7.46 (d,  $J = 8.7$  Hz, 2H), 7.37 (d,  $J = 1.6$  Hz, 1H), 7.30 (dd,  $J = 7.9, 1.7$  Hz, 1H), 6.96 (d,  $J = 8.8$  Hz, 2H), 3.85 (s, 3H), 3.10 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.18, 161.14, 149.19, 137.10, 133.12, 130.40, 128.34, 123.37, 120.37, 120.26, 115.79, 55.53, 24.00. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{NO}_3\text{S}$  [ $\text{M}^+$ ] 299.1, found 299.3. The data are in accordance with those reported in the literature.<sup>52, 53</sup>

#### 5-((4-methoxyphenyl)thio)-2-(trifluoromethyl)pyrimidine (64)



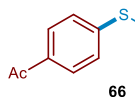
Yellow solid, 78% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 (s, 2H), 7.47 (d,  $J = 8.8$  Hz, 2H), 6.97 (d,  $J = 8.8$  Hz, 2H), 3.83 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.52, 154.30, 153.56, 153.19, 152.83, 152.46, 139.47, 136.94, 123.85, 121.12, 118.39, 118.01, 116.07, 114.68, 55.54. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{12}\text{H}_9\text{F}_3\text{N}_2\text{OS}$  [ $\text{M}^+$ ] 286.0, found 286.2. The data are in accordance with those reported in the literature.<sup>51-53</sup>

#### 6-((4-methoxyphenyl)thio)-[1,2,4]triazolo[4,3-a]pyridine (65)



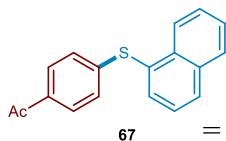
Pale yellow solid, 70% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (s, 1H), 7.91 – 7.86 (m, 1H), 7.62 (dd,  $J = 9.5, 1.0$  Hz, 1H), 7.40 (d,  $J = 8.7$  Hz, 2H), 7.08 (dd,  $J = 9.6, 1.7$  Hz, 1H), 6.90 (d,  $J = 8.8$  Hz, 2H), 3.80 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.54, 135.21, 130.21, 126.30, 122.21, 121.15, 116.11, 115.50, 55.52. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_3\text{OS}$  [ $\text{M}^+$ ] 257.1, found 257.3. The data are in accordance with those reported in the literature.<sup>51-53</sup>

#### 1-(4-(p-tolylthio)phenyl)ethan-1-one (66)



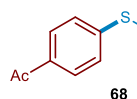
Off-white solid, 77% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (d,  $J = 8.5$  Hz, 2H), 7.40 (d,  $J = 8.2$  Hz, 2H), 7.21 (d,  $J = 7.9$  Hz, 2H), 7.14 (d,  $J = 8.5$  Hz, 2H), 2.52 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.00, 145.90, 139.31, 134.48, 134.13, 130.54, 128.82, 127.91, 126.63, 26.42, 21.28. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{OS}$  [ $\text{M}^+$ ] 242.1, found 242.3. The data are in accordance with those reported in the literature.<sup>54</sup>

#### 1-(4-(naphthalen-1-ylthio)phenyl)ethan-1-one (67)



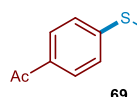
Yellow pasty solid, 78% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 – 8.26 (m, 1H), 7.97 (d,  $J = 8.4$  Hz, 1H), 7.94 – 7.89 (m, 1H), 7.87 (dd,  $J = 7.2, 1.2$  Hz, 1H), 7.74 (d,  $J = 8.5$  Hz, 2H), 7.58 – 7.46 (m, 3H), 7.06 (d,  $J = 8.6$  Hz, 2H), 2.49 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.09, 145.43, 135.19, 134.49, 134.25, 134.08, 130.89, 128.91, 128.84, 128.07, 127.54, 126.76, 126.27, 126.01, 125.78, 26.45. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{OS}$  [ $\text{M}^+$ ] 278.1, found 278.4. The data are in accordance with those reported in the literature.<sup>55</sup>

#### 1-(4-((4-(trifluoromethyl)phenyl)thio)phenyl)ethan-1-one (68)



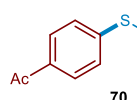
Pale yellow oil, 79% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.5$  Hz, 2H), 7.57 (d,  $J = 8.2$  Hz, 2H), 7.46 (d,  $J = 8.7$  Hz, 2H), 7.36 (d,  $J = 8.5$  Hz, 2H), 2.57 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.19, 141.45, 139.25, 135.87, 131.53, 130.23, 129.66, 129.30, 126.35 (q,  $J = 3.8$  Hz), 125.31, 122.61, 26.58. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{OS}$  [ $\text{M}^+$ ] 296.0, found 296.3. The data are in accordance with those reported in the literature.<sup>52, 54</sup>

#### 1-(4-((4-fluorophenyl)thio)phenyl)ethan-1-one (69)



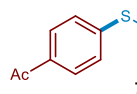
Yellow pasty solid, 75% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.6$  Hz, 2H), 7.53 – 7.38 (m, 2H), 7.32 – 6.99 (m, 4H), 2.52 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.98, 164.50, 162.01, 145.13, 136.55, 136.47, 134.46, 134.21, 128.95, 126.83, 117.09, 116.87, 26.45. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{14}\text{H}_{11}\text{FOS}$  [ $\text{M}^+$ ] 246.1, found 246.3. The data are in accordance with those reported in the literature.<sup>52, 54</sup>

#### 1-(4-(cyclohexylthio)phenyl)ethan-1-one (70)



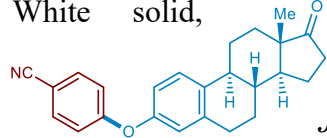
Colorless oil, 81% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.5$  Hz, 2H), 7.29 (d,  $J = 8.5$  Hz, 1H), 3.32 – 3.20 (m, 1H), 2.51 (s, 3H), 2.04 – 1.91 (m, 2H), 1.81 – 1.69 (m, 2H), 1.64 – 1.54 (m, 1H), 1.45 – 1.17 (m, 5H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.02, 143.51, 134.12, 128.65, 128.27, 44.82, 33.02, 26.38, 25.86, 25.64. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{14}\text{H}_{18}\text{OS}$  [ $\text{M}^+$ ] 234.1, found 234.3. The data are in accordance with those reported in the literature.<sup>56</sup>

#### 1-(4-(phenethylthio)phenyl)ethan-1-one (71)

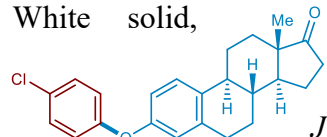


Yellow solid, 77% yield;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.5$  Hz, 2H), 7.38 – 7.31 (m, 4H), 7.27 – 7.19 (m, 3H), 3.29 – 3.20 (m, 2H), 3.03 – 2.94 (m, 2H), 2.57 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.03, 144.23, 139.67, 133.92, 128.80, 128.61, 128.48, 126.67, 126.47, 35.11, 33.41, 26.41. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{OS}$  [ $\text{M}^+$ ] 256.1, found 256.3. The data are in accordance with those reported in the literature.<sup>57</sup>

#### 4-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)benzonitrile (72)

White solid,  75% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 8.7$  Hz, 2H), 7.29 (d,  $J = 8.6$  Hz, 1H), 6.98 (d,  $J = 8.8$  Hz, 2H), 6.83 (dd,  $J = 8.5, 2.7$  Hz, 1H), 6.78 (d,  $J = 2.7$  Hz, 1H), 2.96 – 2.86 (m, 2H), 2.50 (dd,  $J = 19.0, 8.8$  Hz, 1H), 2.44 – 2.37 (m, 1H), 2.29 (td,  $J = 11.0, 4.1$  Hz, 1H), 2.21 – 1.91 (m, 4H), 1.69 – 1.39 (m, 6H), 0.92 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  220.63, 161.95, 152.60, 138.92, 136.81, 134.08, 127.13, 120.50, 118.94, 117.75, 105.48, 50.43, 47.95, 44.15, 38.10, 35.86, 31.58, 29.47, 26.35, 25.85, 21.61, 13.88. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{25}\text{H}_{25}\text{NO}_2$  [ $\text{M}^+$ ] 371.2, found 371.3. The data are in accordance with those reported in the literature.<sup>58</sup>

**(8R,9S,13S,14S)-3-(4-chlorophenoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (73)**

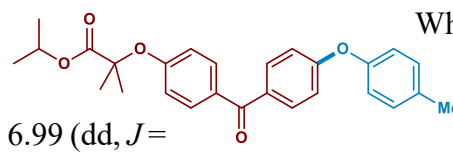
White solid,  68% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.21 (m, 3H), 6.91 (d,  $J = 9.0$  Hz, 2H), 6.78 (dd,  $J = 8.5, 2.8$  Hz, 1H), 6.73 (d,  $J = 2.8$  Hz, 1H), 2.87 (dd,  $J = 10.6, 7.0$  Hz, 2H), 2.50 (dd,  $J = 18.7, 9.1$  Hz, 1H), 2.44 – 2.35 (m, 1H), 2.27 (td,  $J = 11.0, 4.2$  Hz, 1H), 2.20 – 1.93 (m, 4H), 1.69 – 1.38 (m, 6H), 0.92 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  220.61, 156.24, 154.62, 138.41, 135.24, 129.60, 127.82, 126.76, 119.78, 119.08, 116.44, 50.40, 47.93, 44.07, 38.16, 35.84, 31.58, 29.48, 26.41, 25.86, 21.59, 13.85. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{24}\text{H}_{25}\text{ClO}_2$  [ $\text{M}^+$ ] 380.2, found 380.2. The data are in accordance with those reported in the literature.<sup>59</sup>

**(8R,9S,13S,14S)-13-methyl-3-(pyridin-3-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (74)**

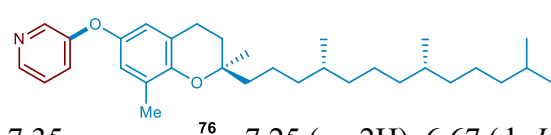
White solid, 83% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (d,  $J = 2.8$  Hz, 1H), 8.32 (d,  $J = 4.6$  Hz, 1H), 7.31 – 7.21 (m, 3H), 6.80 (dd,  $J = 8.5, 2.7$  Hz, 1H), 6.75 (d,  $J = 2.5$  Hz, 1H), 2.87 (dd,  $J = 7.6, 3.3$  Hz, 2H), 2.50 (dd,  $J = 19.1, 9.0$  Hz, 1H), 2.44 – 2.33 (m, 1H), 2.28 (t,  $J = 9.0$  Hz, 1H), 2.20 – 2.10 (m, 1H), 2.08 – 1.89 (m, 3H), 1.69 – 1.38 (m, 6H), 0.91 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  220.78, 154.18, 144.03, 141.17, 138.73, 135.82, 127.01, 125.40, 124.14, 119.19, 116.53, 50.50, 48.03, 44.17, 38.22, 35.93, 31.64, 29.57, 26.45, 25.93, 21.67, 13.94.

**HRMS (ESI)**  $m/z$  calcd for  $(C_{23}H_{26}NO_2)^+$   $[M^+ + H^+]$  348.1958, found 348.1955. The data are in accordance with those reported in the literature.<sup>60</sup>

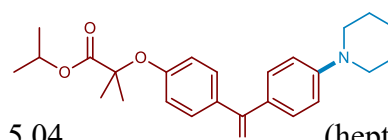
**isopropyl 2-methyl-2-(4-(4-(p-tolxyloxy)benzoyl)phenoxy)propanoate (75)**

 White solid, 65% yield; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d,  $J$  = 16.4 Hz, 4H), 7.19 (d,  $J$  = 7.8 Hz, 2H), 6.99 (dd,  $J$  = 8.6, 3.6 Hz, 4H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 5.08 (hept,  $J$  = 6.3 Hz, 1H), 2.36 (s, 3H), 1.65 (s, 6H), 1.20 (d,  $J$  = 6.3 Hz, 6H). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  194.50, 173.34, 161.86, 159.43, 153.33, 134.36, 132.25, 131.93, 131.12, 130.66, 120.29, 117.33, 116.87, 79.48, 69.42, 25.50, 21.65, 20.93. **HRMS (ESI)**  $m/z$  calcd for  $C_{27}H_{29}O_5^+$   $[M^+ + H^+]$  433.2010, found 433.2000. The data are in accordance with those reported in the literature.<sup>19</sup>

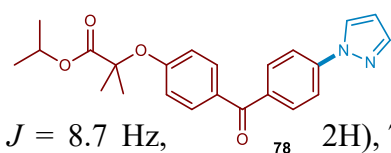
**3-(((R)-2,8-dimethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)pyridine (76)**

 Yellow pasty solid, 68% yield; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (s, 1H), 8.29 (s, 1H), 7.35 (s, 1H), 7.25 (m, 2H), 6.67 (d,  $J$  = 2.9 Hz, 1H), 6.60 (d,  $J$  = 2.9 Hz, 1H), 2.72 (q,  $J$  = 6.4 Hz, 2H), 2.15 (s, 3H), 1.79 (dq,  $J$  = 28.1, 6.9 Hz, 2H), 1.62 – 1.01 (m, 26H), 0.85 (dd,  $J$  = 10.2, 6.6 Hz, 13H). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.98, 149.31, 147.10, 141.96, 138.94, 128.30, 125.34, 124.49, 121.94, 120.07, 117.80, 40.25, 39.50, 37.58, 37.54, 37.42, 32.93, 32.82, 31.15, 28.11, 24.93, 24.58, 24.29, 22.85, 22.76, 22.65, 21.10, 19.89, 19.80, 16.32. **HRMS (ESI)**  $m/z$  calcd for  $(C_{32}H_{50}NO_2)^+$   $[M^+ + H^+]$  480.3836, found 480.3829.

**isopropyl 2-methyl-2-(4-(4-(piperidin-1-yl)benzoyl)phenoxy)propanoate (77)**

 White solid, 71% yield; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (dd,  $J$  = 18.3, 8.5 Hz, 4H), 6.82 (t,  $J$  = 10.2 Hz, 4H), 5.04 (hept,  $J$  = 6.5 Hz, 1H), 3.32 (t,  $J$  = 5.3 Hz, 4H), 1.84 – 1.48 (m, 12H), 1.16 (d,  $J$  = 6.4 Hz, 6H). **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  194.04, 173.33, 158.63, 154.10, 132.35, 132.08, 131.43, 126.65, 117.24, 113.27, 79.27, 69.23, 48.73, 25.39, 25.37, 24.35, 21.54. **GCMS (EI)**  $m/z$  calcd for  $C_{25}H_{31}NO_4$   $[M^+]$  409.2, found 409.3. The data are in accordance with those reported in the literature.<sup>61</sup>

**isopropyl 2-(4-(4-(1H-pyrazol-1-yl)benzoyl)phenoxy)-2-methylpropanoate (78)**



White solid, 85% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 2.6$  Hz, 1H), 7.86 (d,  $J = 8.7$  Hz, 2H), 7.81 (d,  $J = 8.7$  Hz, 2H), 7.78 – 7.72 (m, 3H), 6.87 (d,  $J = 8.8$  Hz, 2H), 6.50 (t,  $J = 2.1$  Hz, 1H), 5.08 (hept,  $J = 6.3$  Hz, 1H), 1.66 (s, 6H), 1.20 (d,  $J = 6.3$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  194.37, 173.22, 159.70, 142.72, 142.01, 135.79, 132.01, 131.55, 130.63, 126.99, 118.34, 117.35, 108.55, 79.50, 69.43, 25.47, 21.62. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_4$  [ $\text{M}^+$ ] 392.2, found 392.2. The data are in accordance with those reported in the literature.<sup>62</sup>

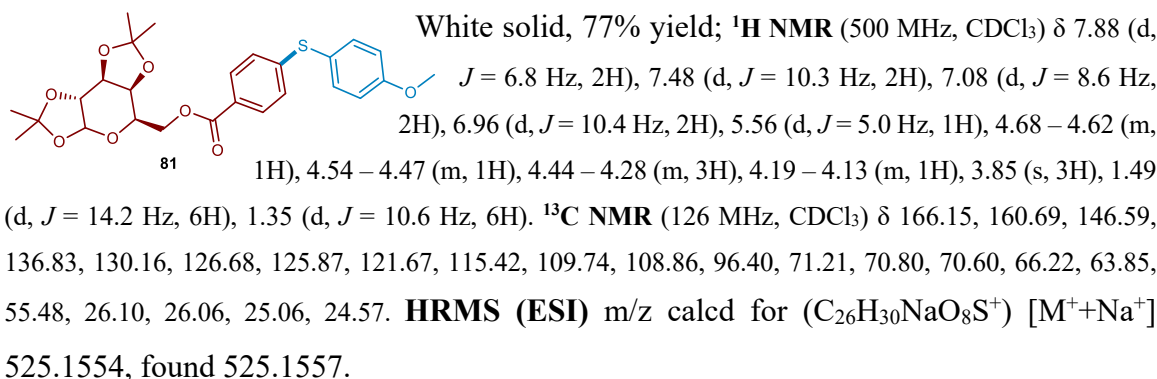
**3-(4-(2-chloro-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)piperidin-1-yl)pyridine (79)**

Pale yellow solid, 74% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (dd,  $J = 4.8, 1.7$  Hz, 1H), 8.28 (s, 1H), 8.05 (s, 1H), 7.45 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.24 – 7.11 (m, 5H), 7.11 (dd,  $J = 7.7, 4.8$  Hz, 1H), 3.60 – 3.48 (m, 2H), 3.46 – 3.30 (m, 2H), 3.07 – 2.97 (m, 2H), 2.90 – 2.75 (m, 2H), 2.69 (ddd,  $J = 14.2, 9.7, 4.5$  Hz, 1H), 2.56 (ddd,  $J = 14.0, 9.5, 4.5$  Hz, 1H), 2.52 – 2.42 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.09, 146.97, 146.74, 139.71, 139.34, 137.75, 137.73, 137.49, 133.89, 133.57, 133.07, 130.73, 129.12, 126.30, 123.87, 123.13, 122.45, 49.99, 49.87, 31.82, 31.63, 30.48, 30.22. **GCMS (EI)**  $m/z$  calcd for  $\text{C}_{25}\text{H}_{22}\text{ClN}_3$  [ $\text{M}^+$ ] 387.2, found 387.2.

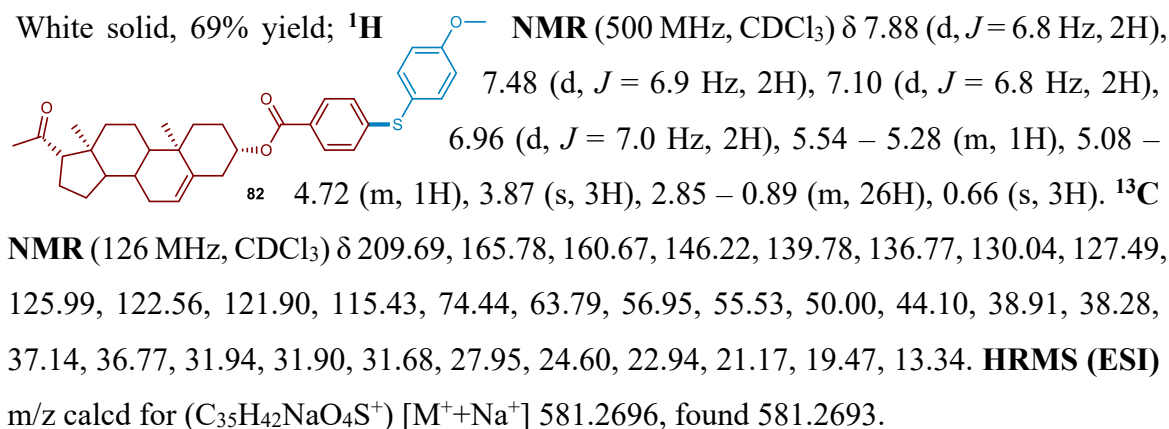
**(10R,13S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((4-methoxyphenyl)thio)benzoate (80)**

White solid, 68% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.6$  Hz, 2H), 7.48 (d,  $J = 8.7$  Hz, 2H), 7.10 (d,  $J = 8.5$  Hz, 2H), 6.96 (d,  $J = 6.8$  Hz, 2H), 5.05 – 4.77 (m, 1H), 3.86 (s, 3H), 2.03 – 0.82 (m, 46H), 0.68 (d,  $J = 1.8$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.90, 160.64, 146.01, 136.73, 130.04, 127.72, 126.03, 122.03, 115.41, 74.40, 56.55, 56.40, 55.52, 54.36, 44.82, 42.72, 40.12, 39.65, 36.92, 36.30, 35.94, 35.62, 34.25, 32.13, 28.76, 28.38, 28.14, 27.71, 24.34, 23.98, 22.96, 22.70, 21.35, 18.81, 12.41, 12.21. **HRMS (ESI)**  $m/z$  calcd for  $(\text{C}_{41}\text{H}_{58}\text{NaO}_3\text{S})^+$  [ $\text{M}^+ + \text{Na}^+$ ] 653.3999, found 653.3979.

**((5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-((4-methoxyphenyl)thio)benzoate (81)**



**(10S,13R)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((4-methoxyphenyl)thio)benzoate (82)**



**Supporting Information References:**

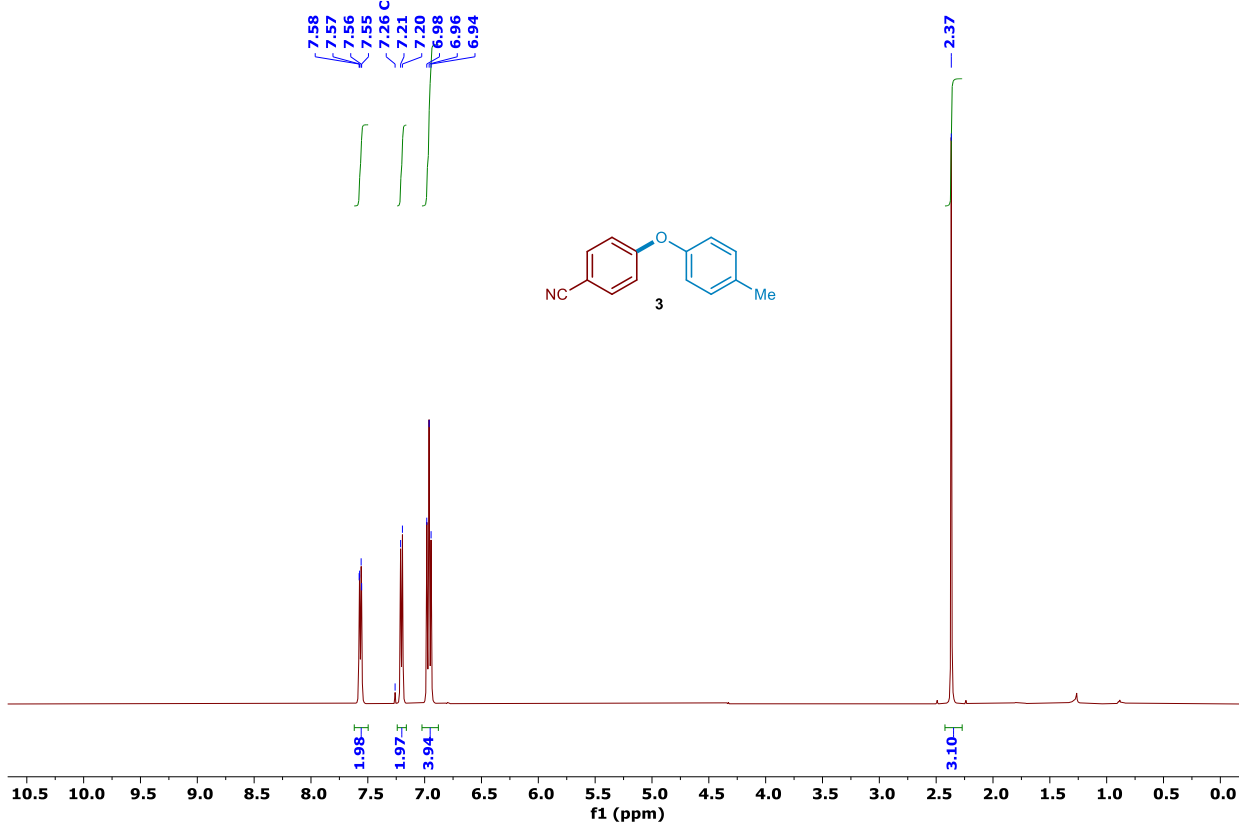
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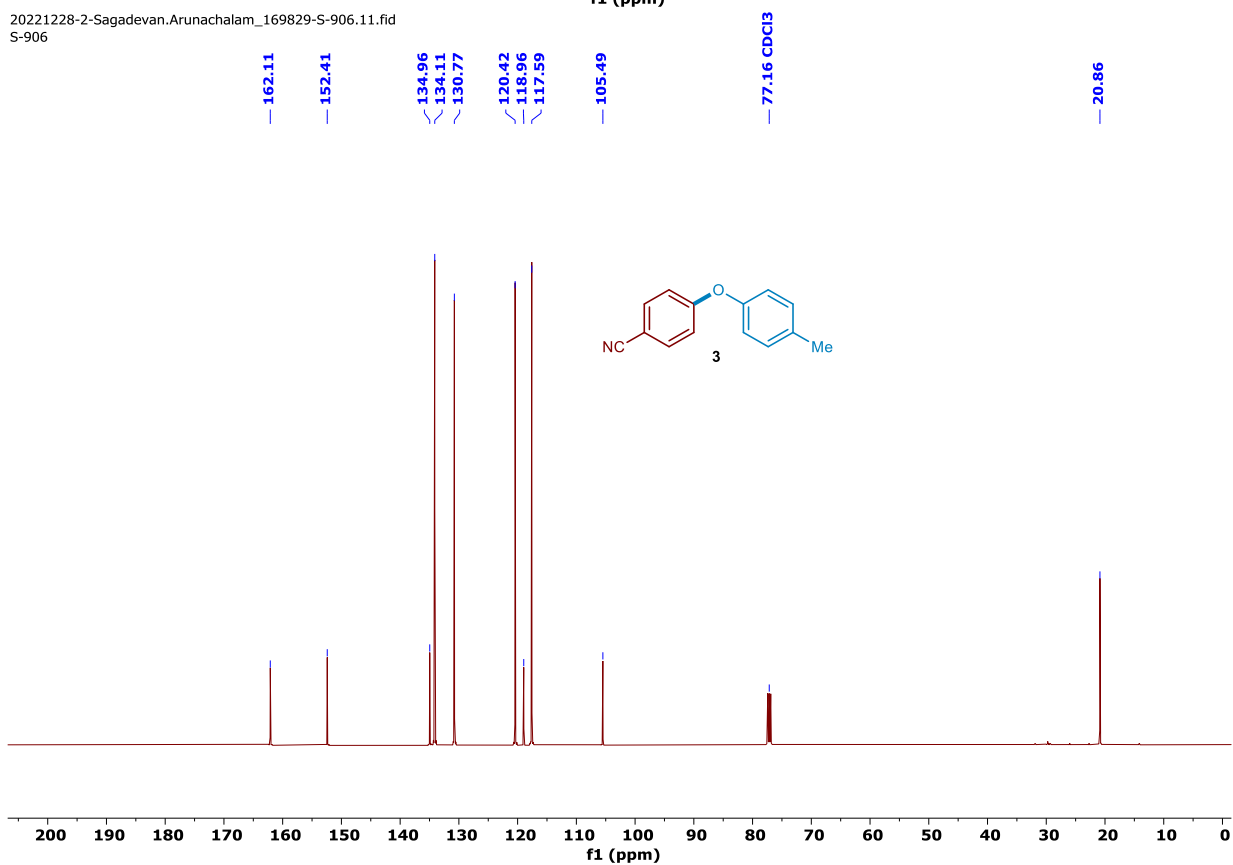


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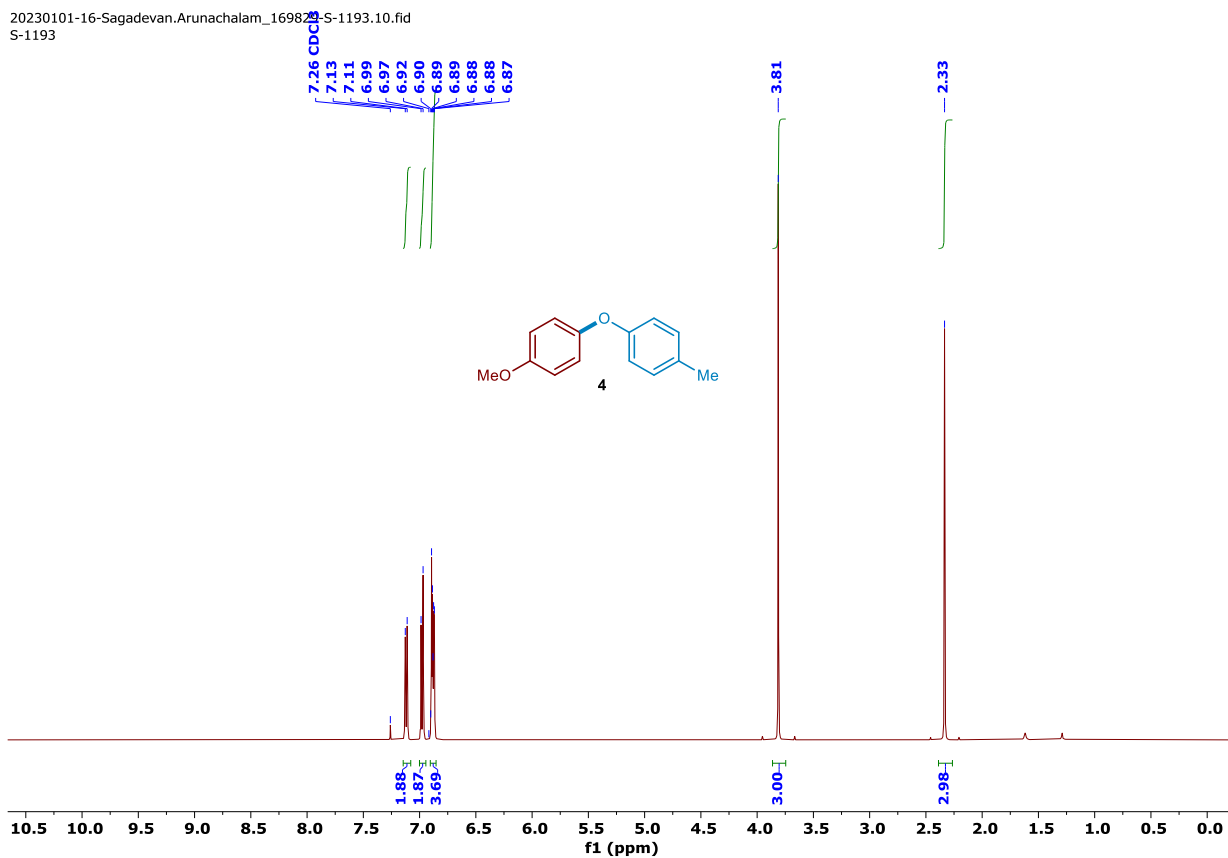
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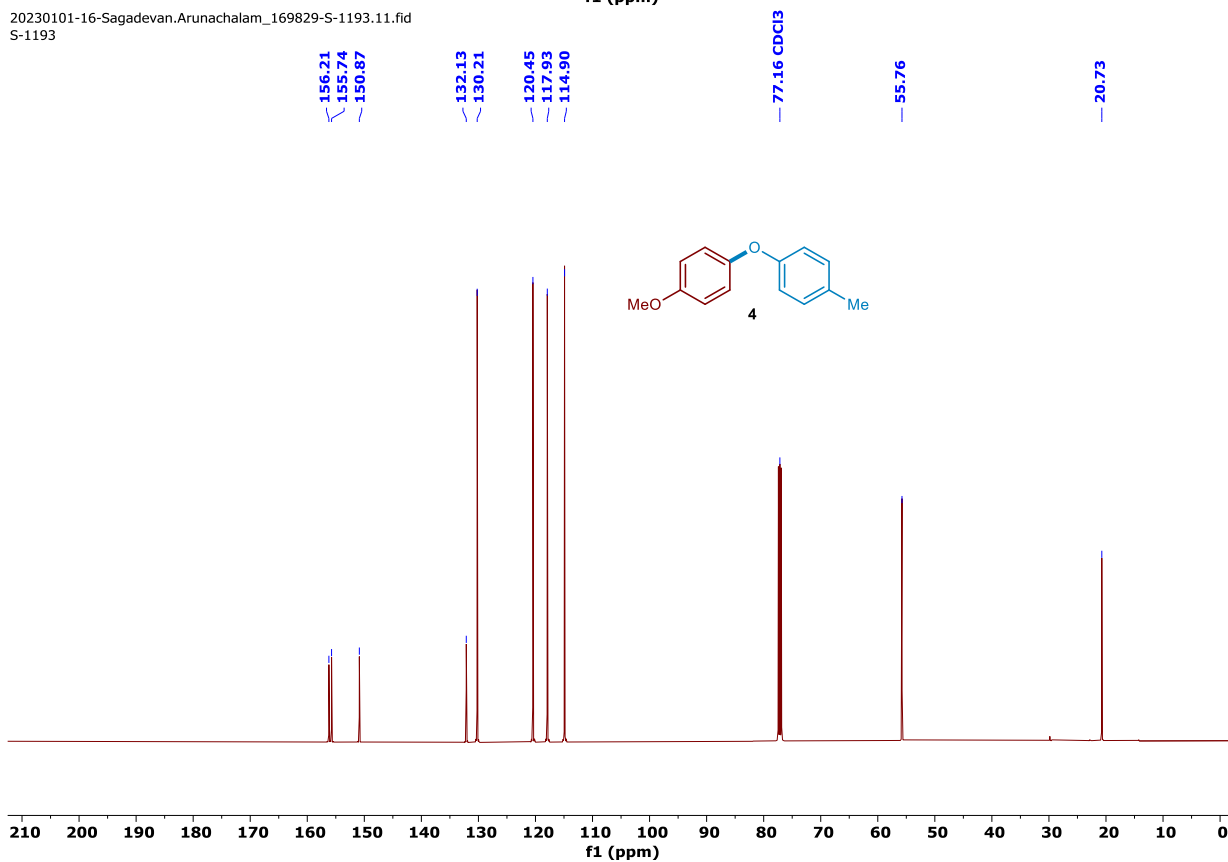
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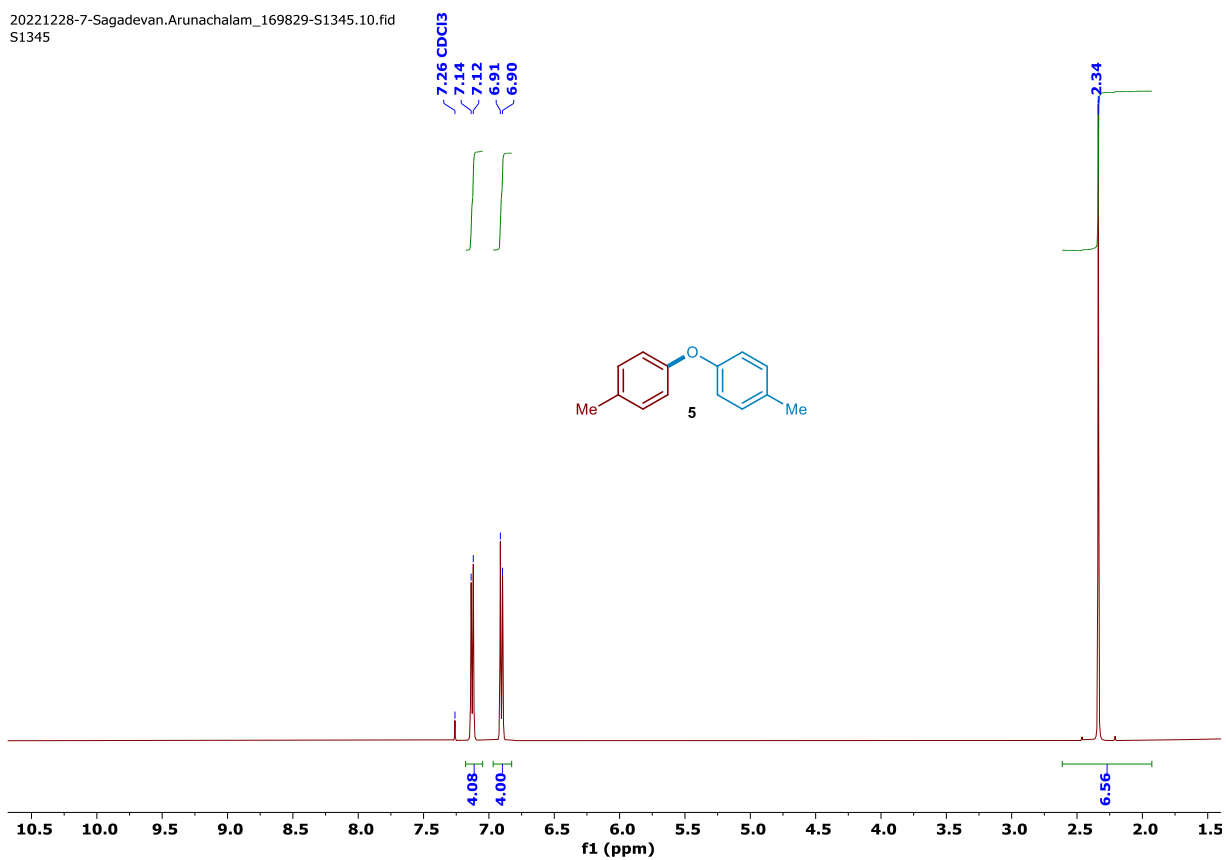
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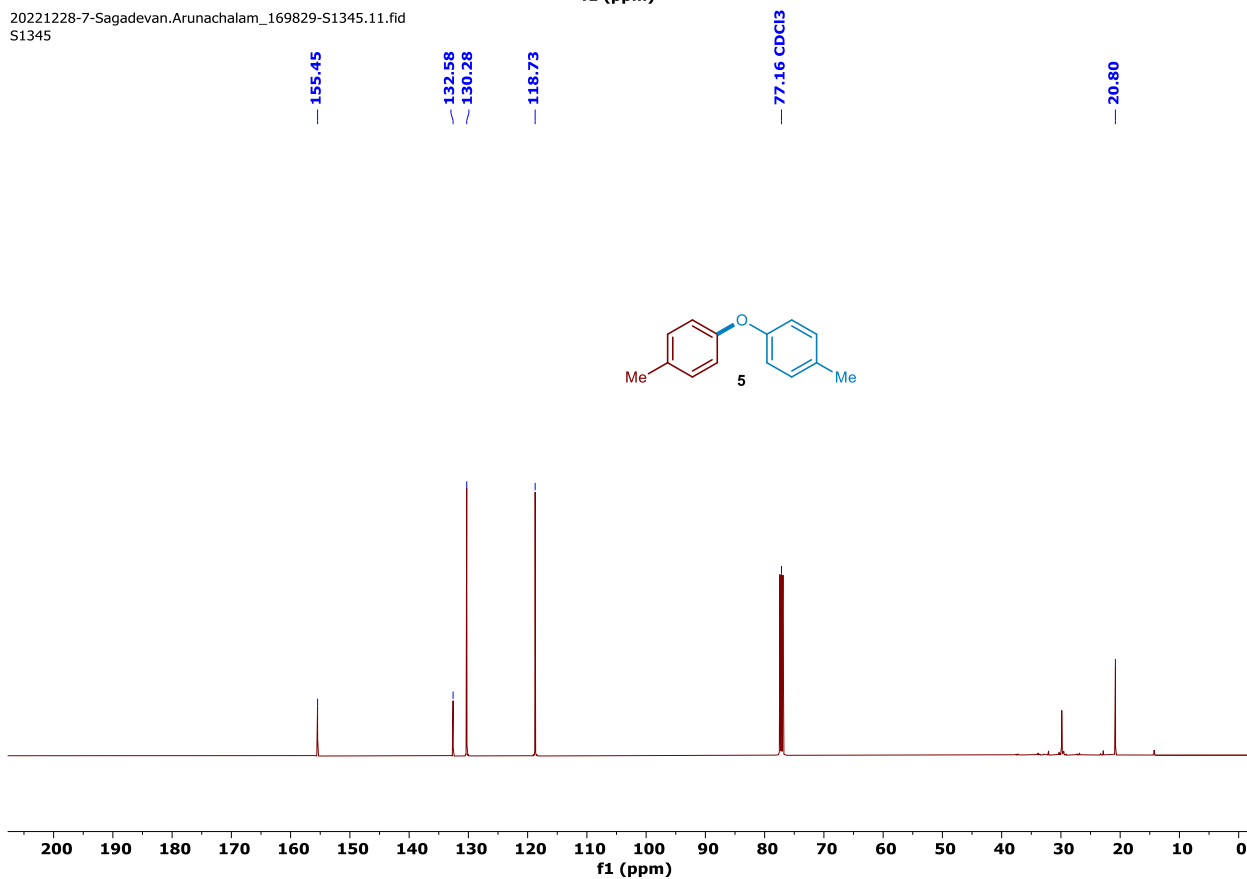
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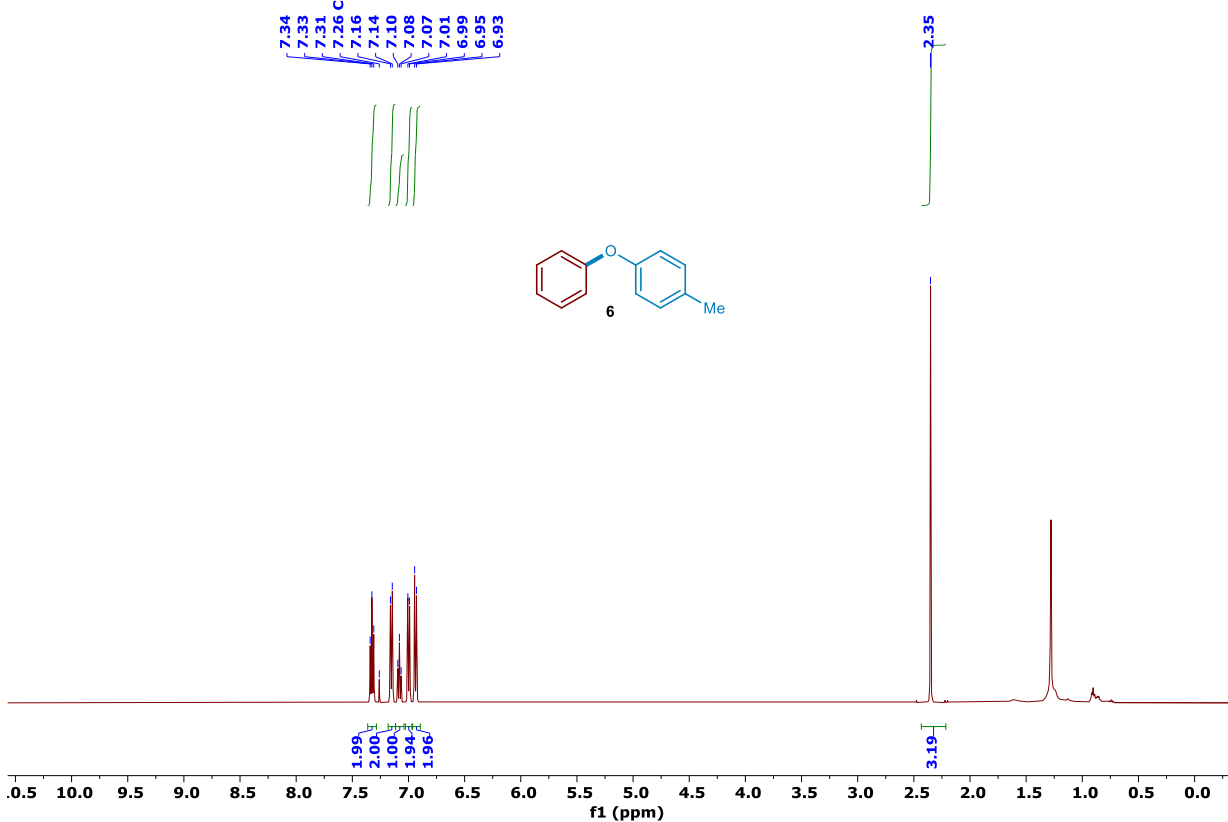
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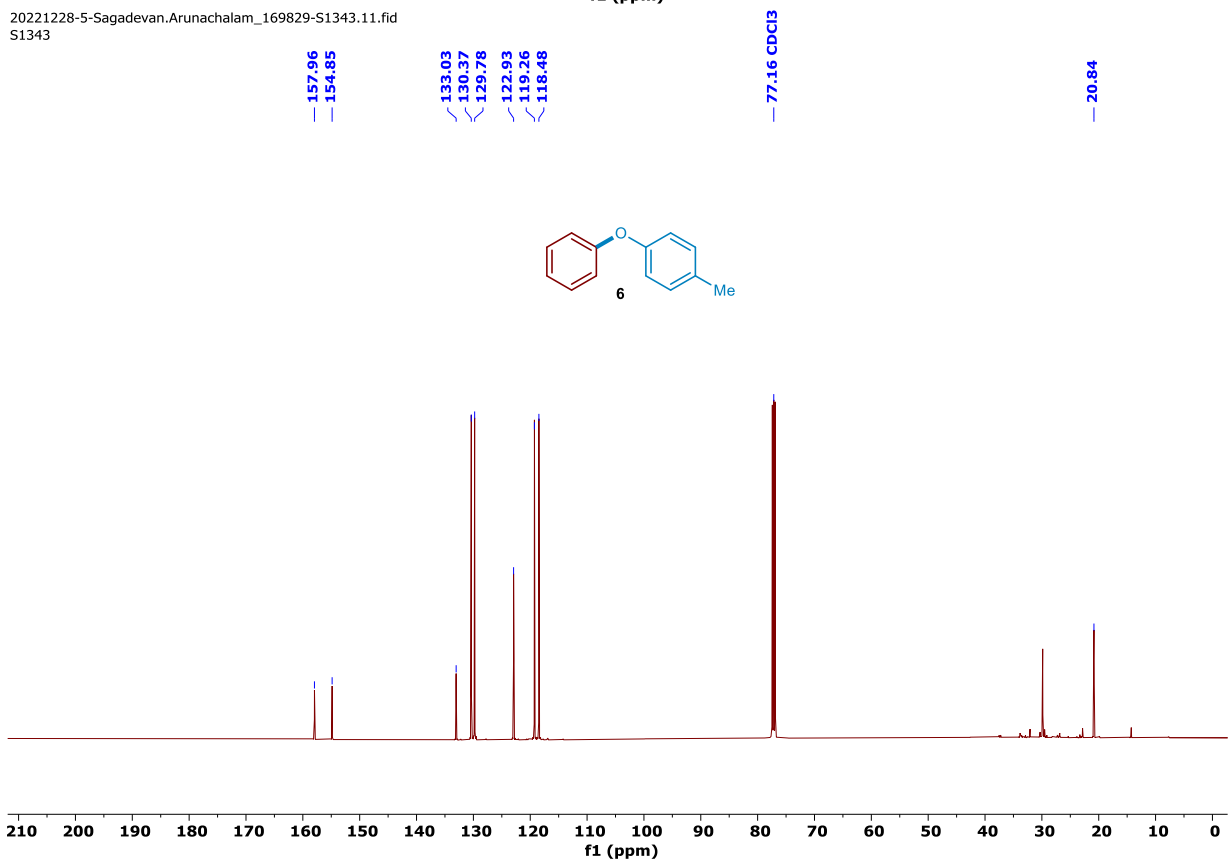
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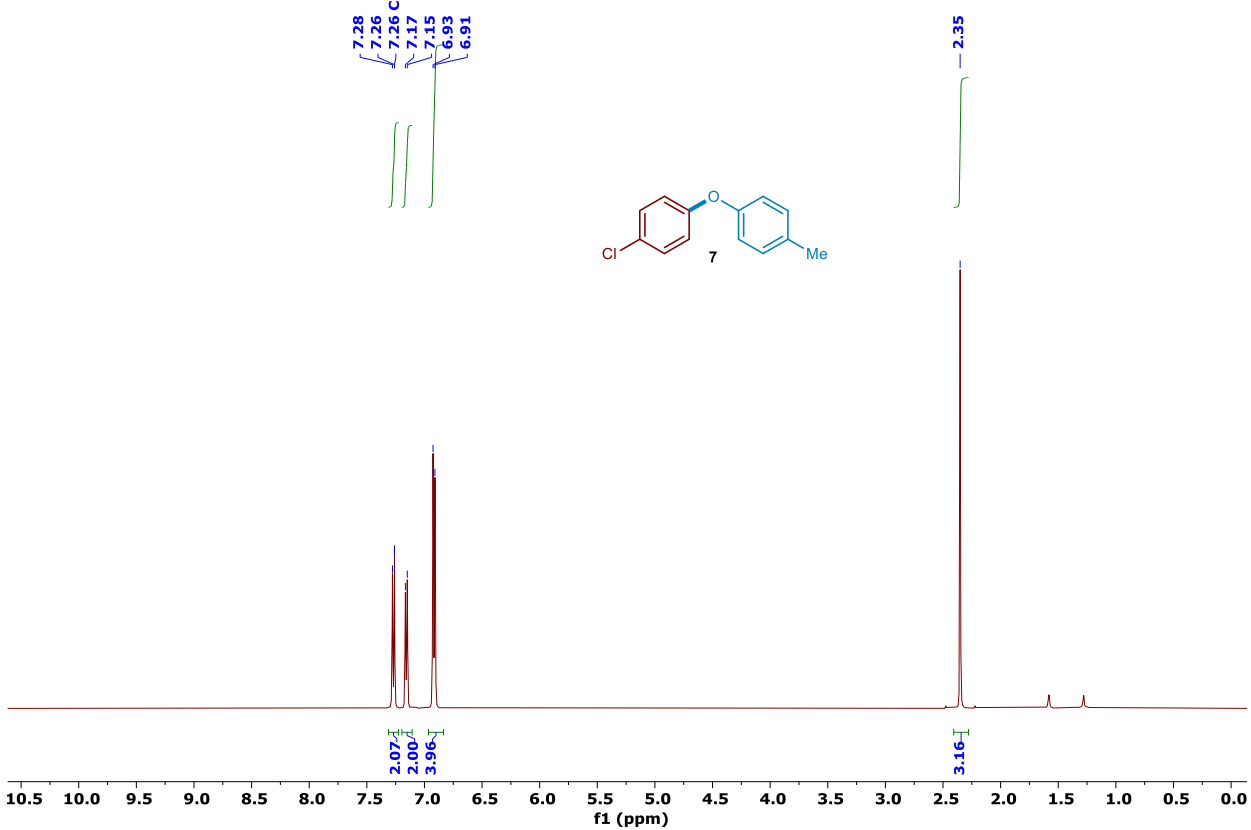
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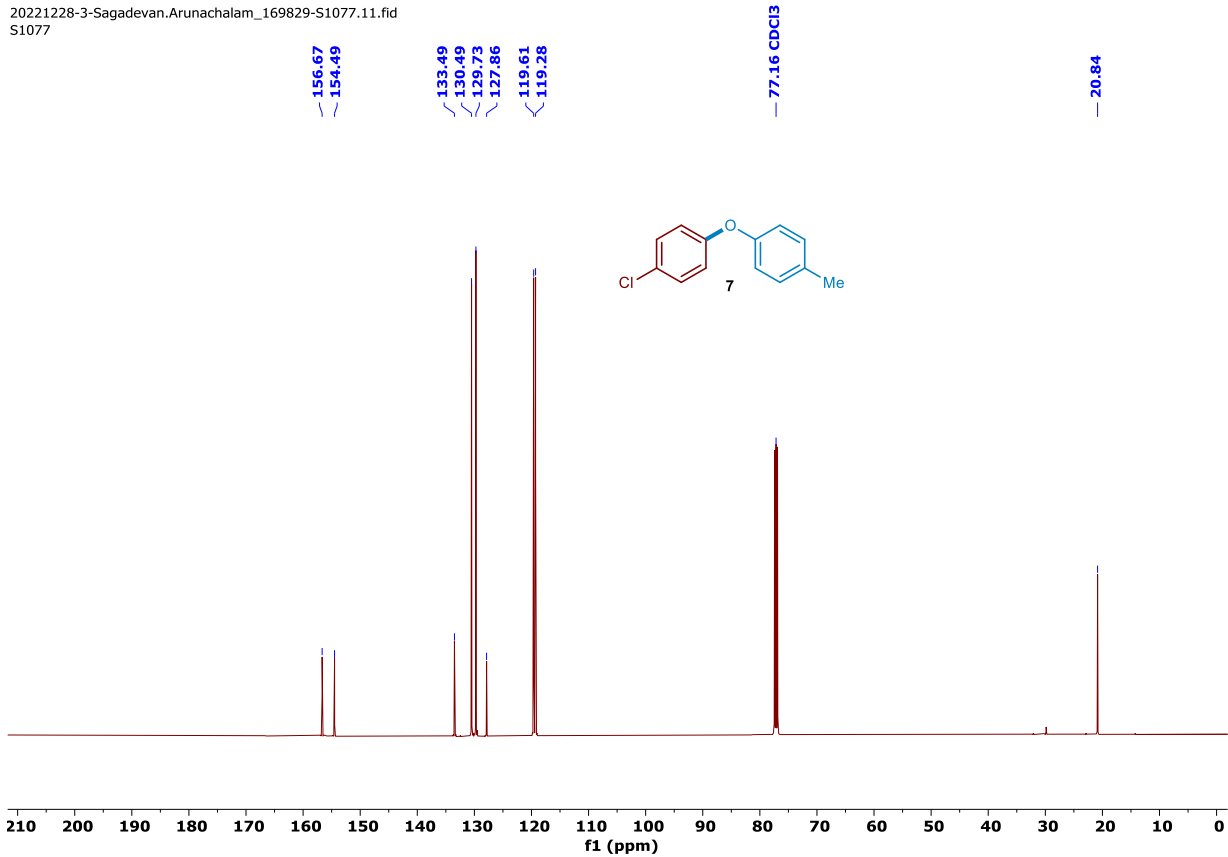
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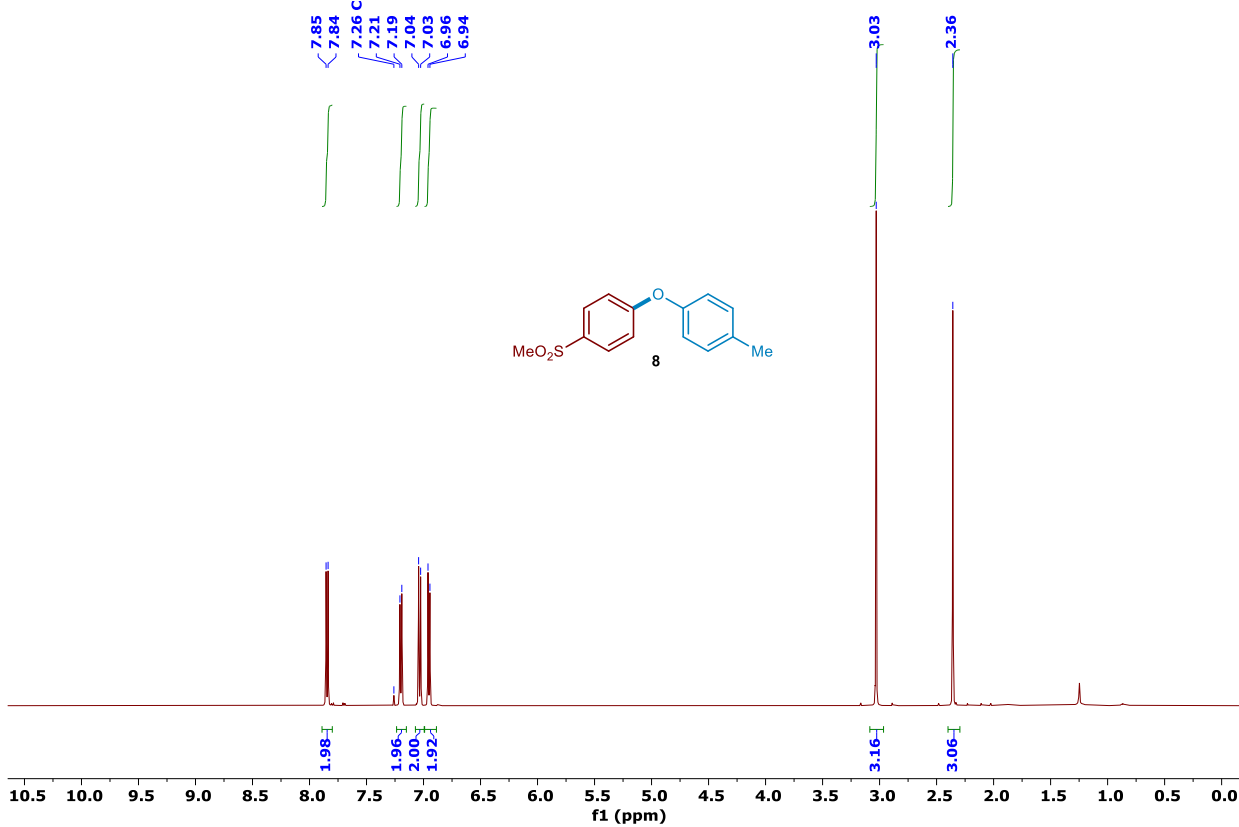
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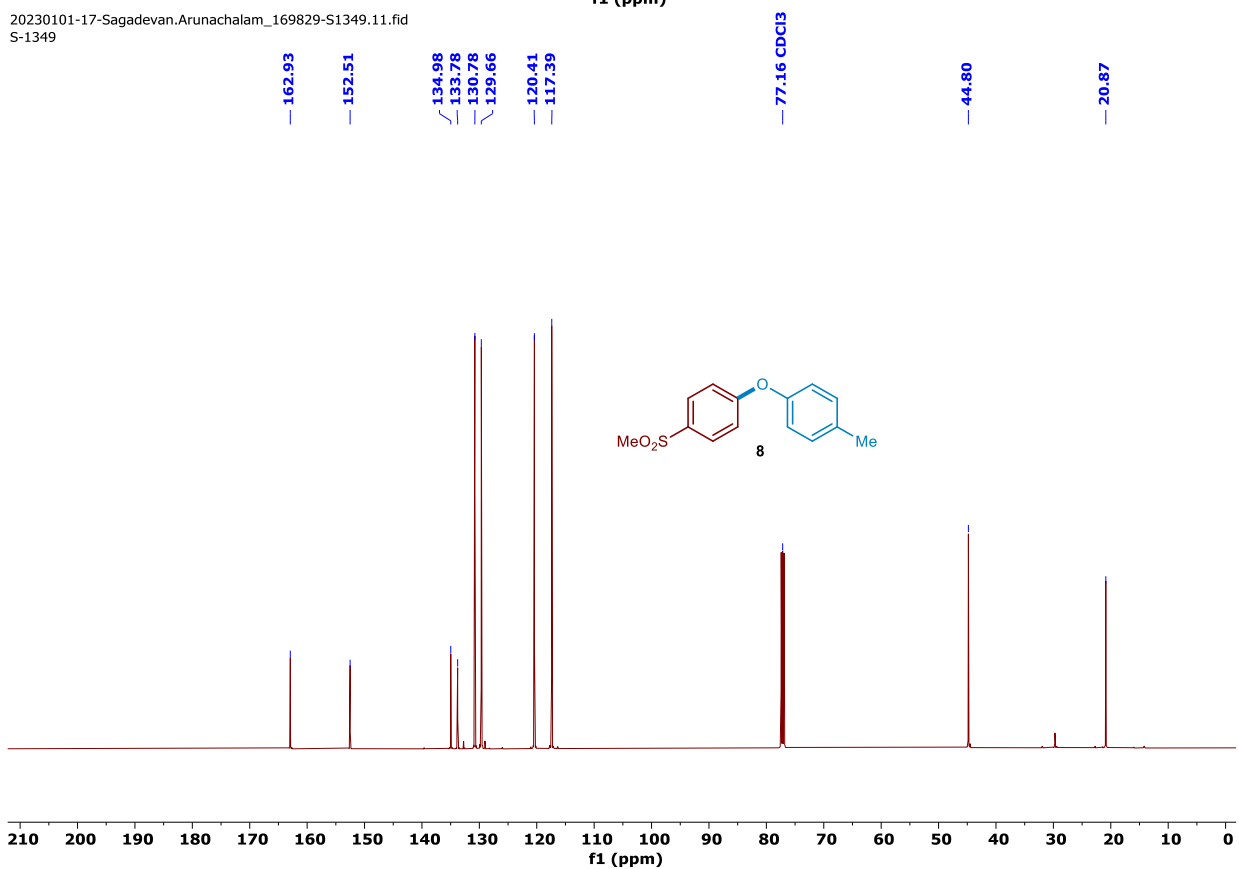
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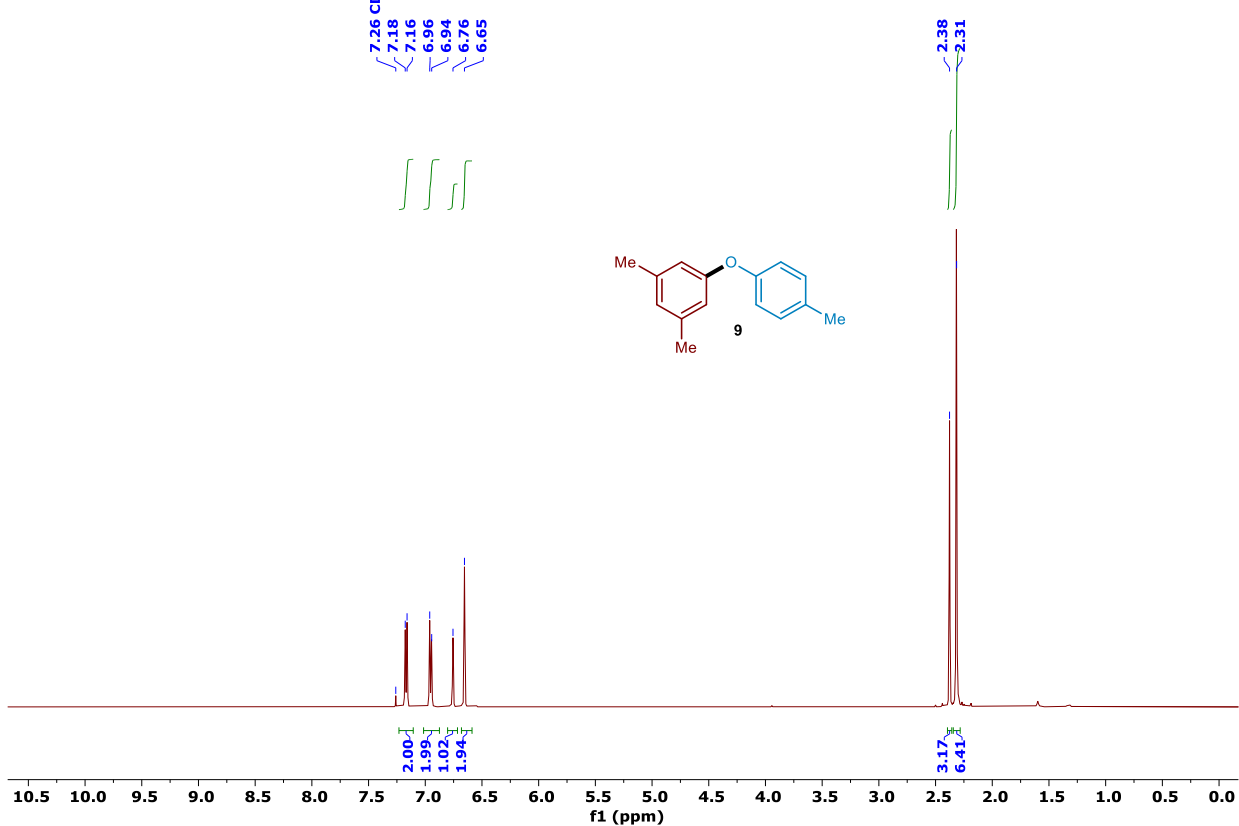
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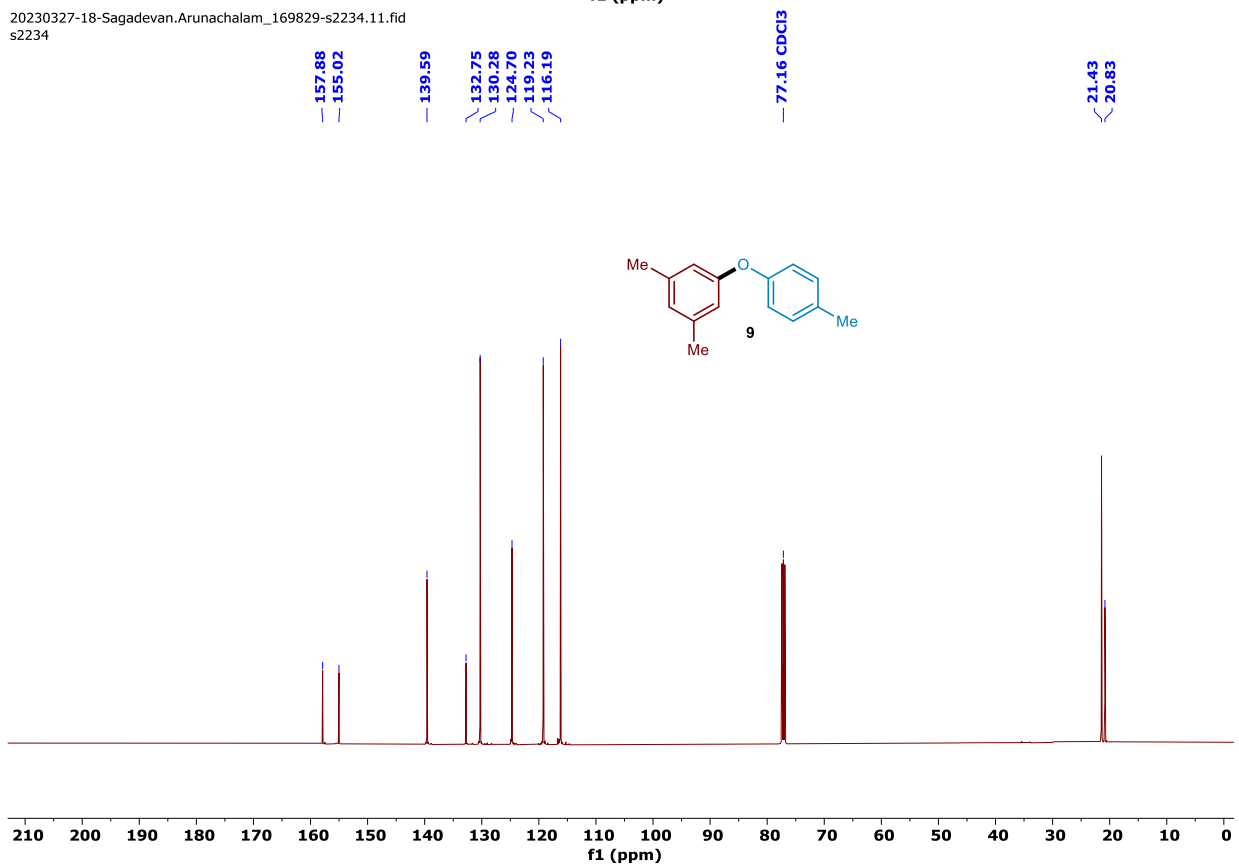
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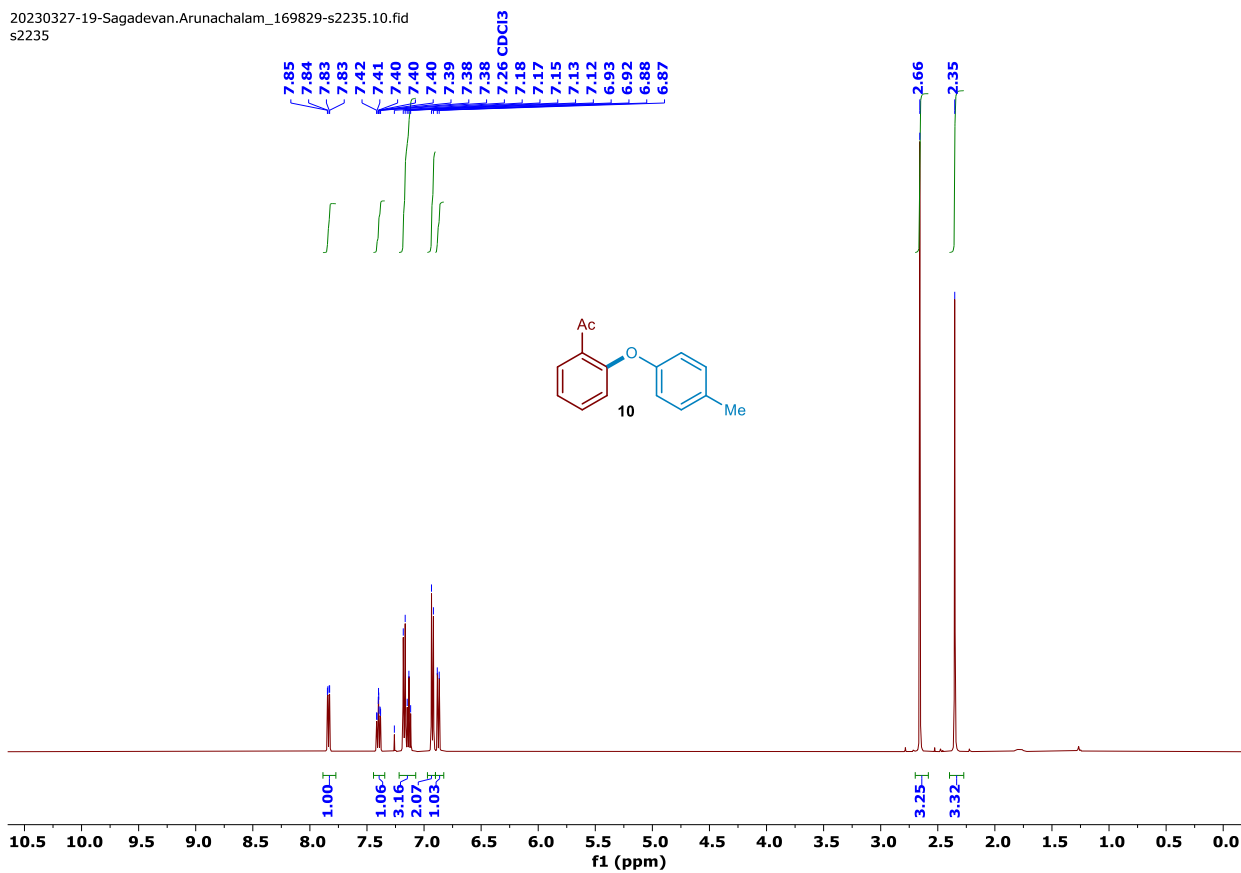


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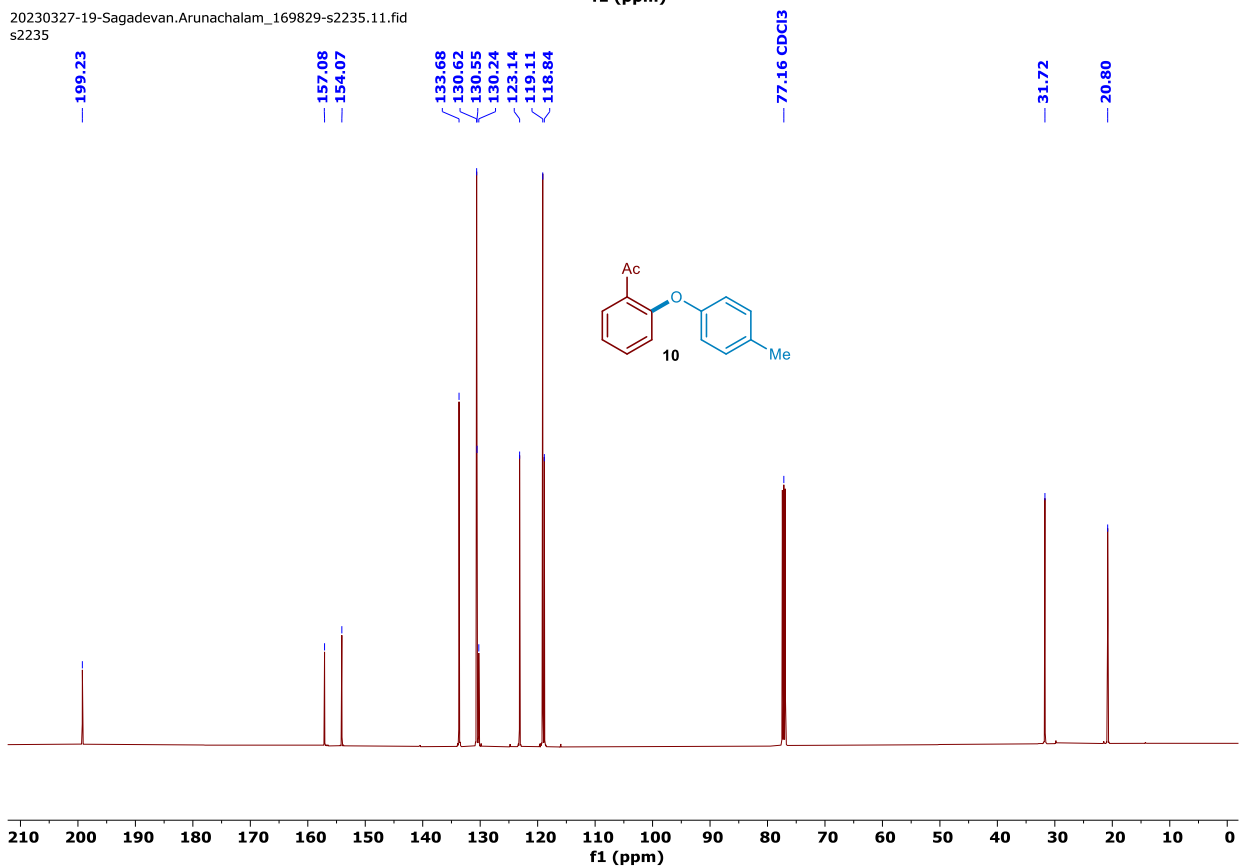




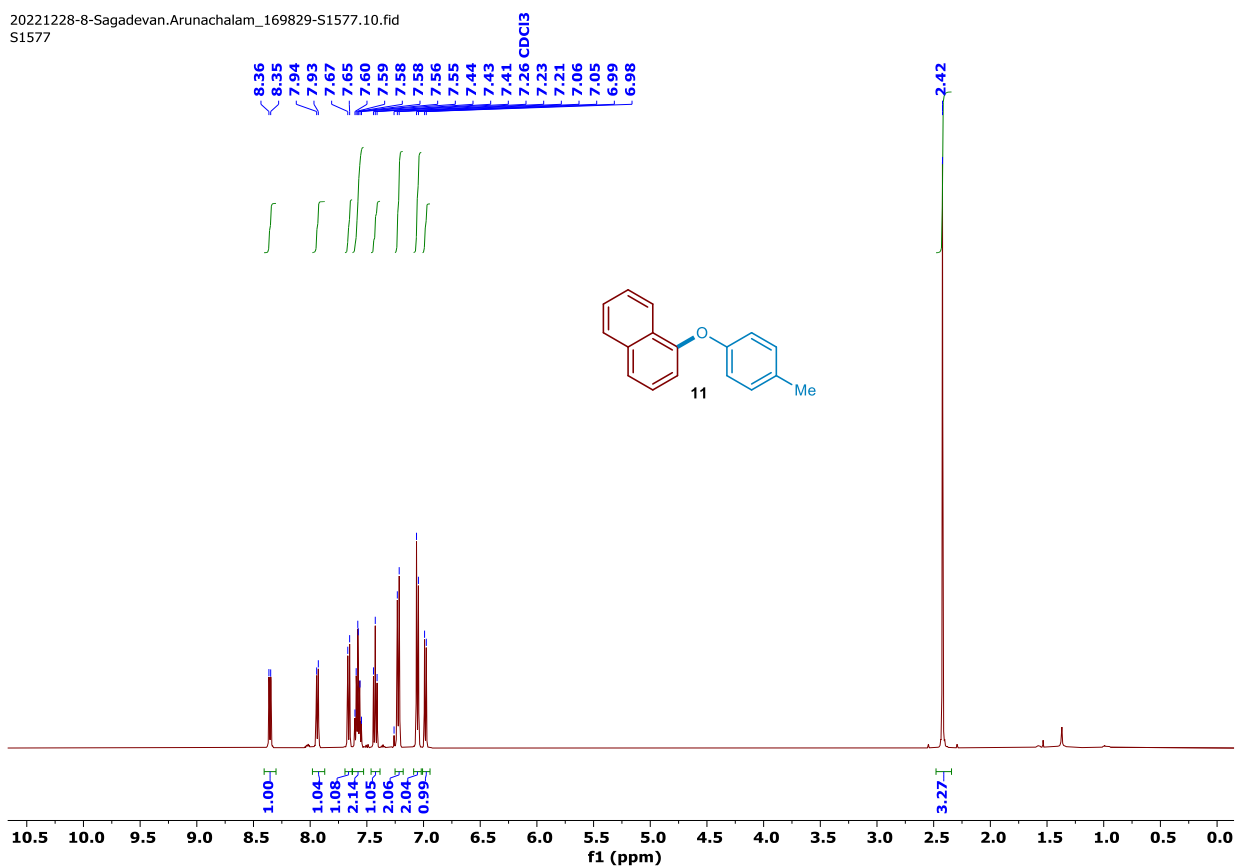
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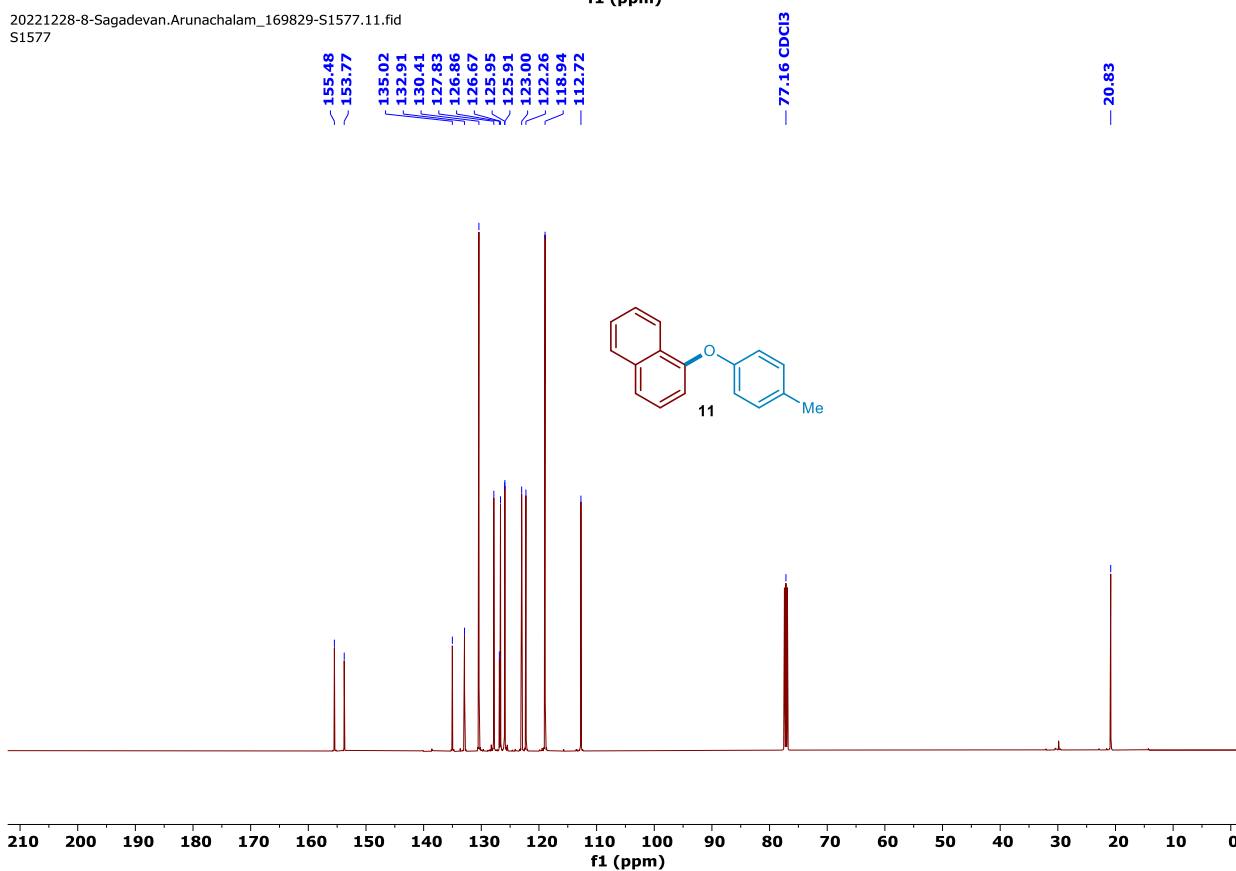
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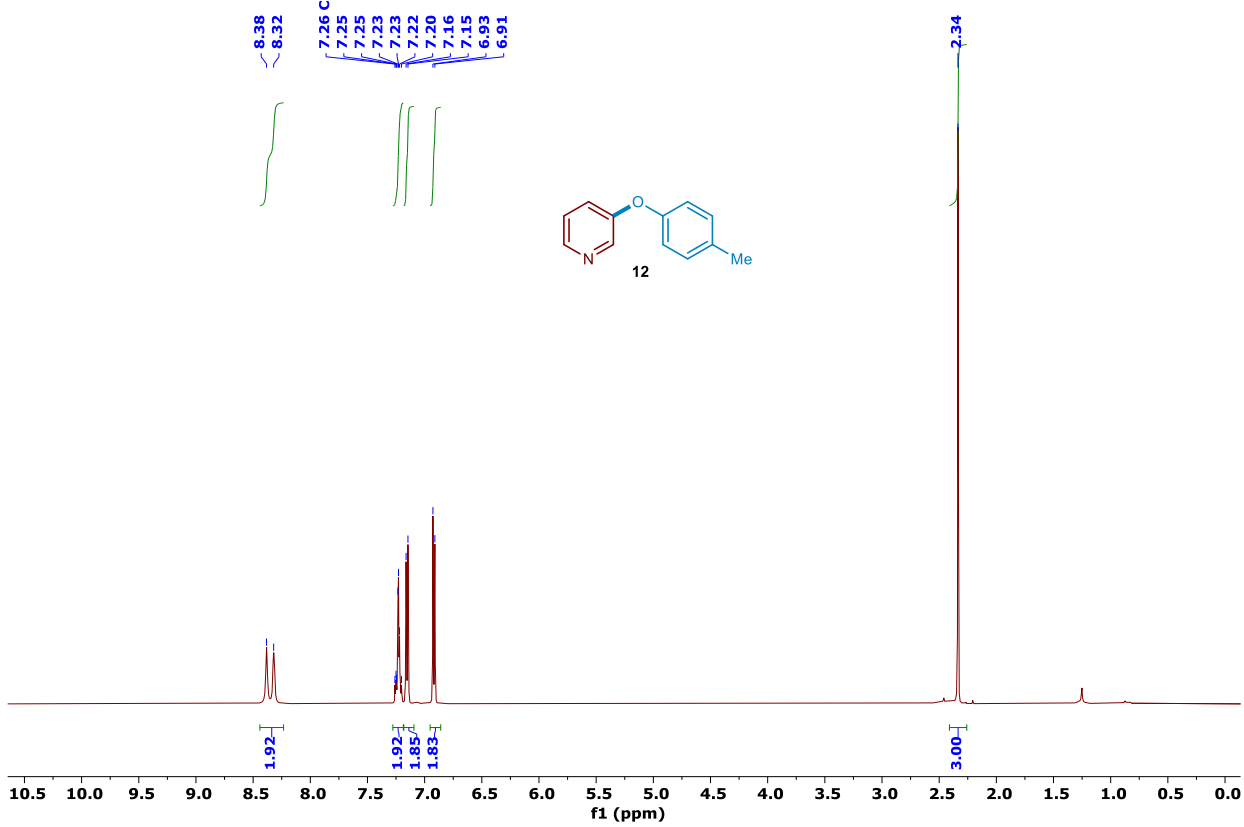
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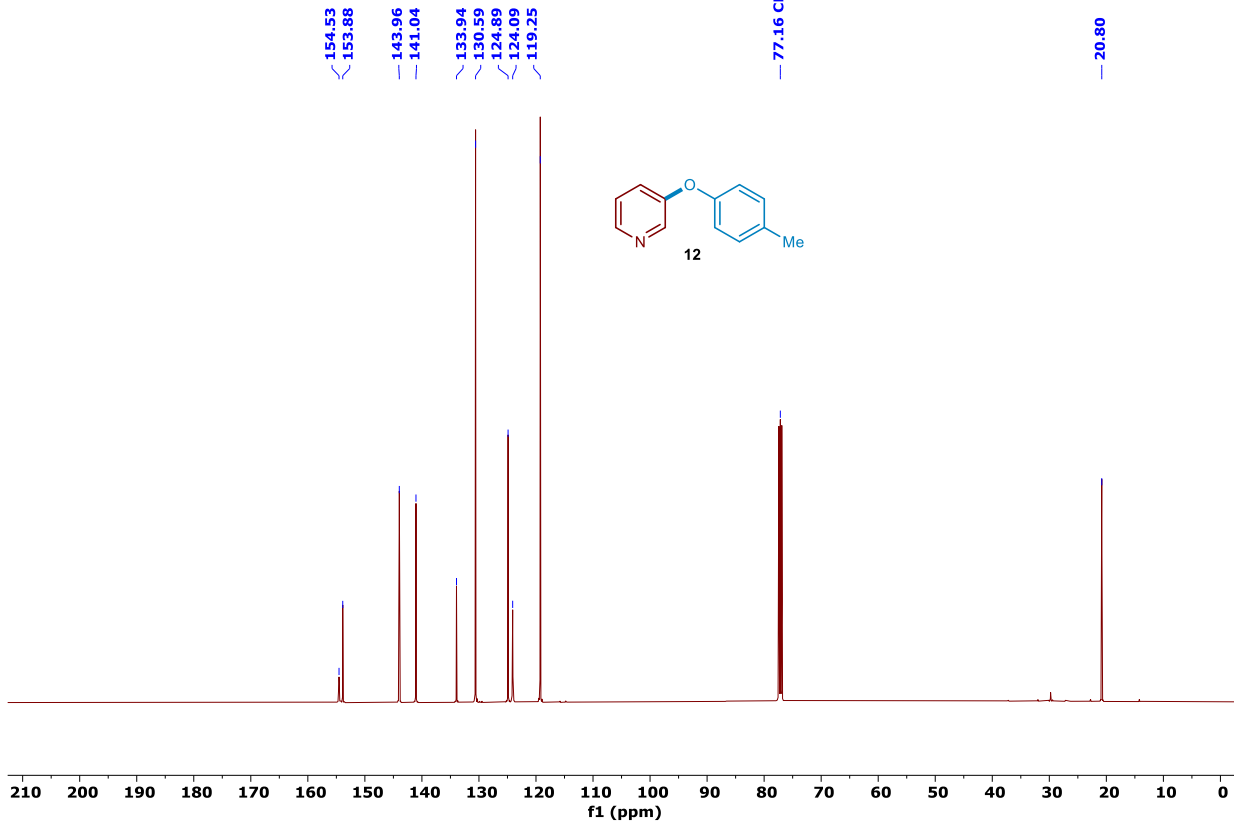
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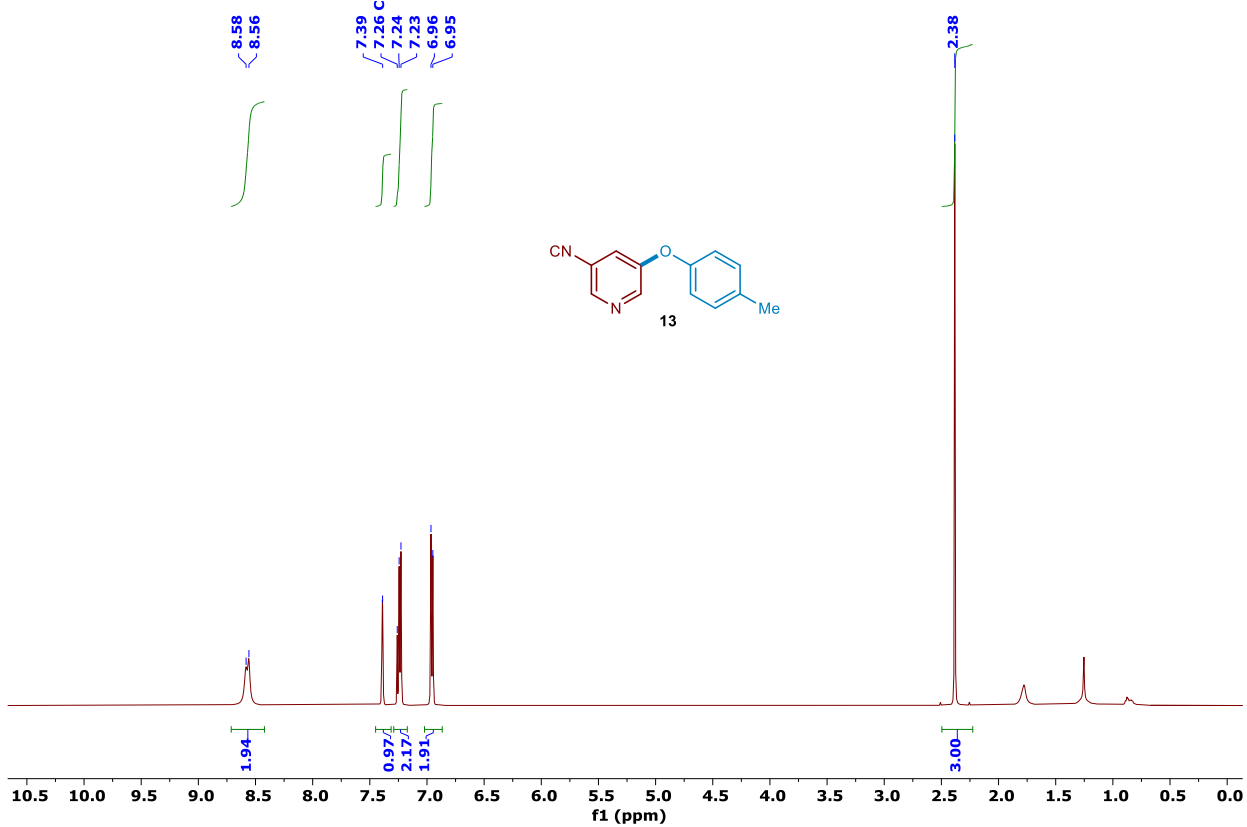
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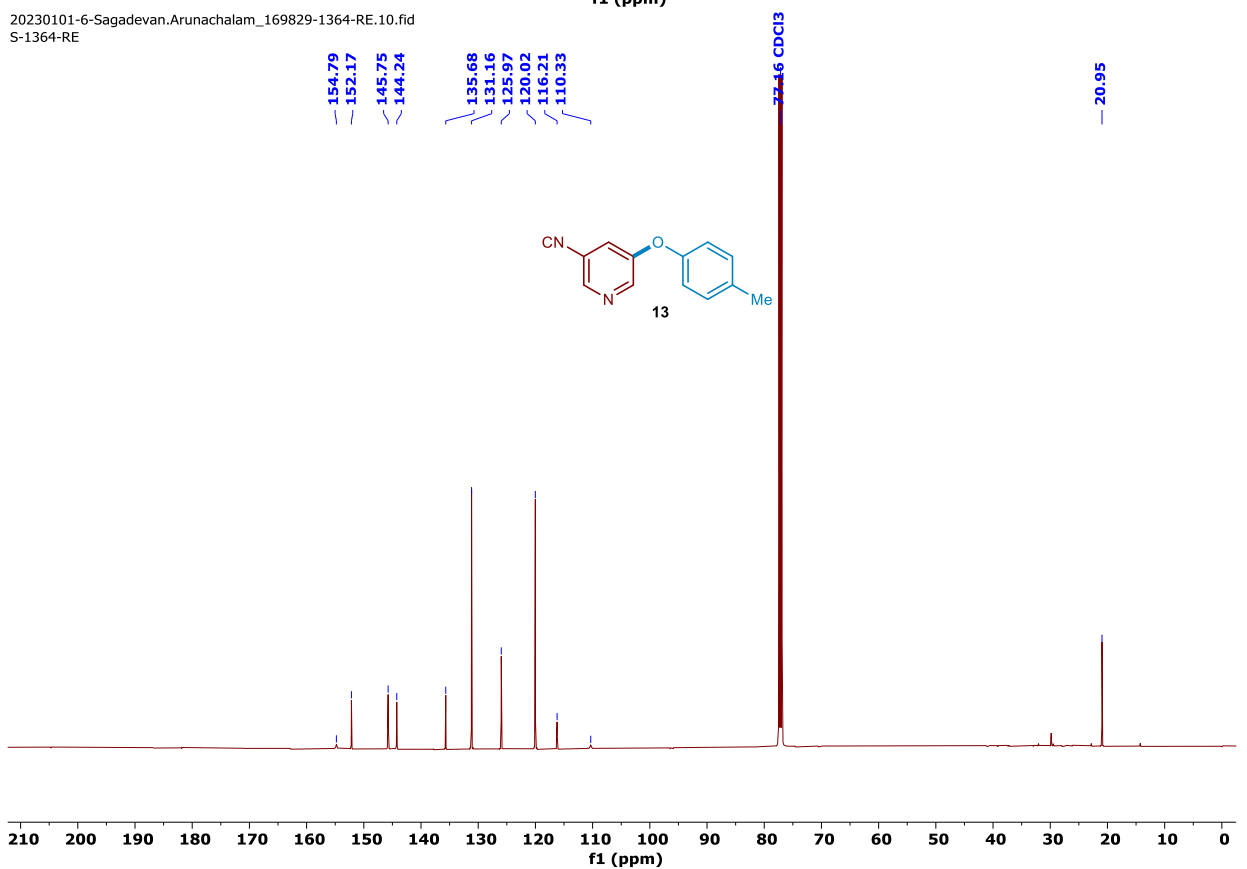
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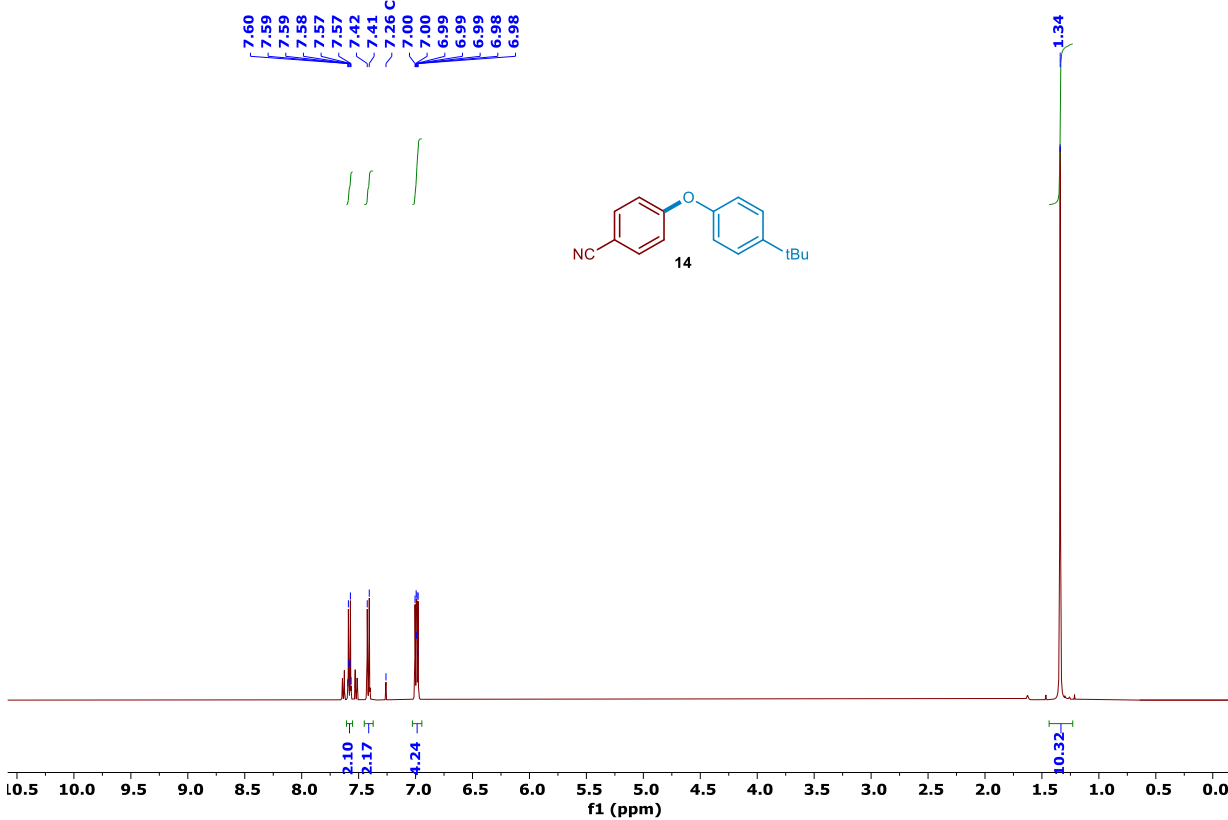
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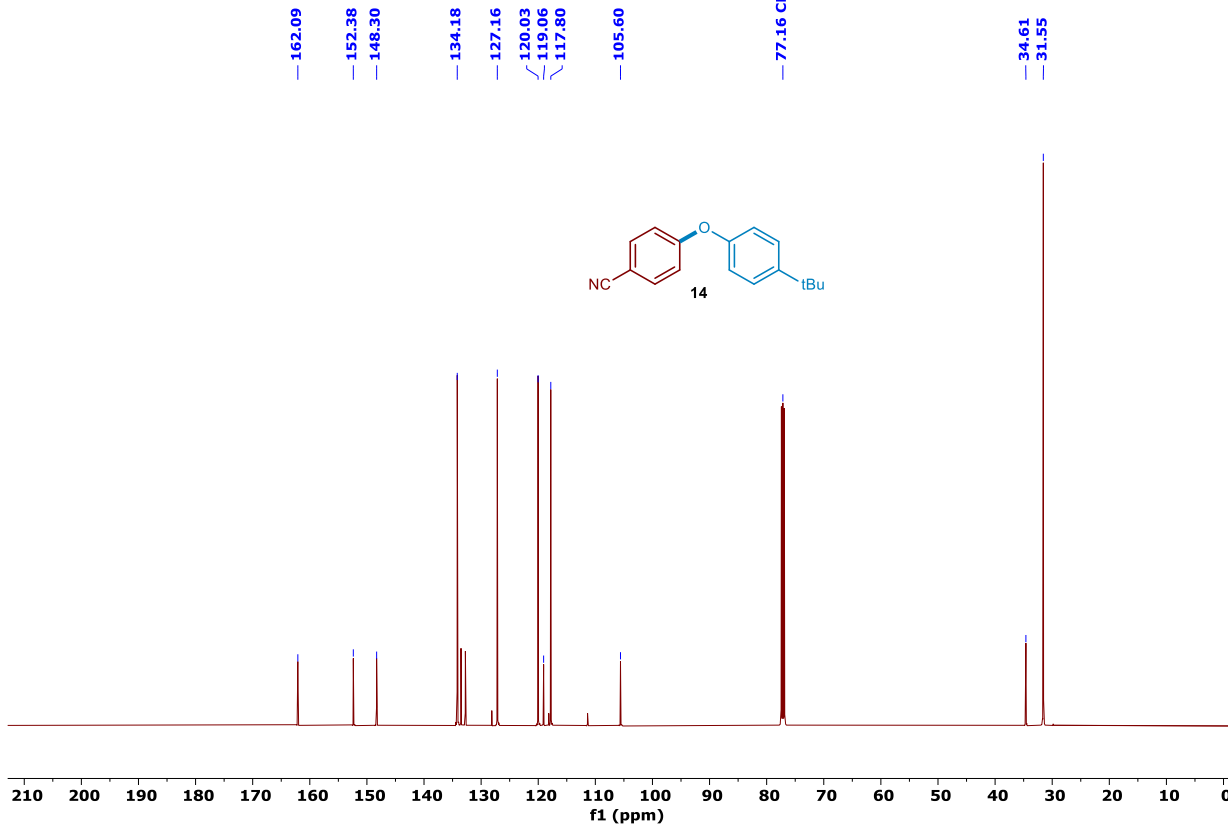
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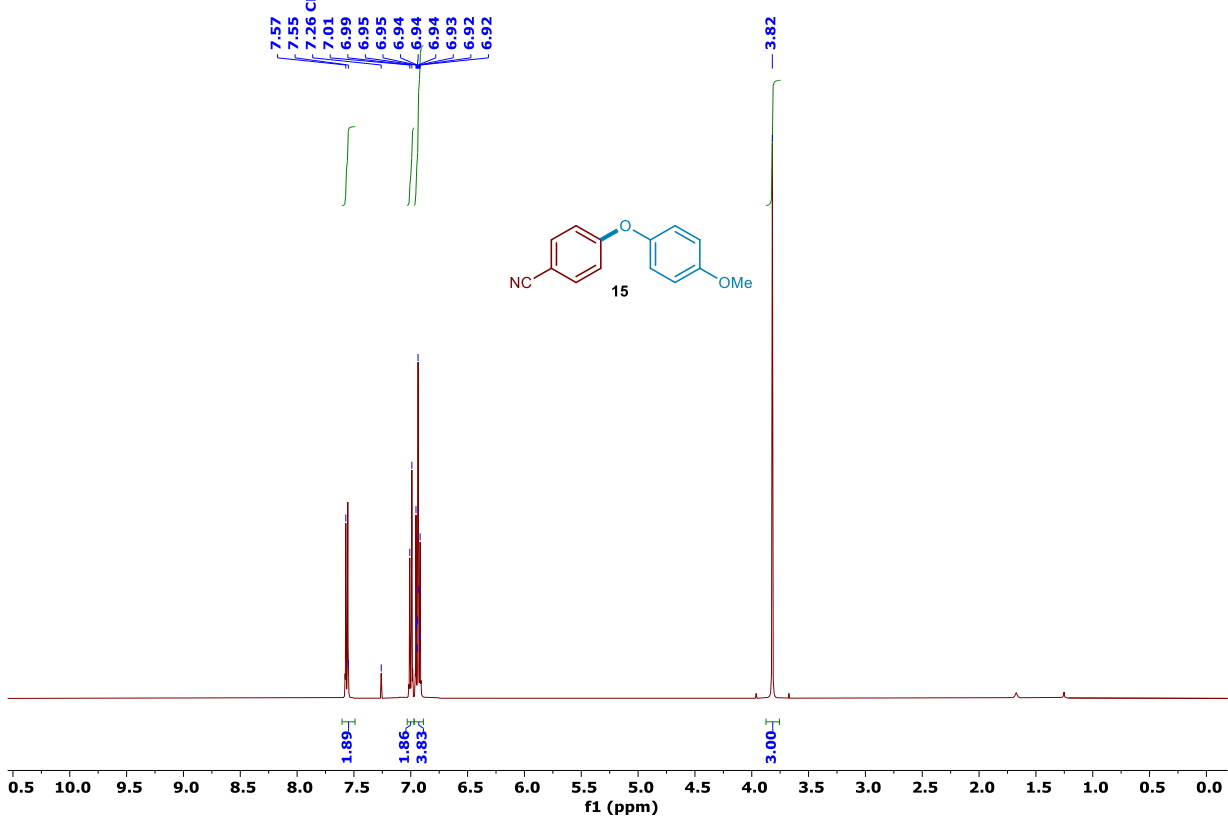
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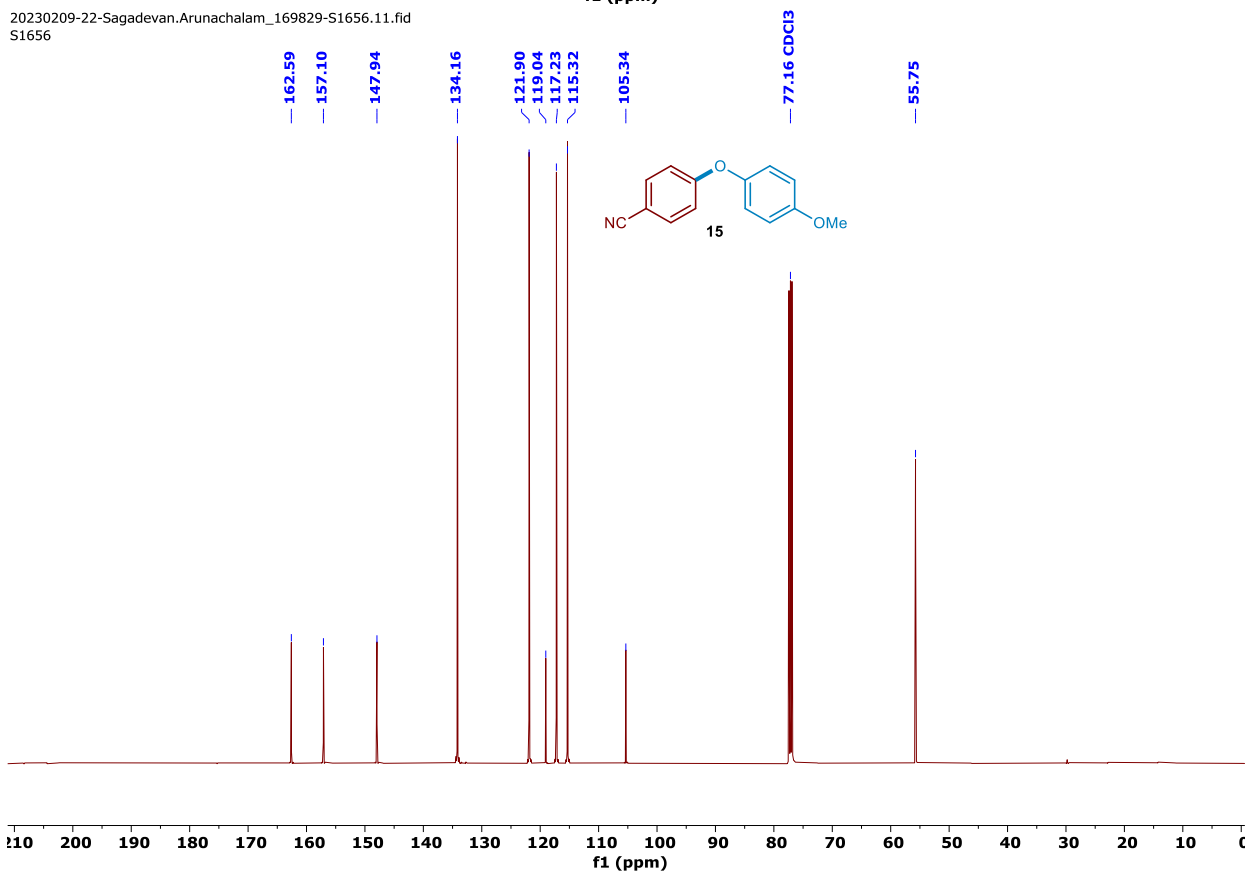
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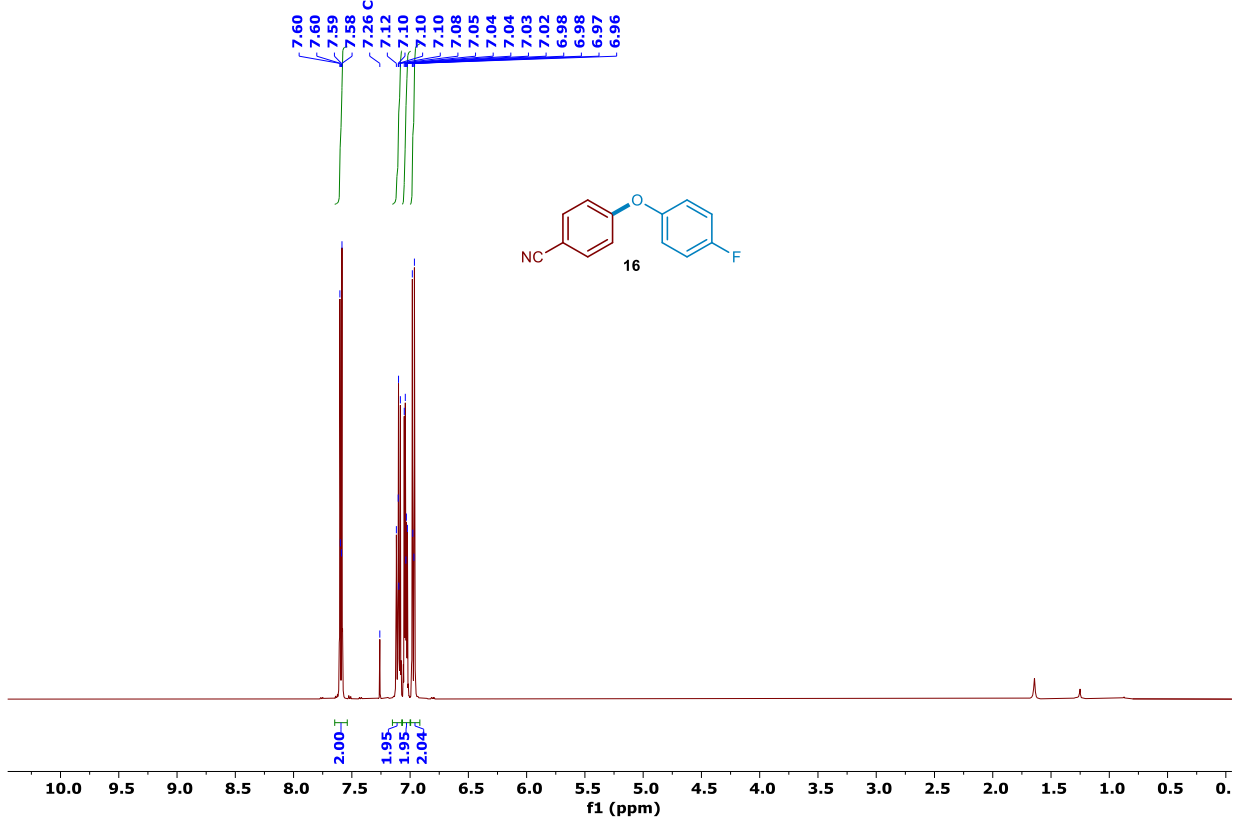
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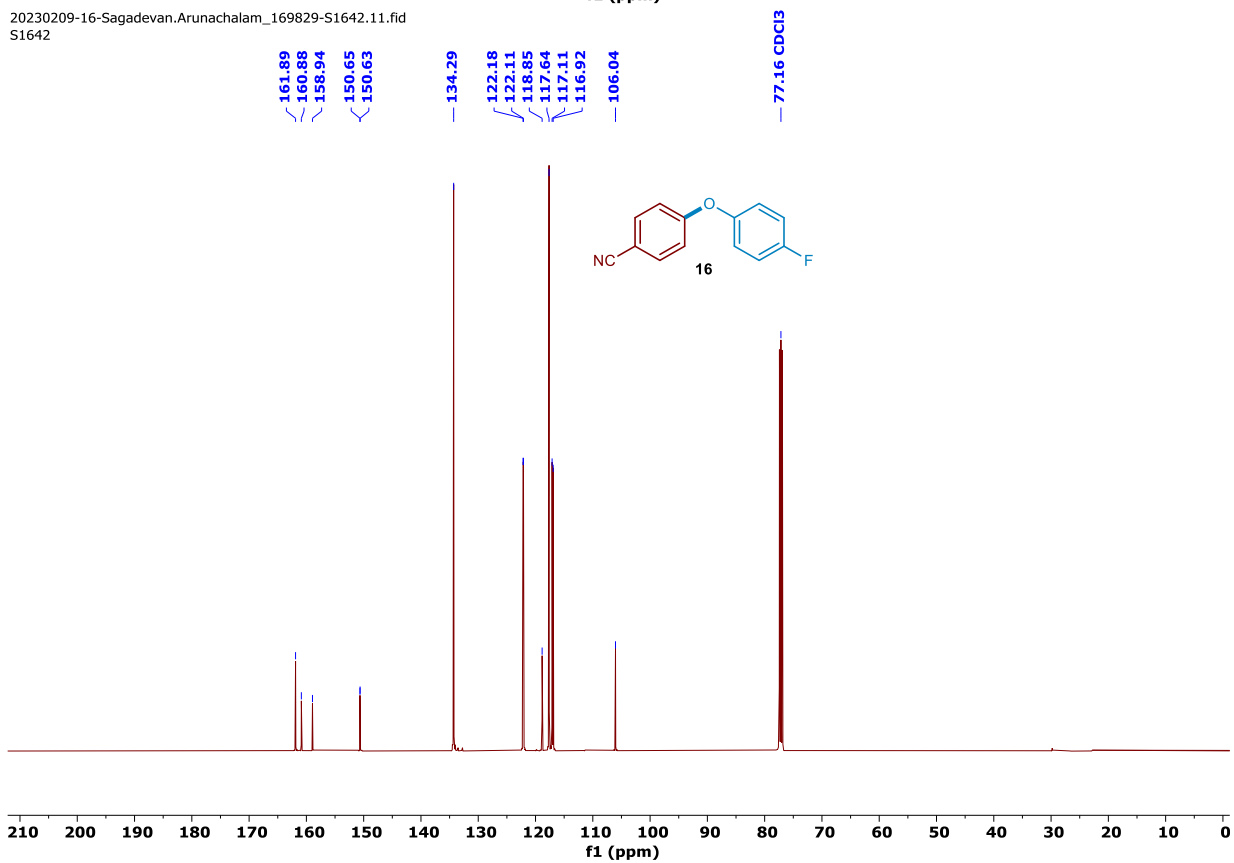
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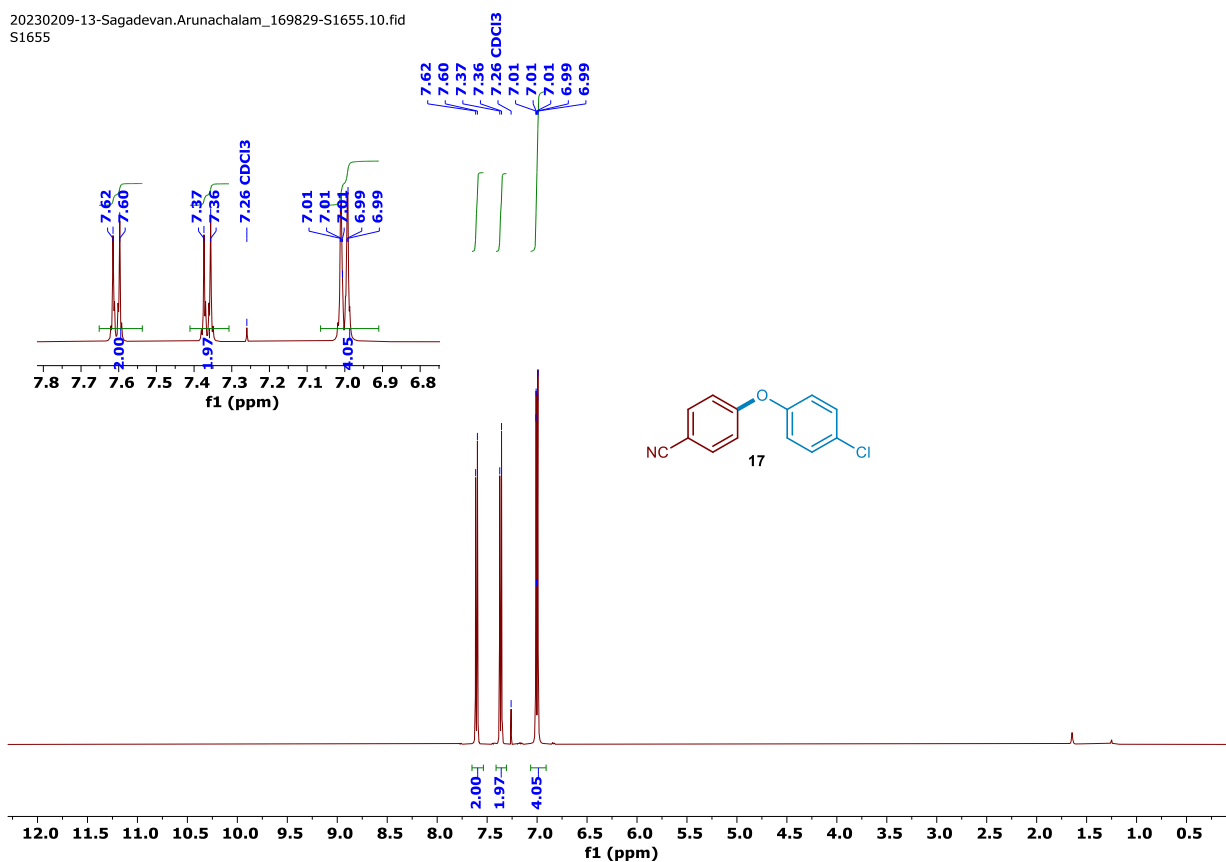
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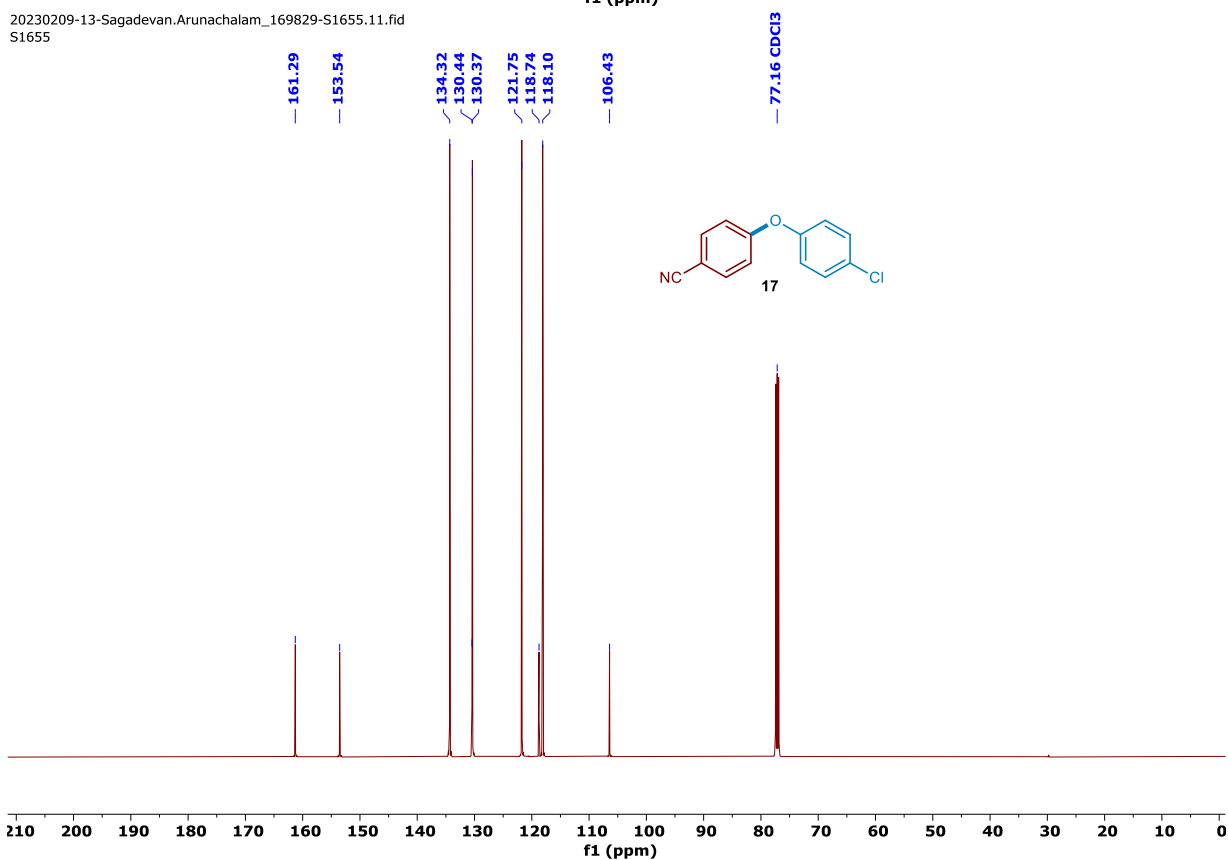
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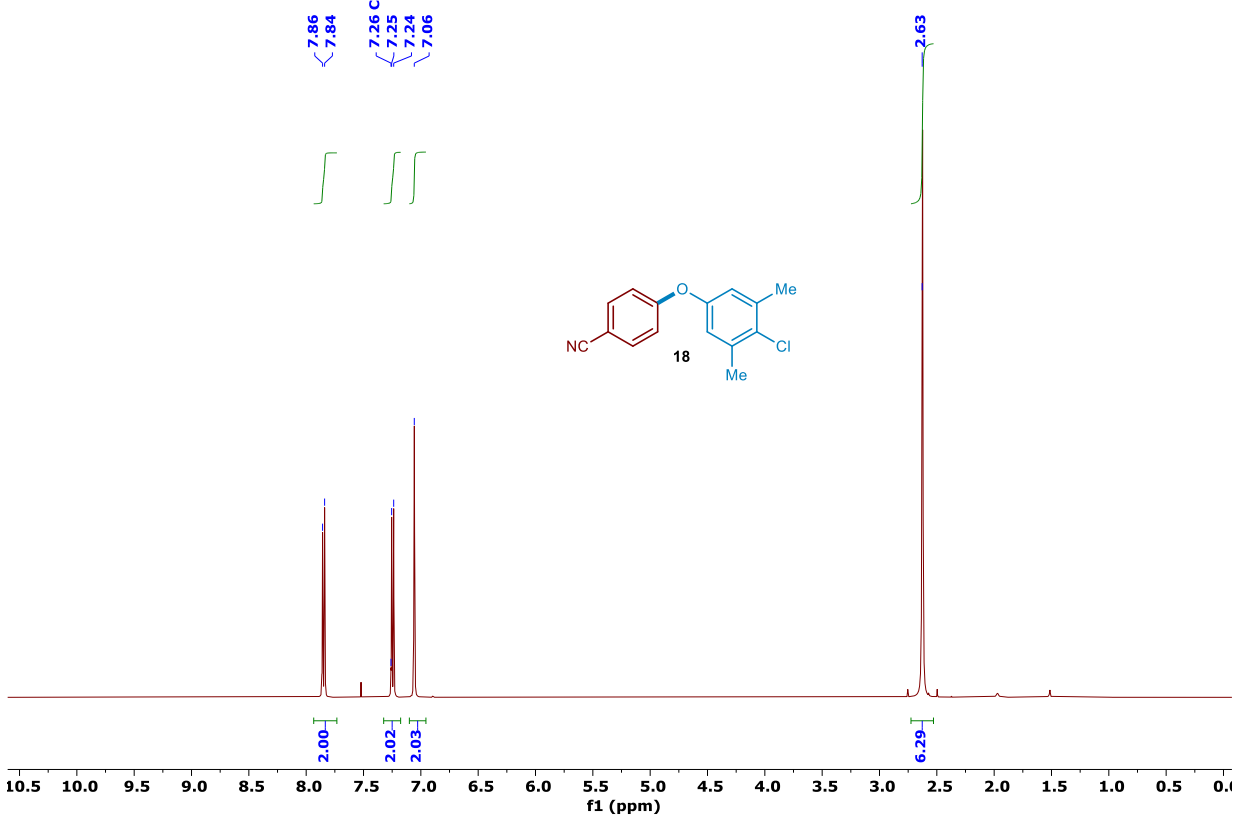


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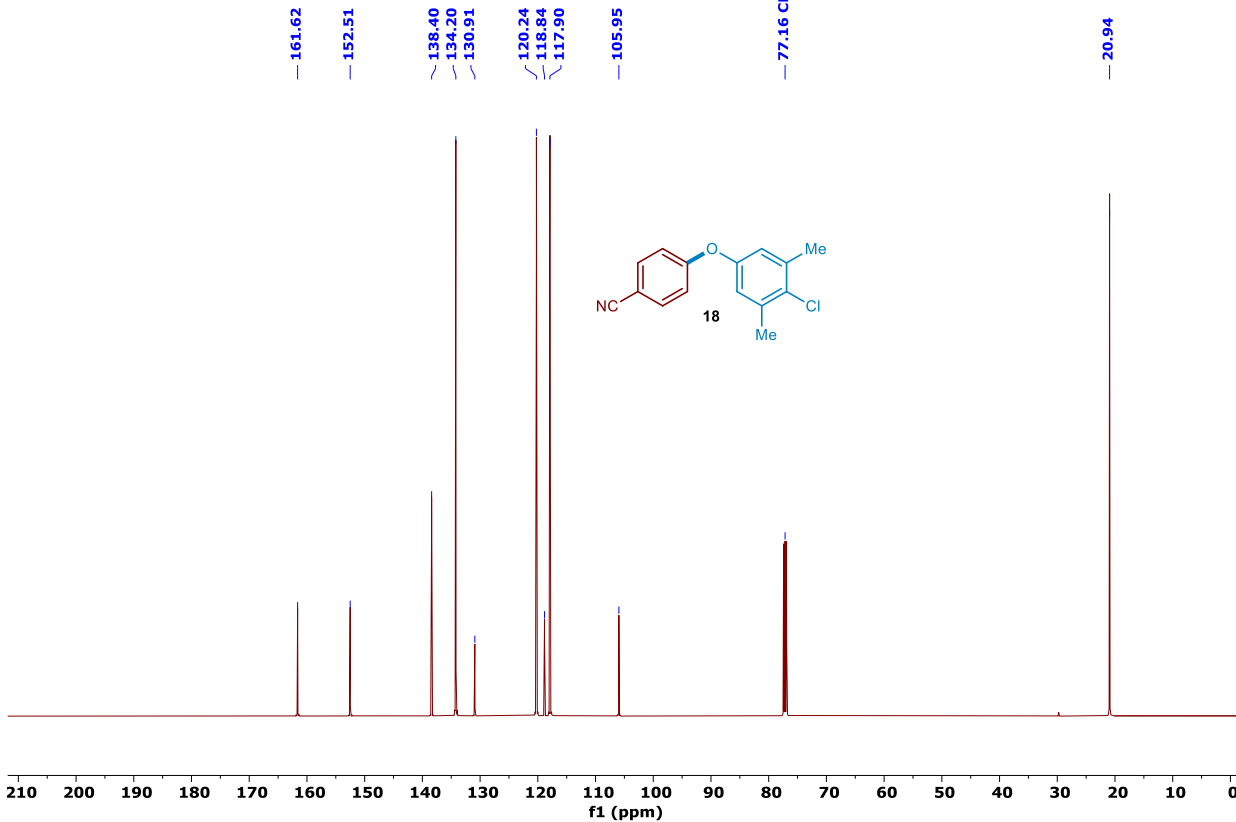




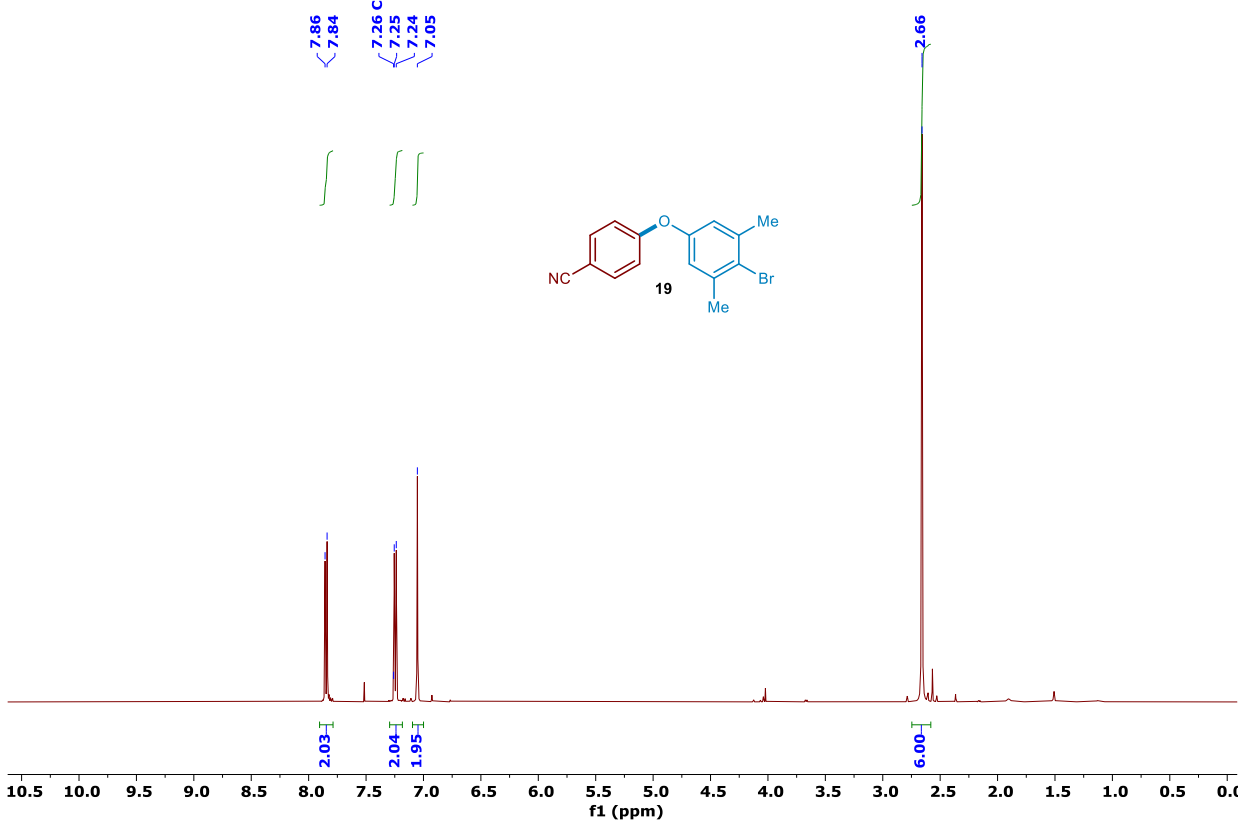
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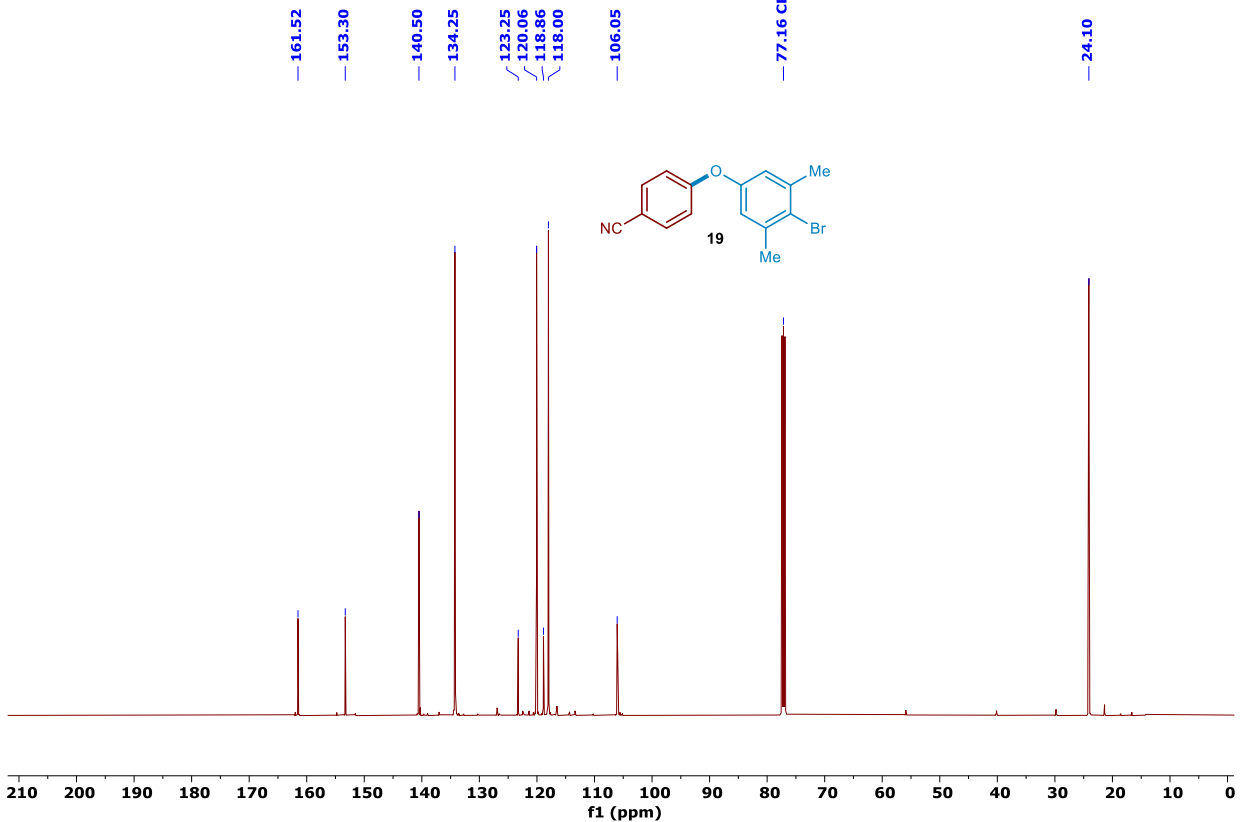
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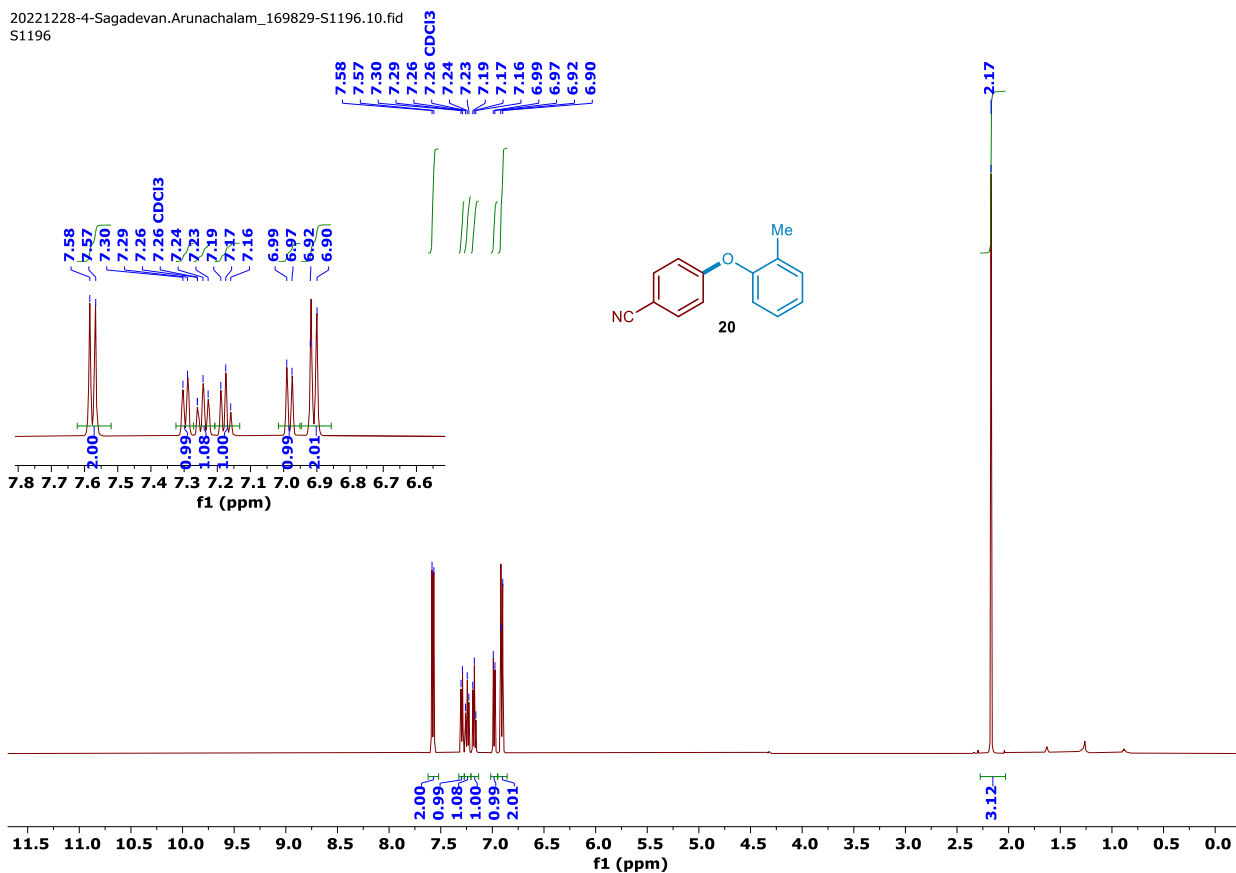
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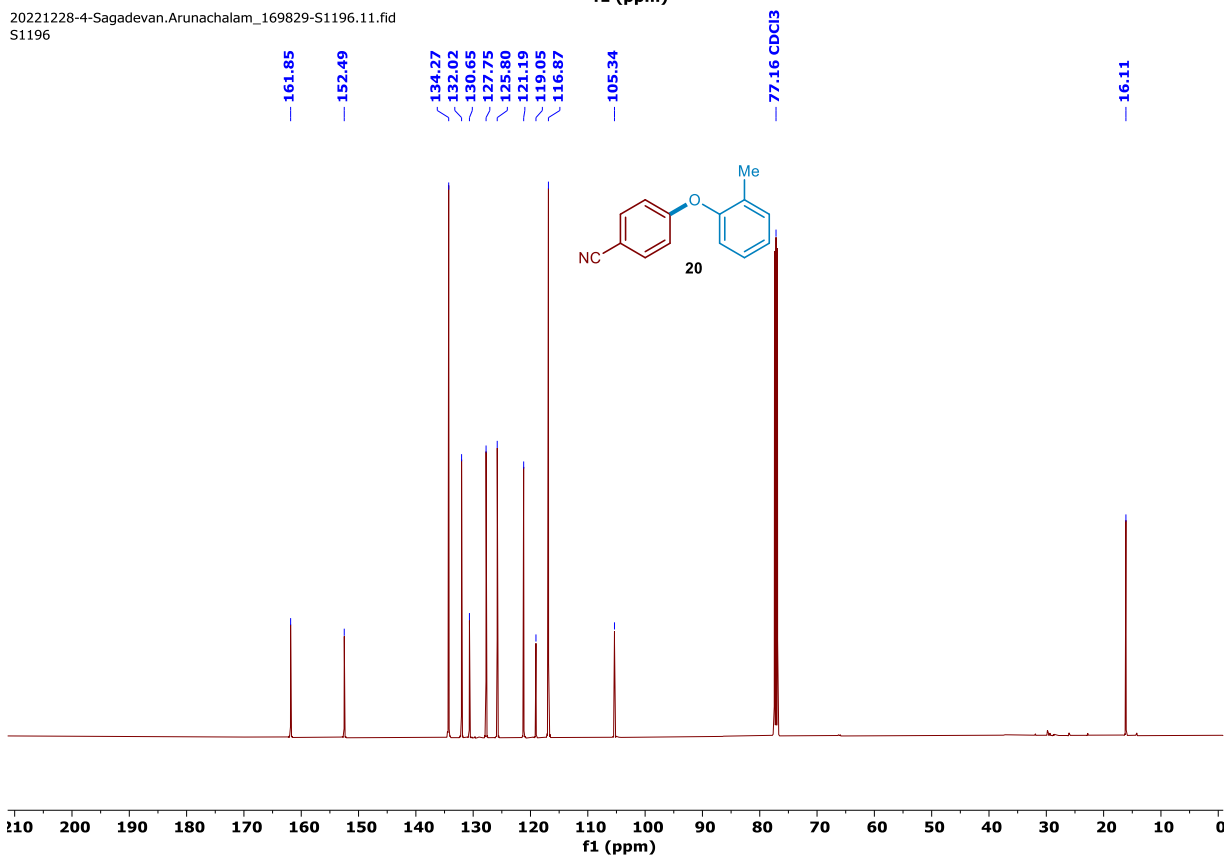
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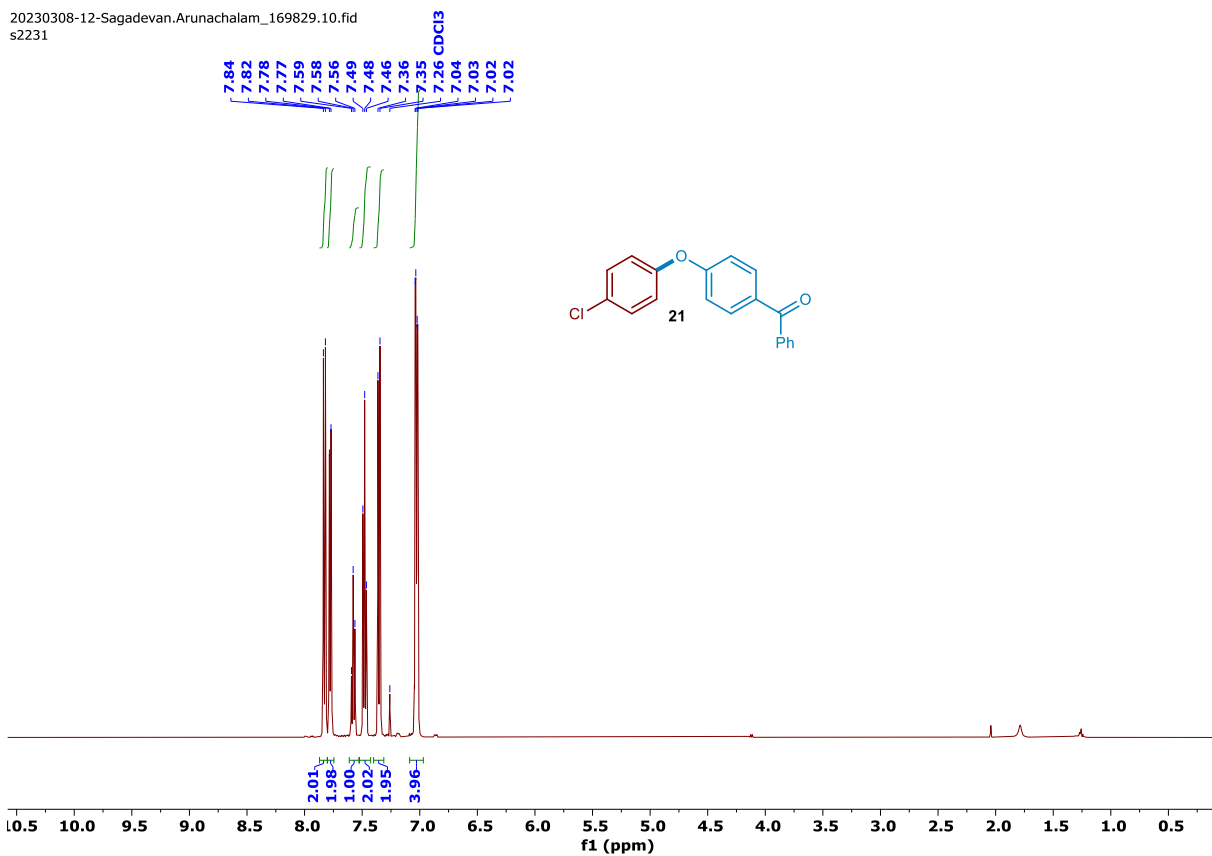
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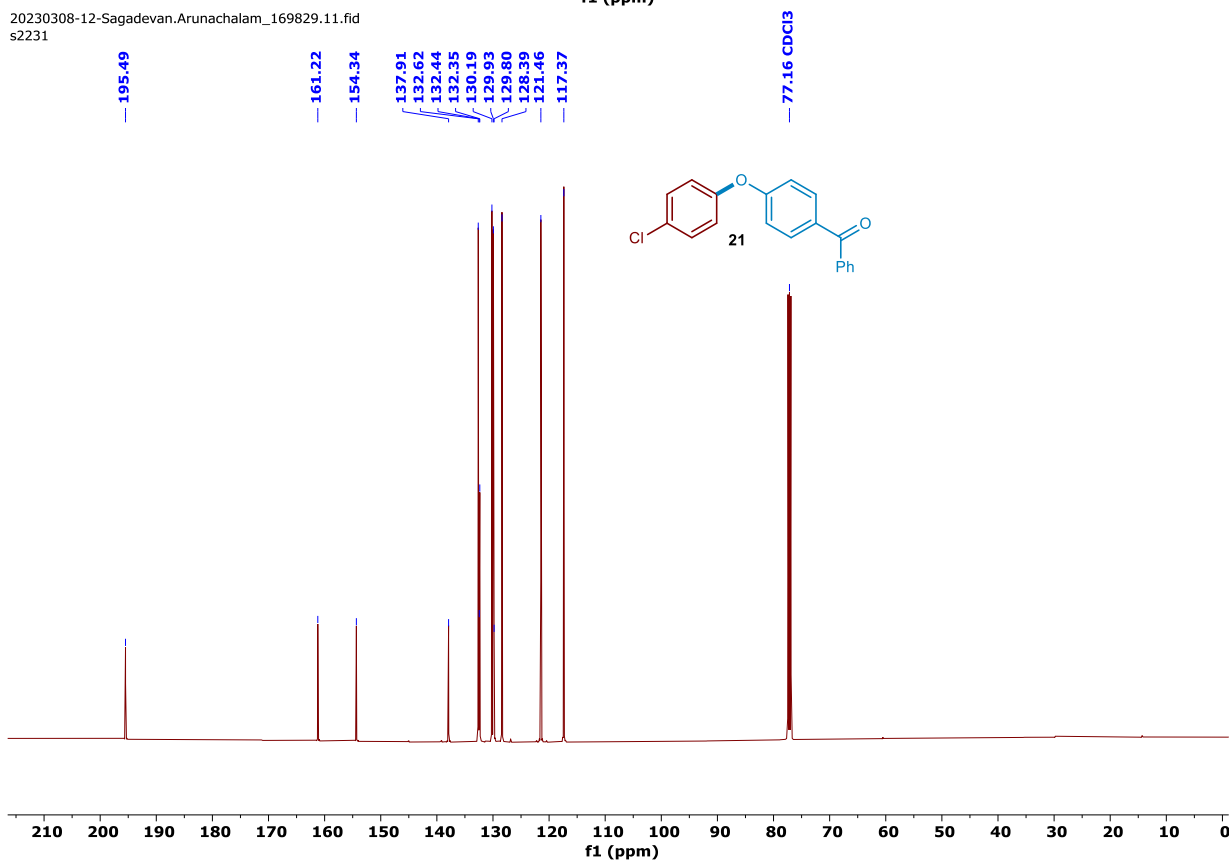
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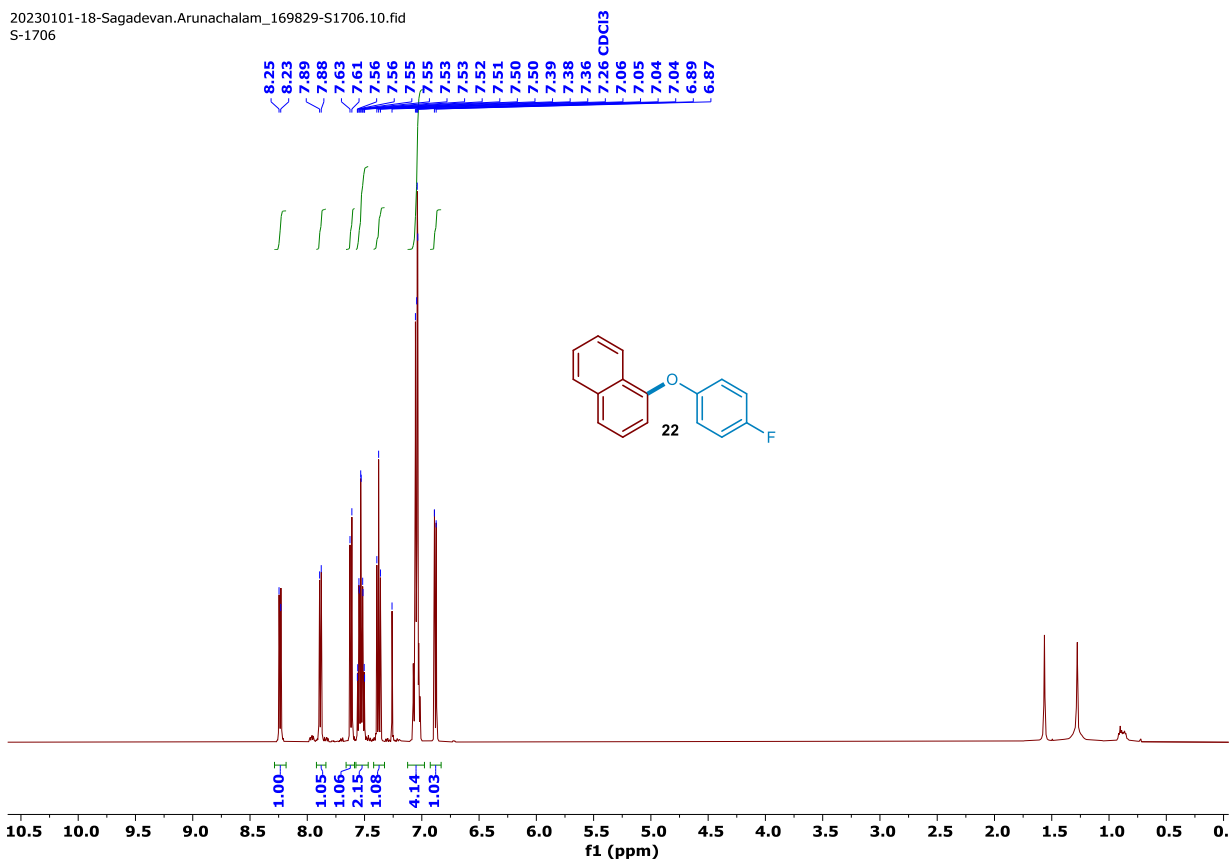
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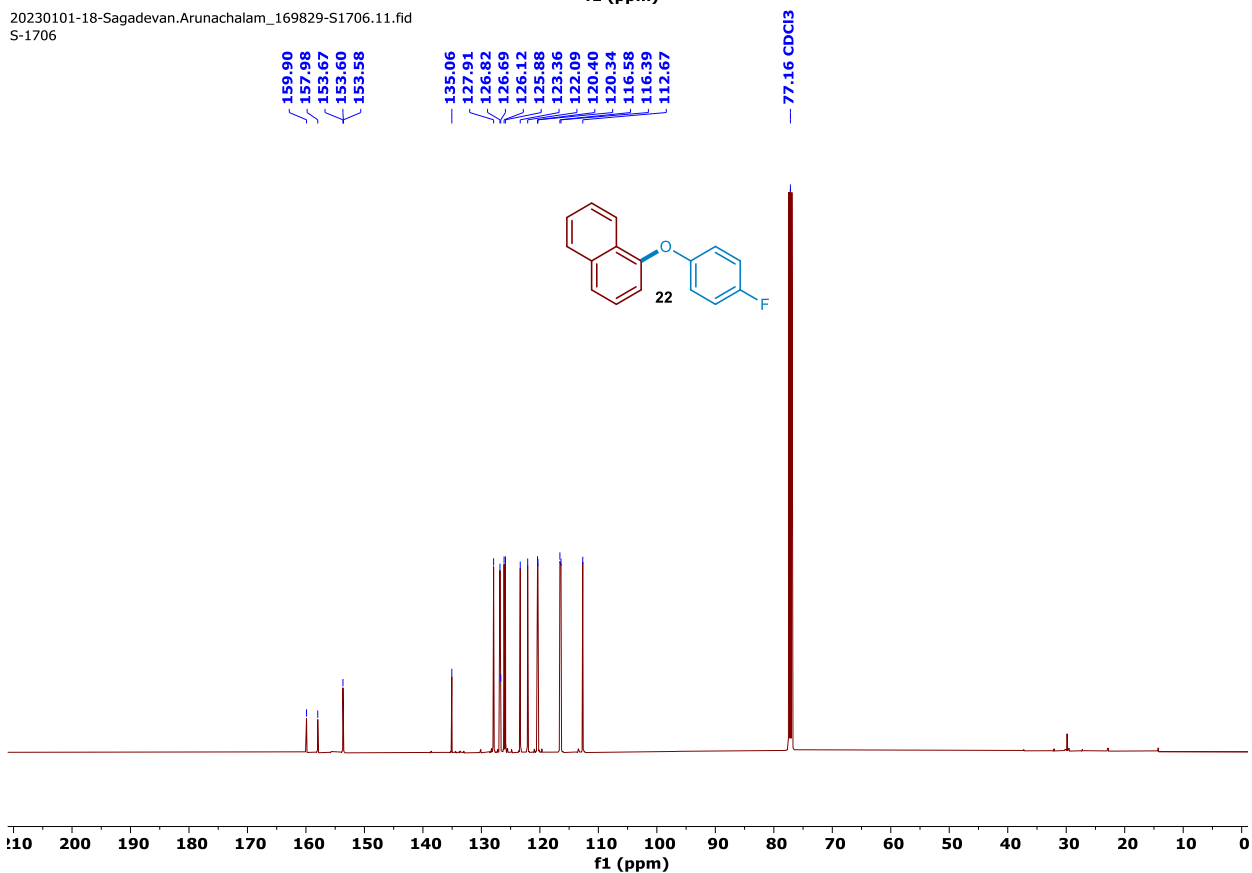
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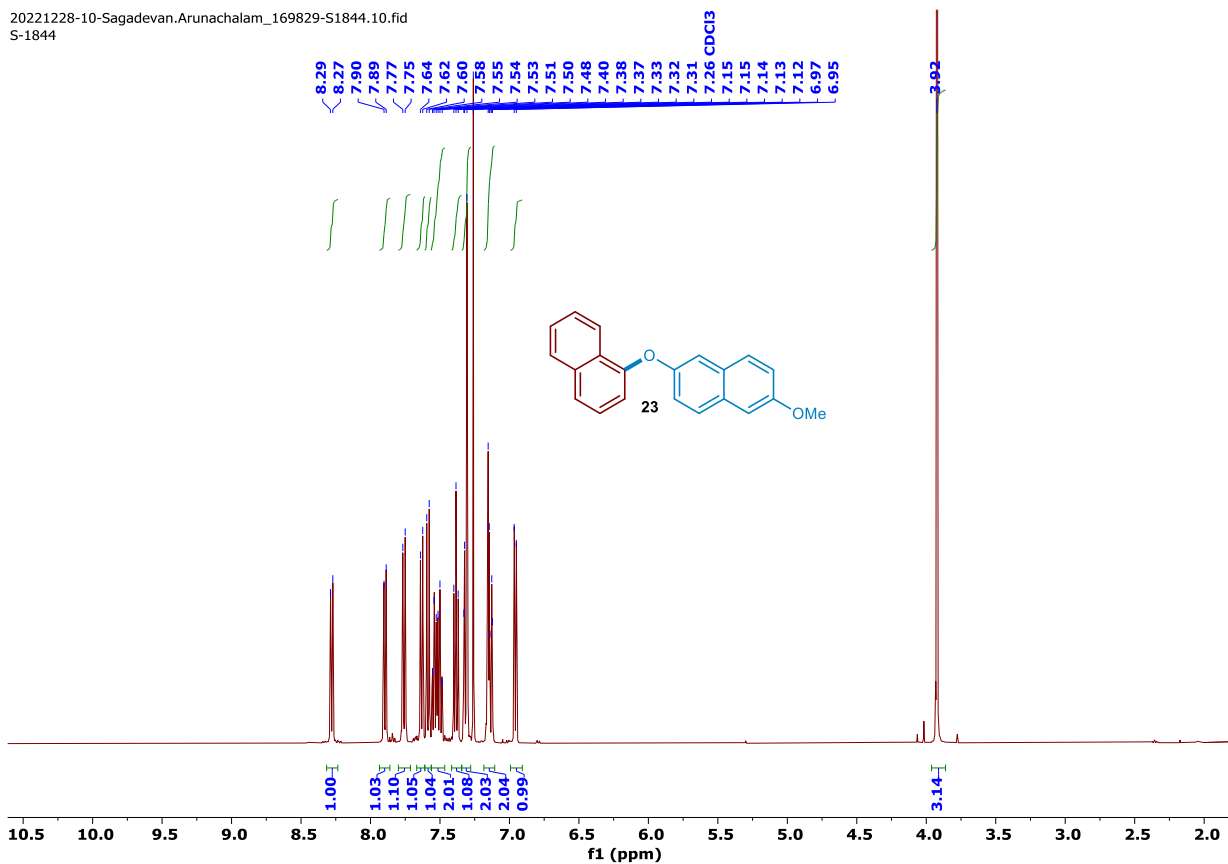
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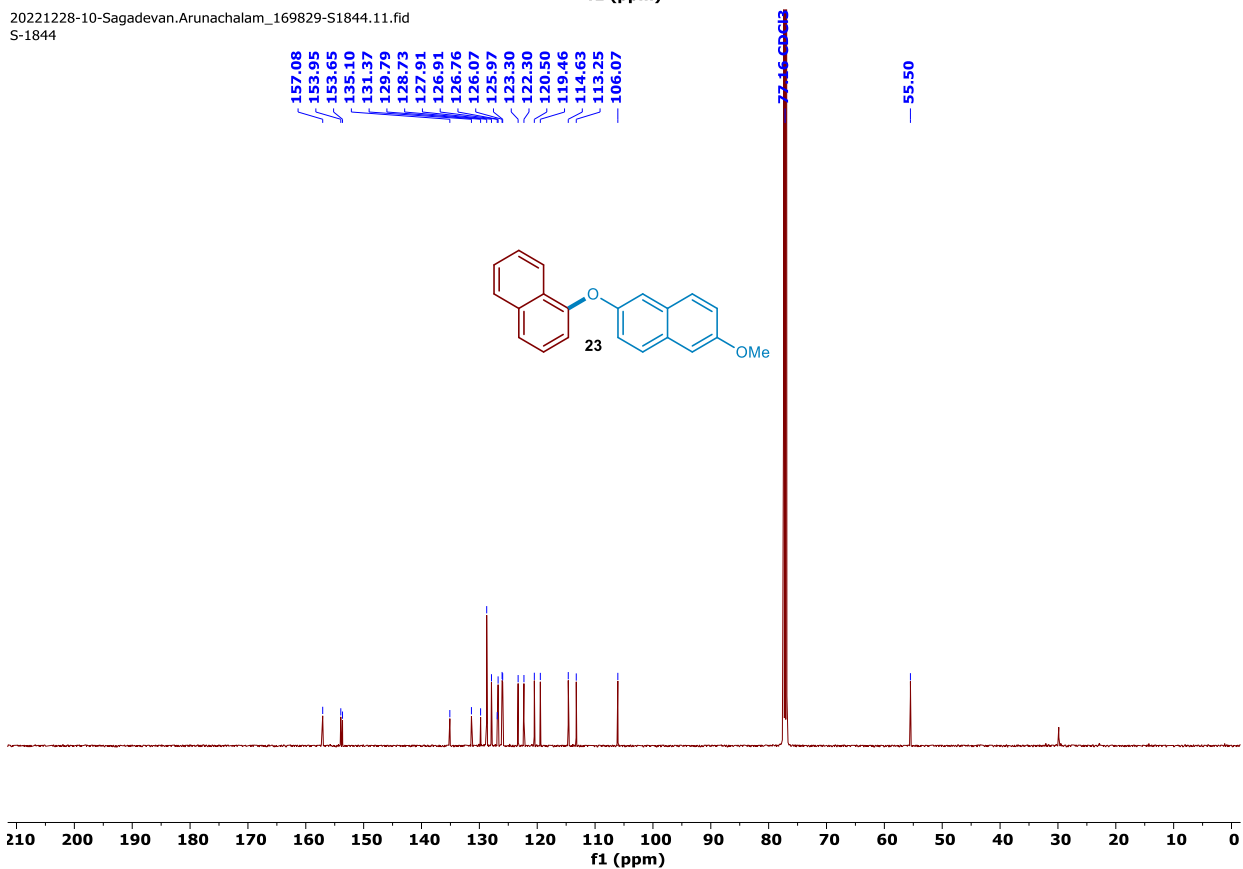
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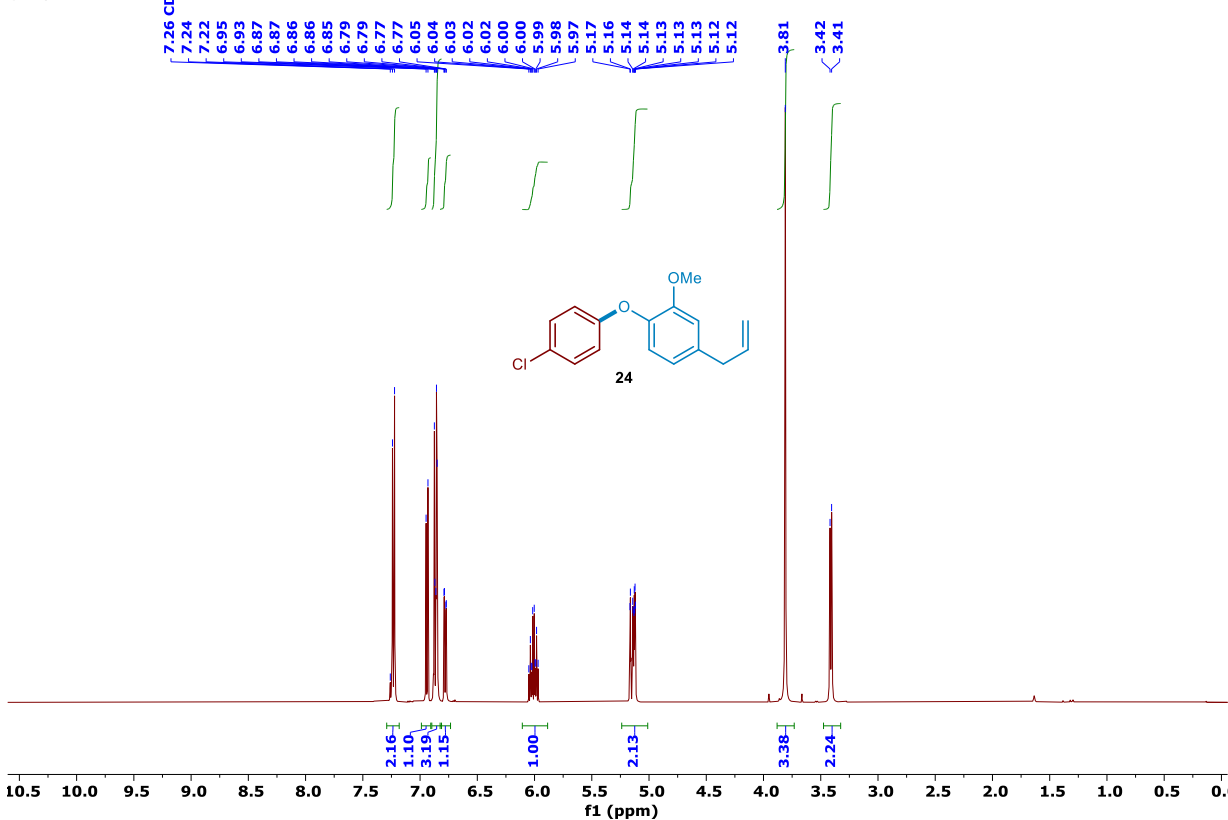
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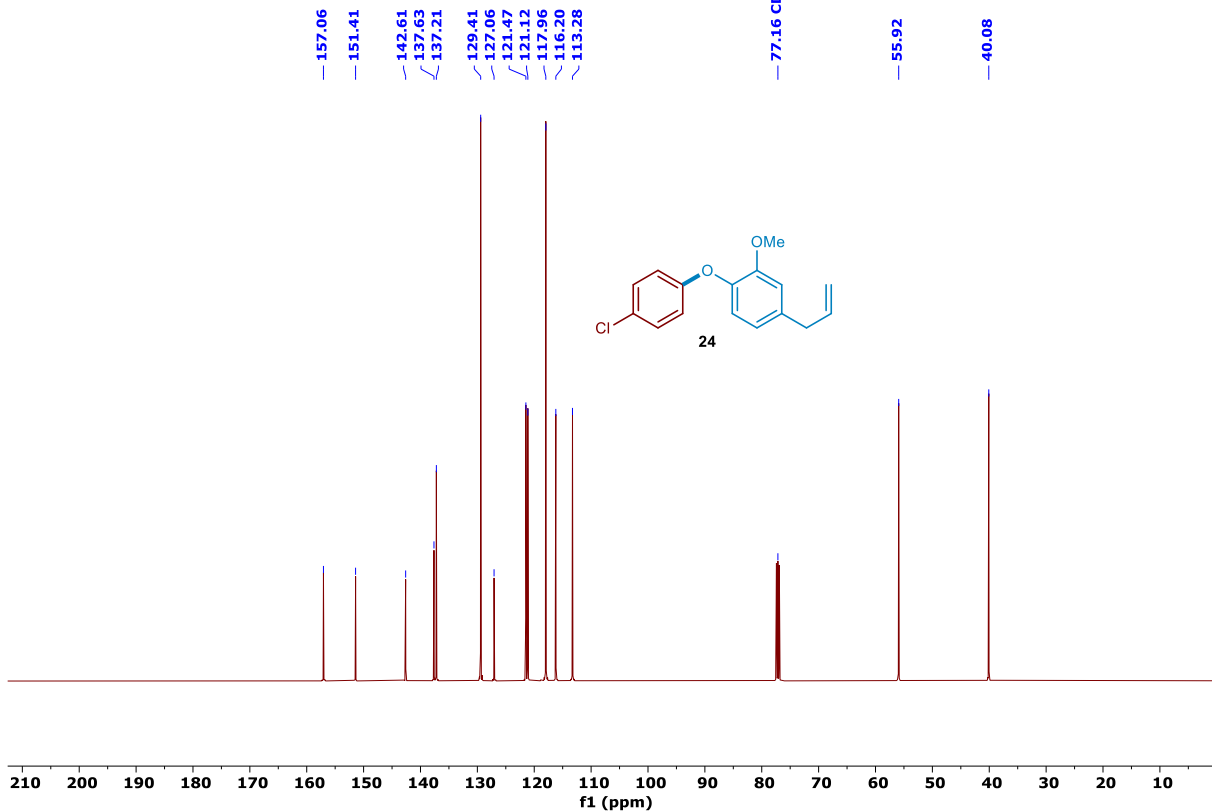
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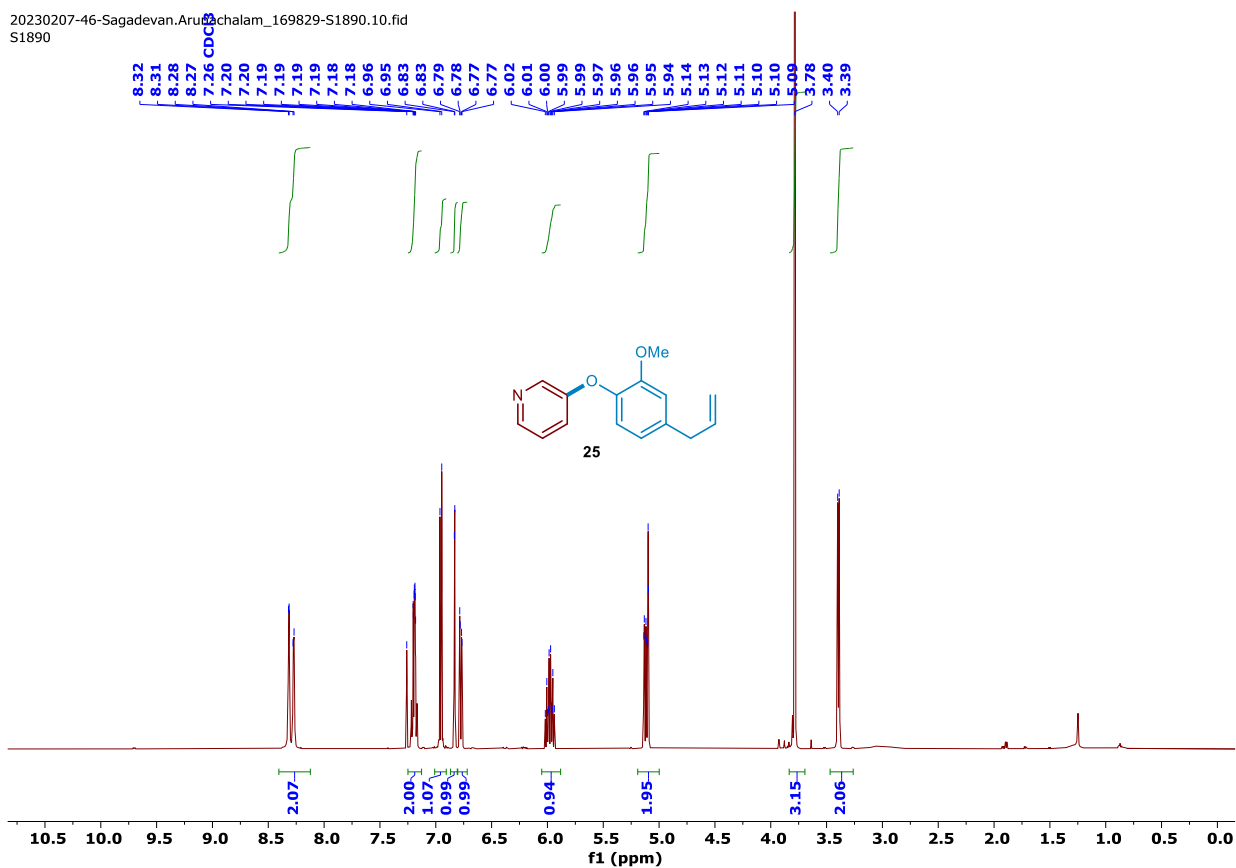
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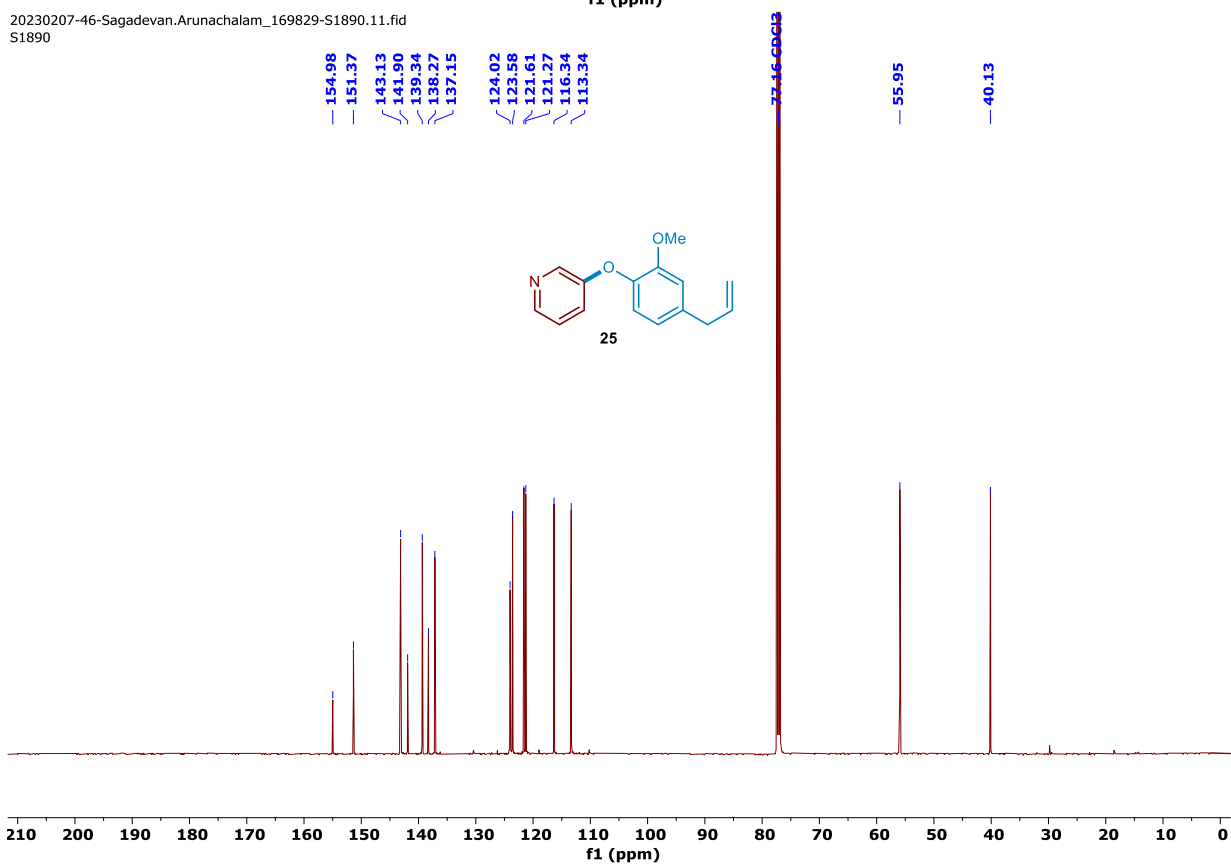
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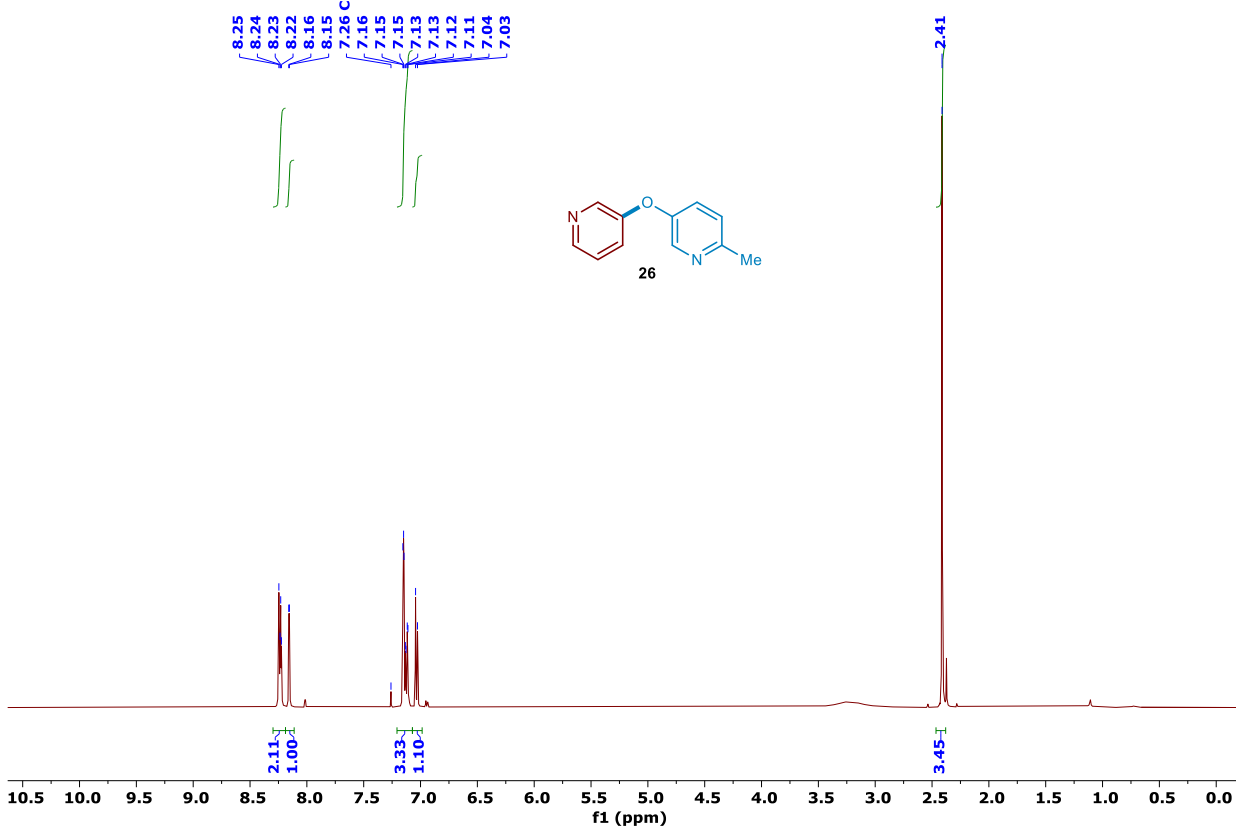


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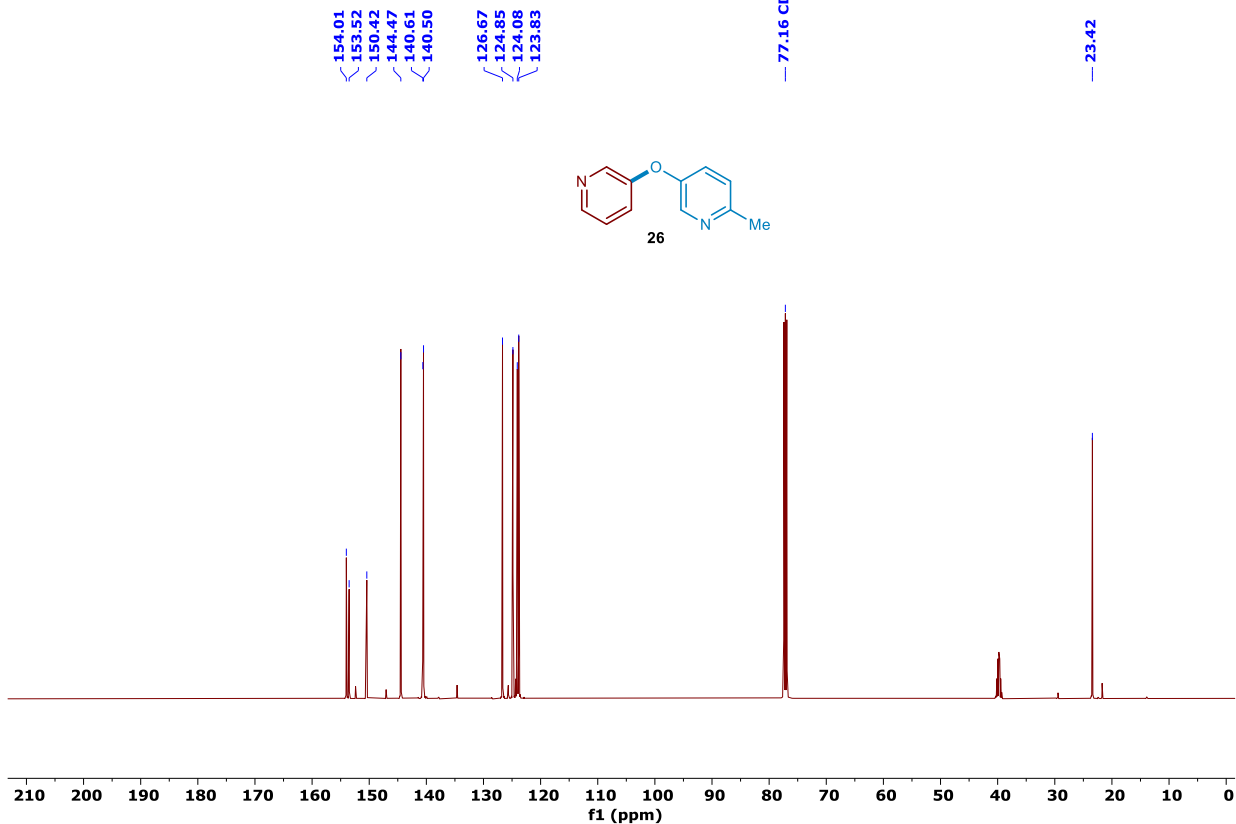




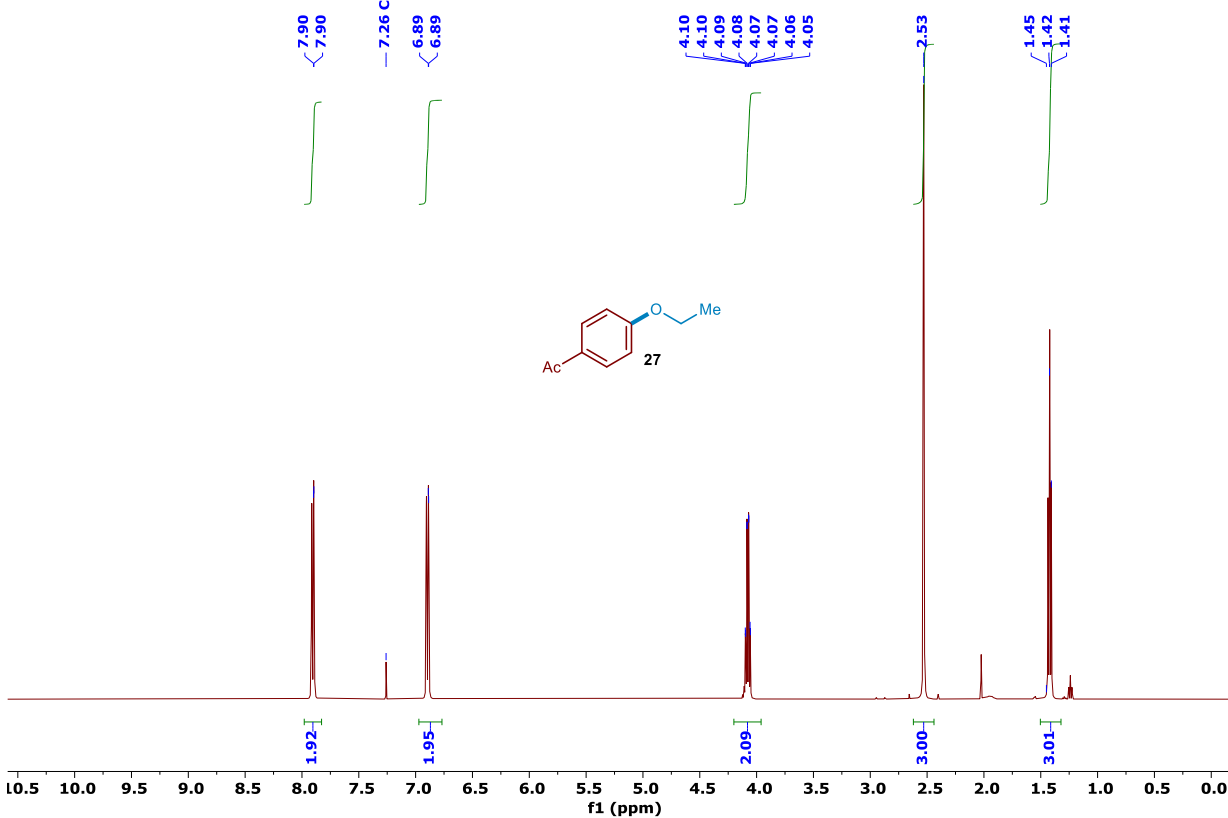
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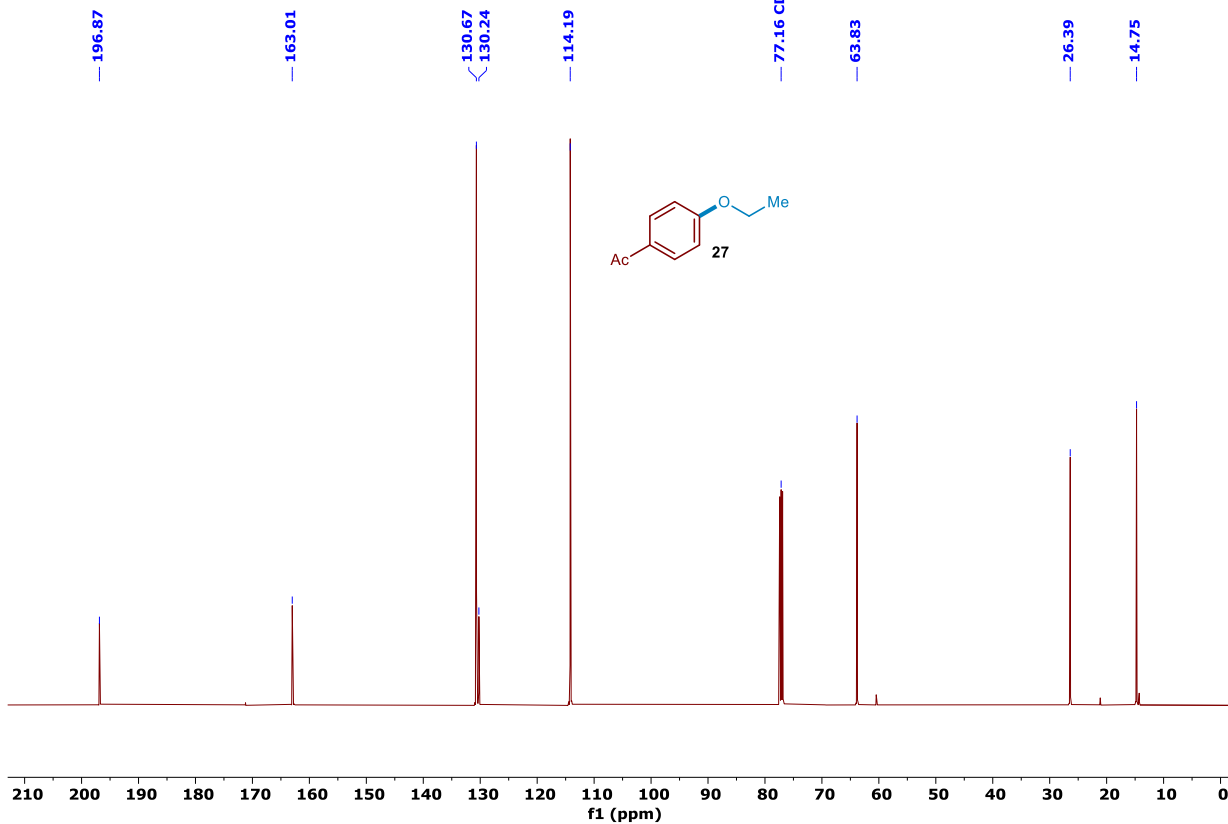
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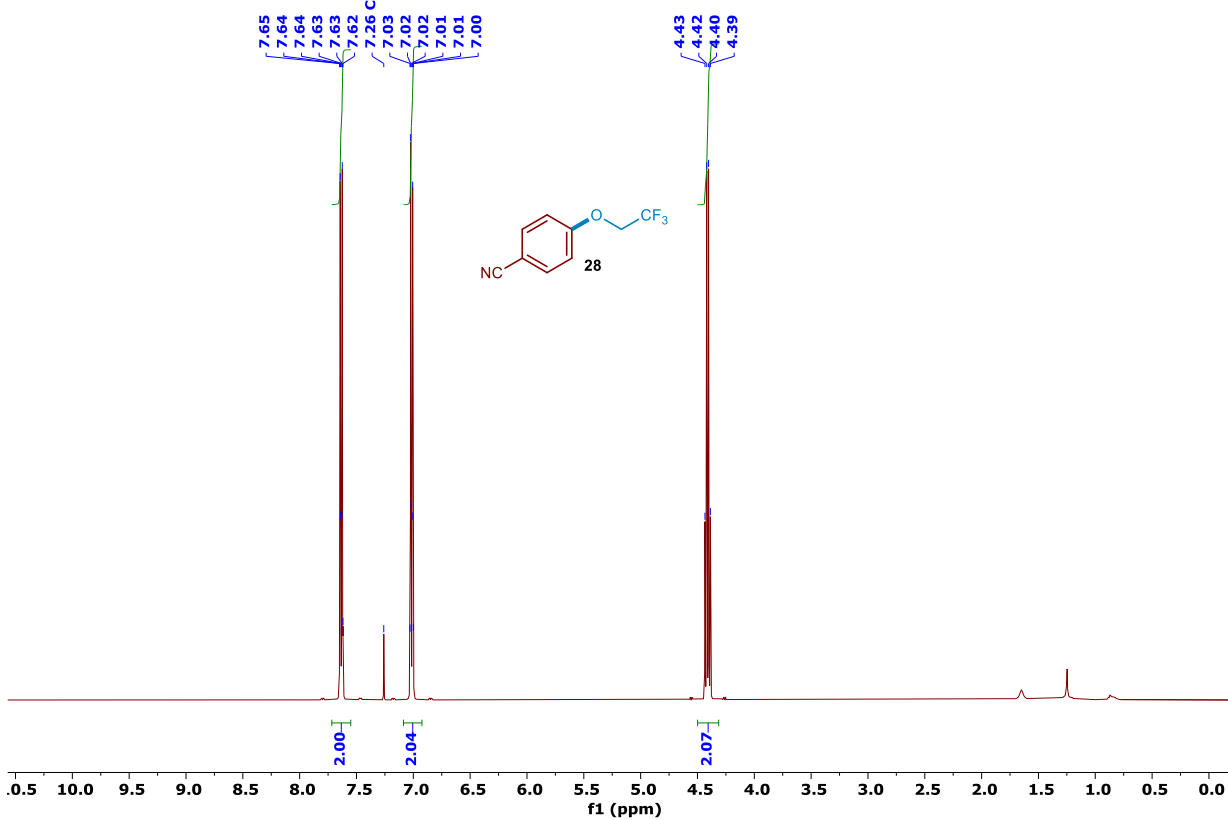
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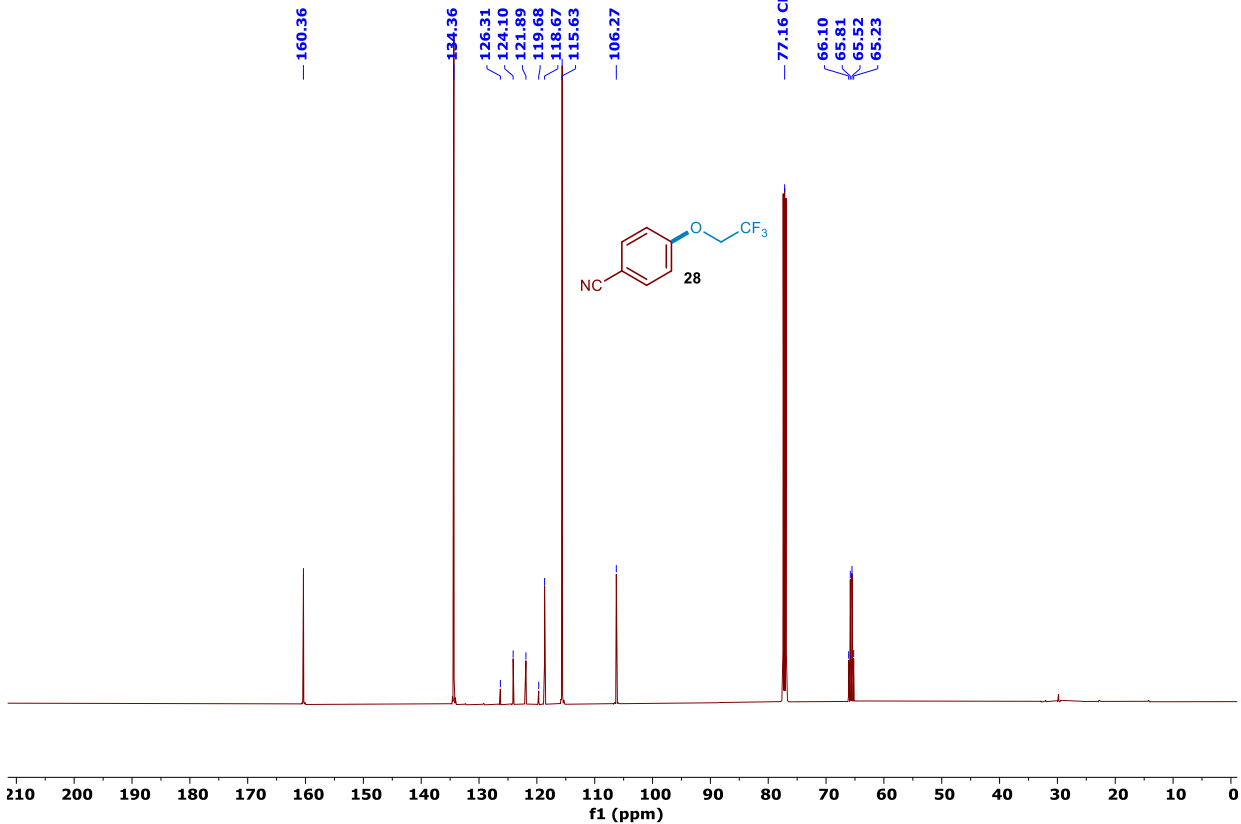
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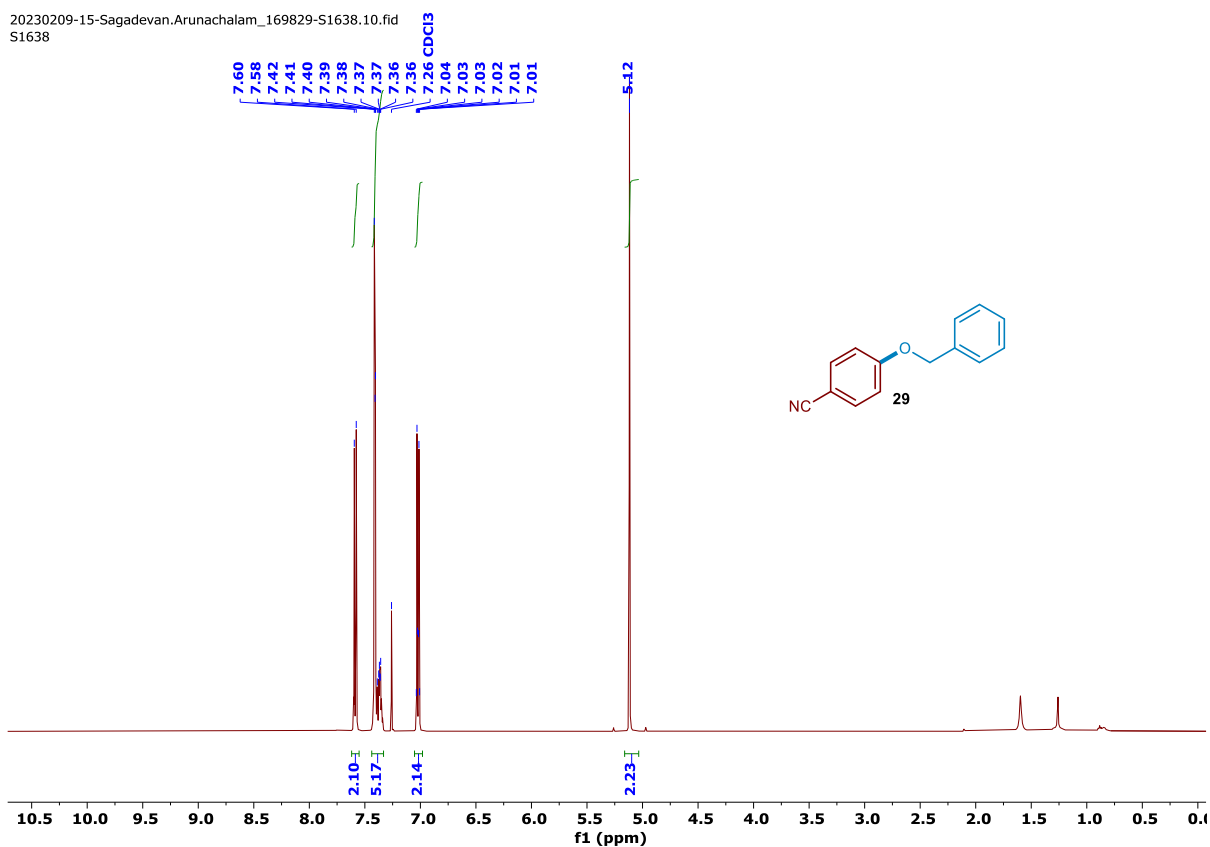
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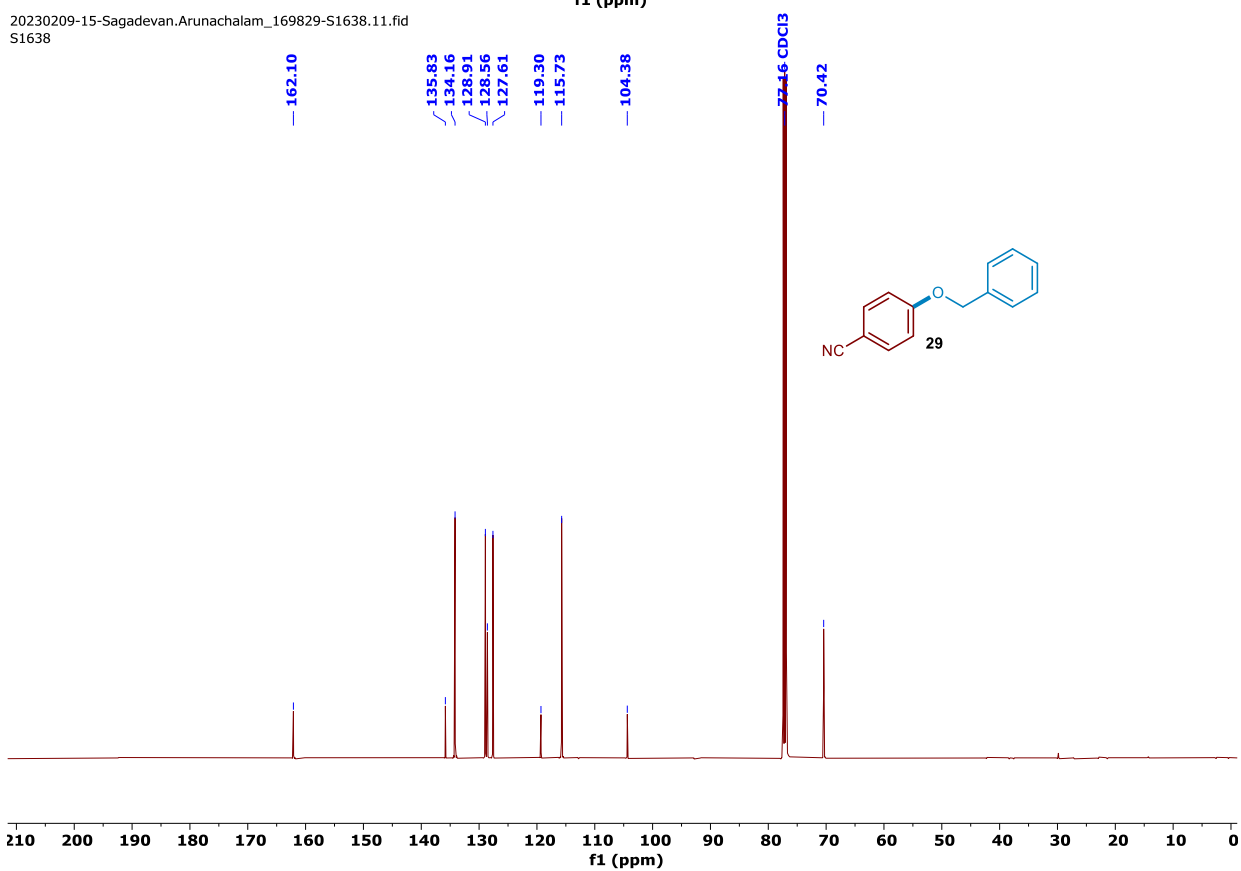
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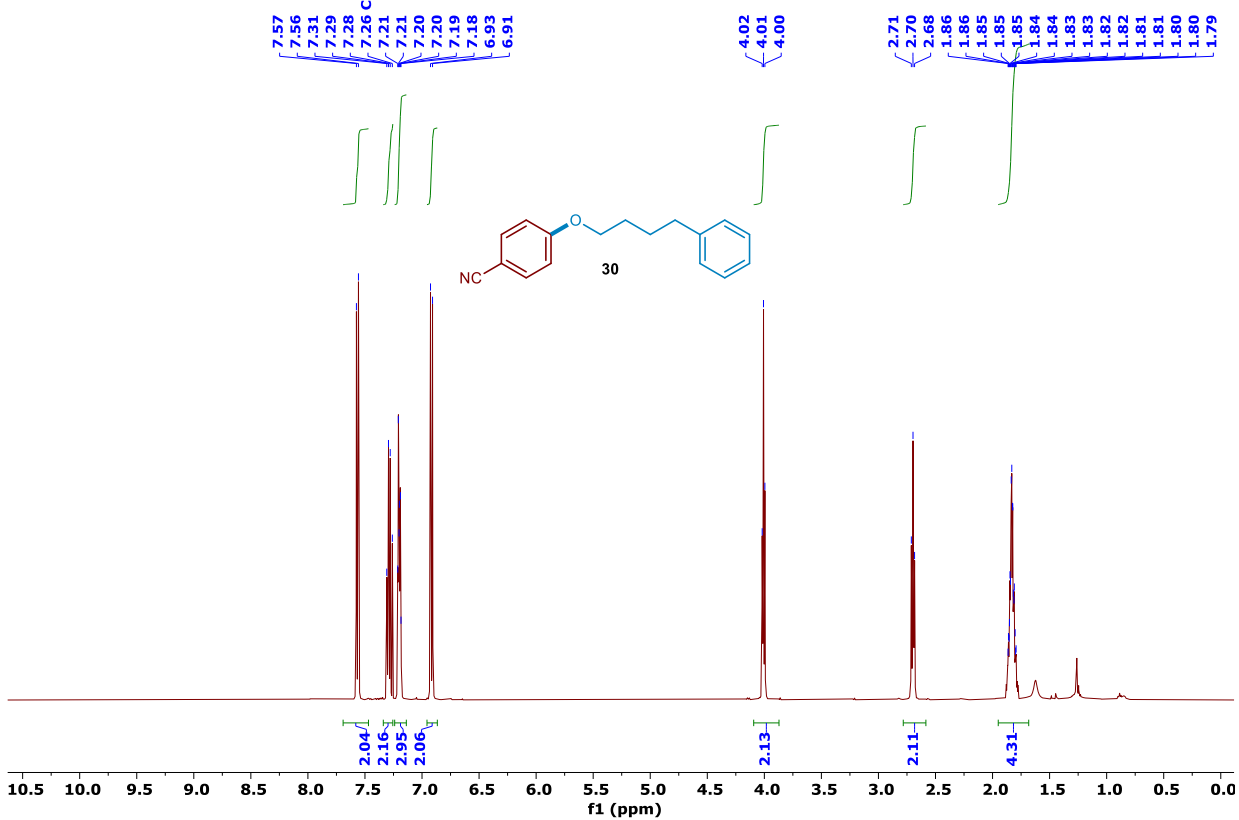
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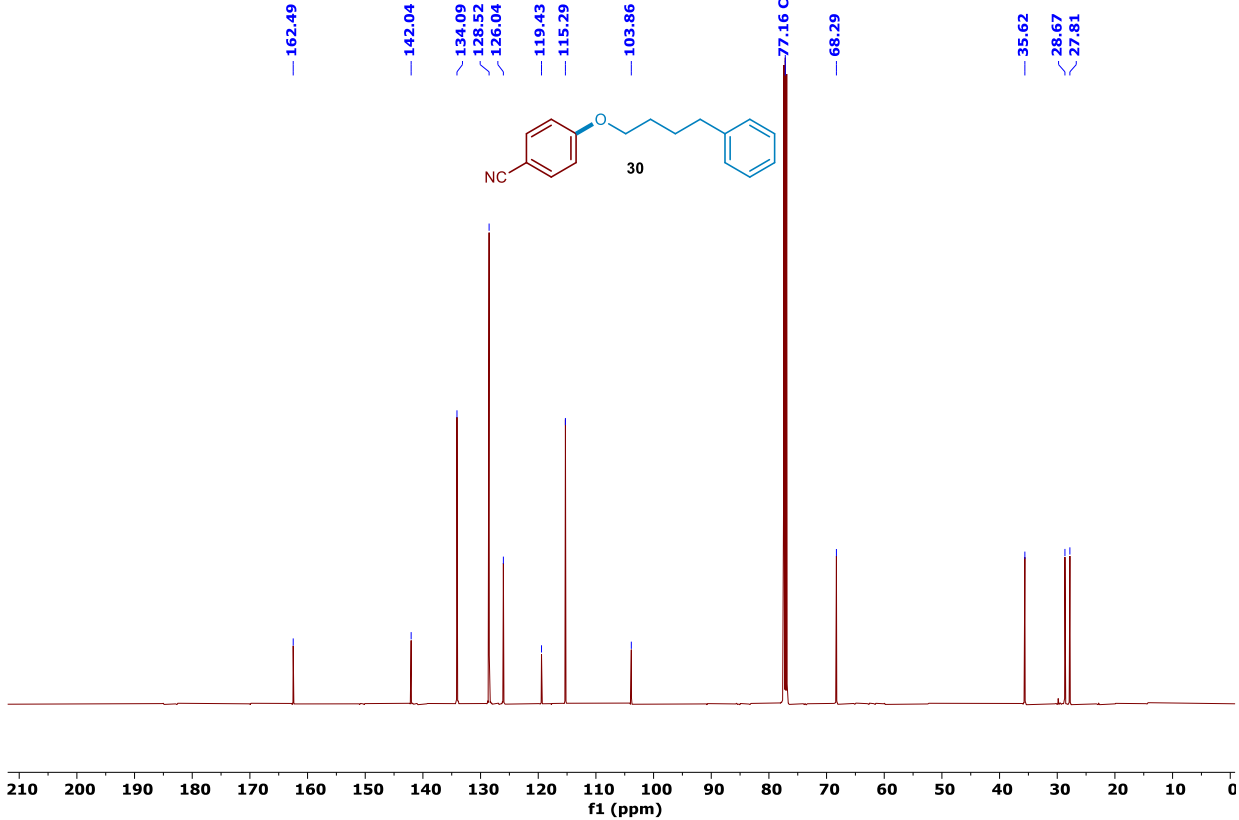
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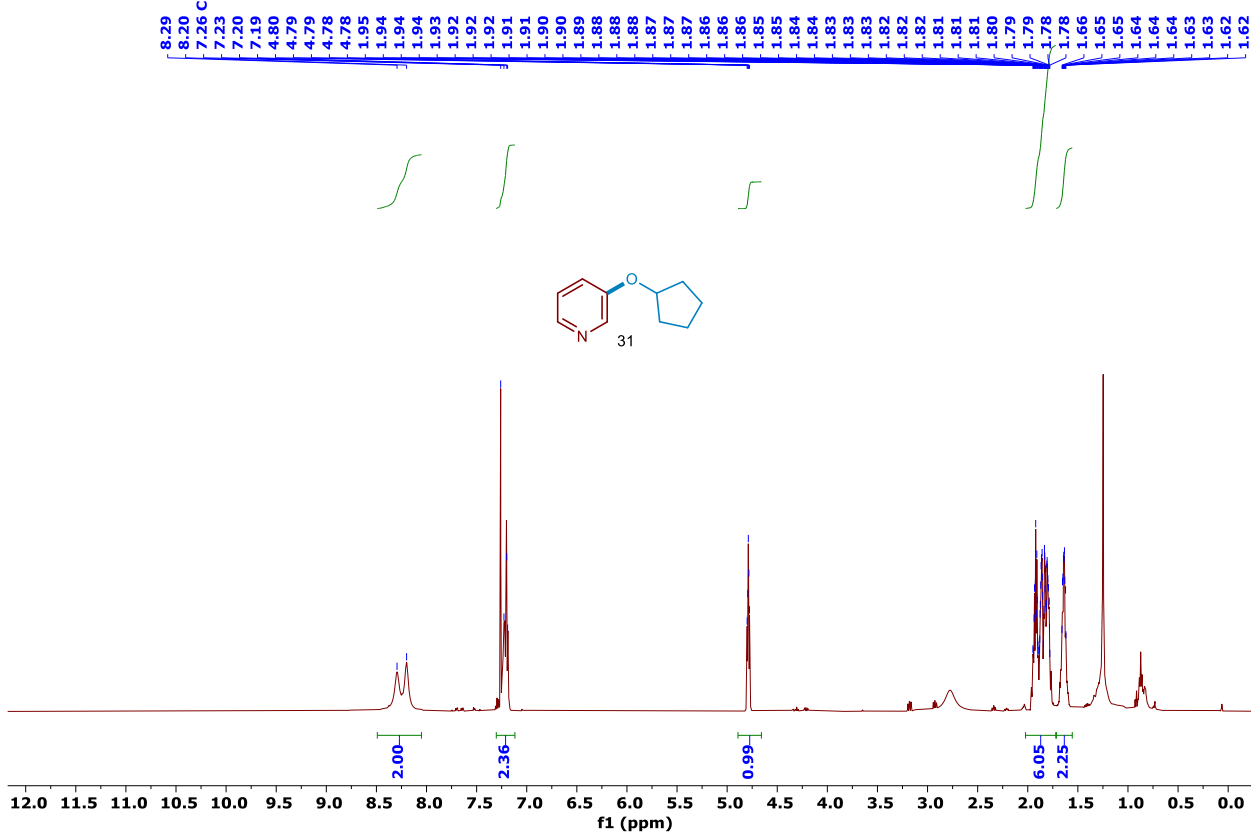
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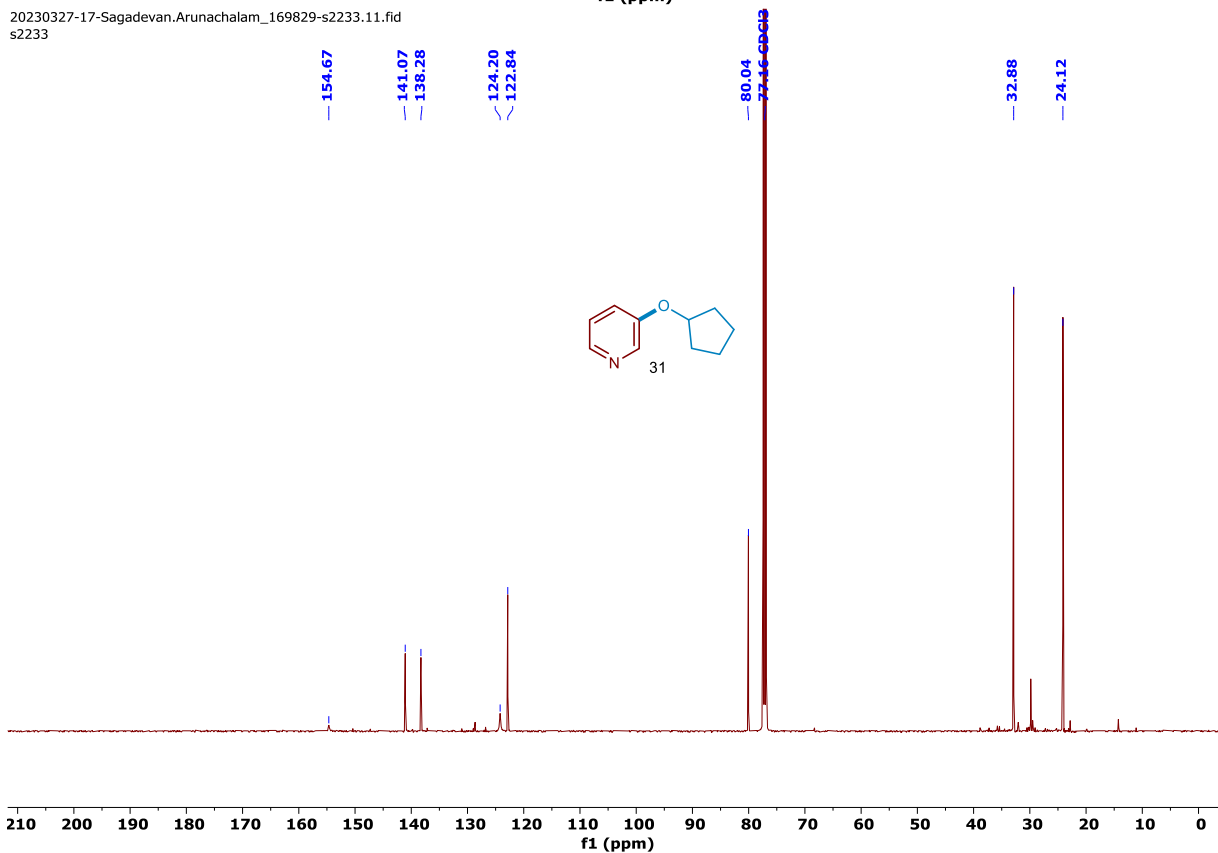
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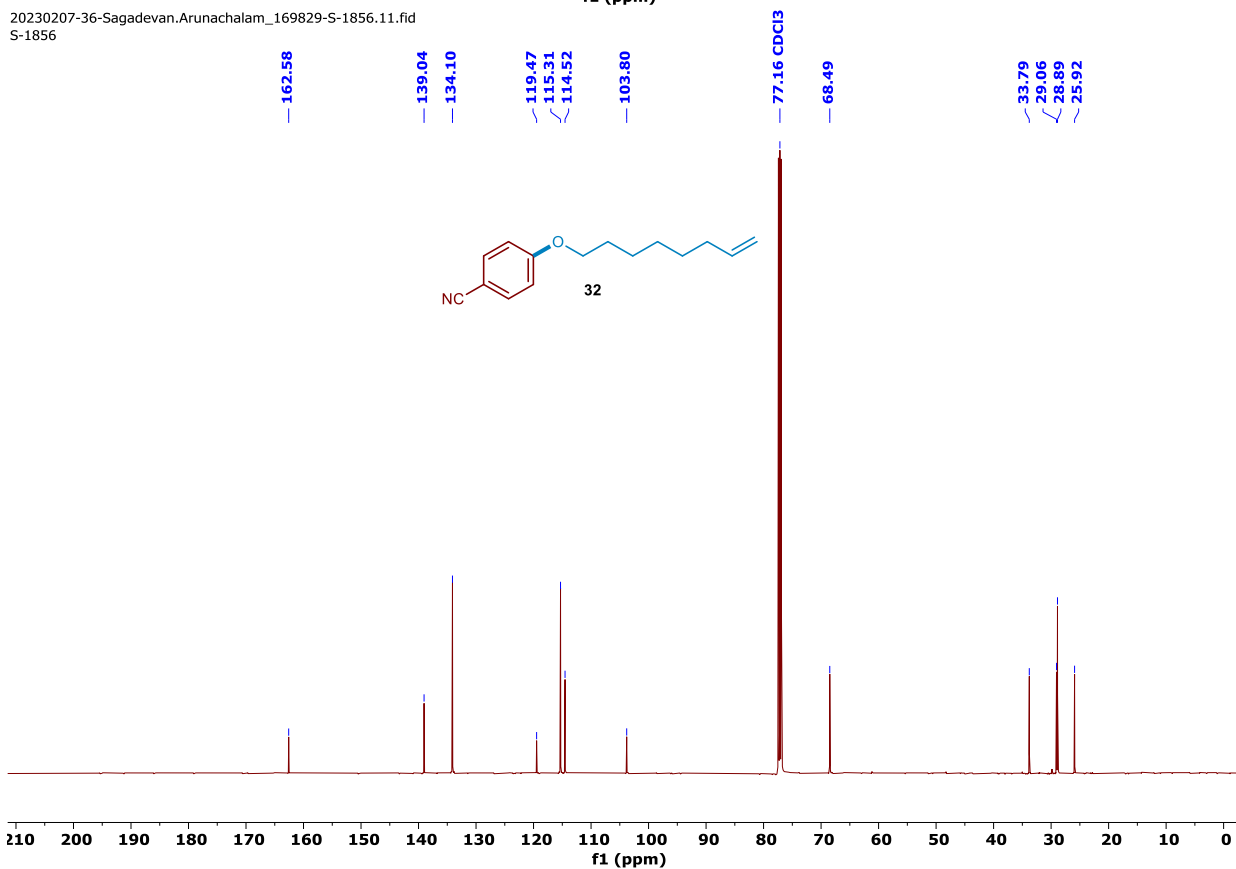
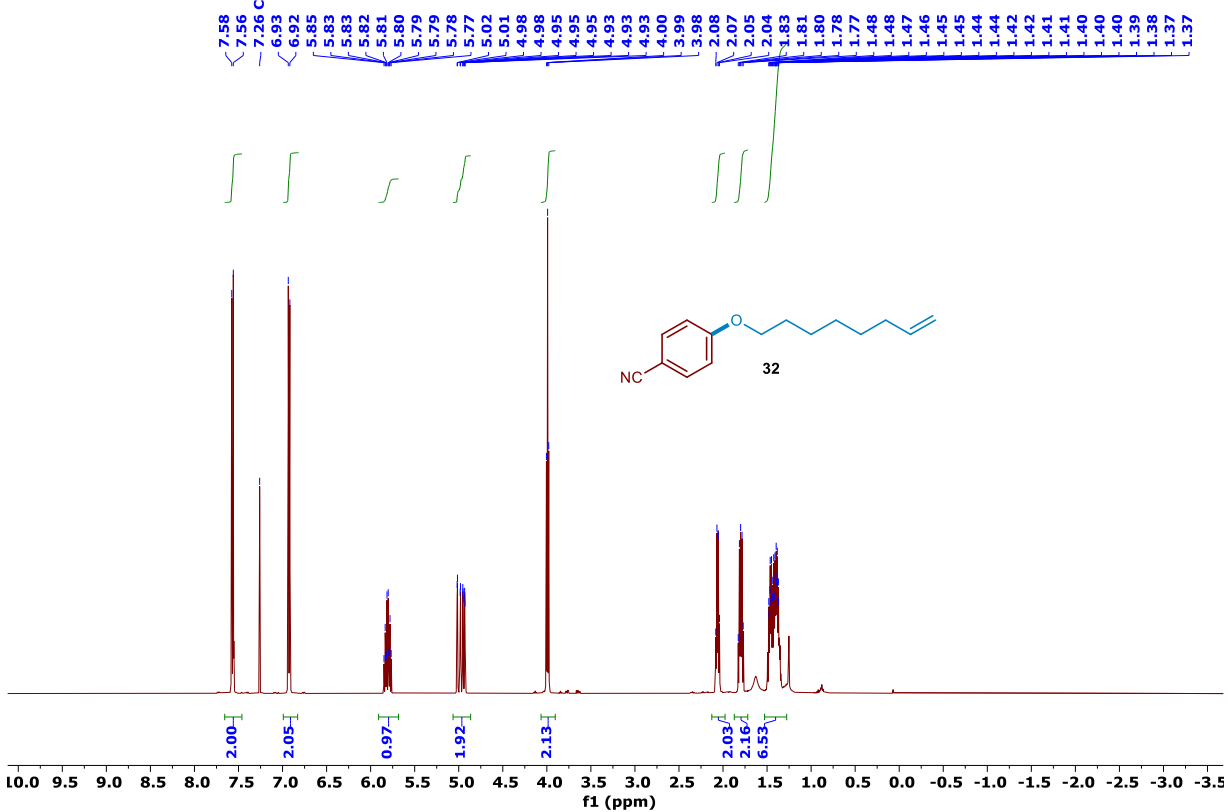


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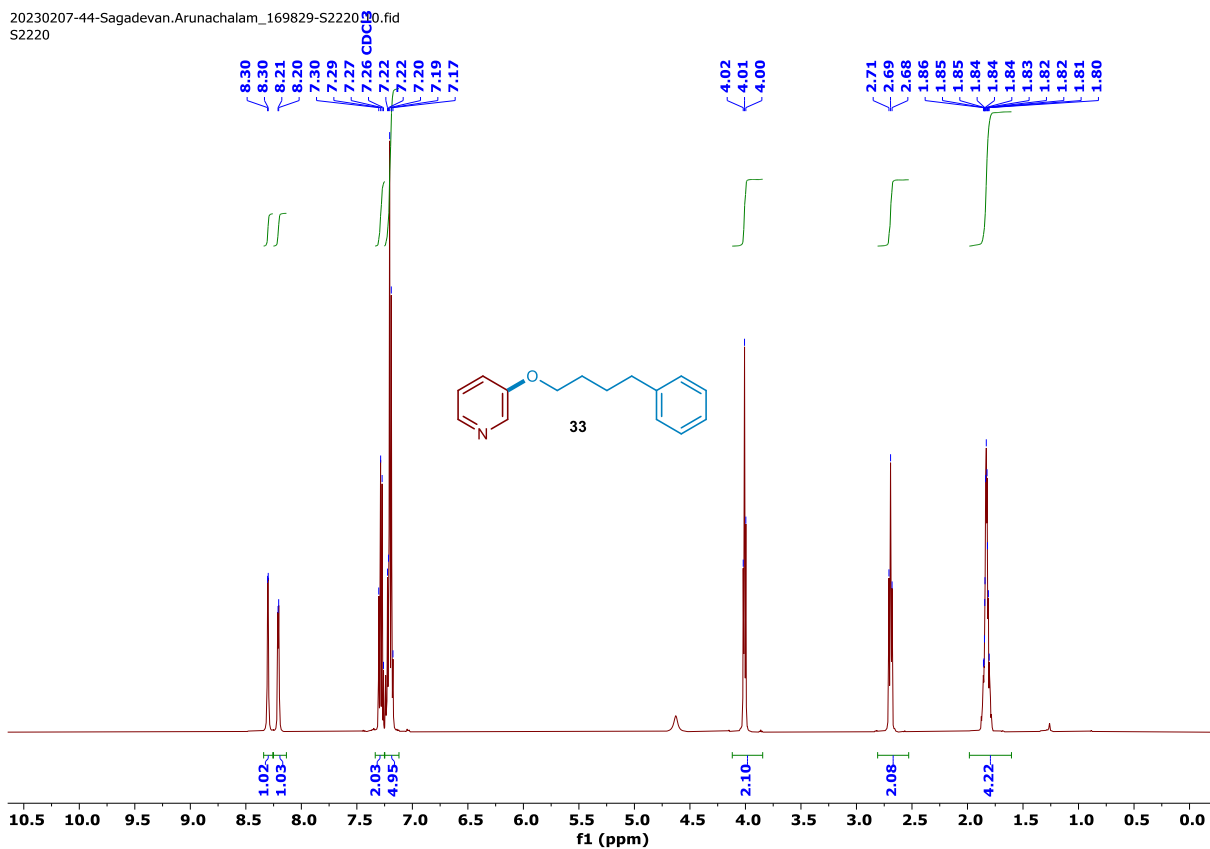


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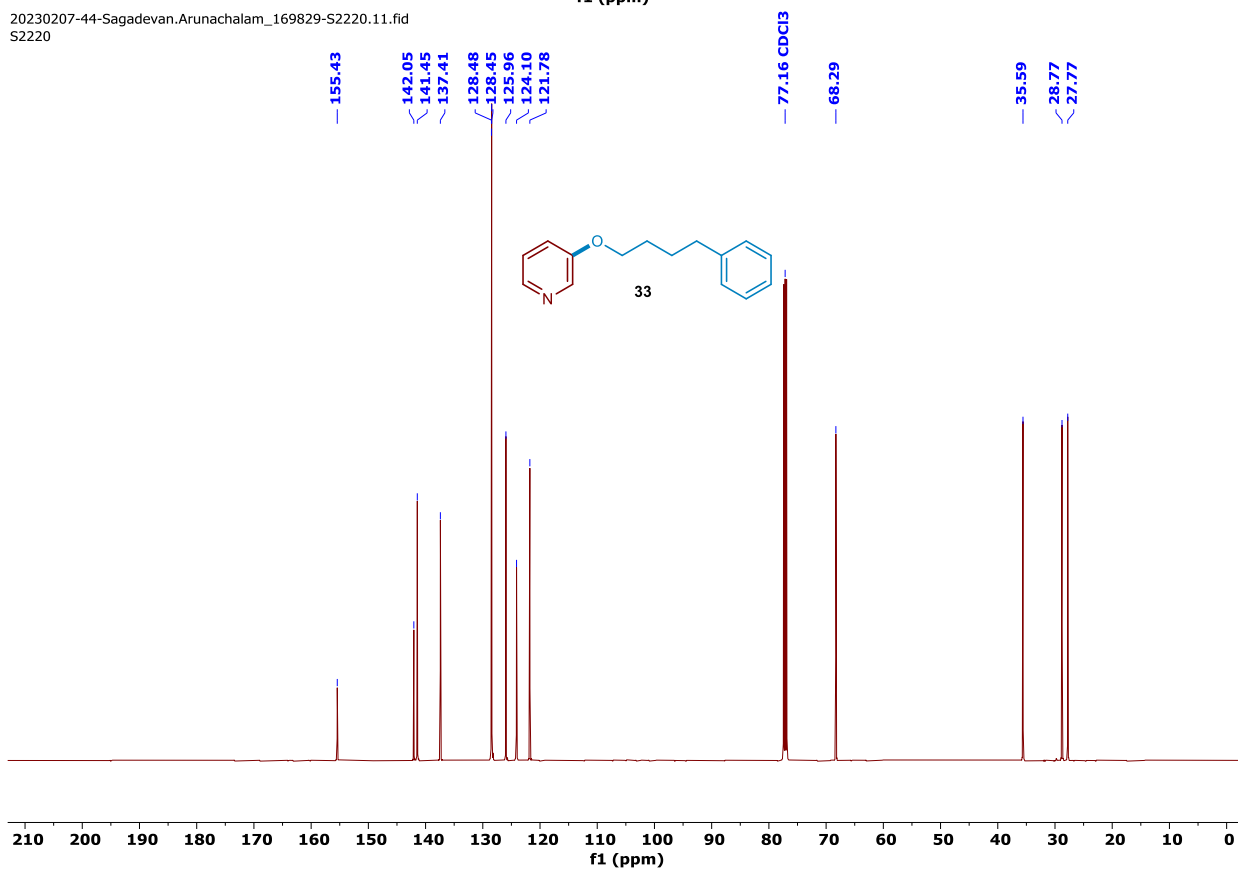




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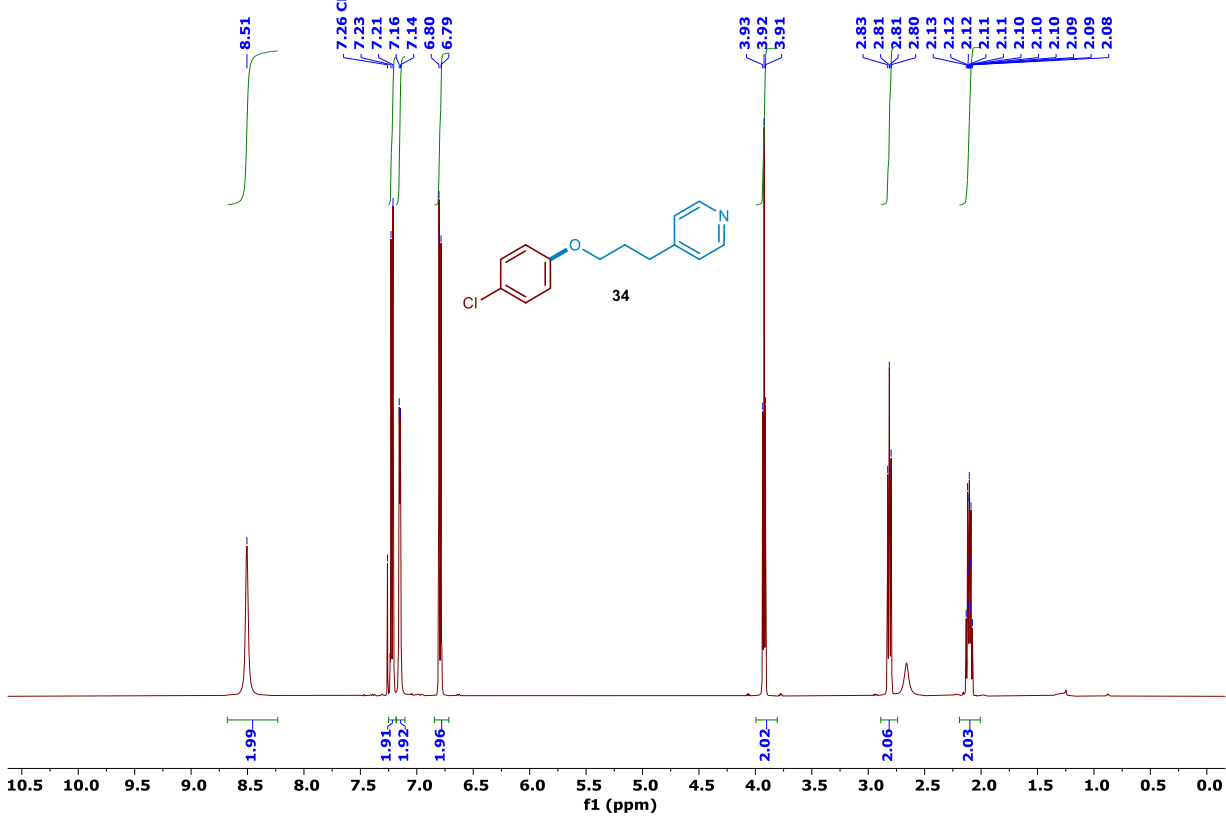


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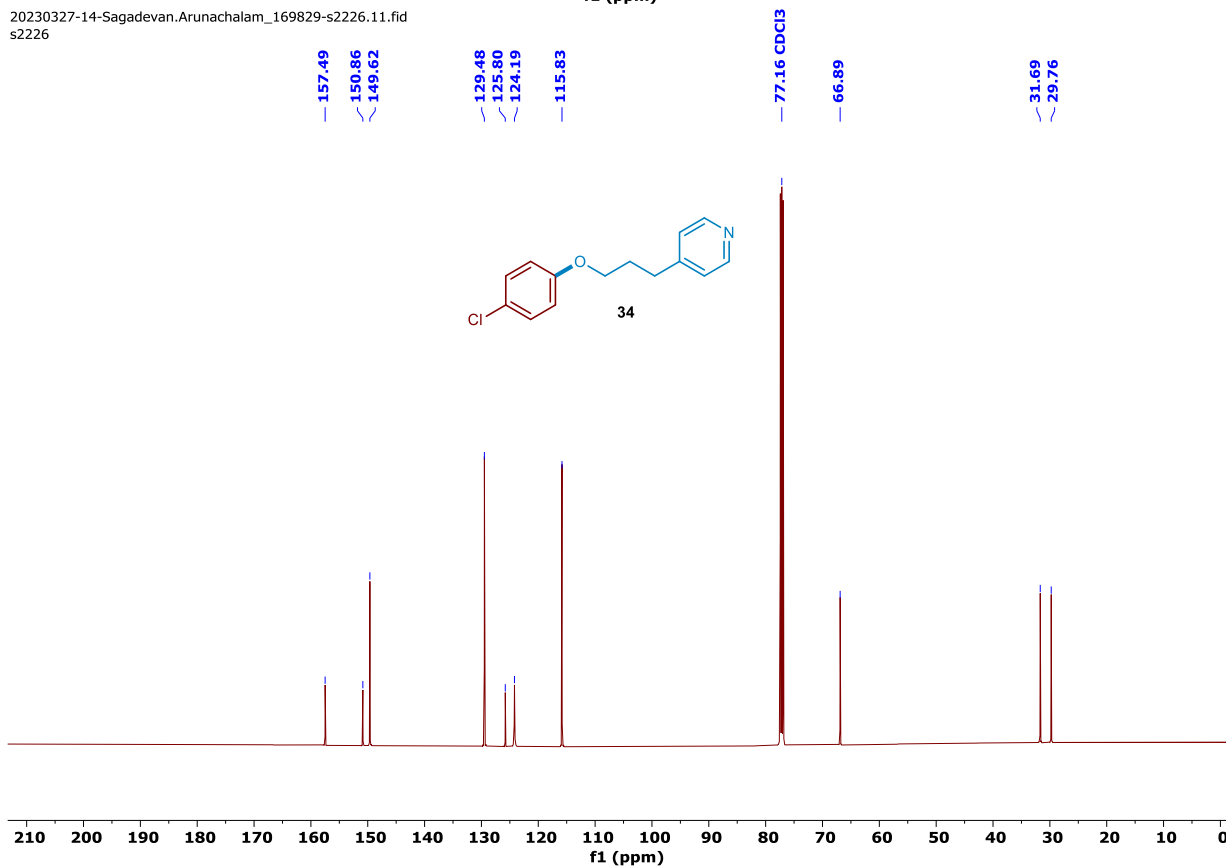




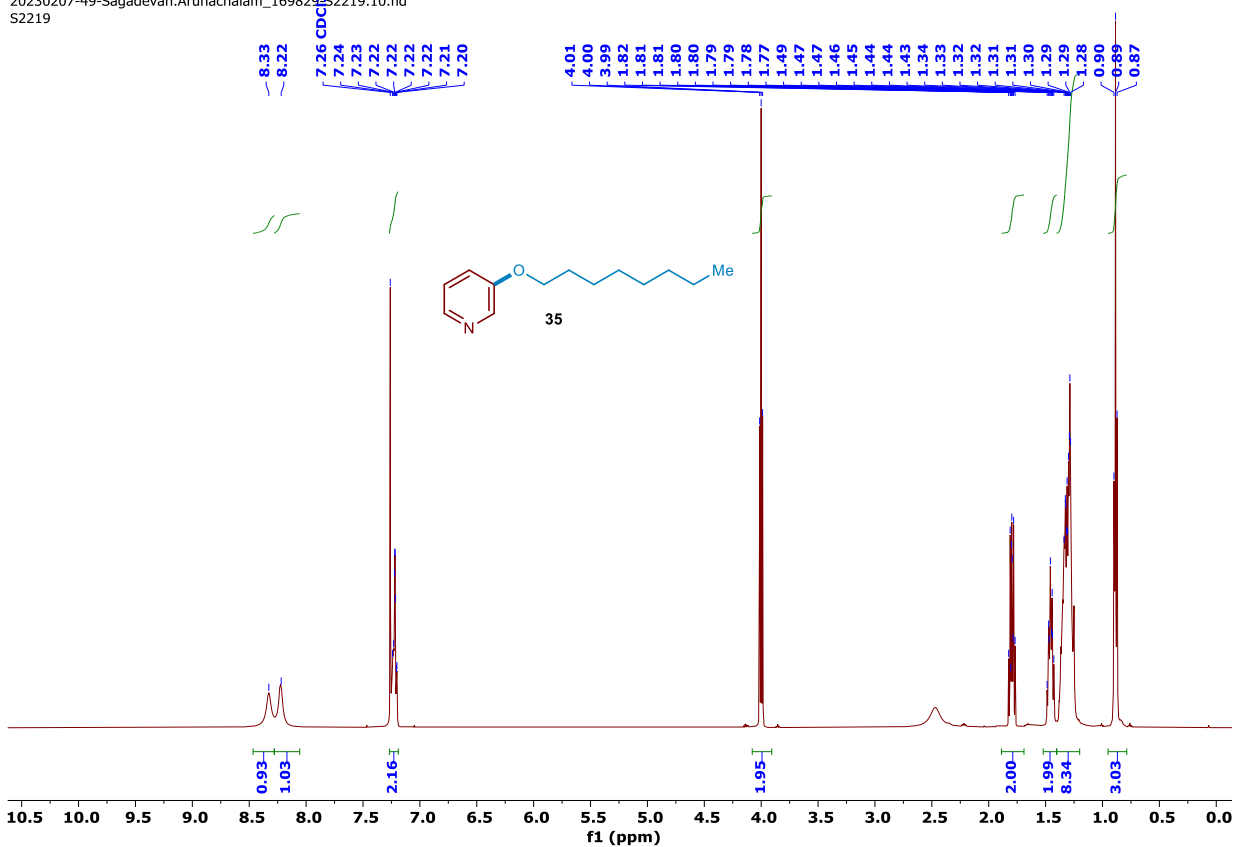
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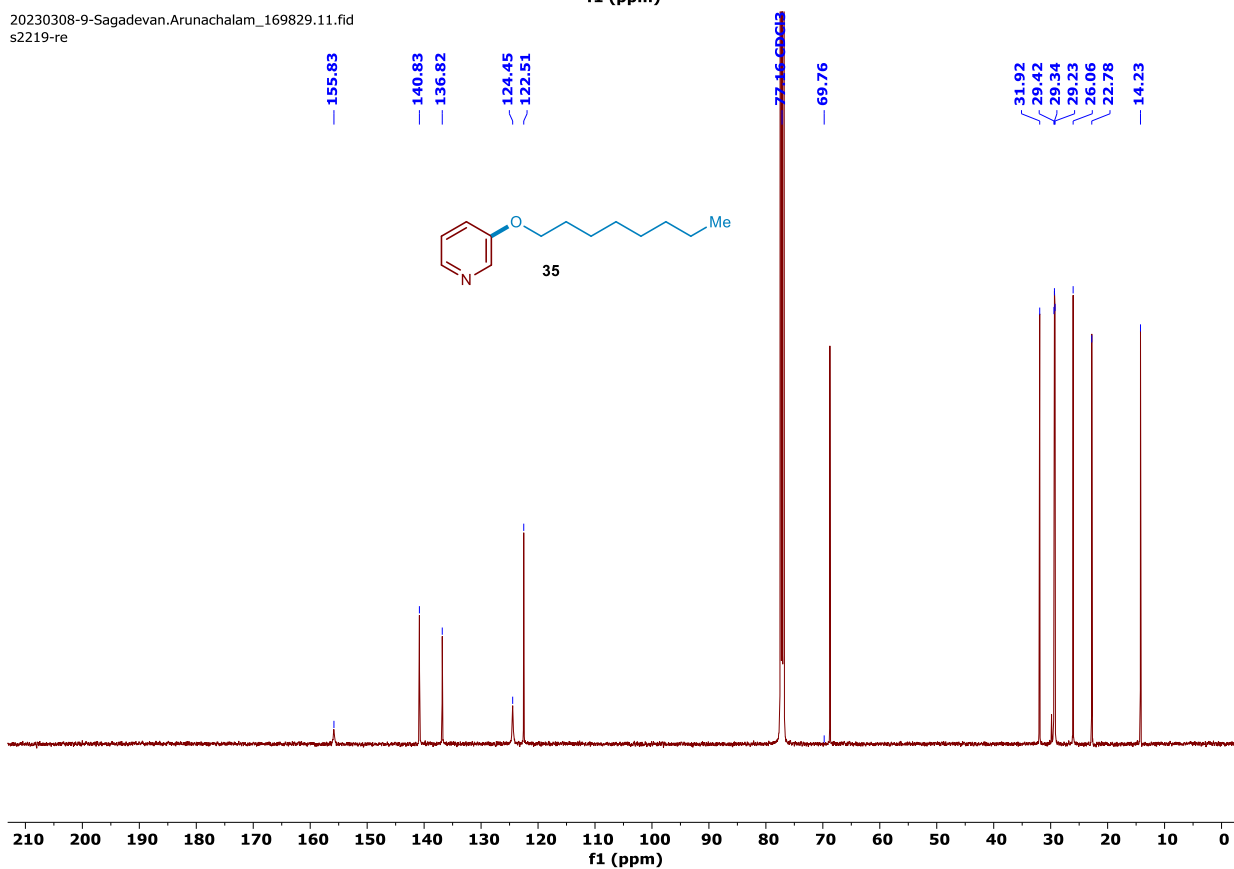
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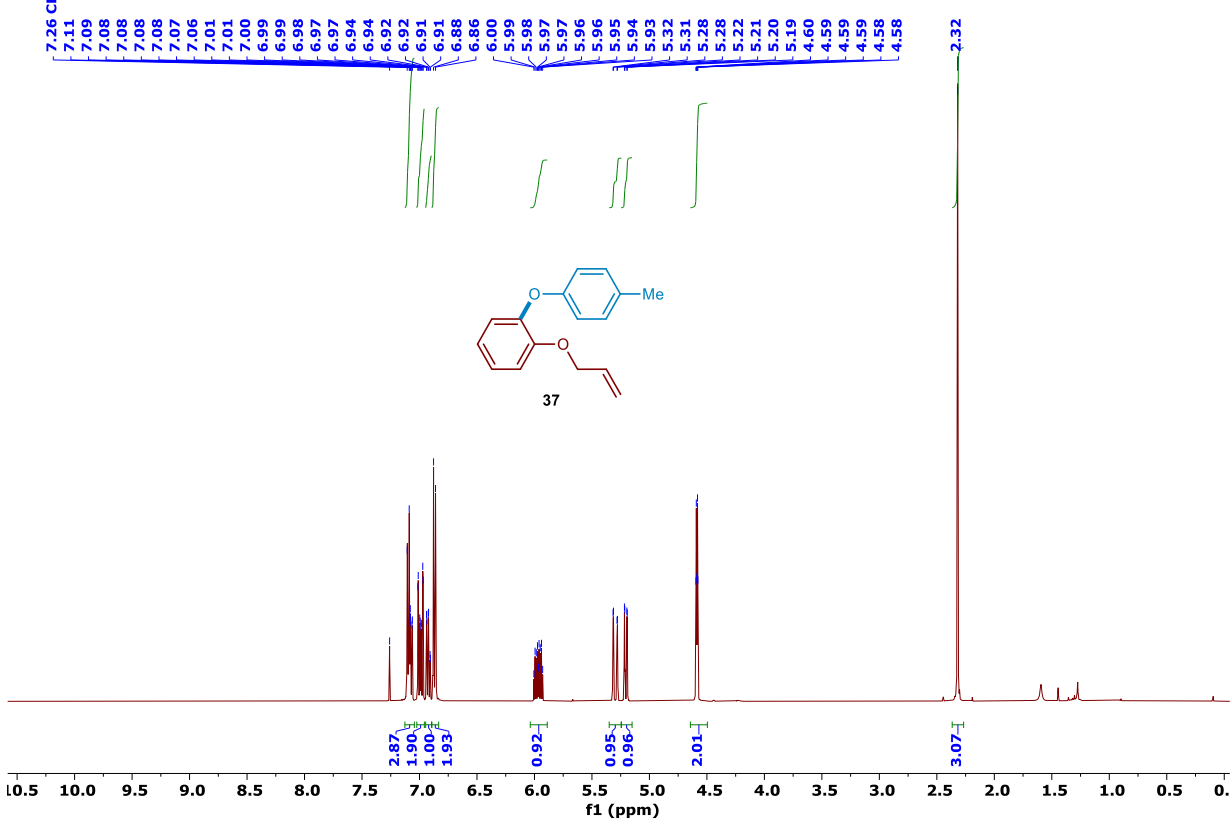
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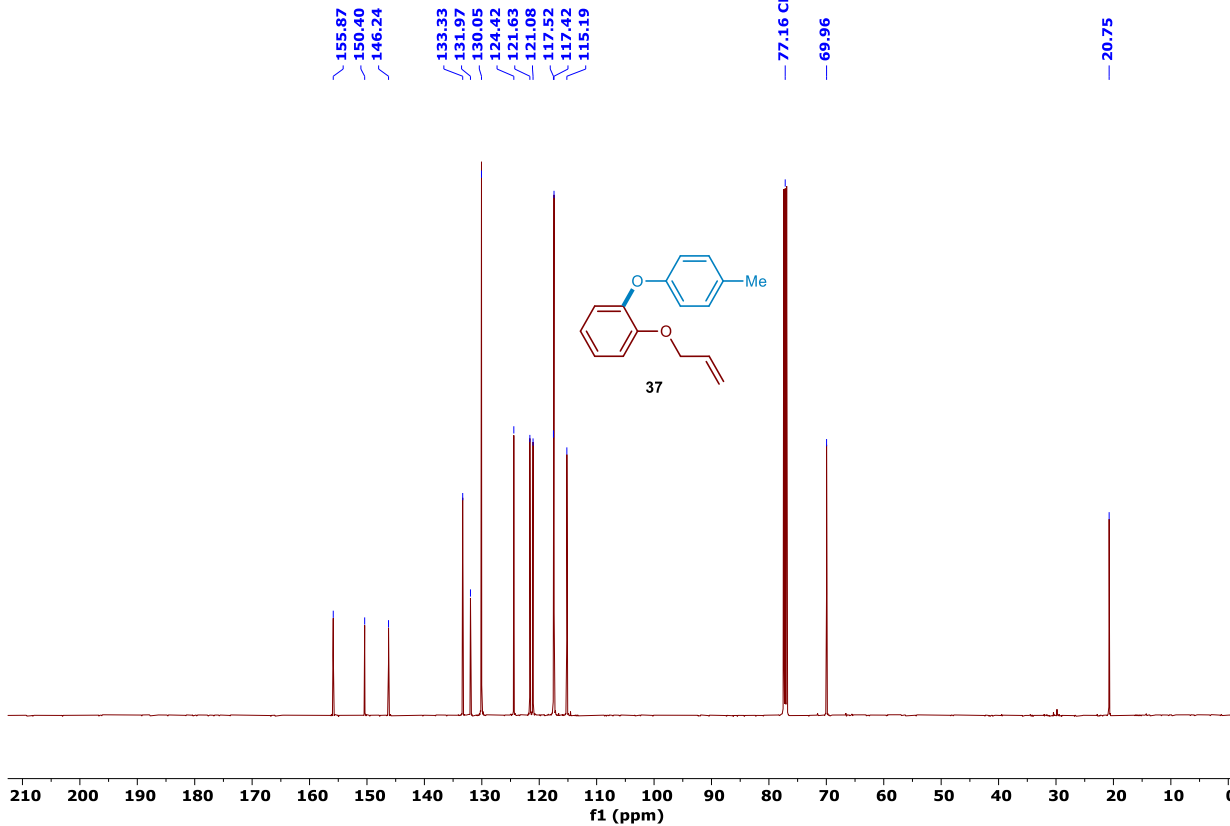
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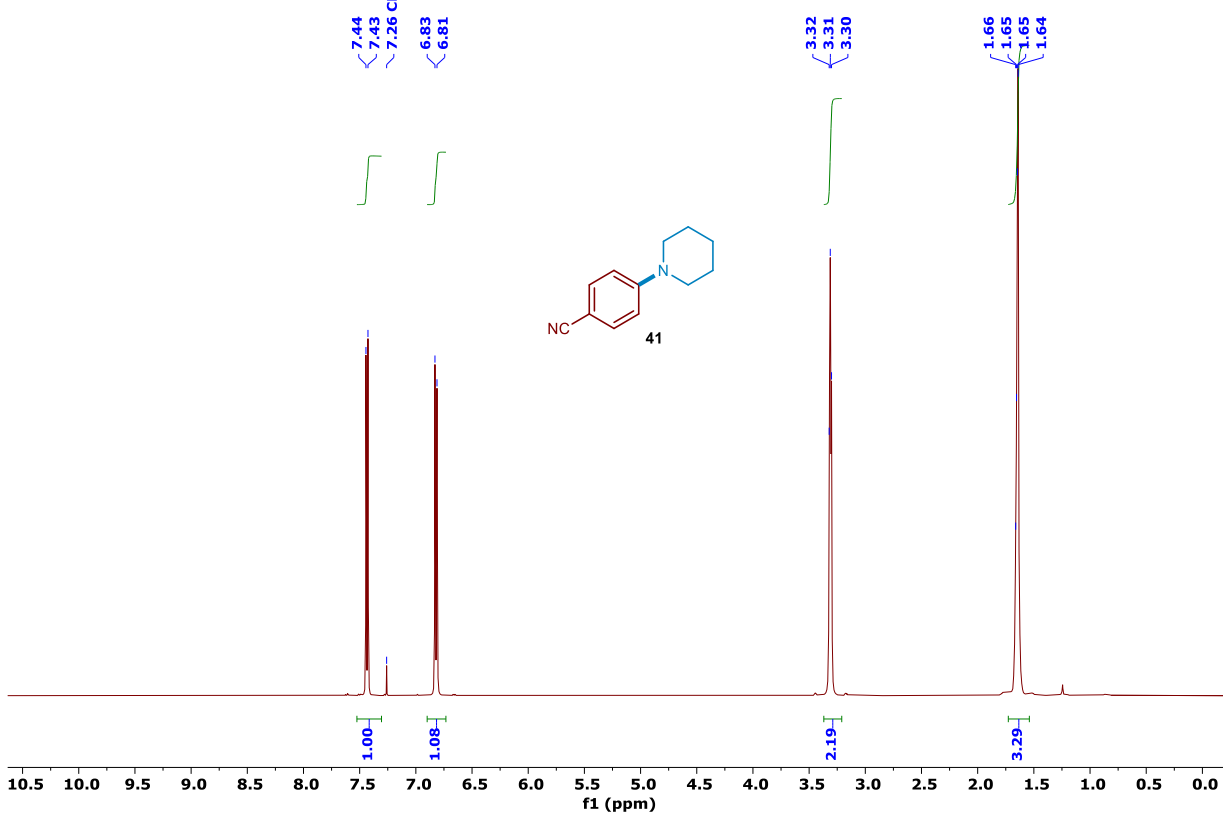
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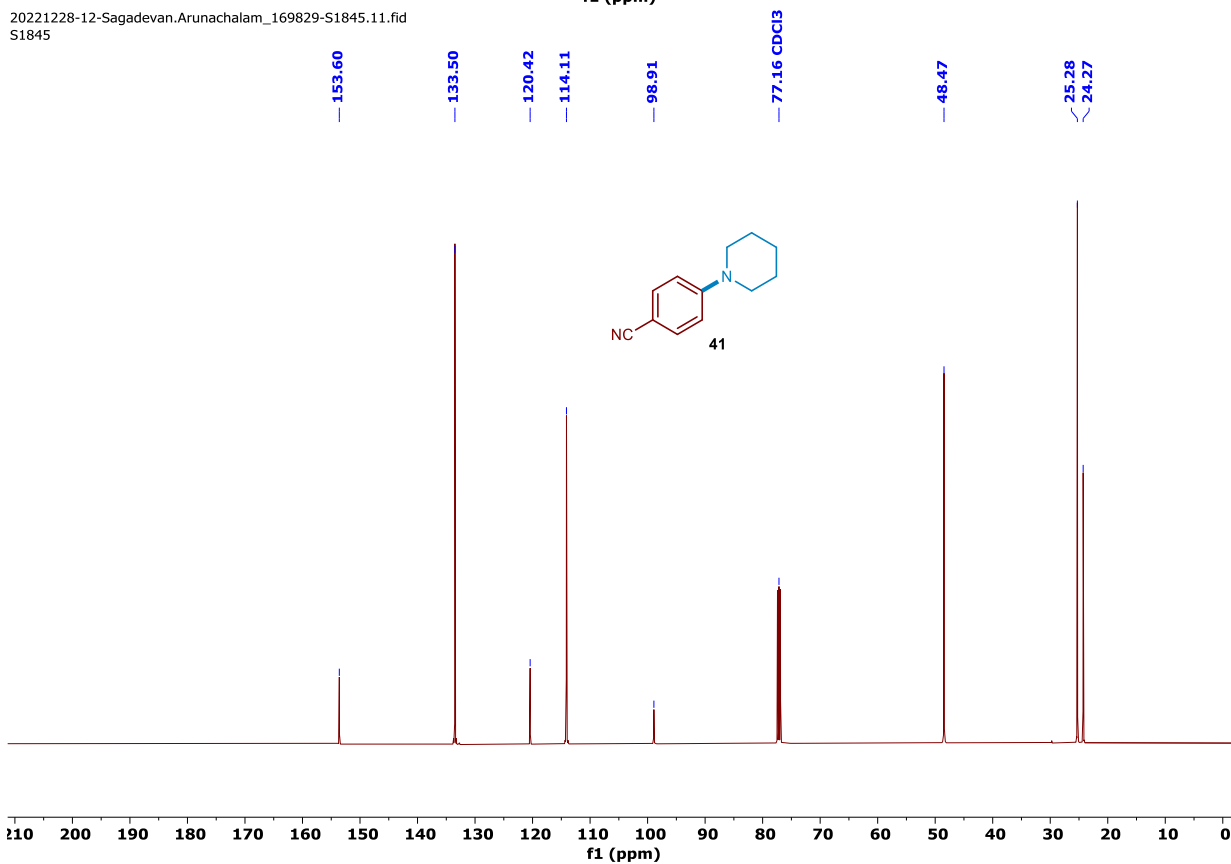
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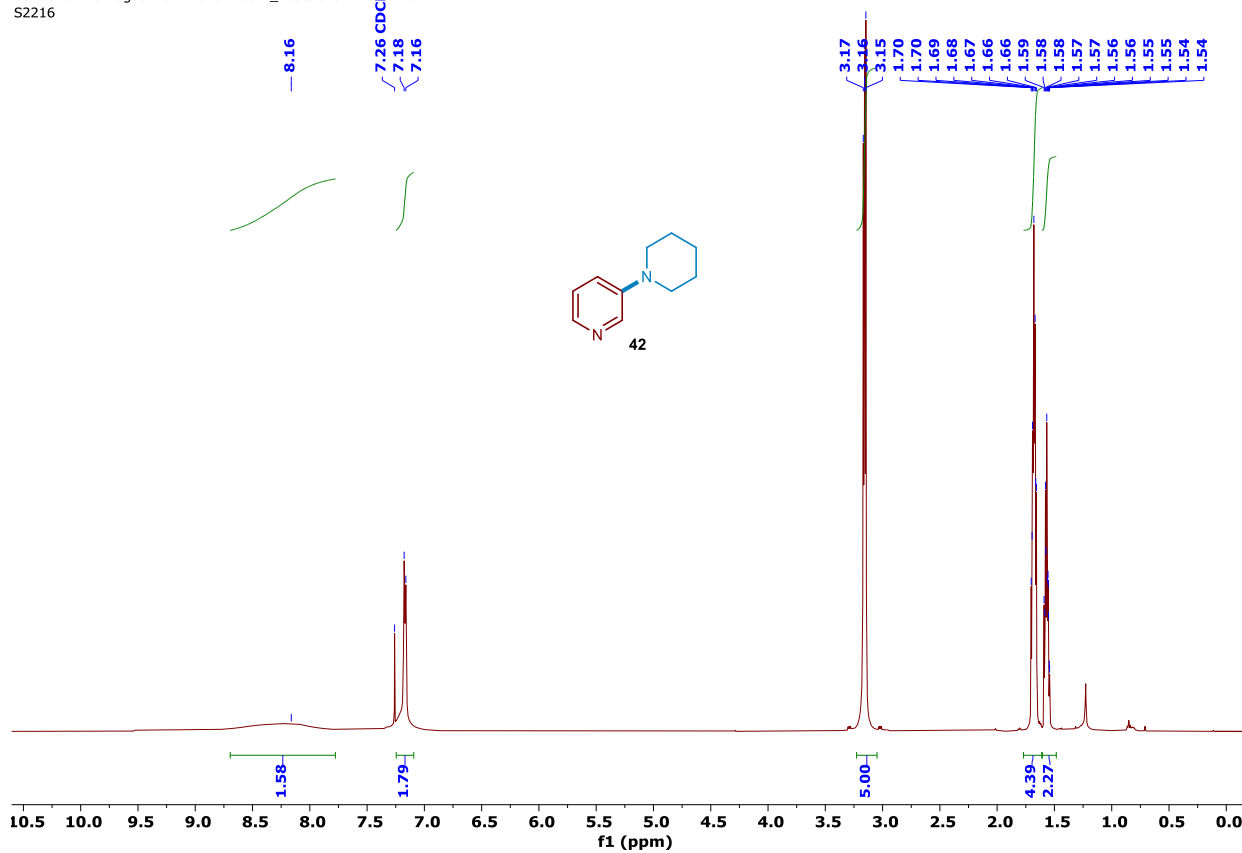
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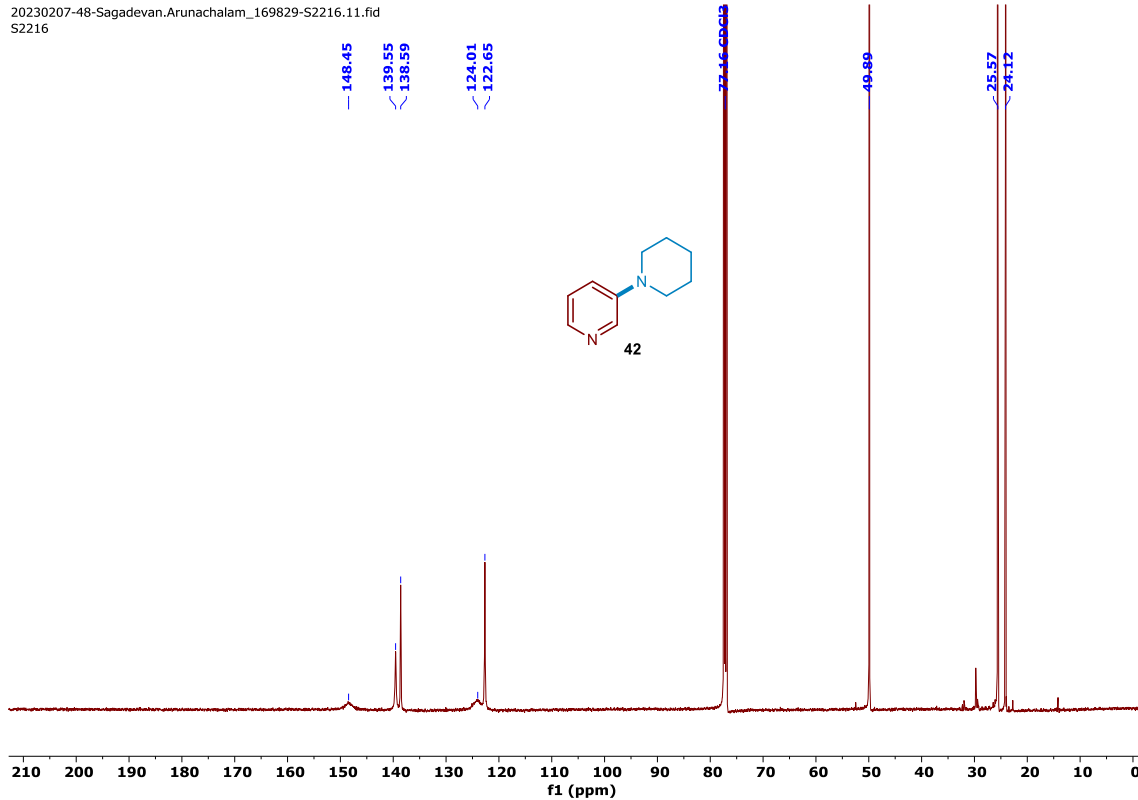
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S1845



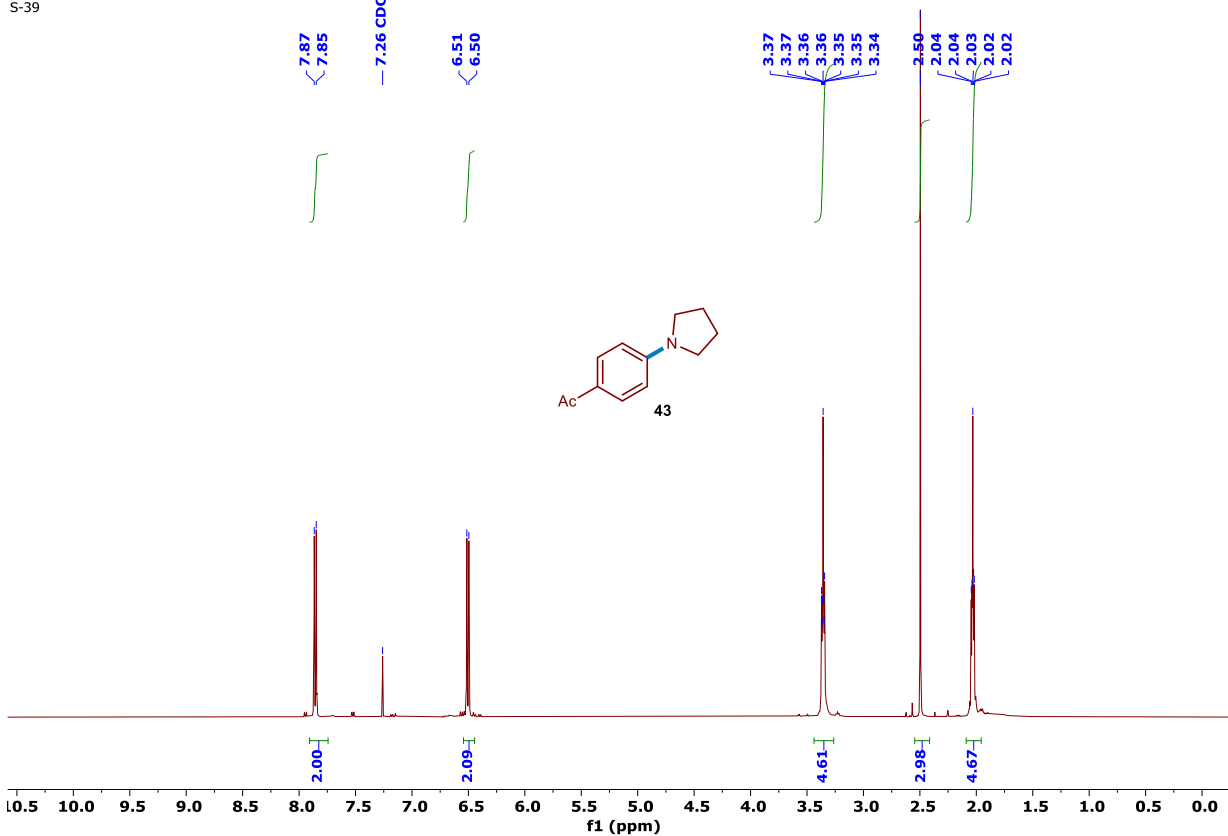
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S2216



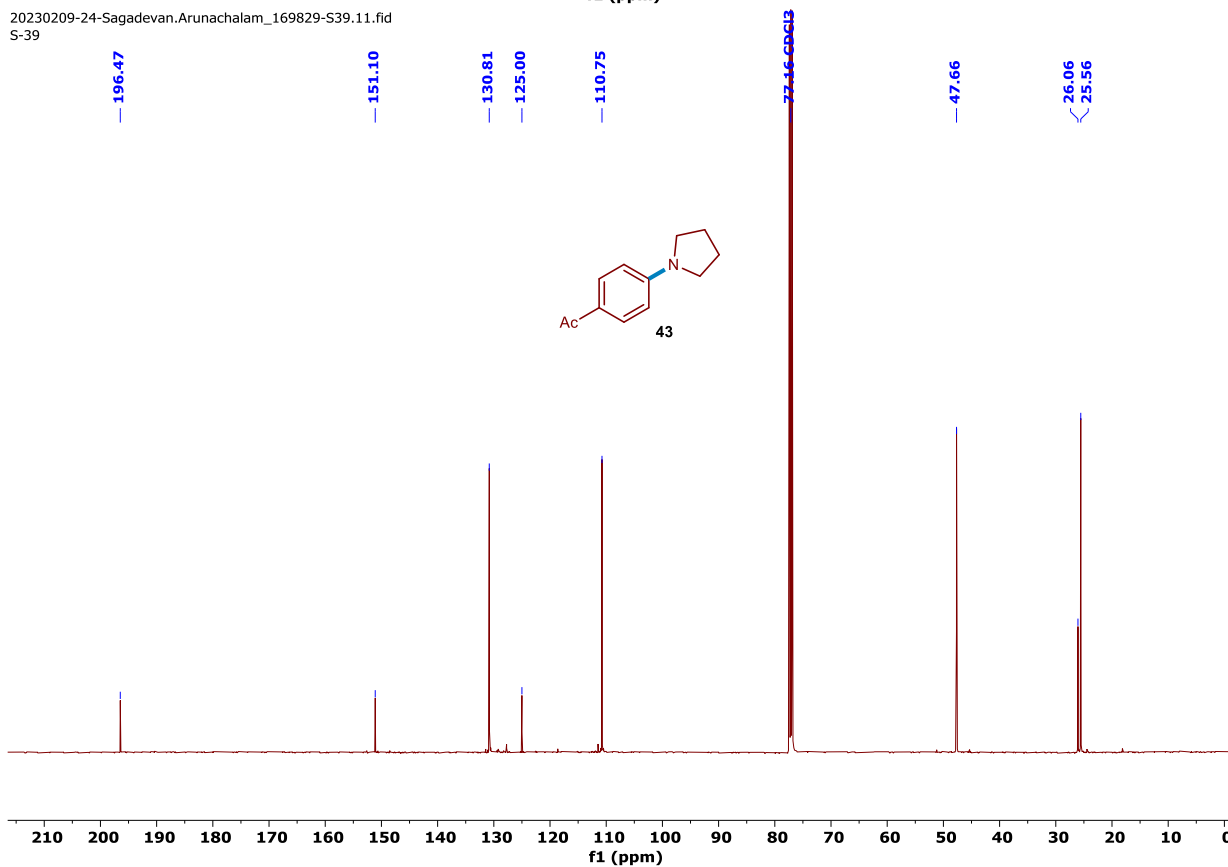
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S2216



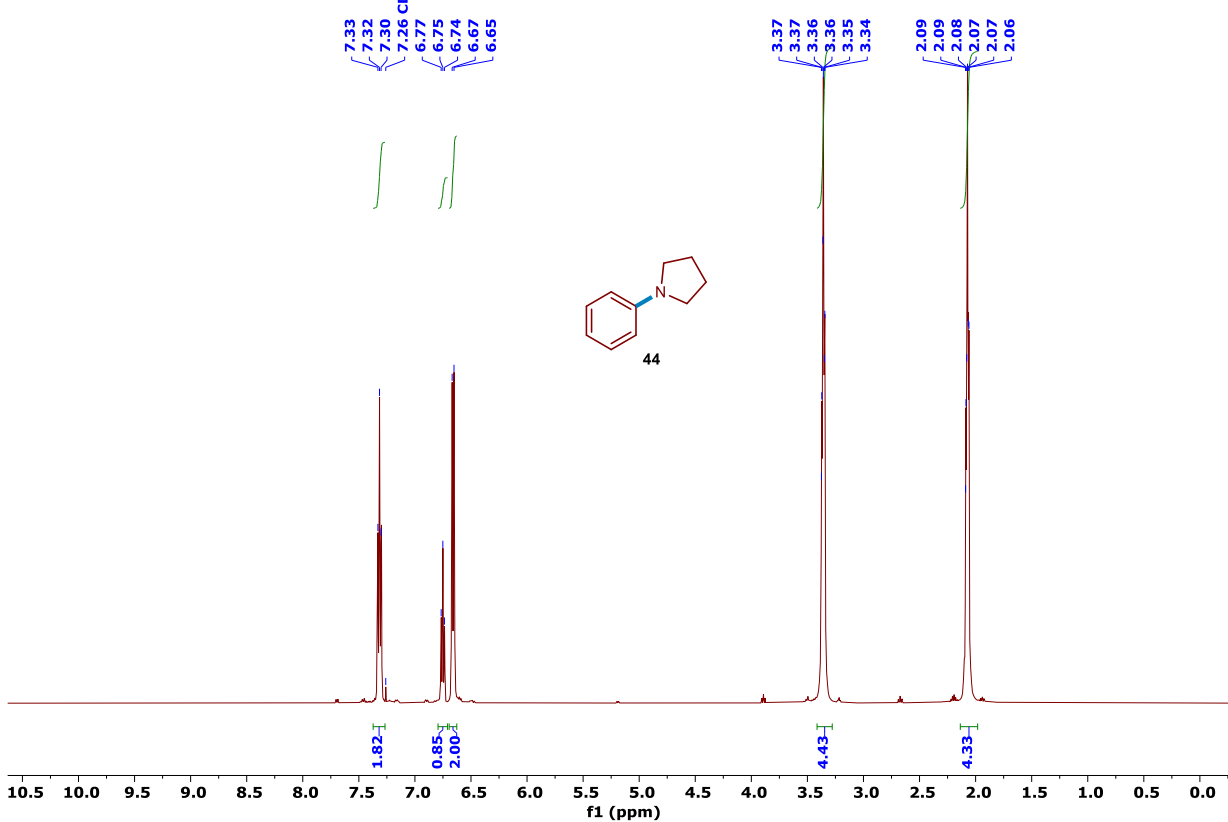
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S-39



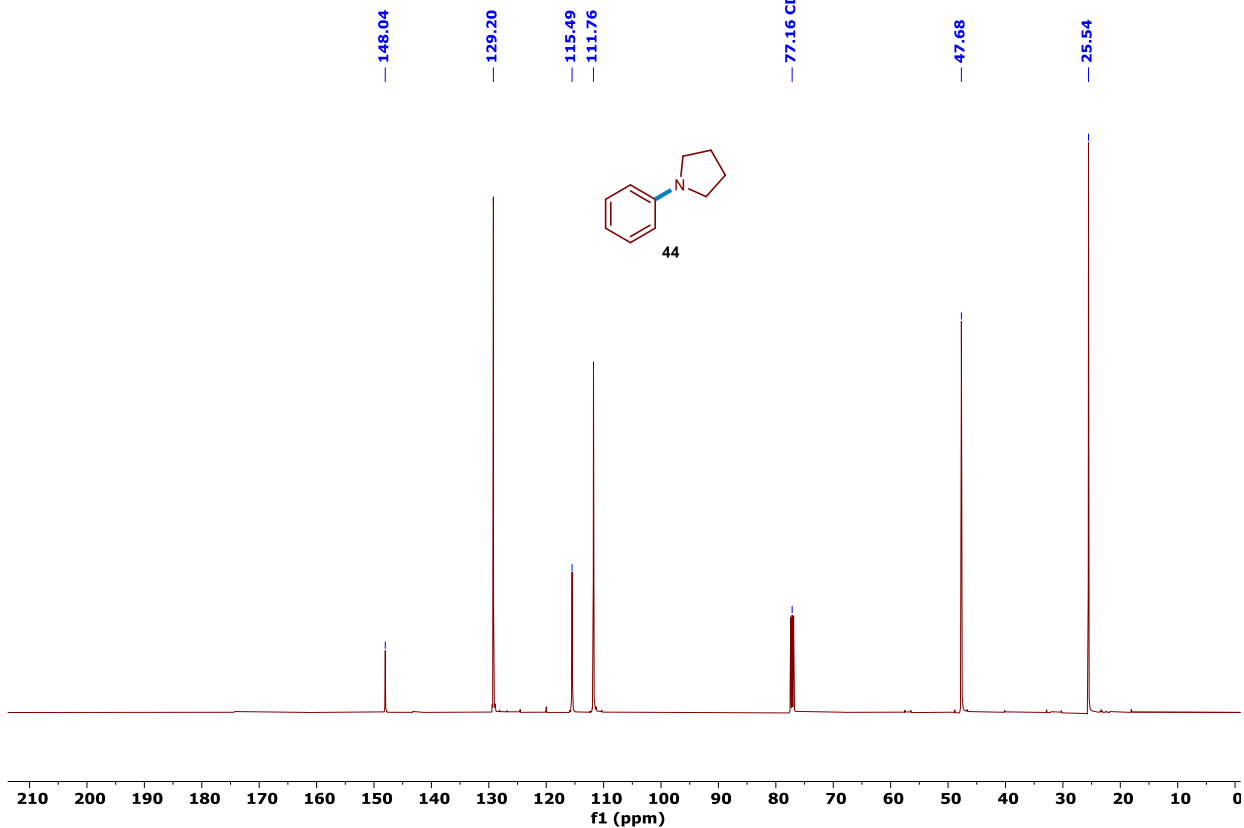
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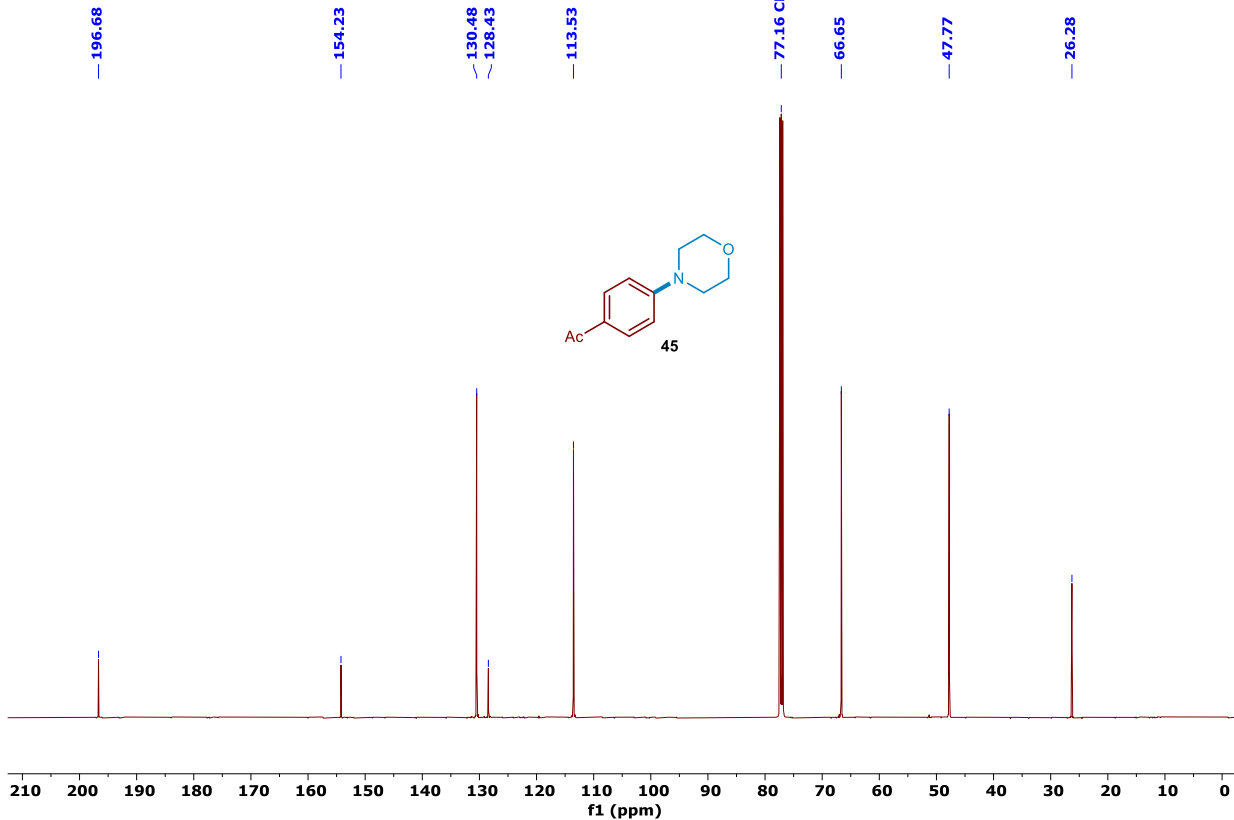
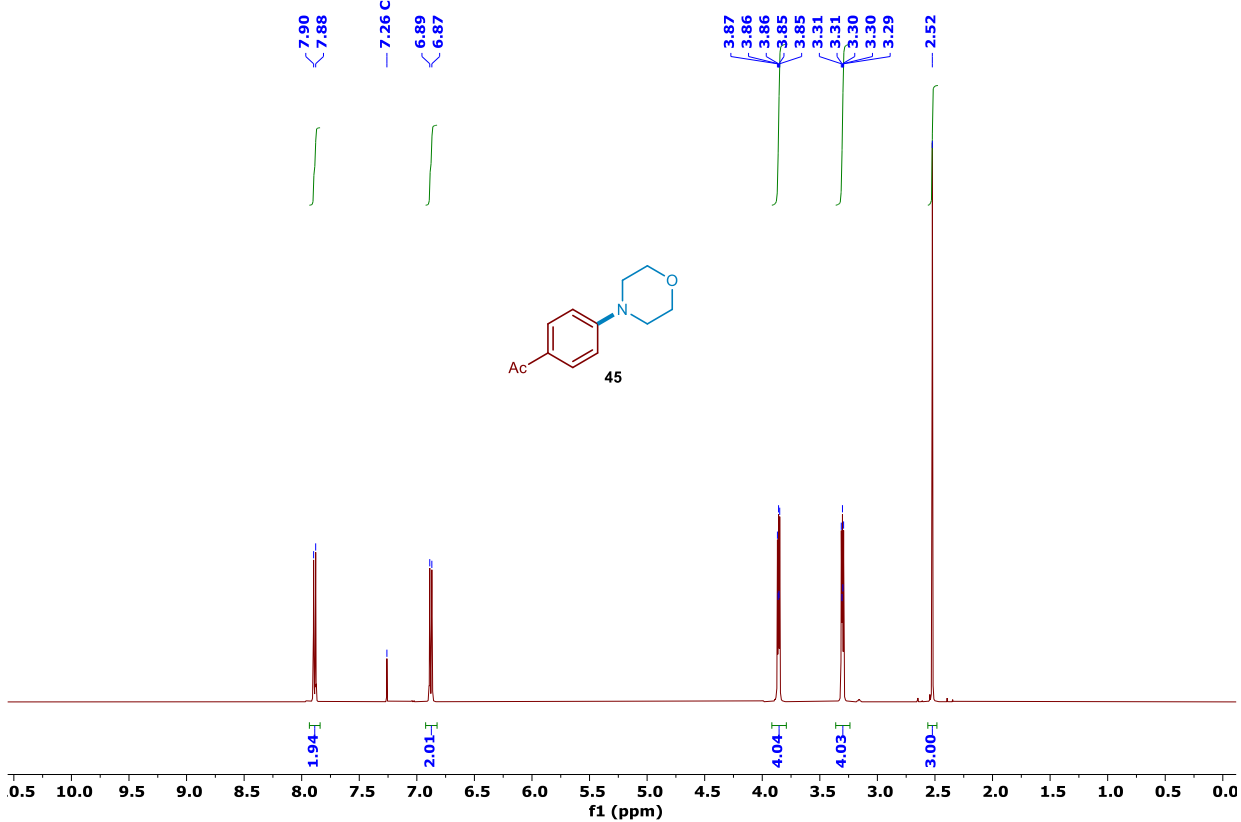


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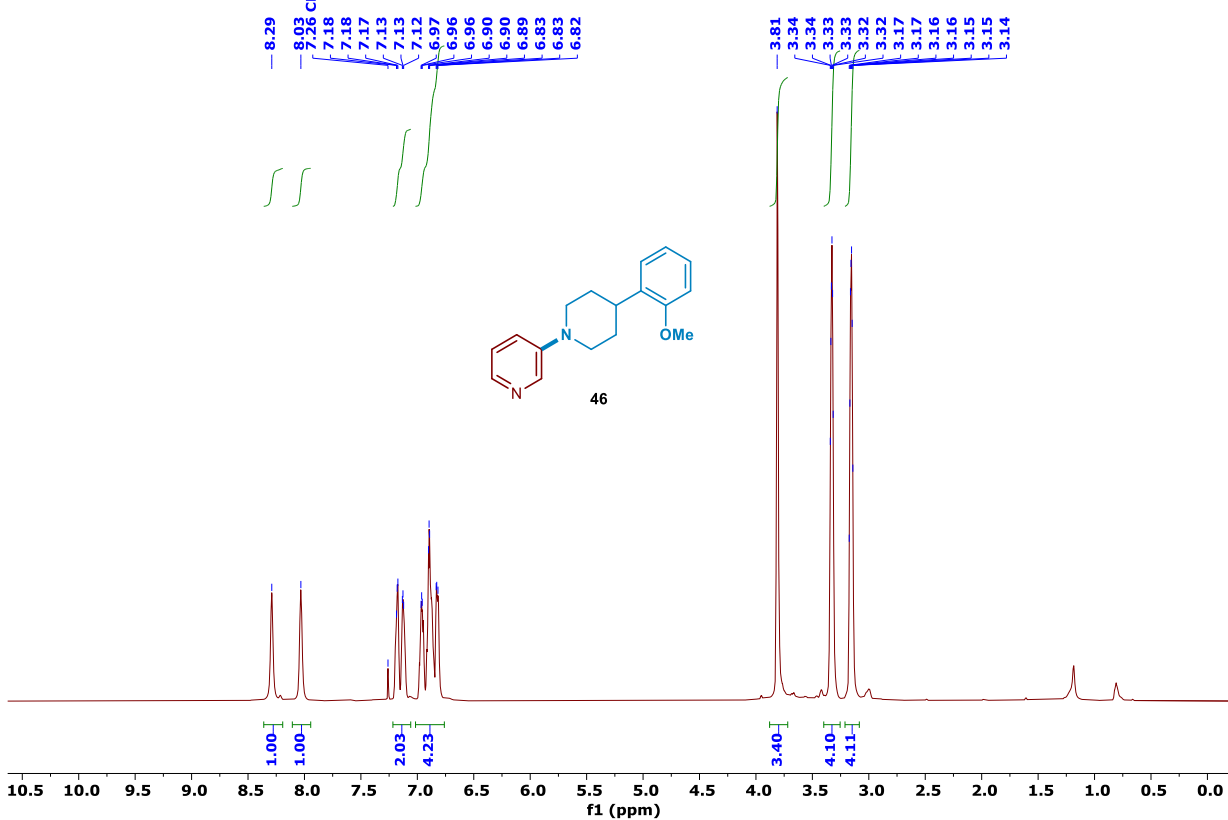
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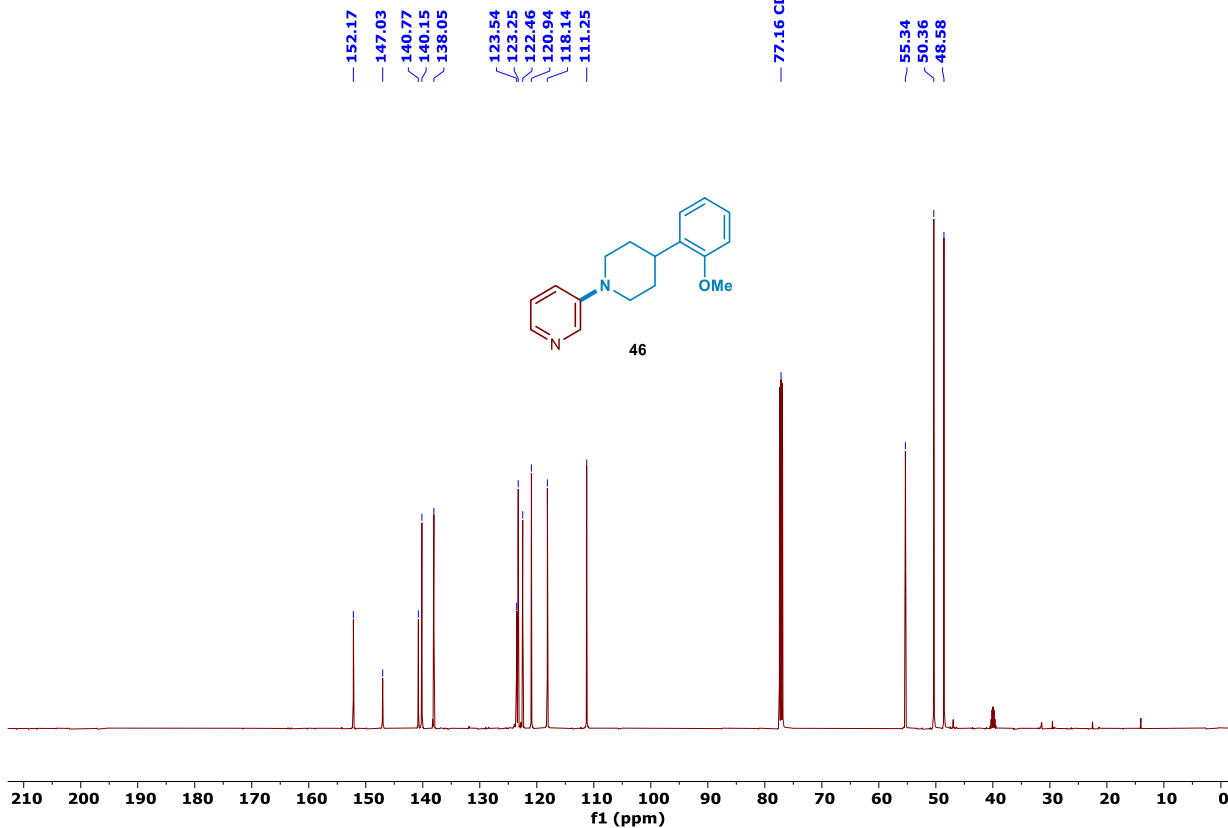




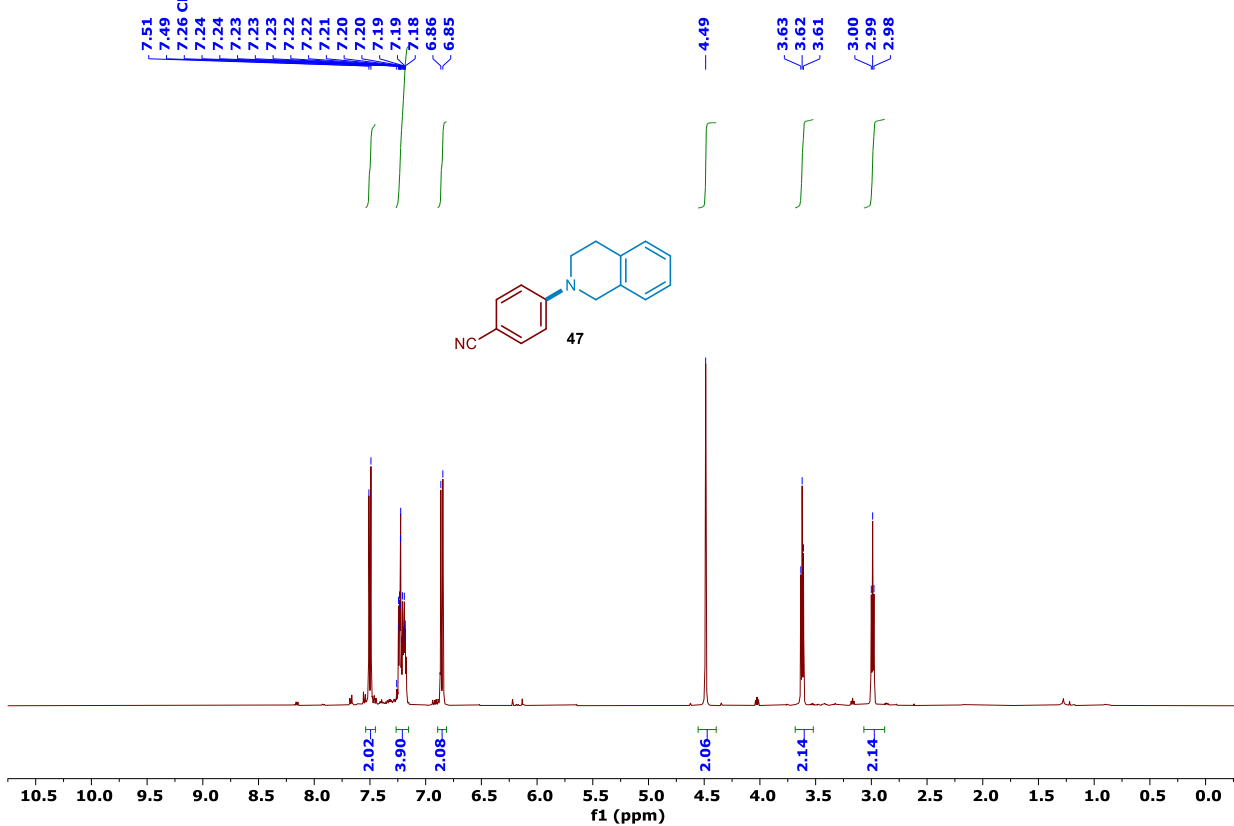
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S2217



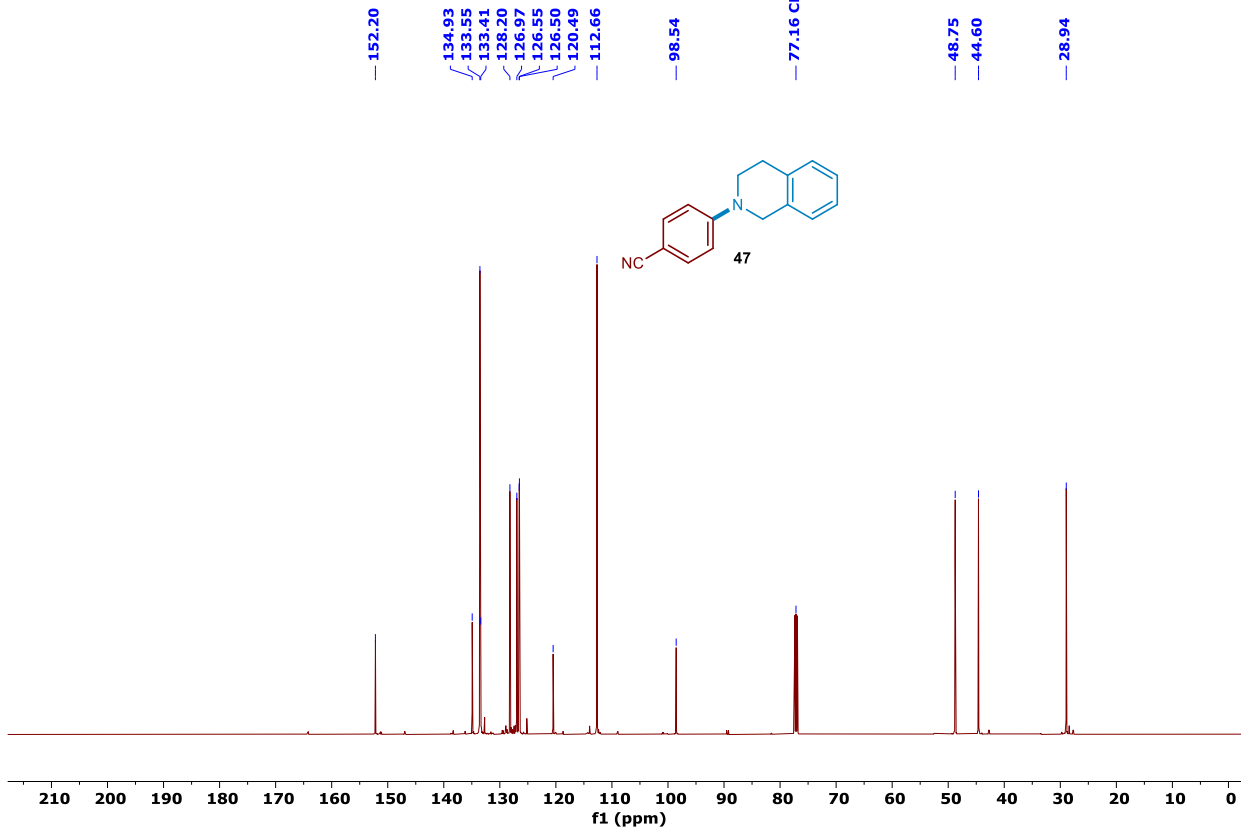
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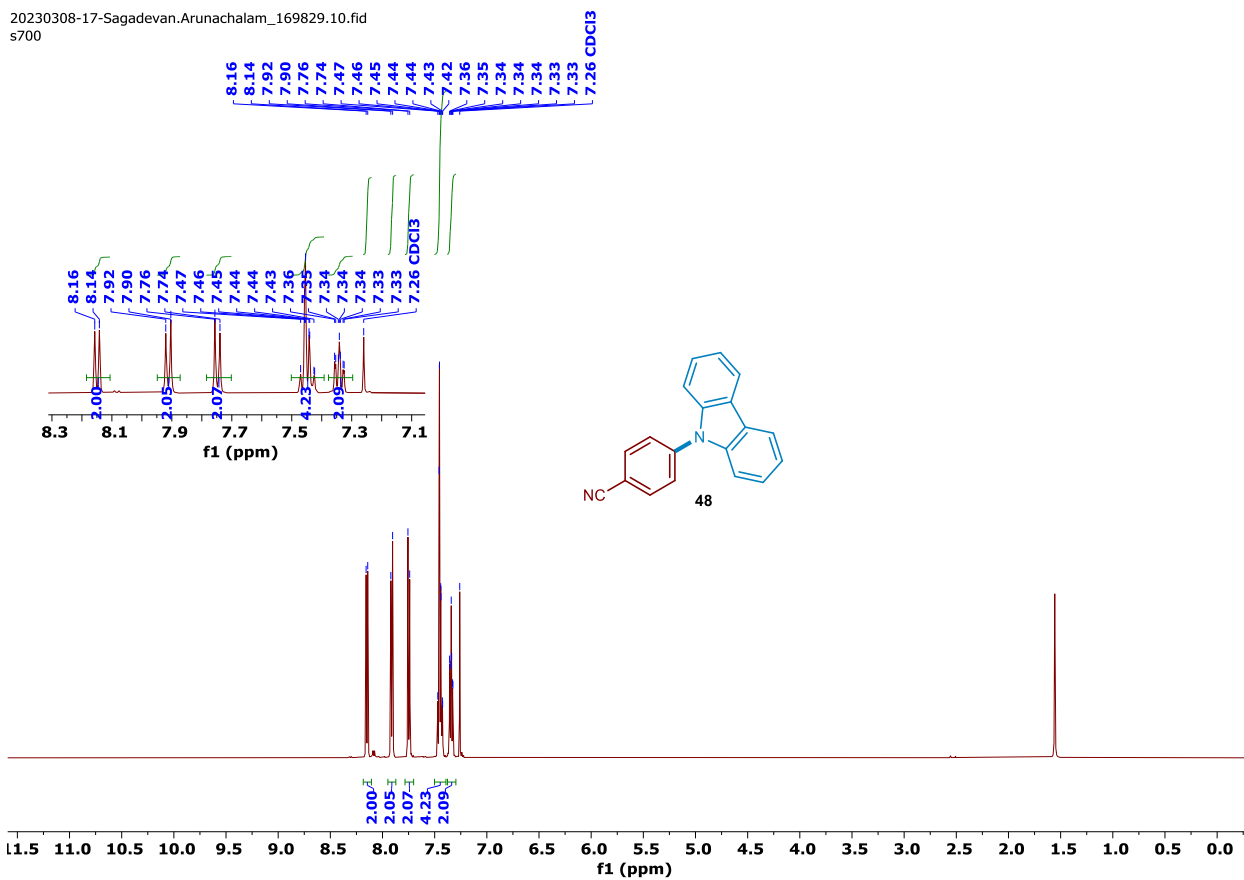
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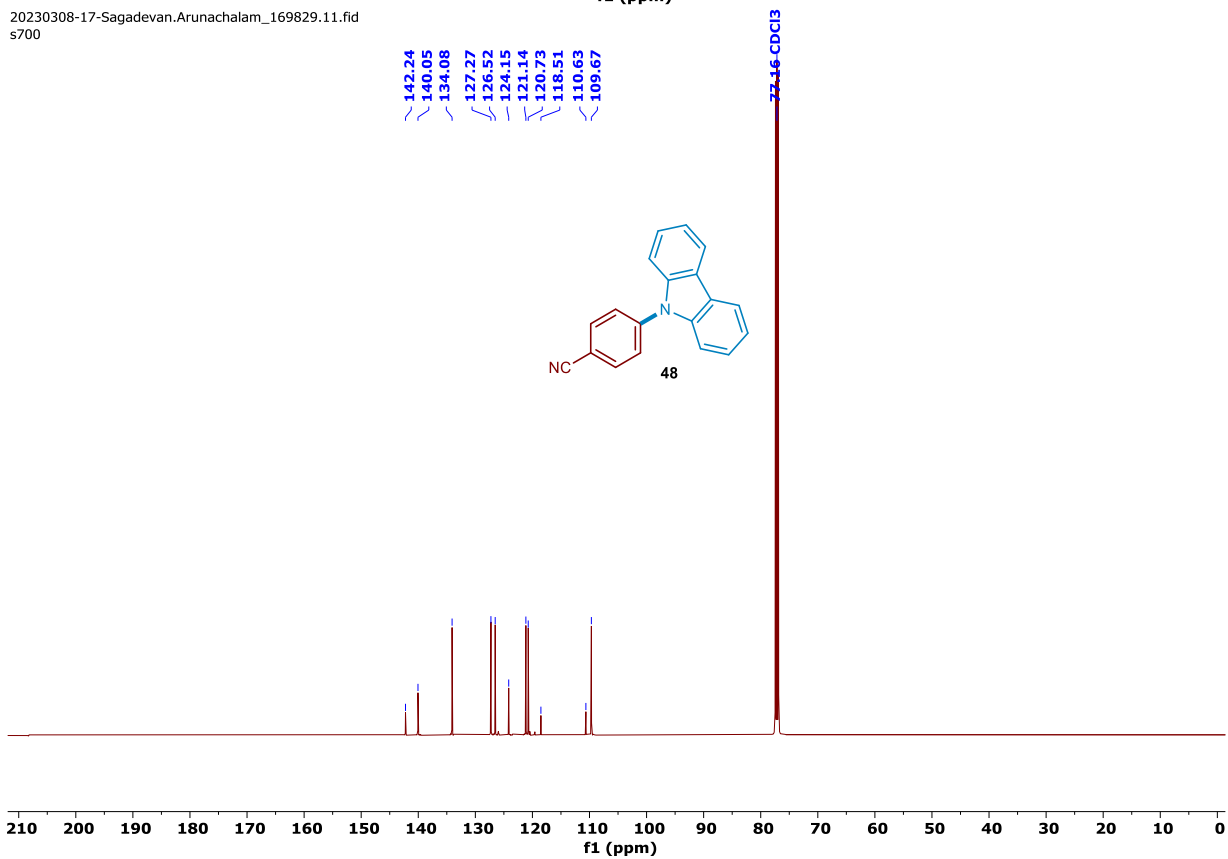
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S2196



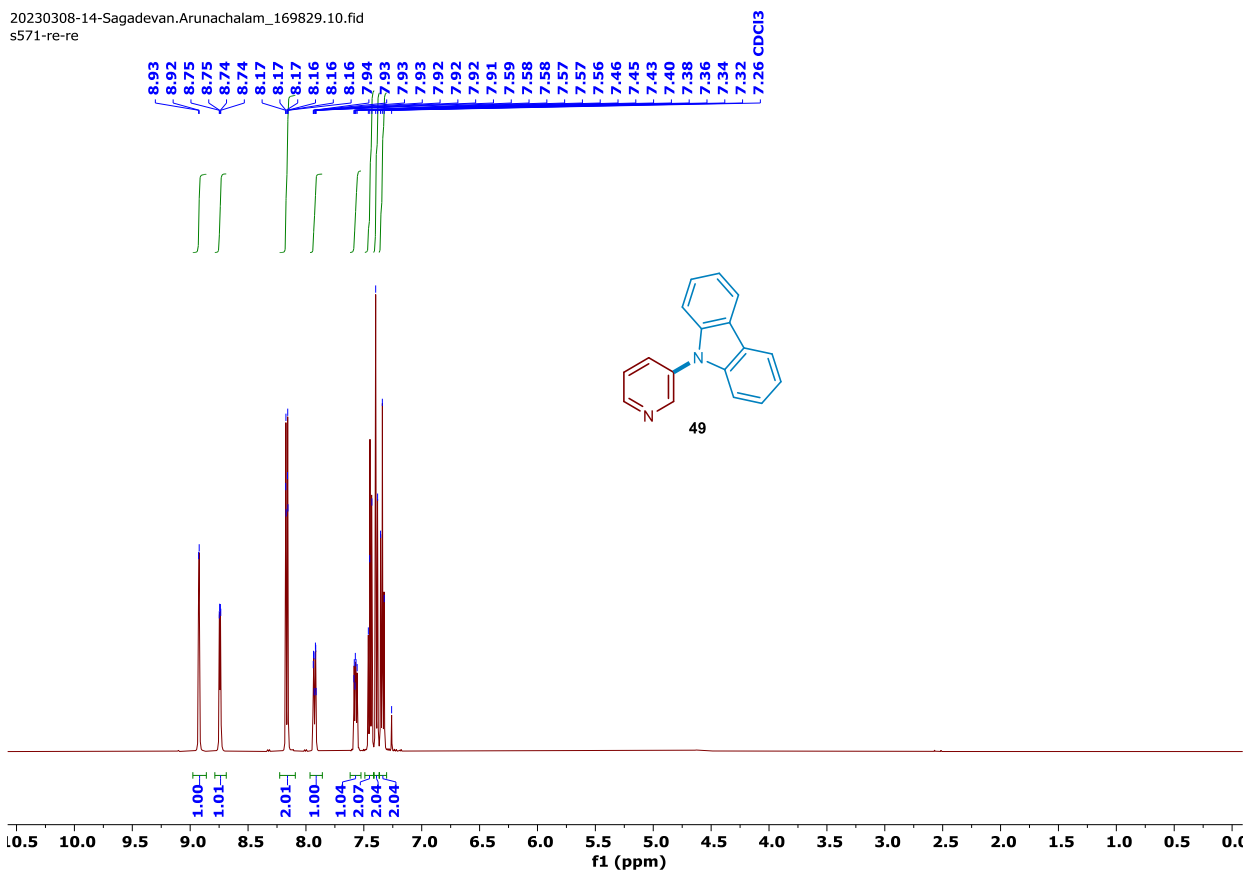
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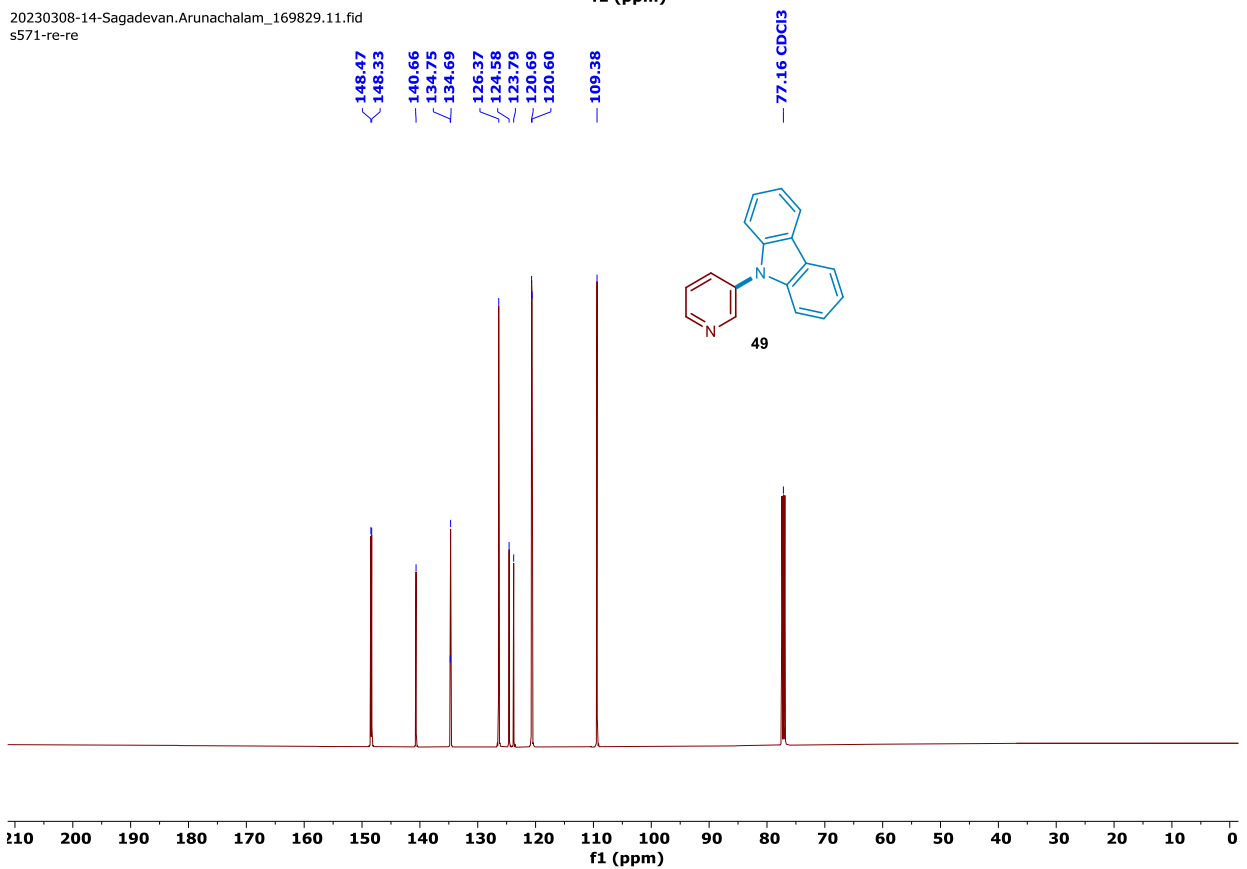
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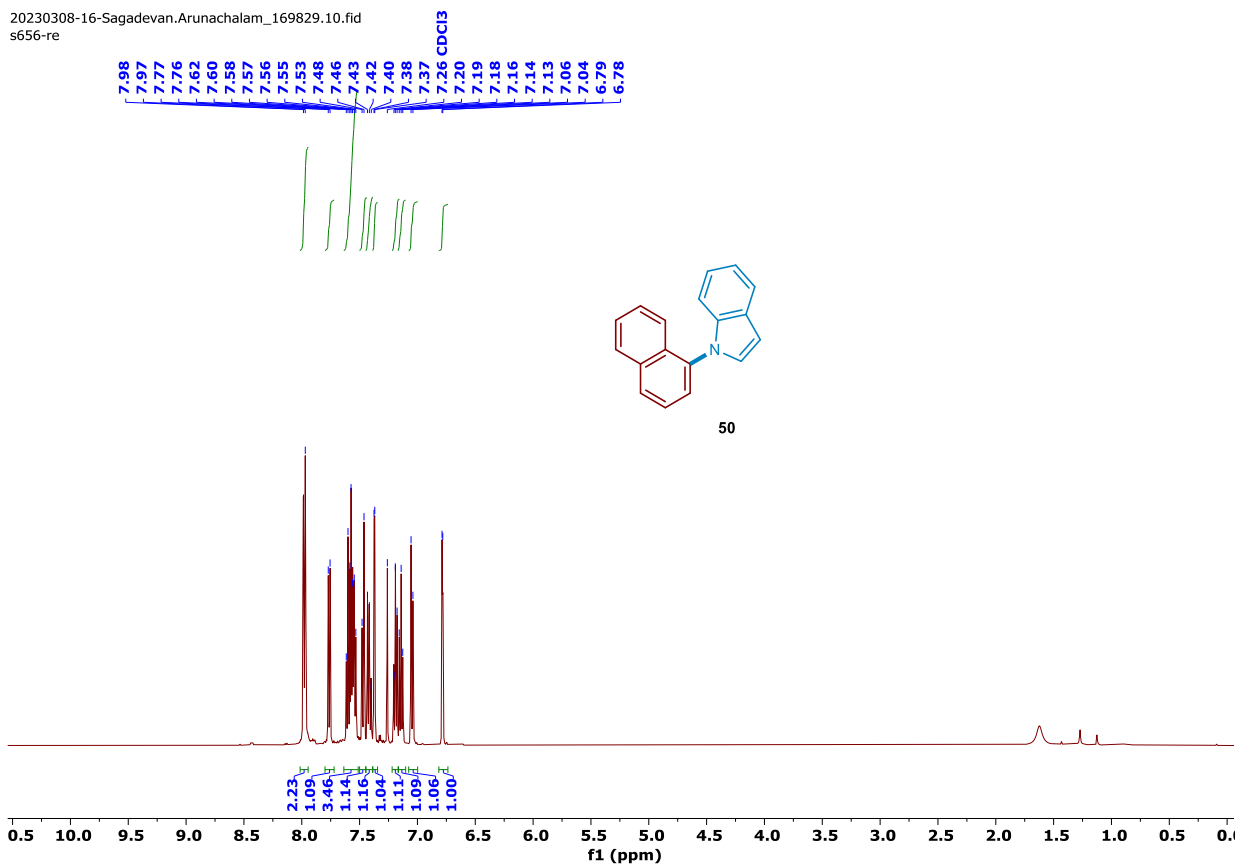
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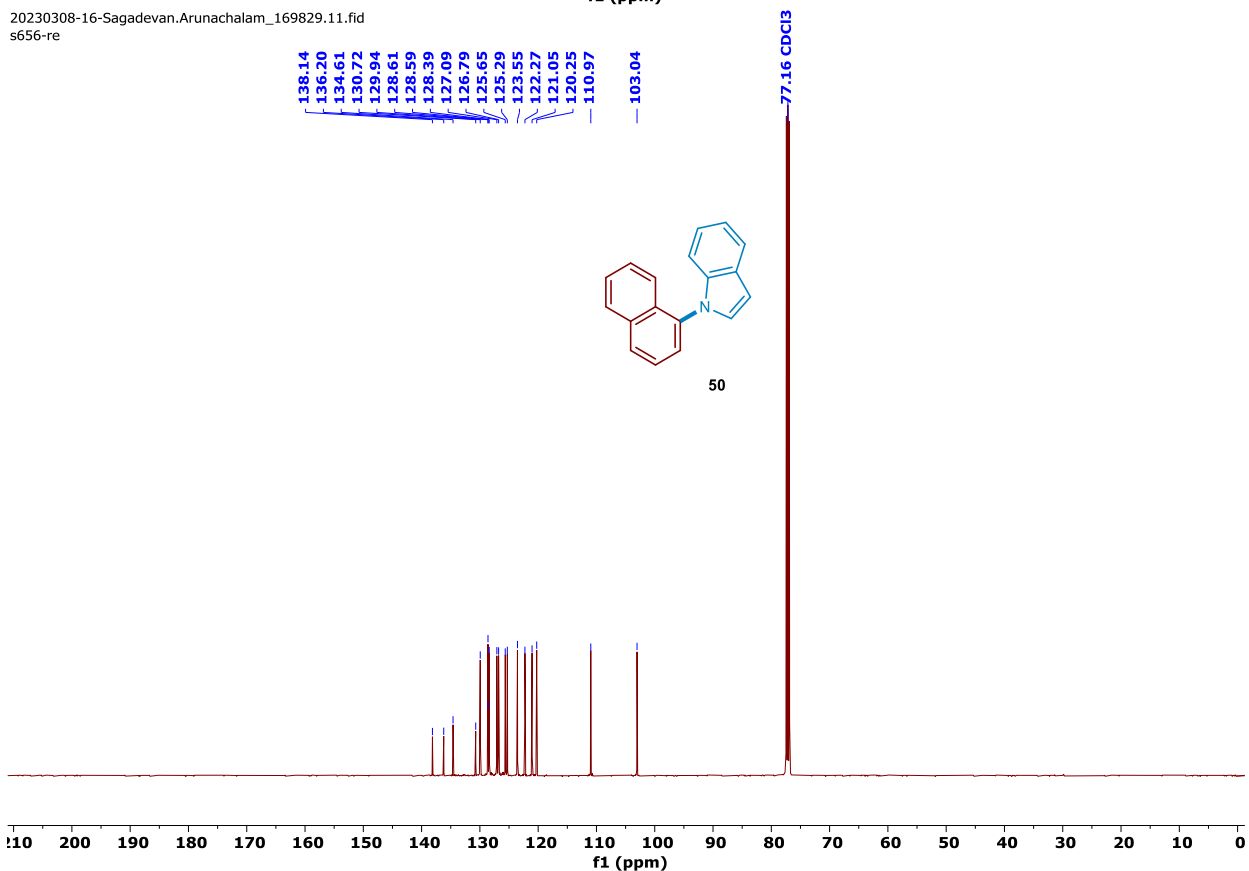
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s571-re-re



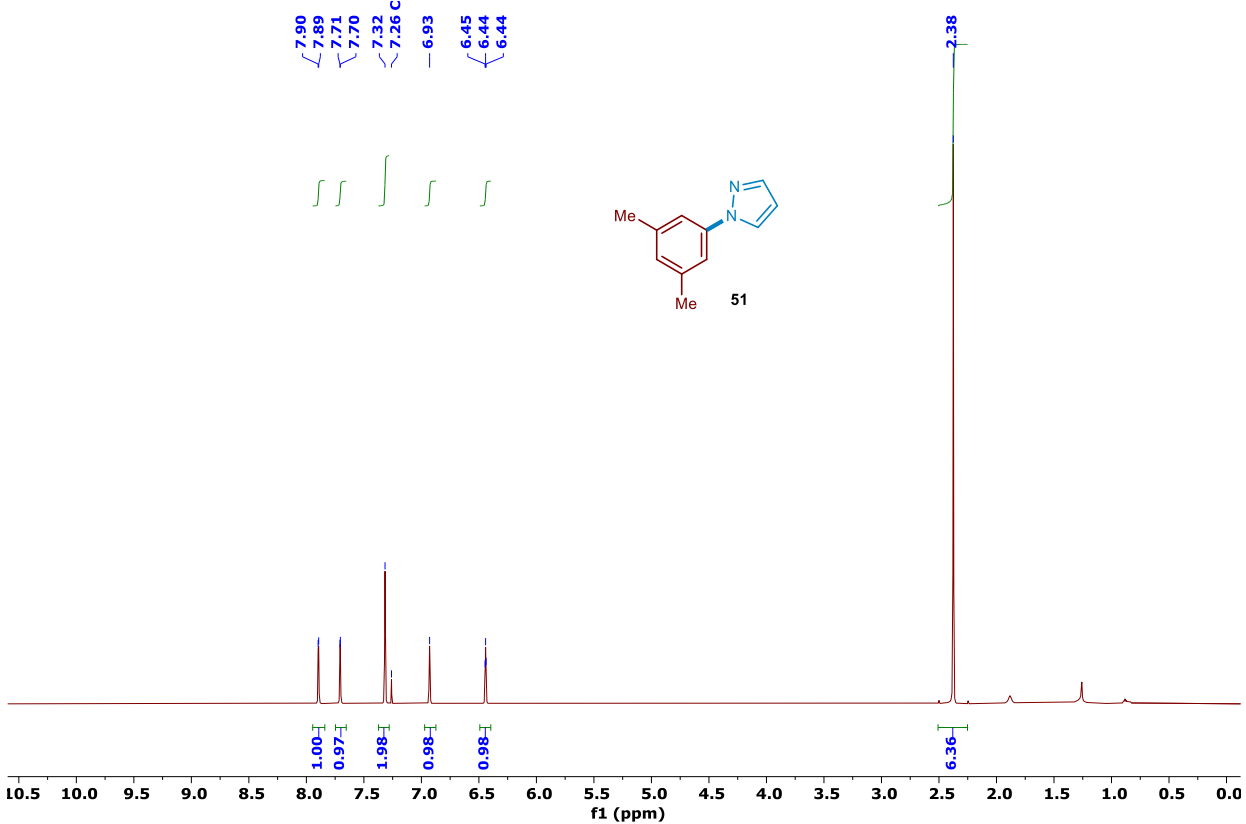
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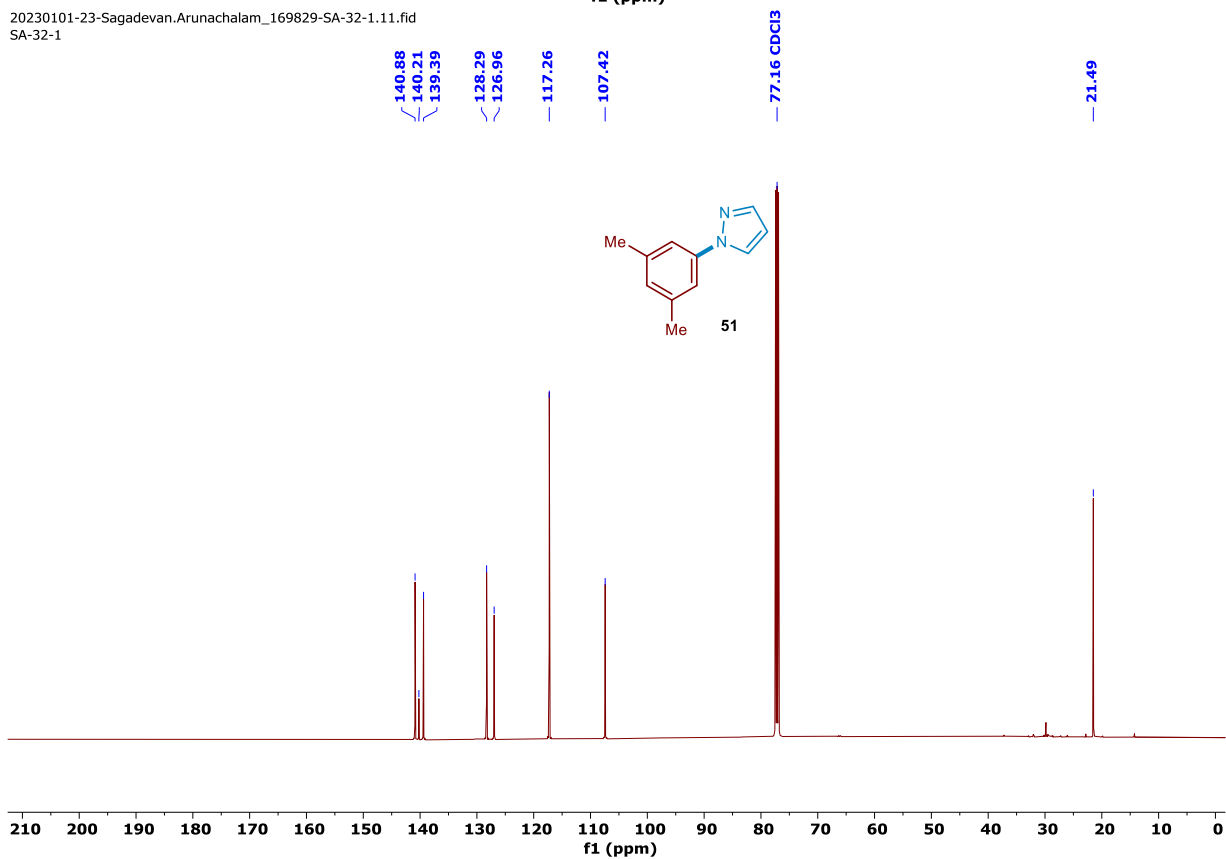
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s656-re



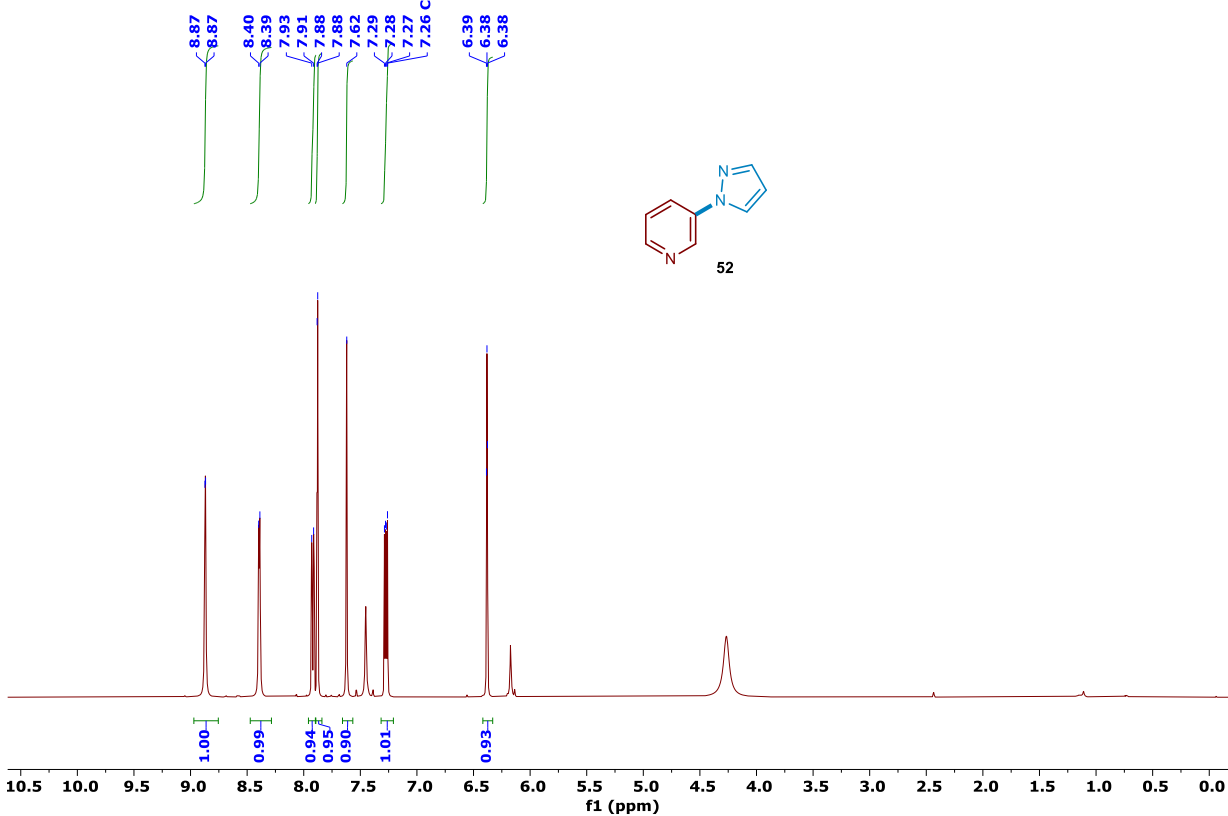
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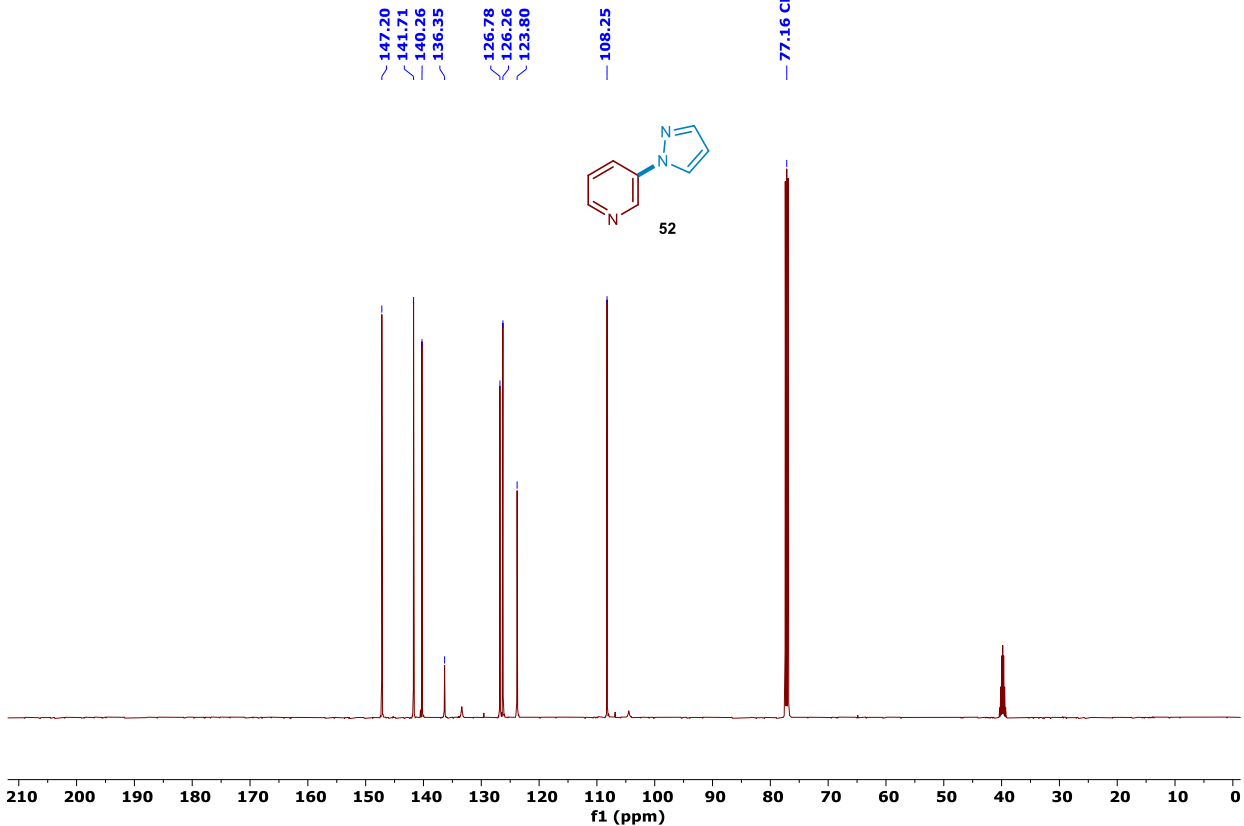
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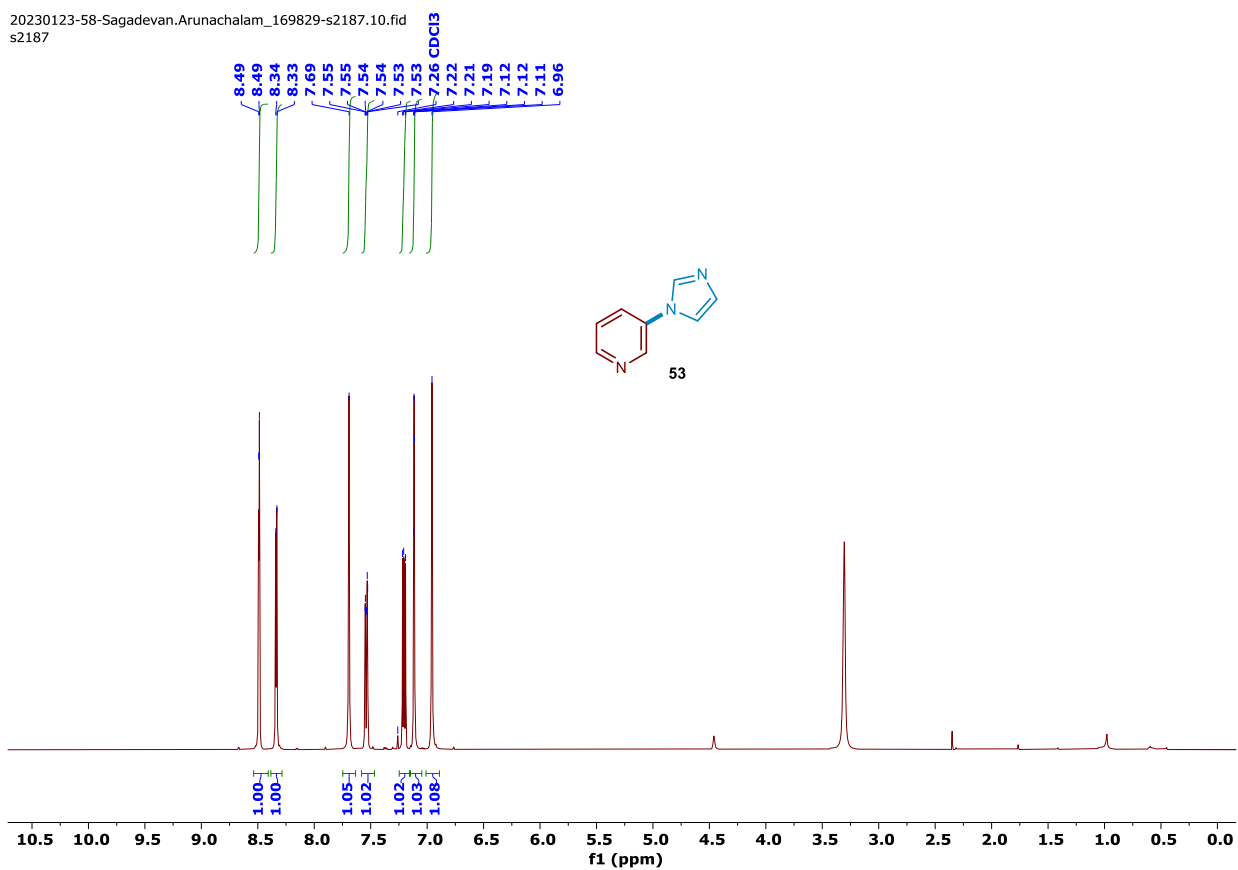
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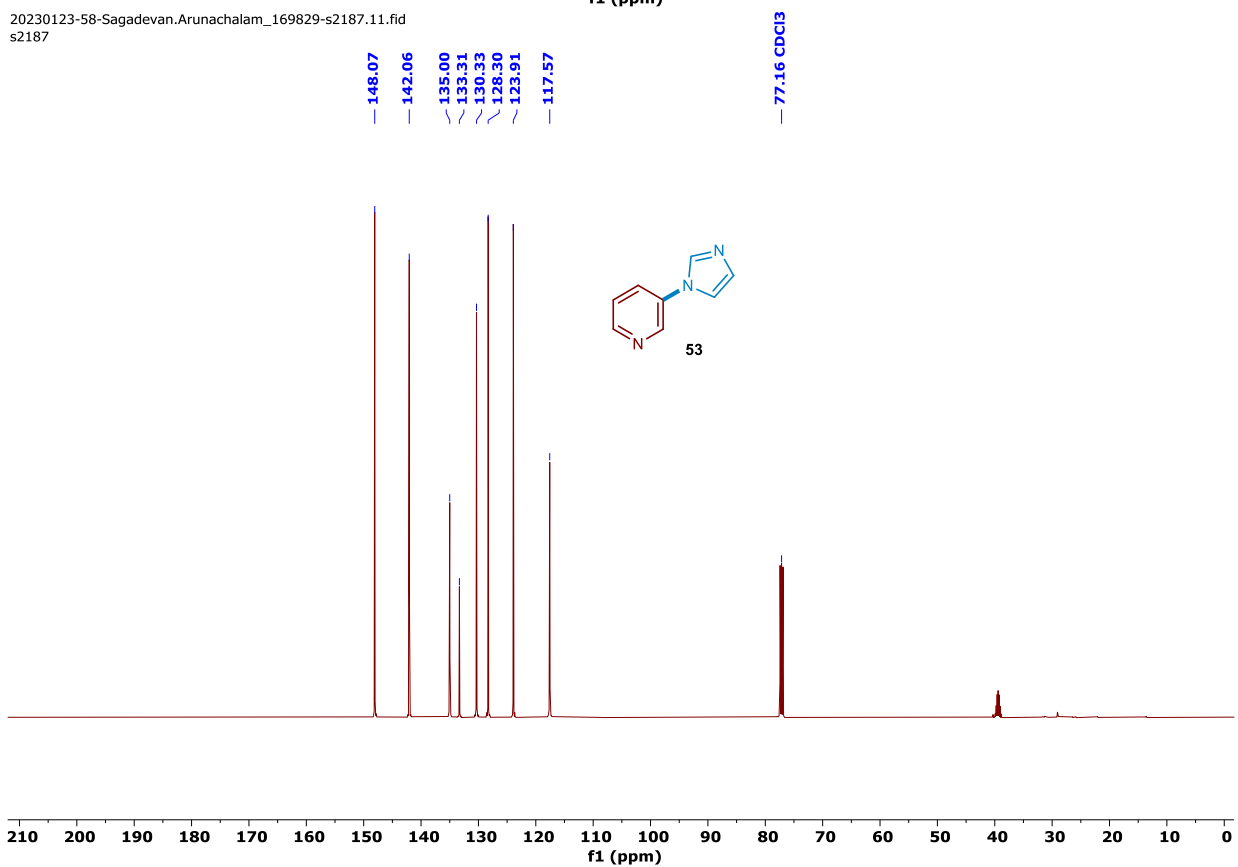
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S2179



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s2187

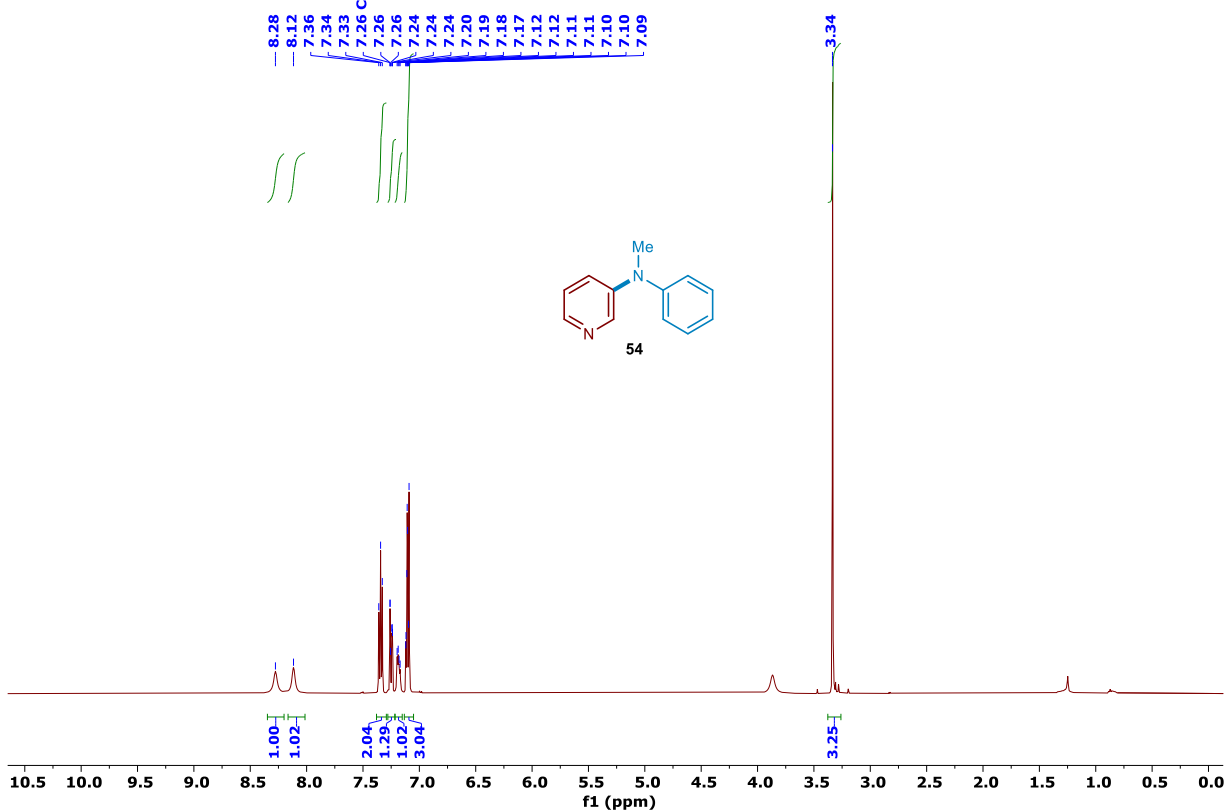


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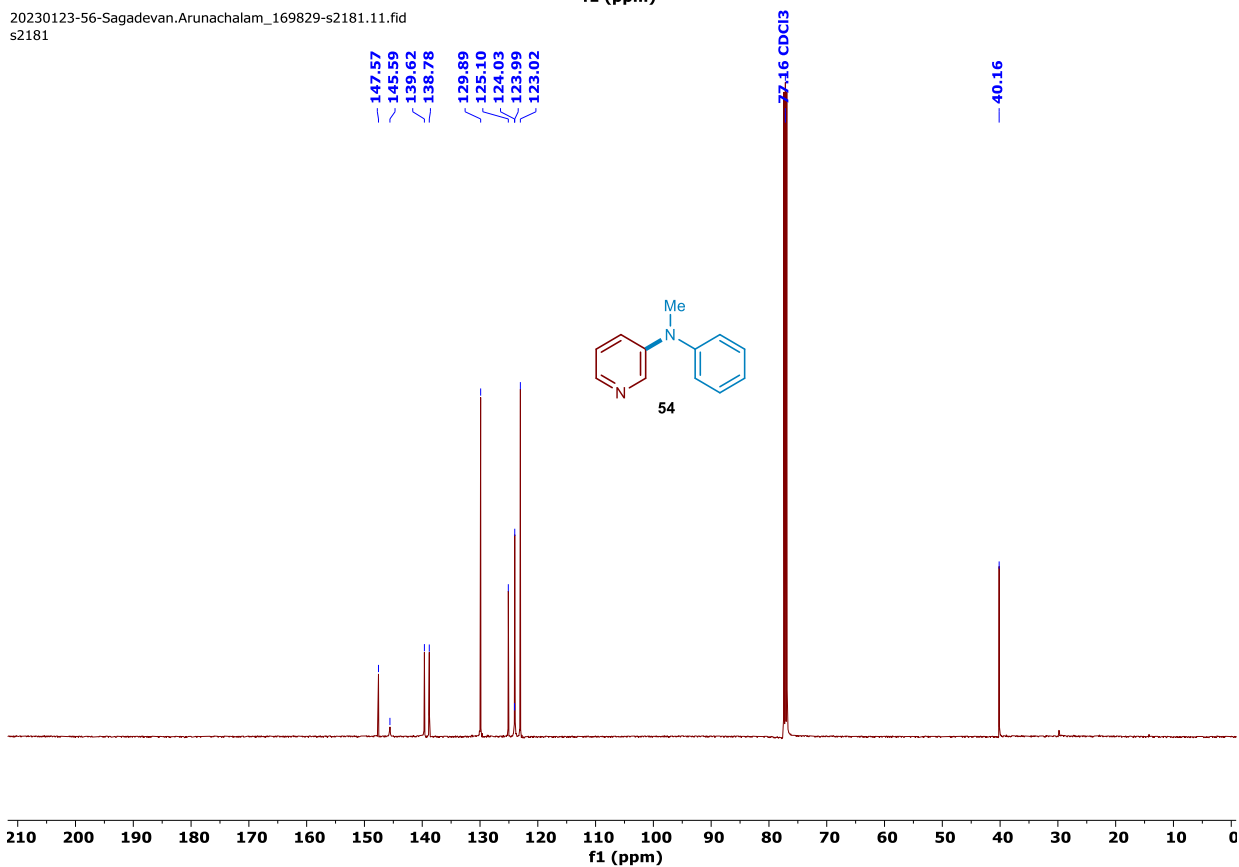




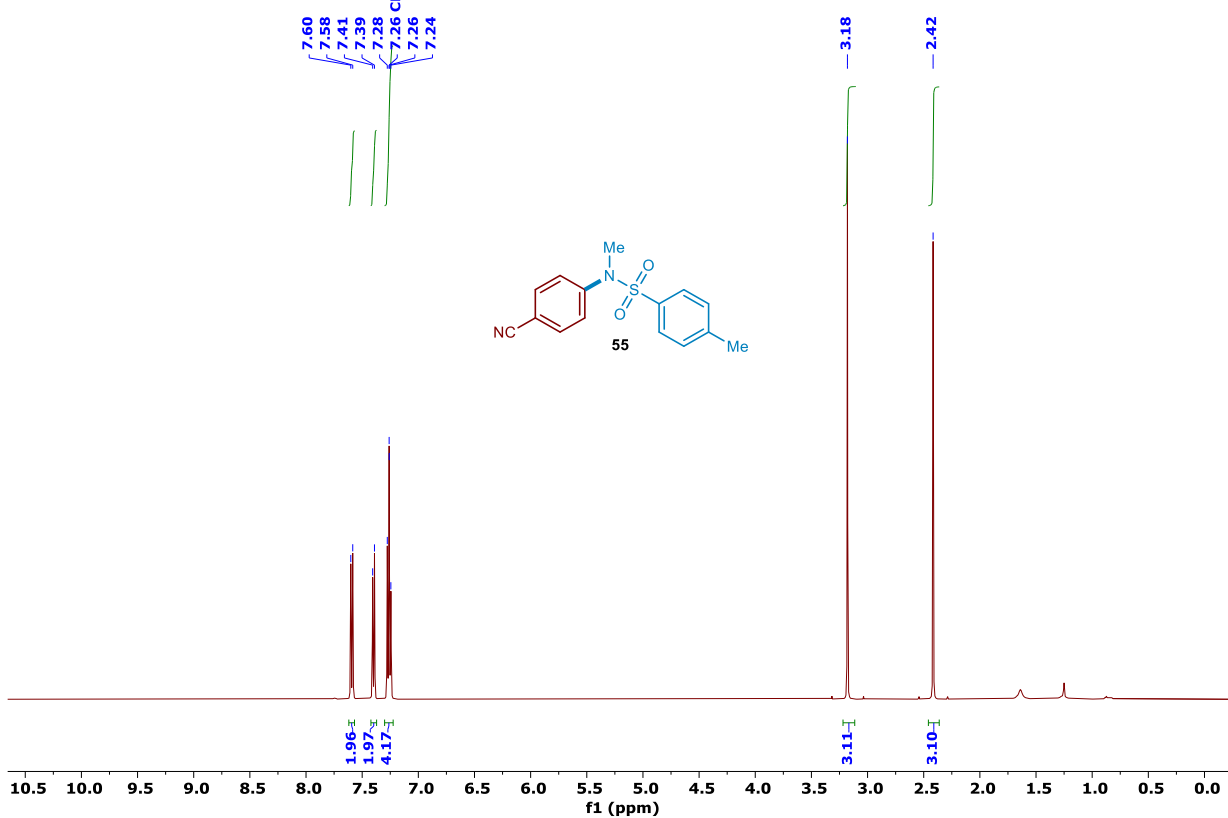
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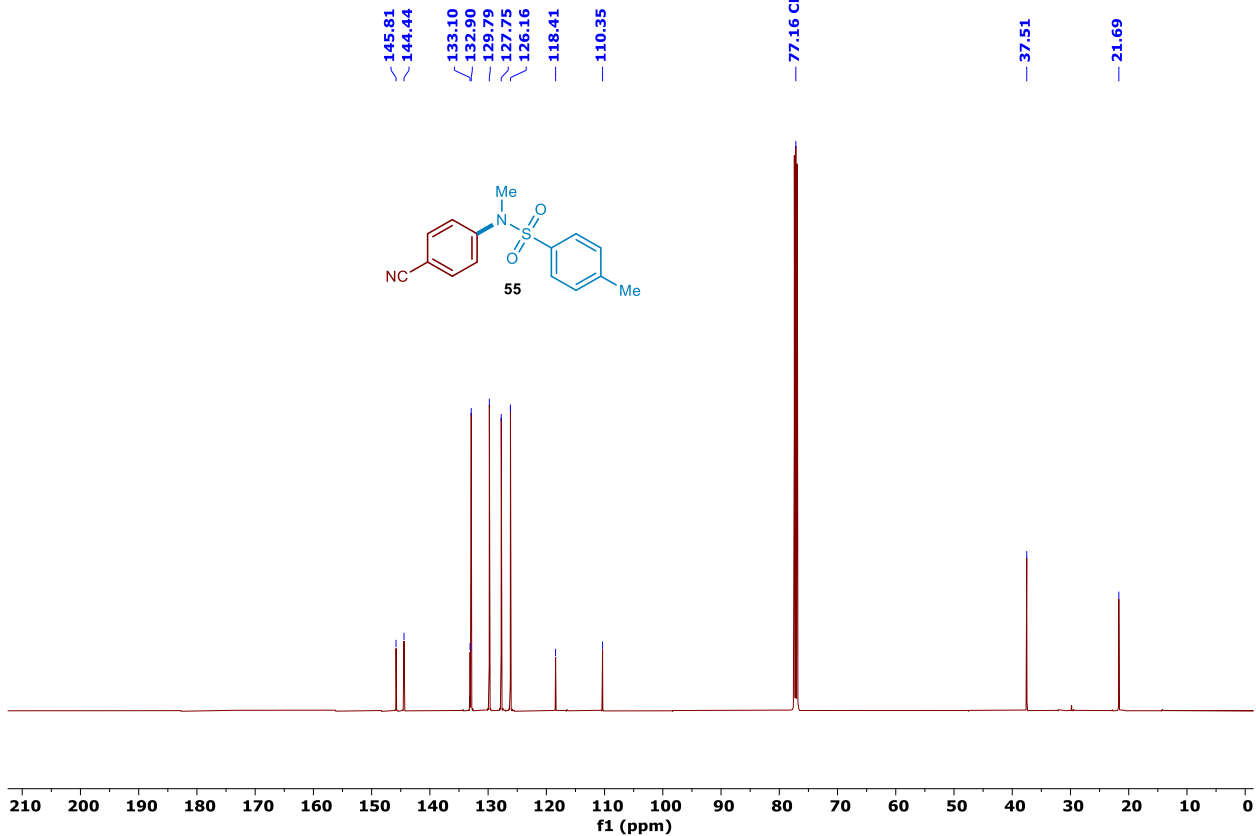
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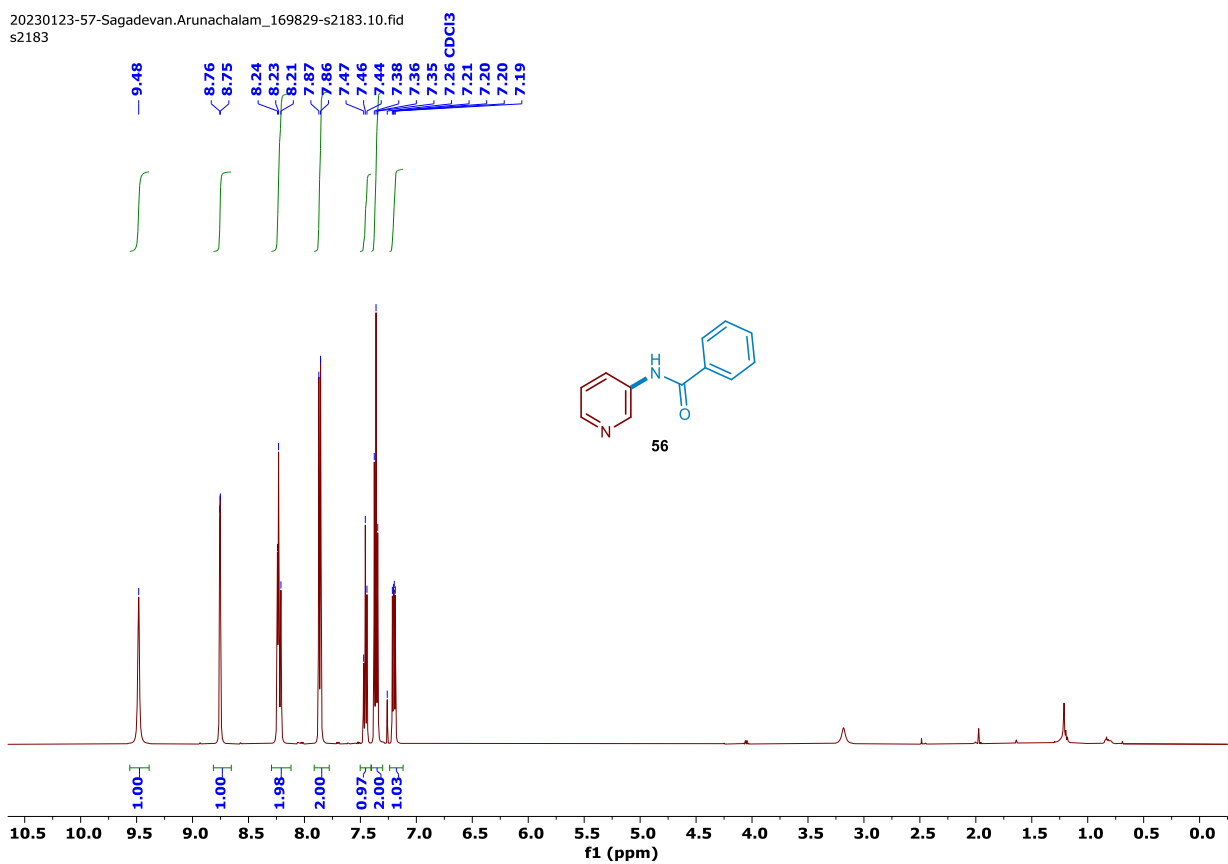
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SA-29



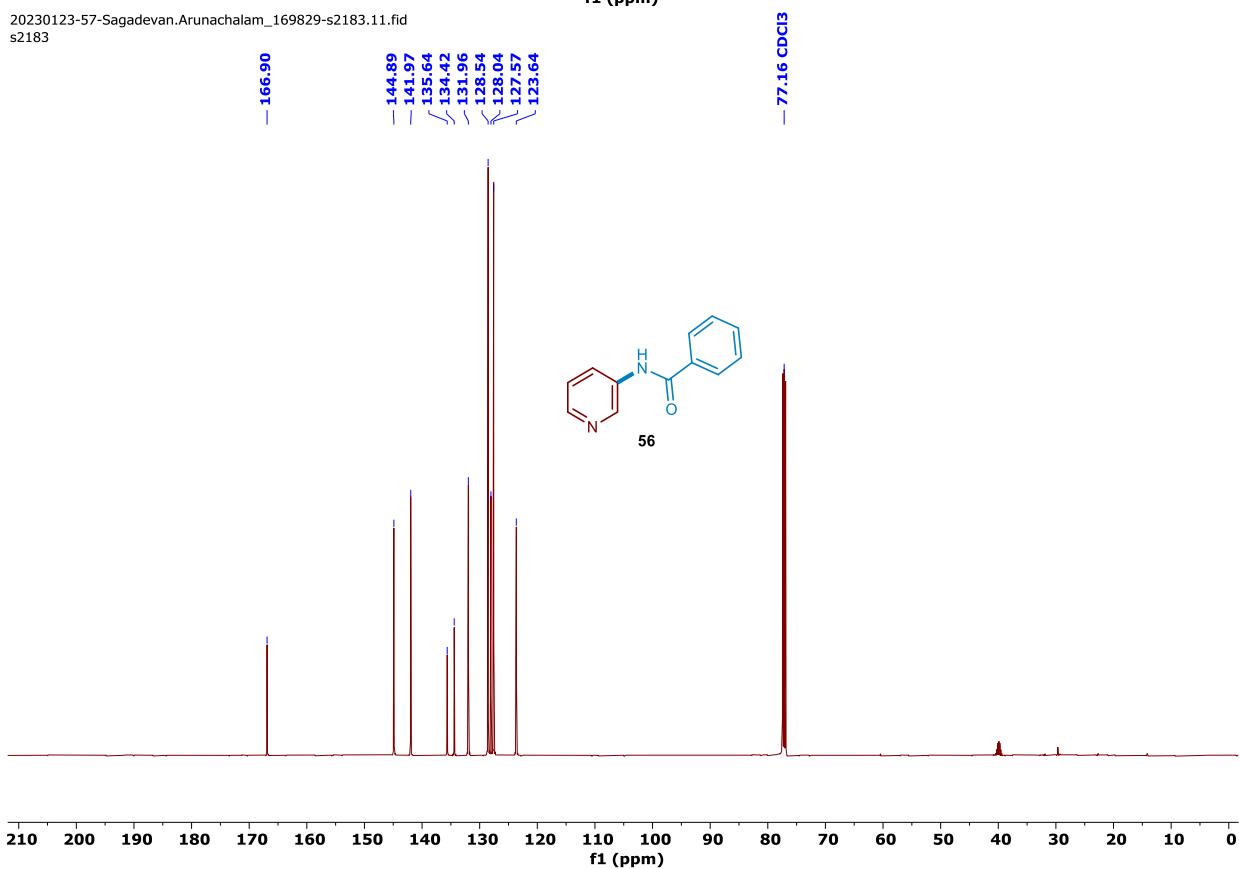
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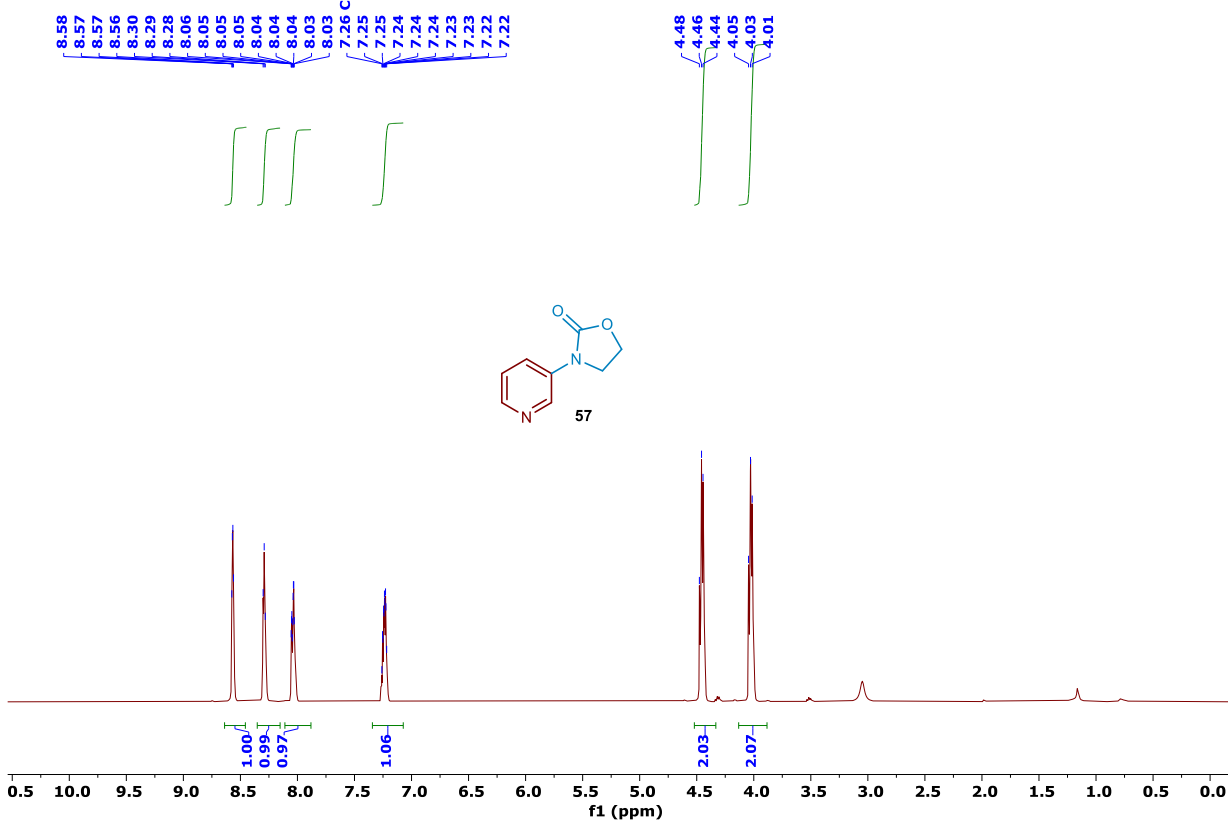
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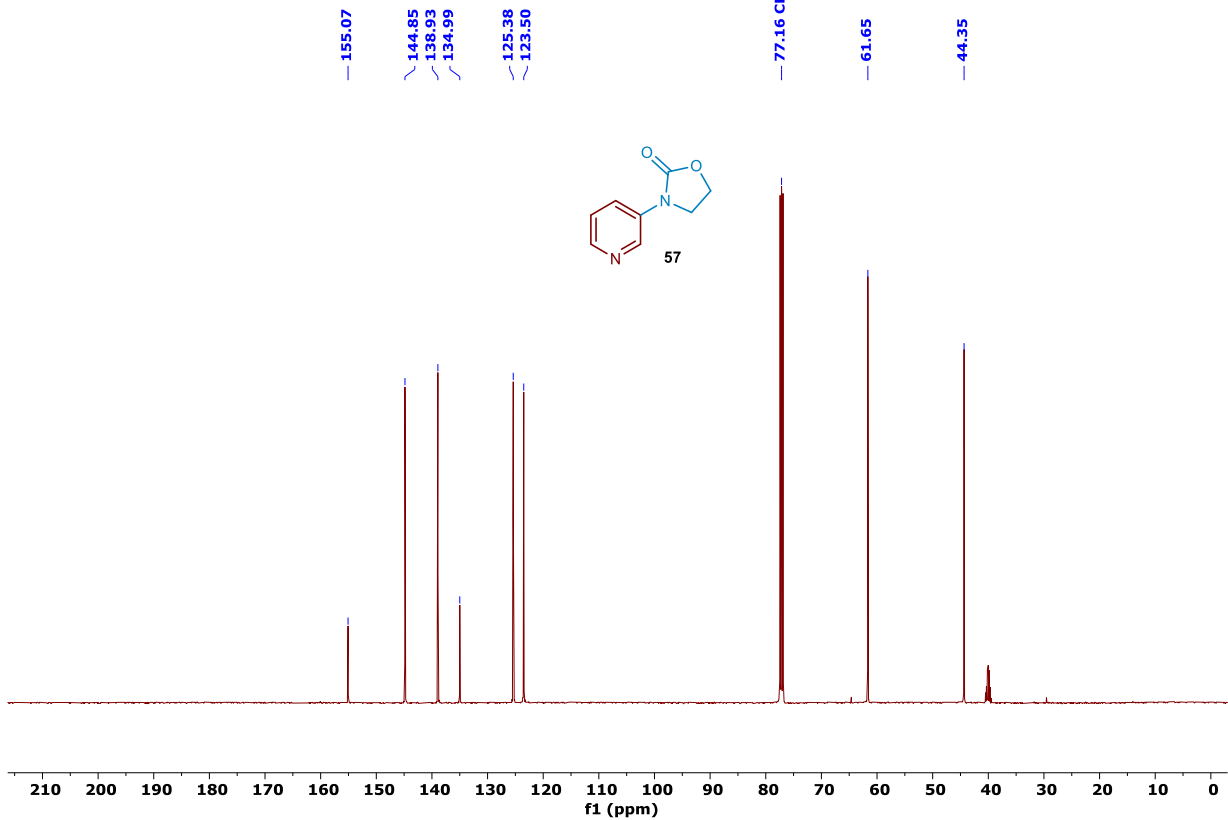
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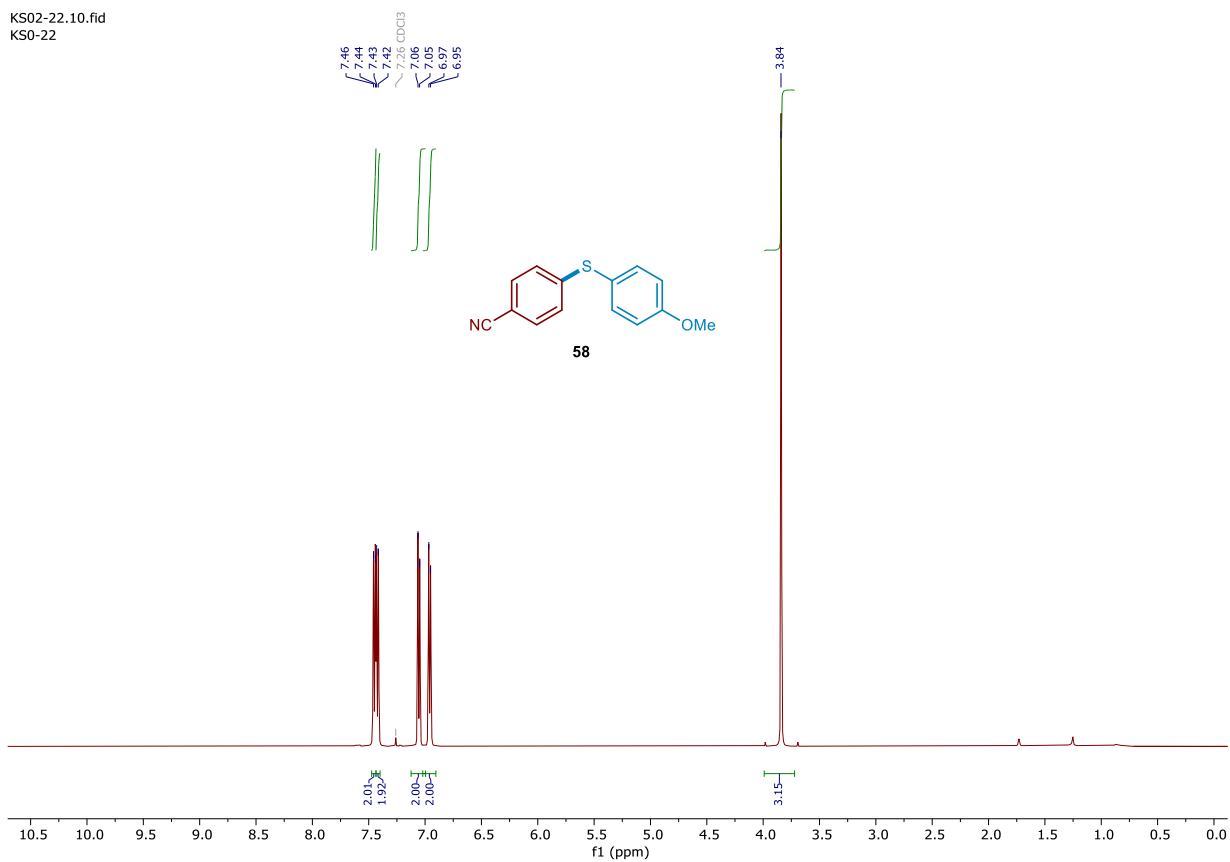
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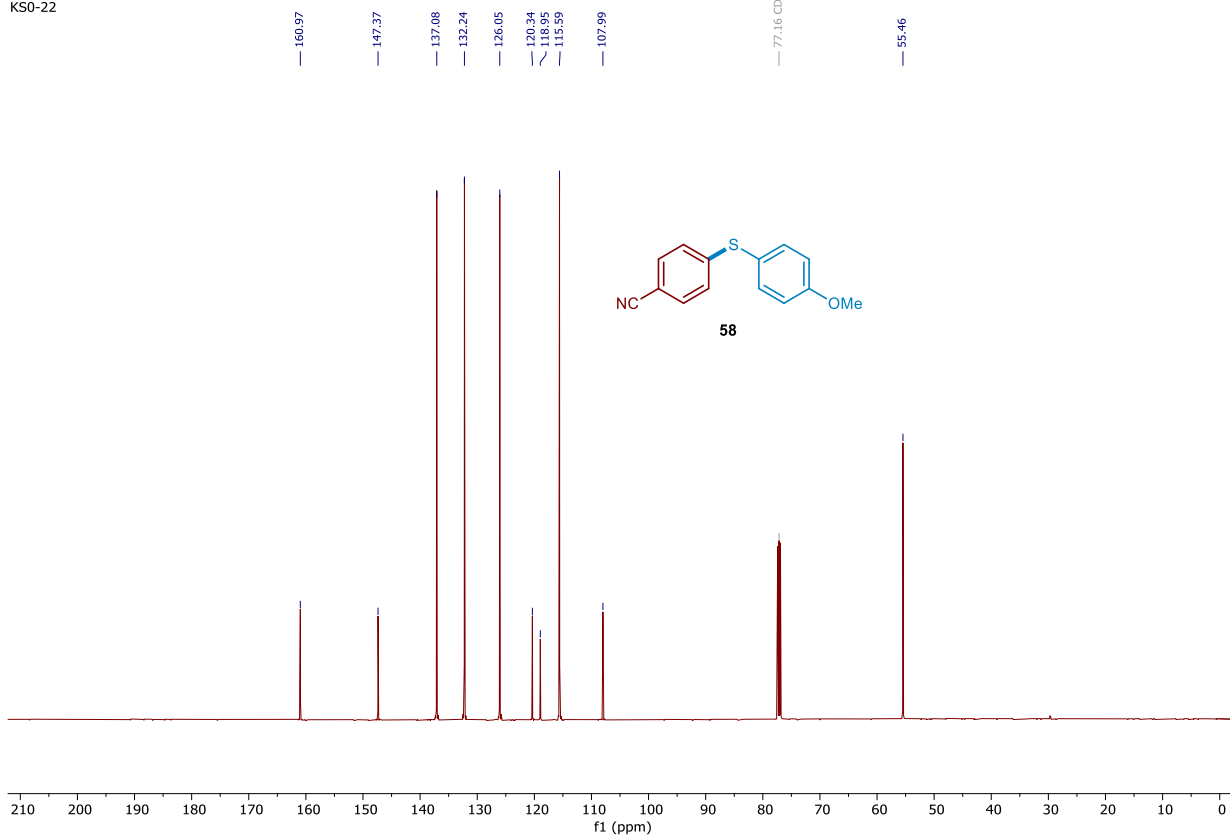
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S2185



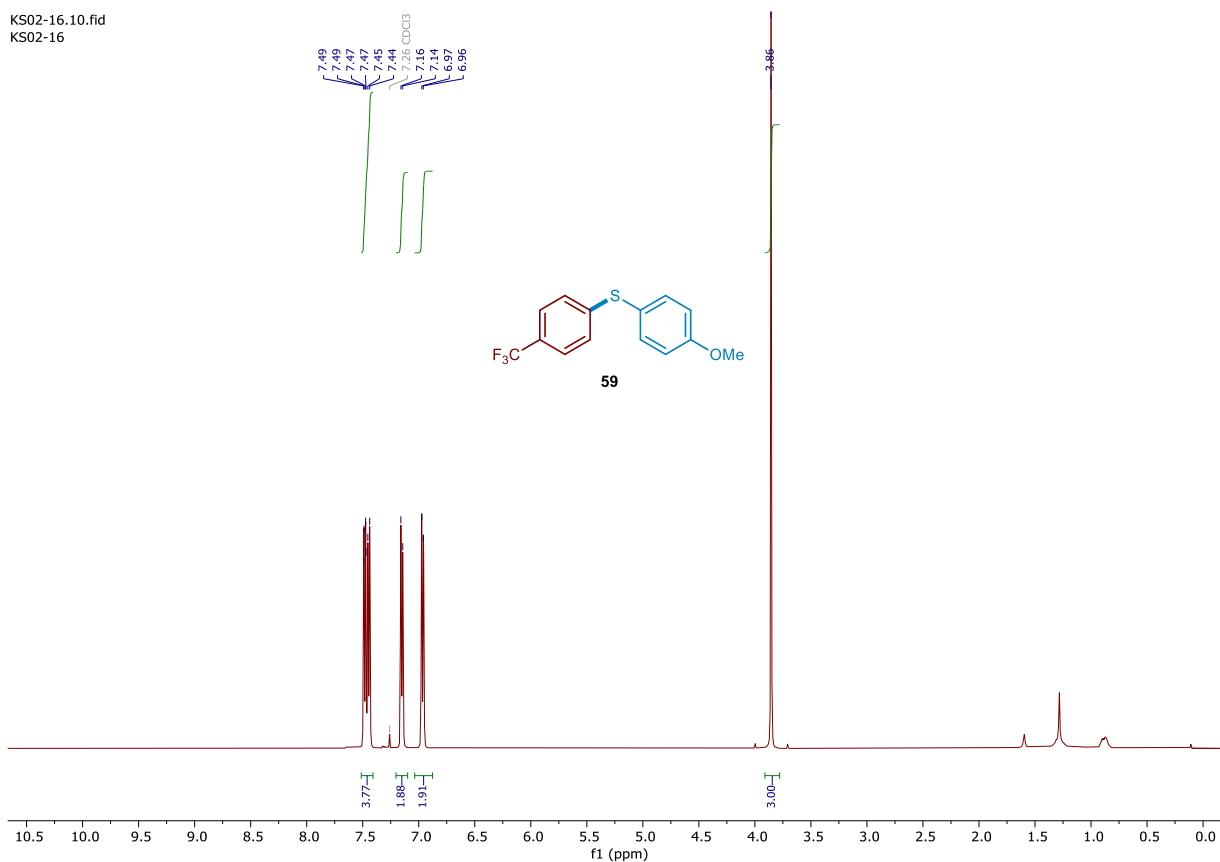
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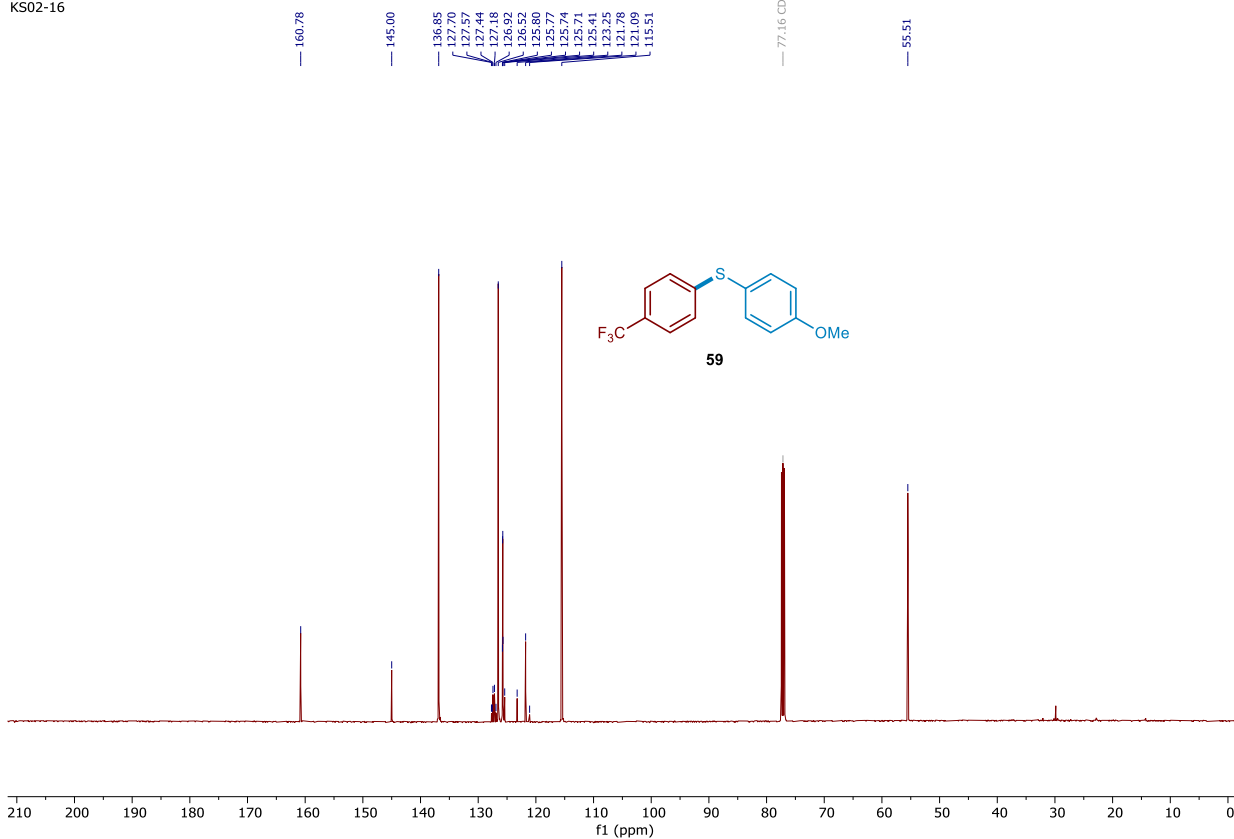
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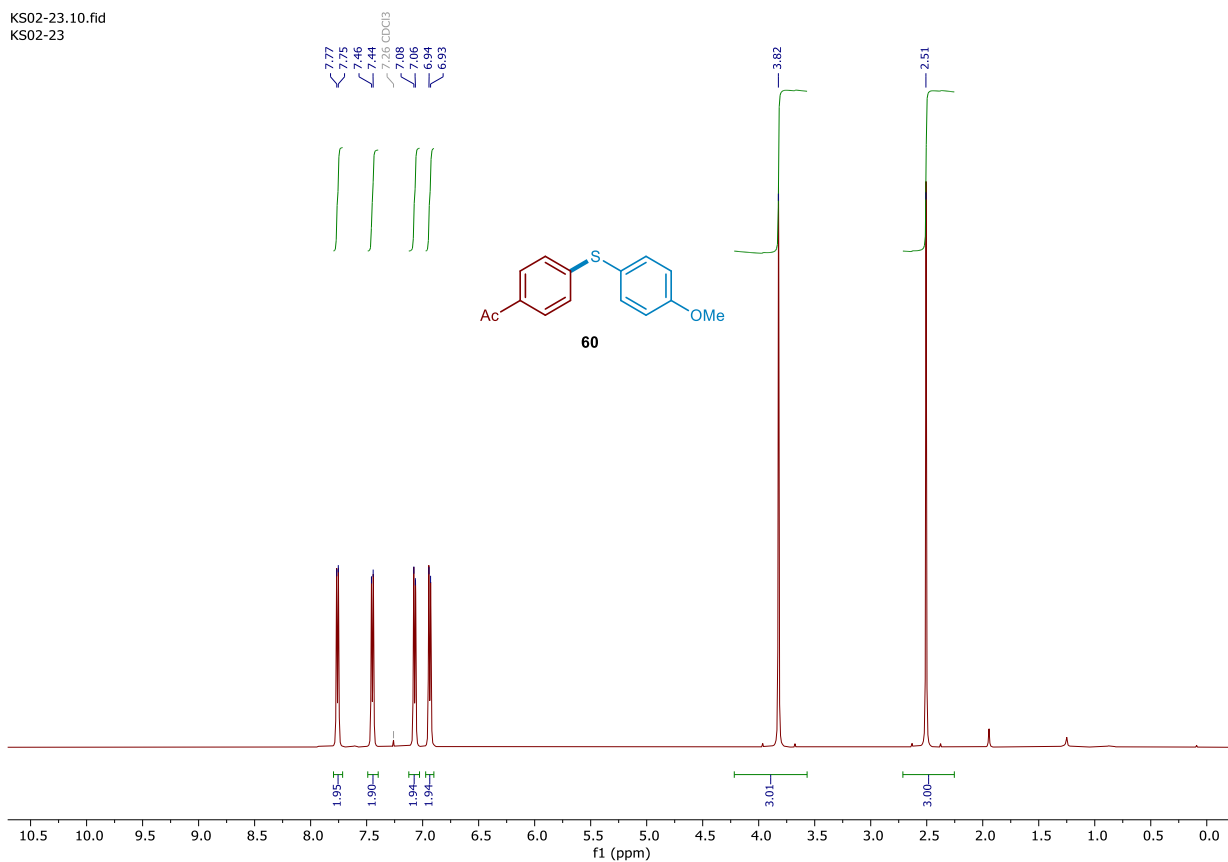
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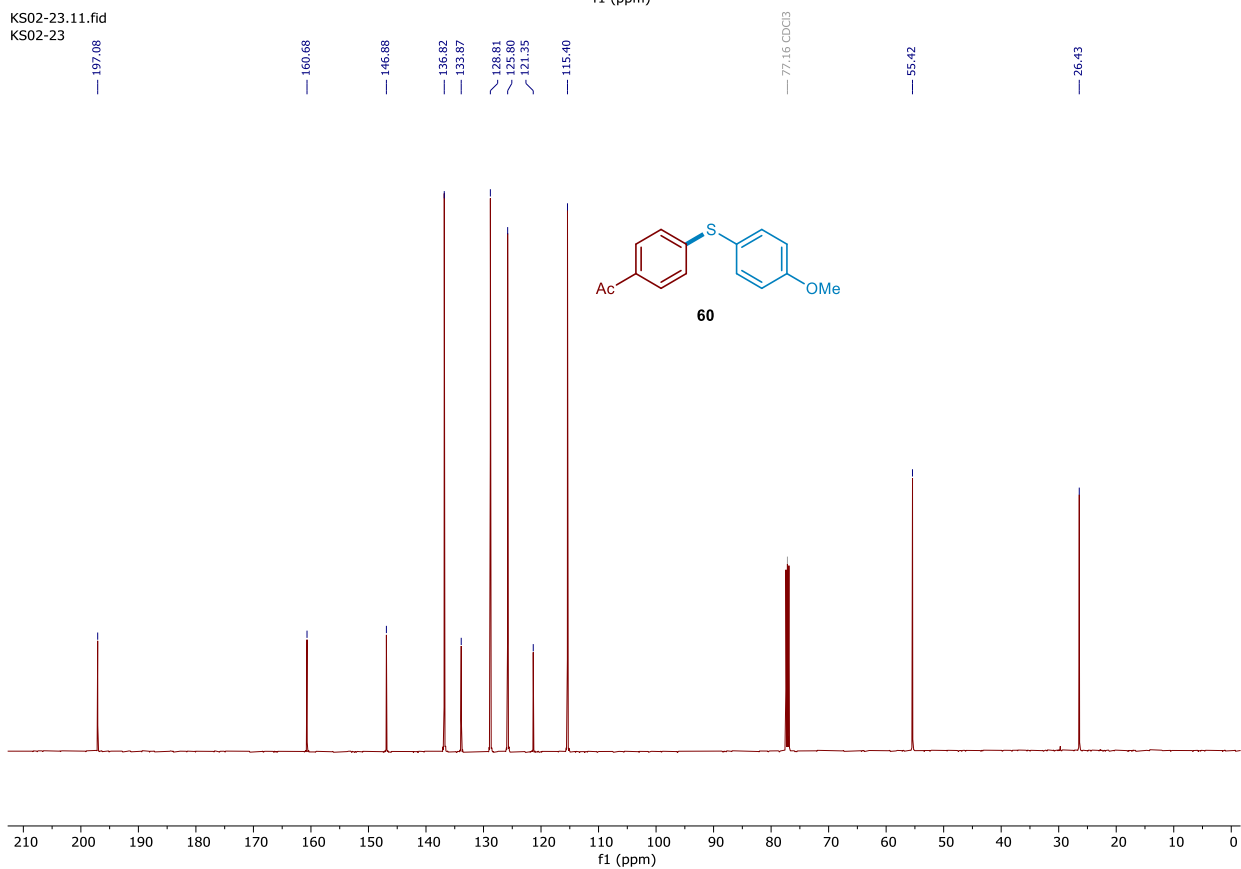
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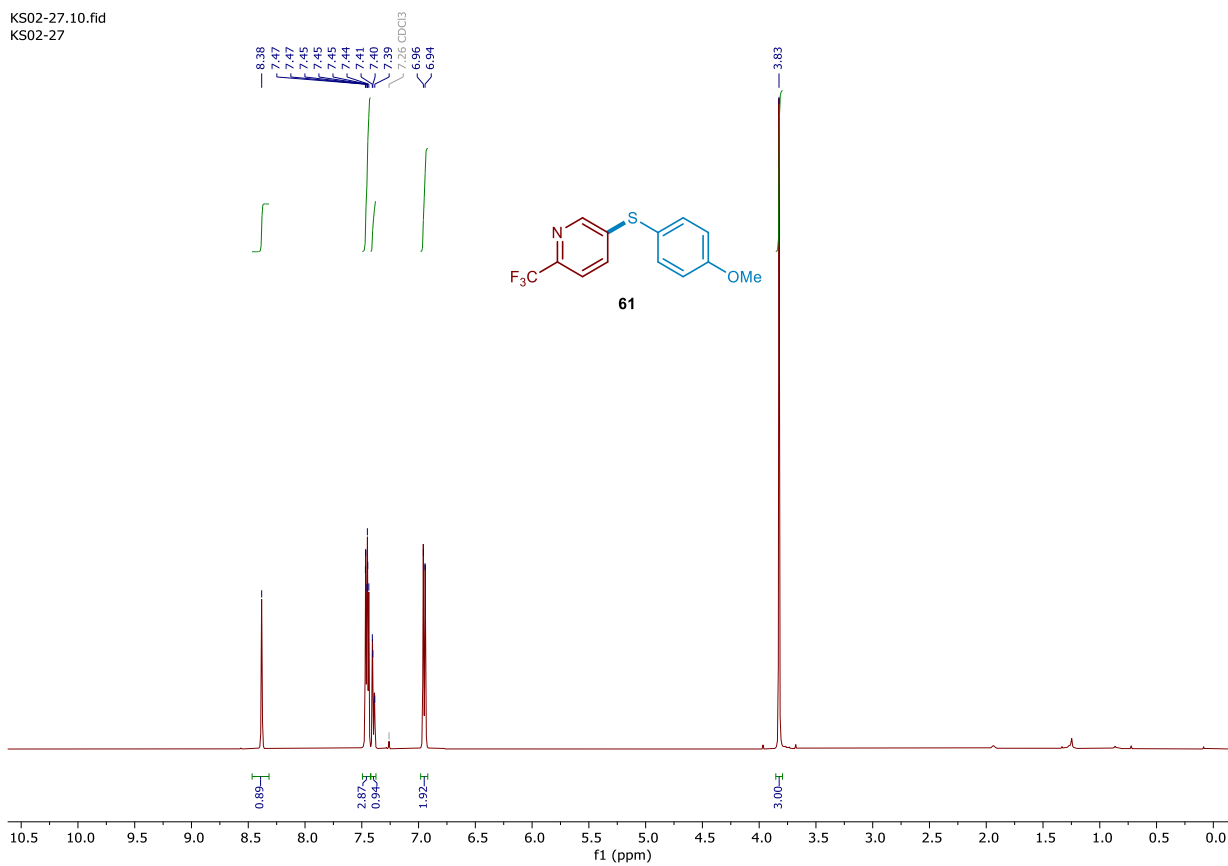
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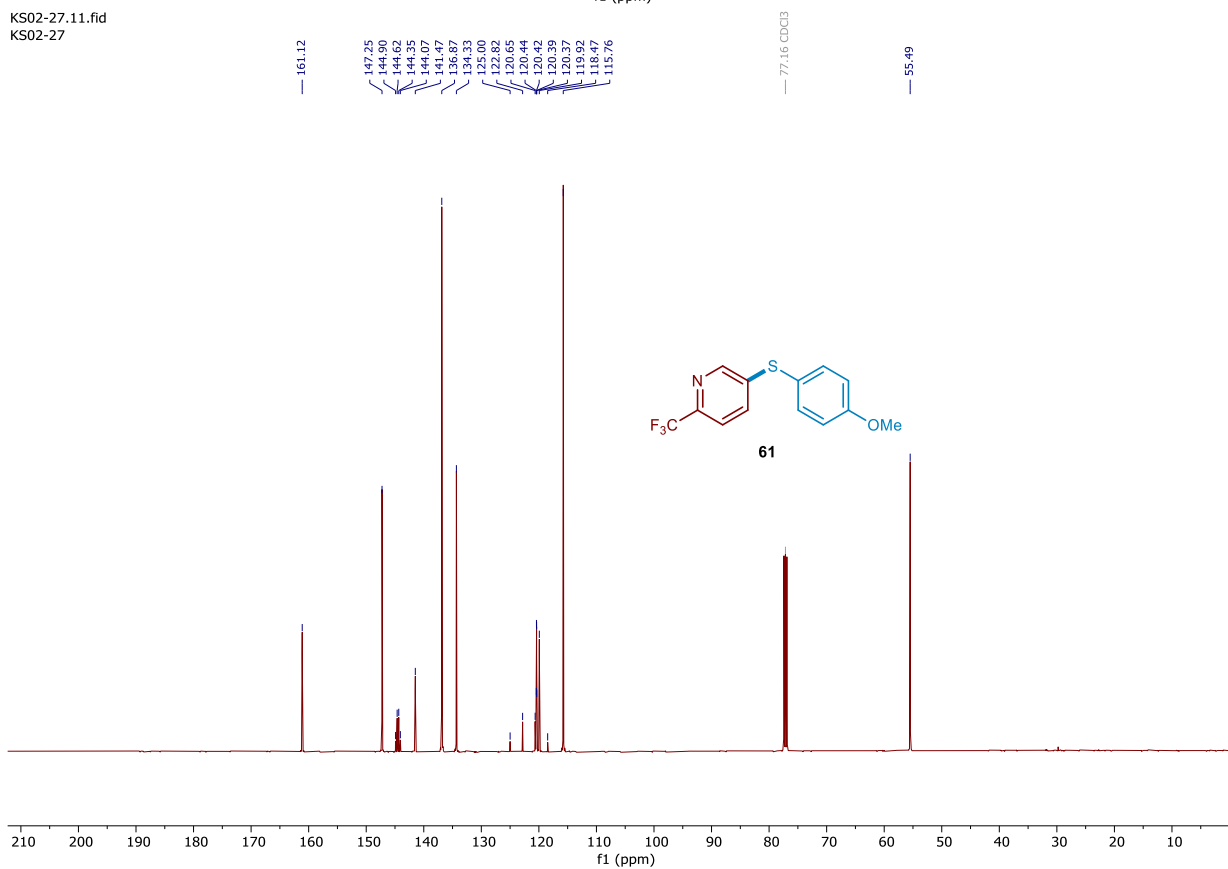
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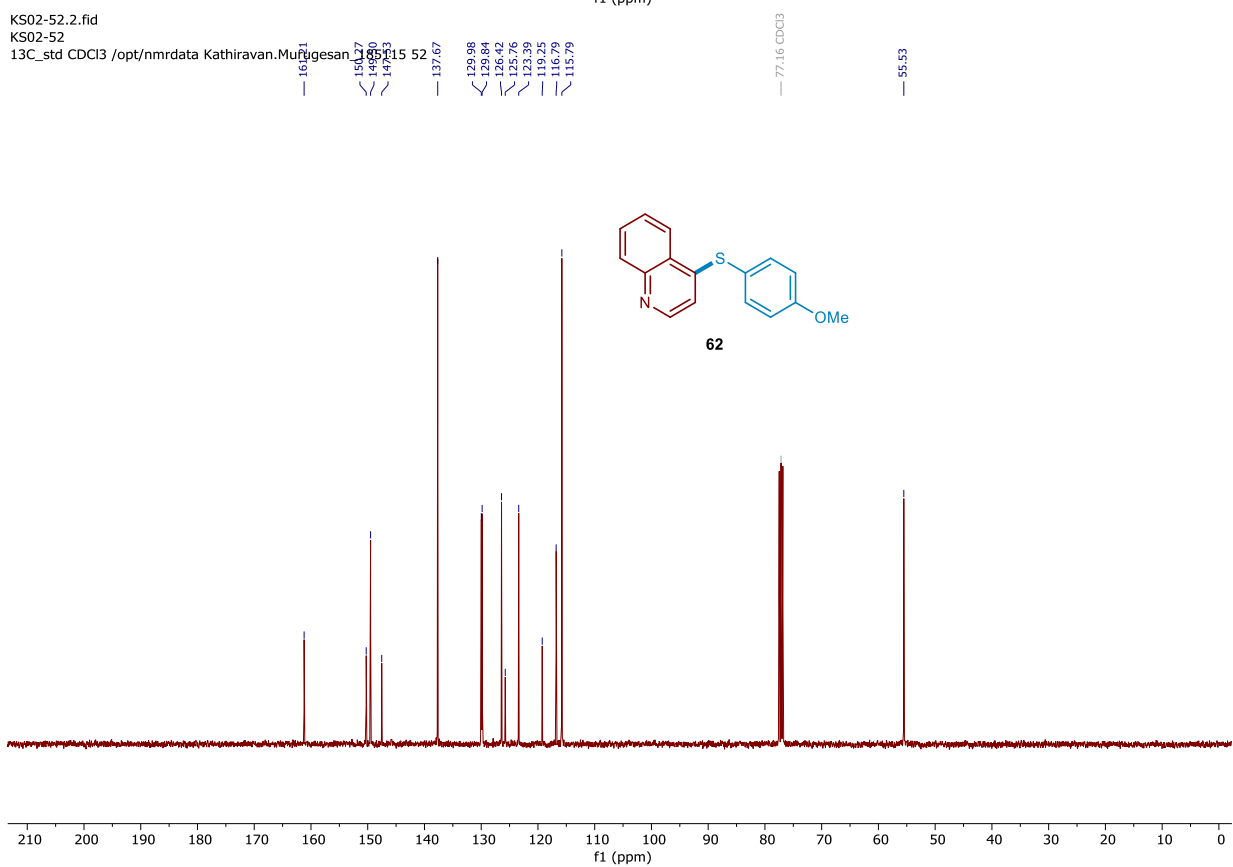
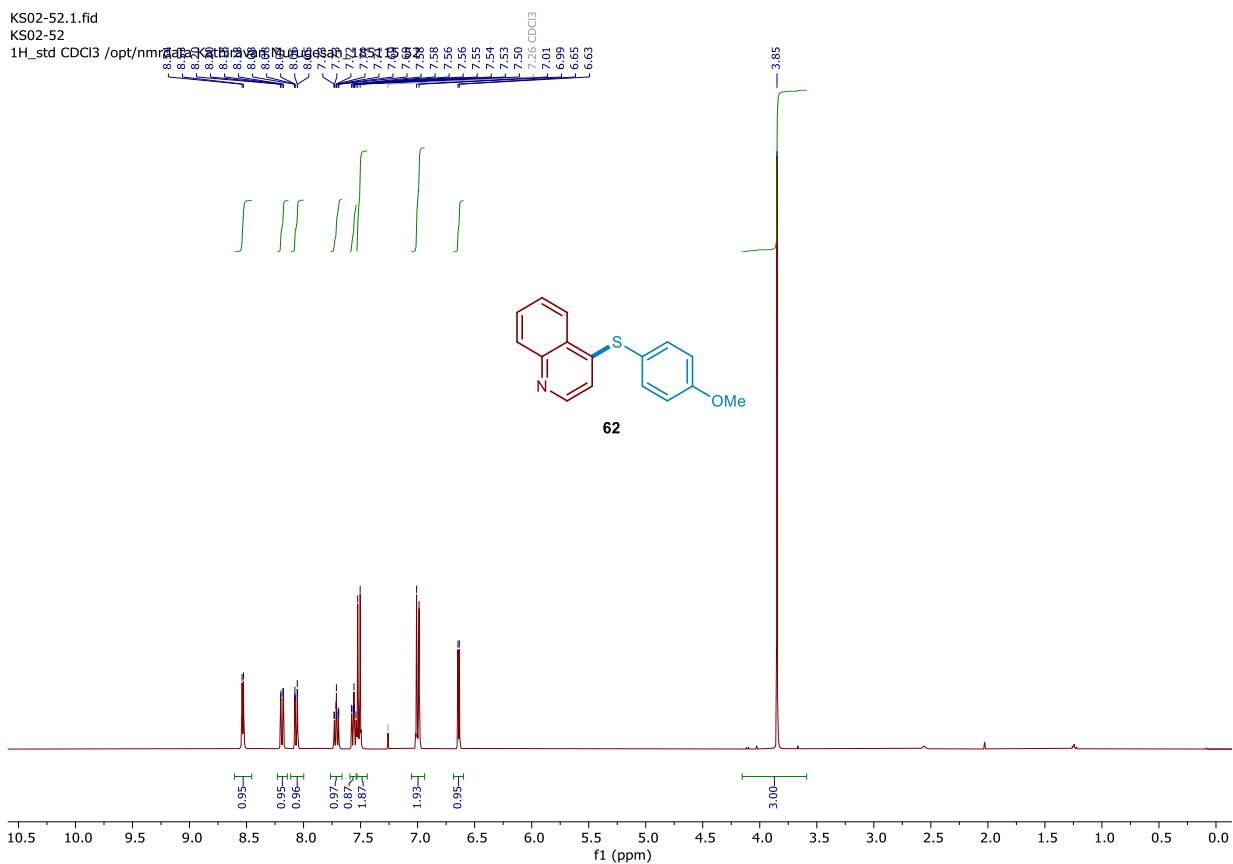
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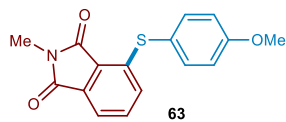
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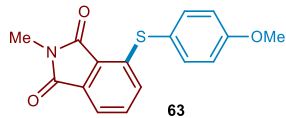




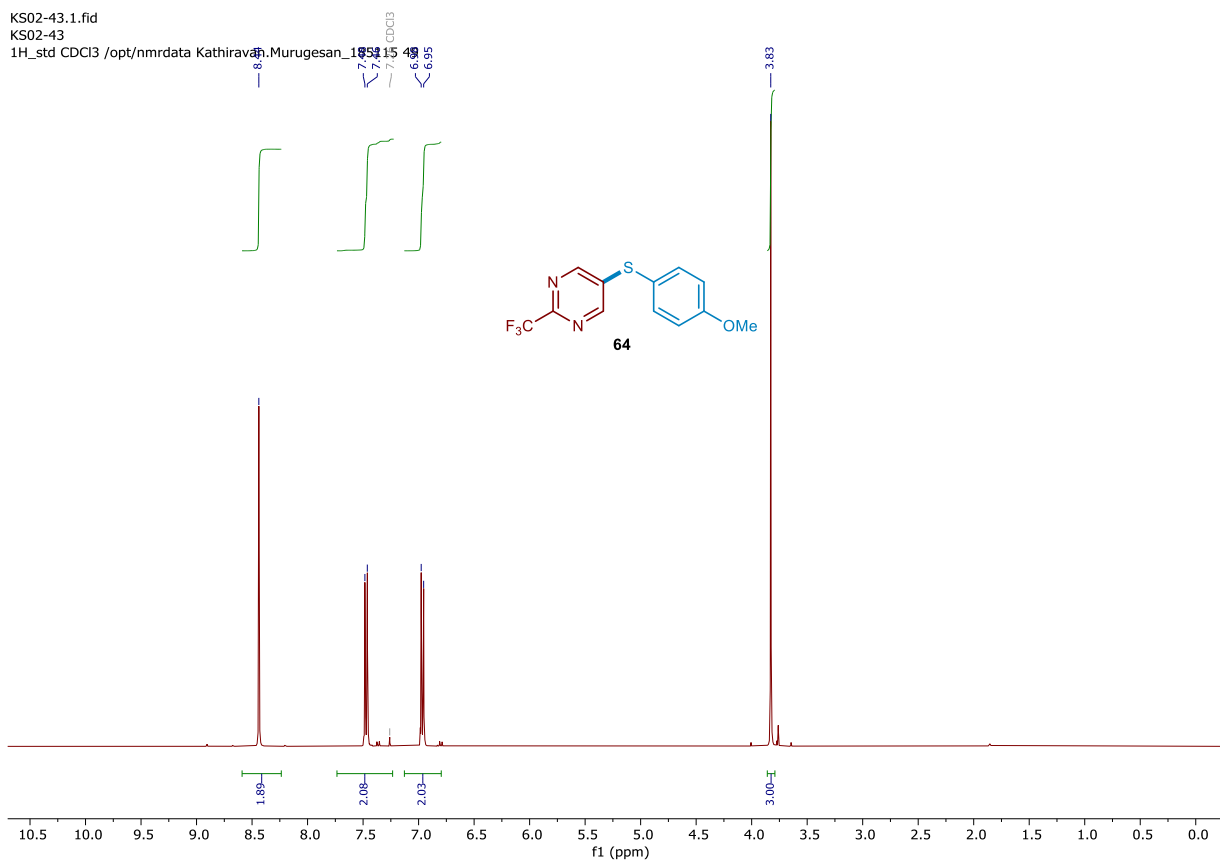
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CDC13



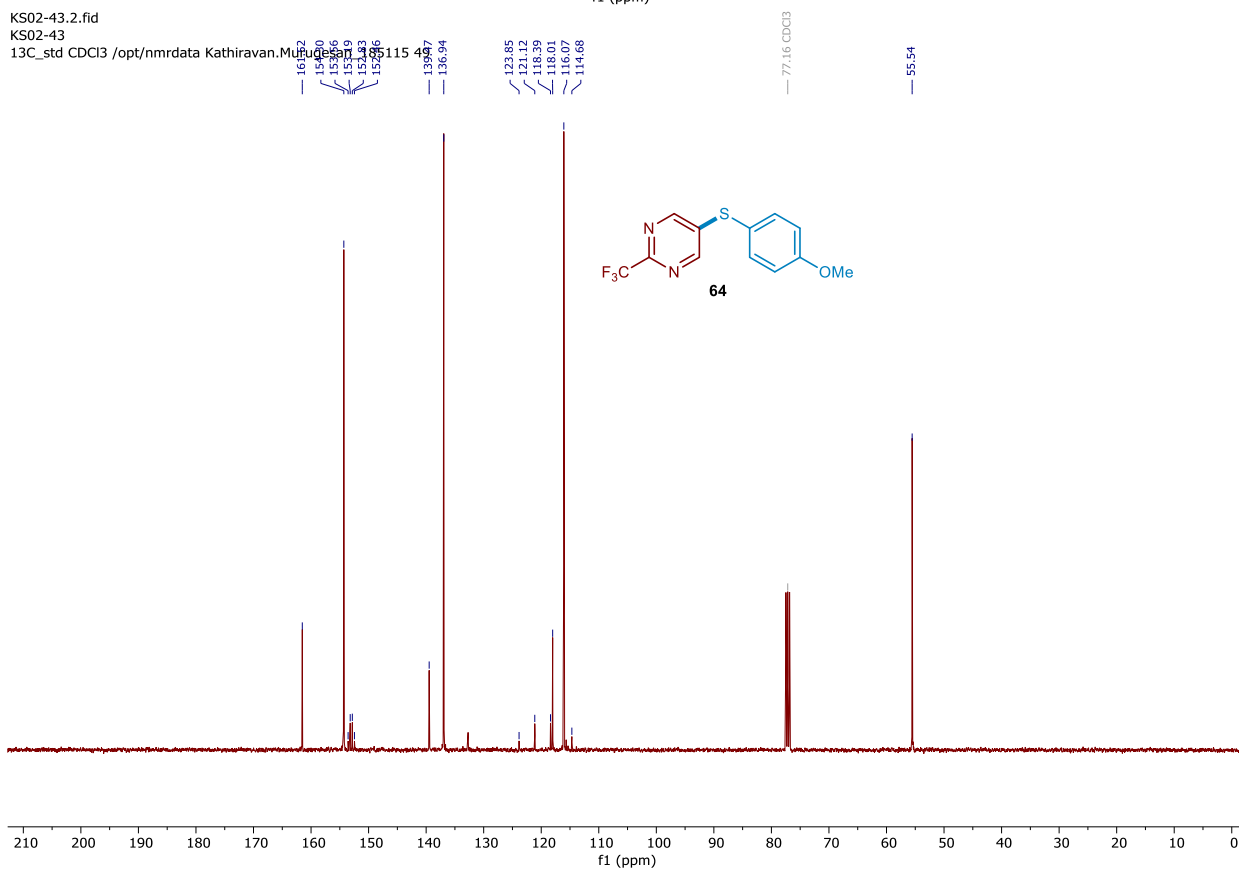
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KS02-43.1.fid  
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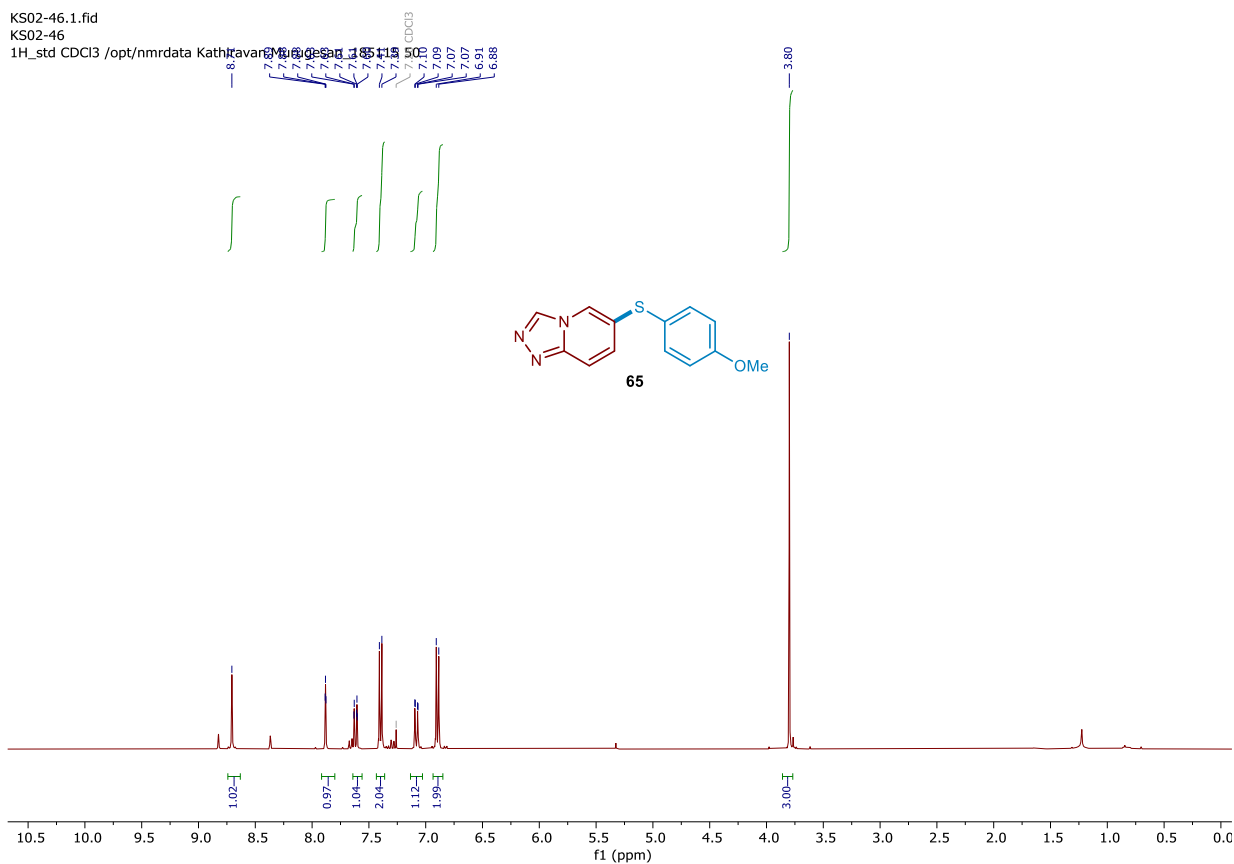


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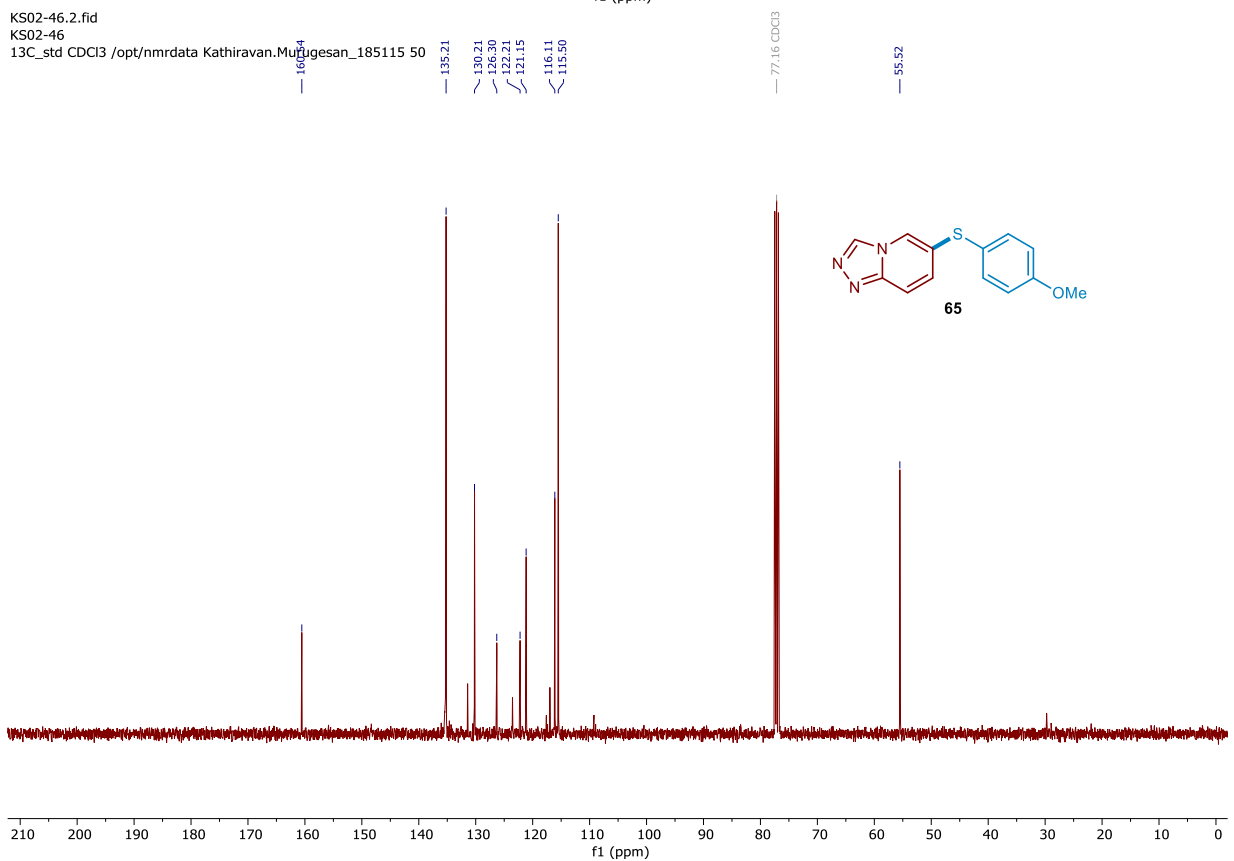
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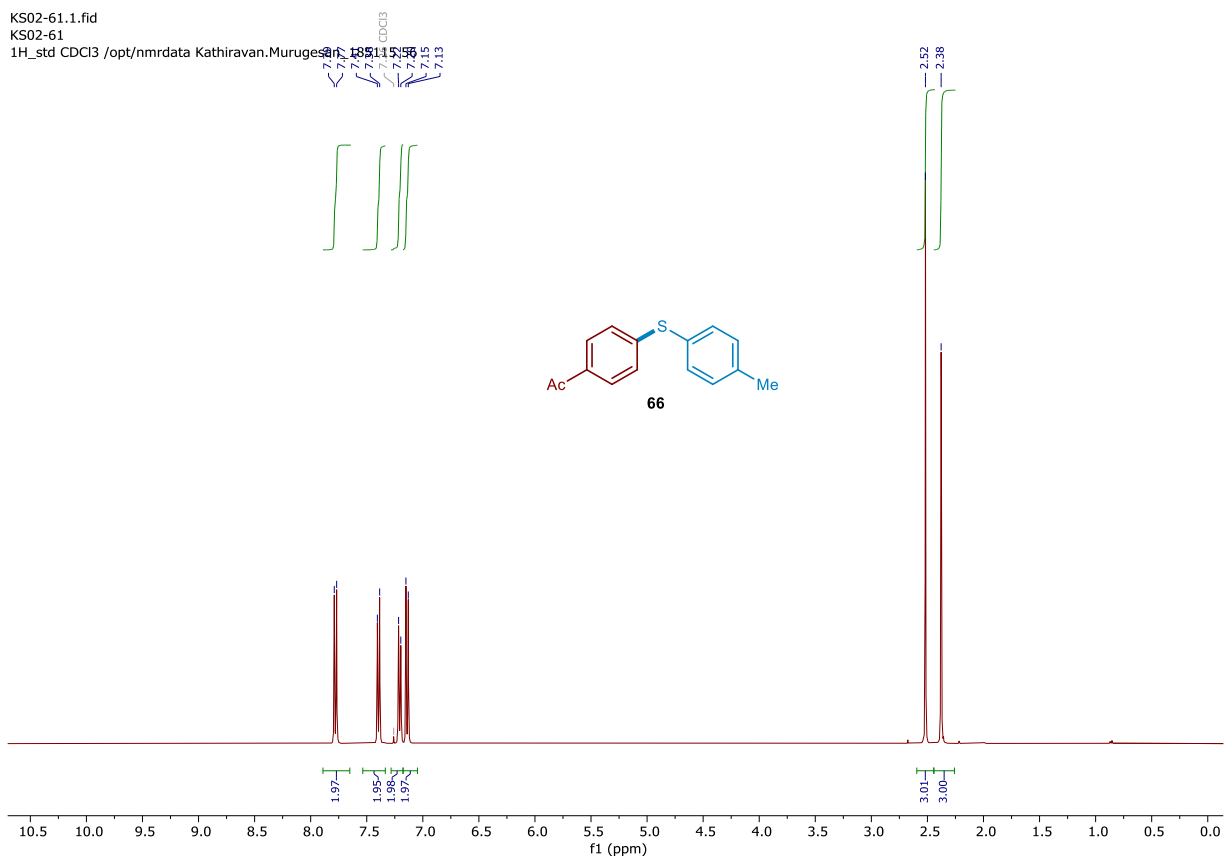
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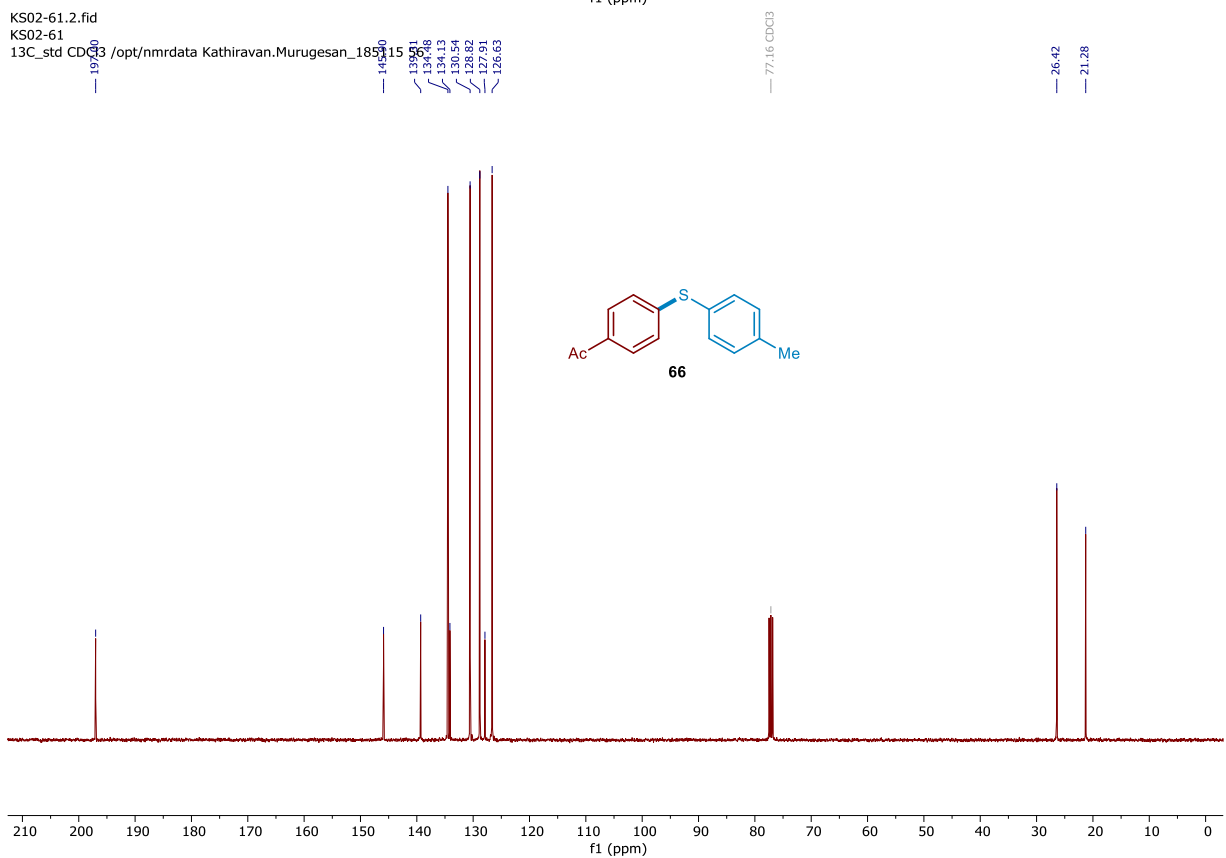
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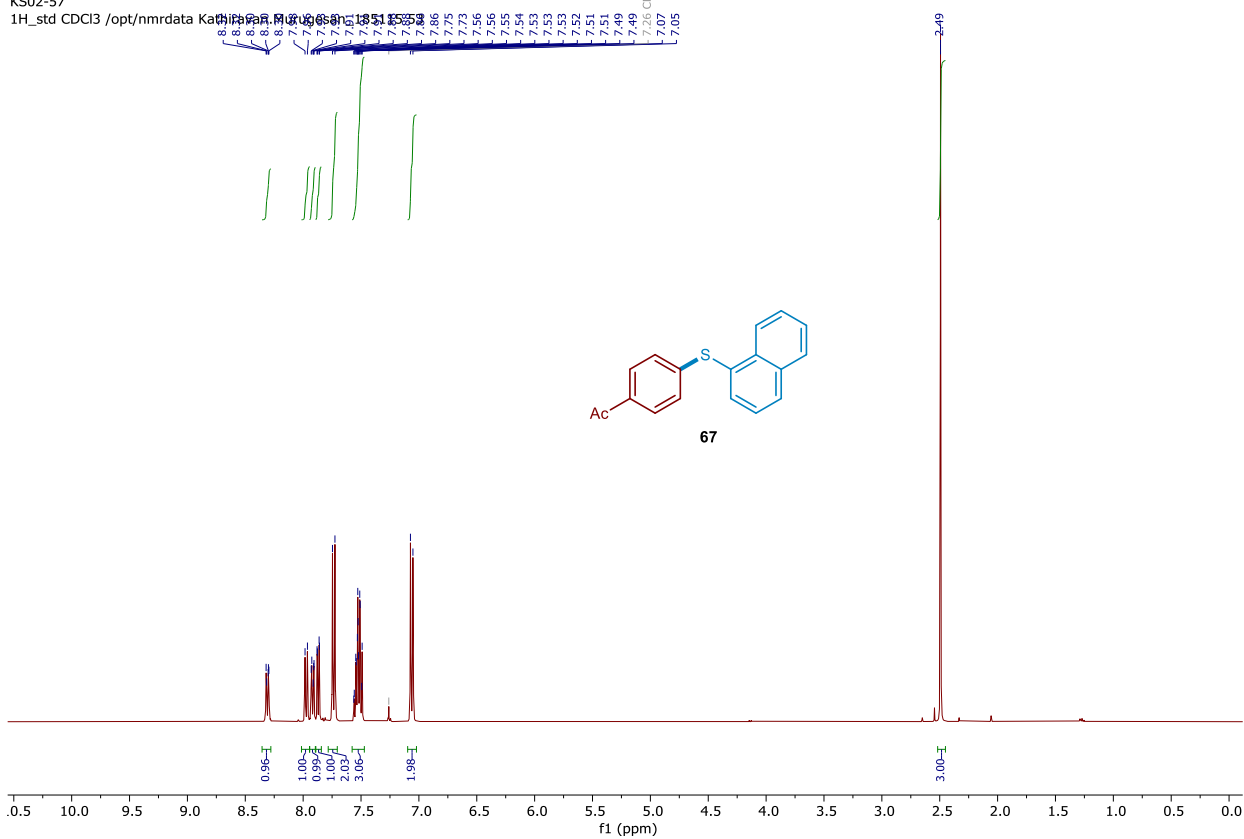
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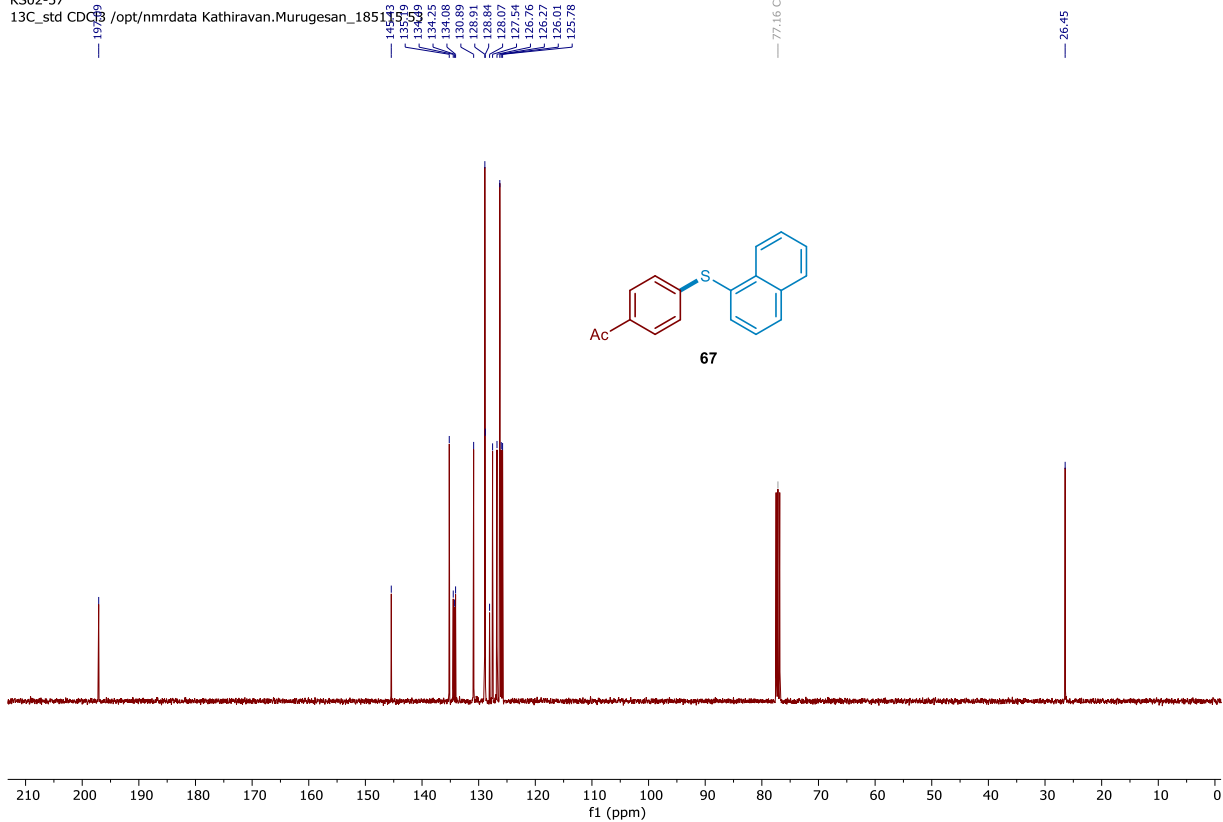
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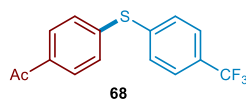


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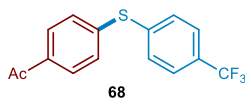
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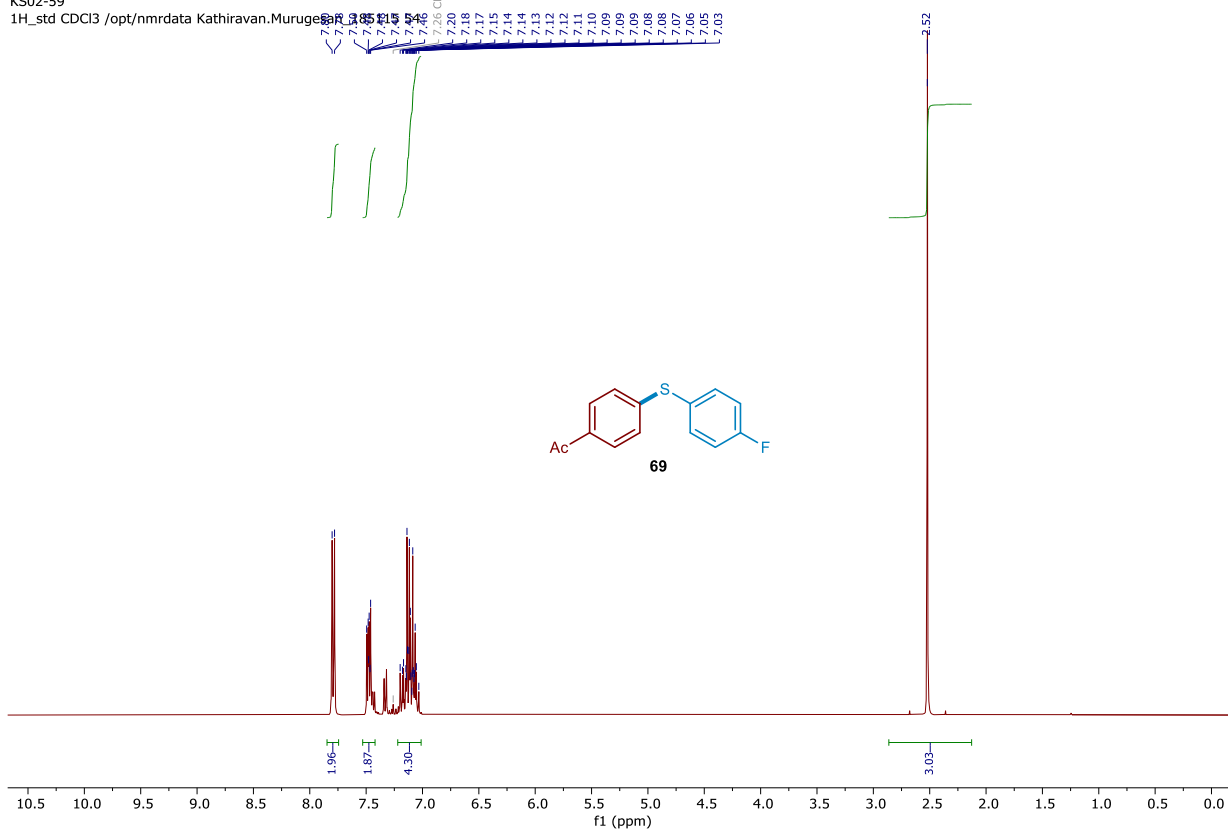


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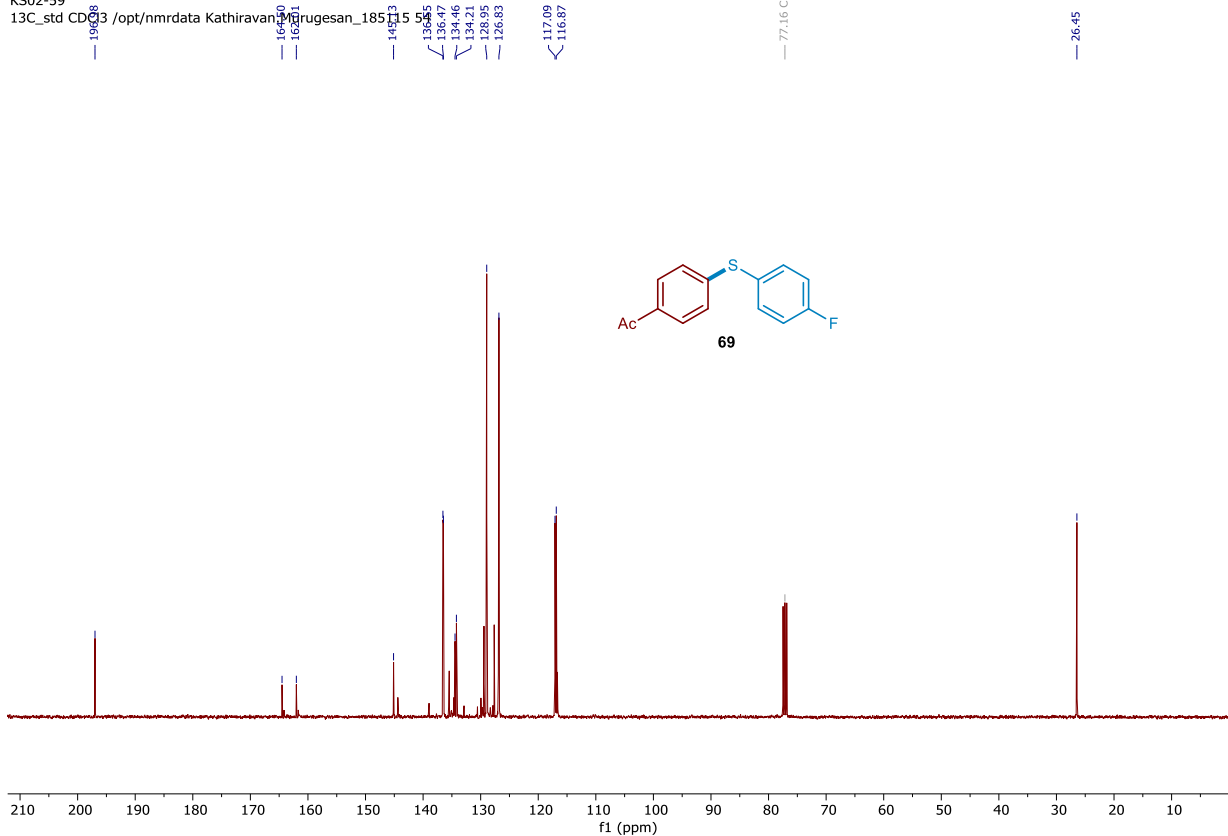
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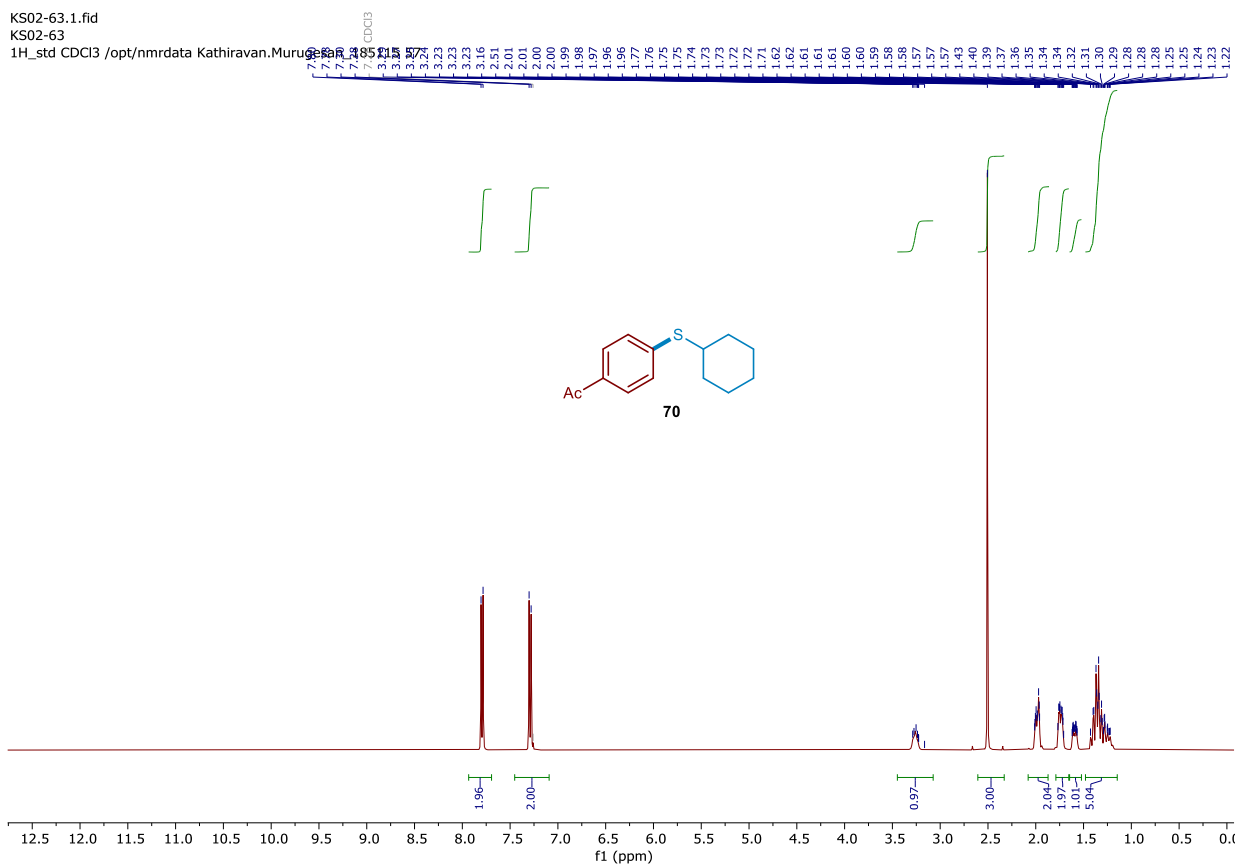
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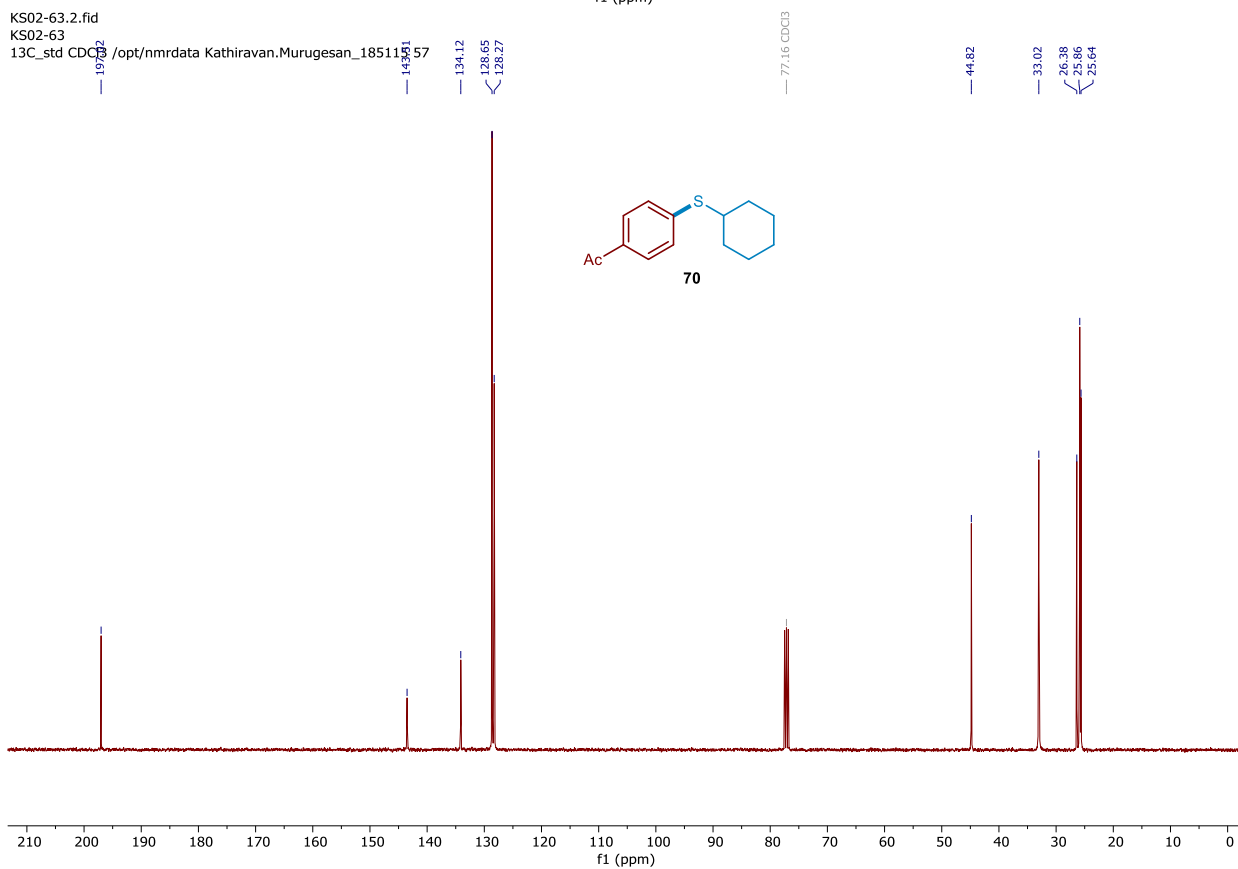
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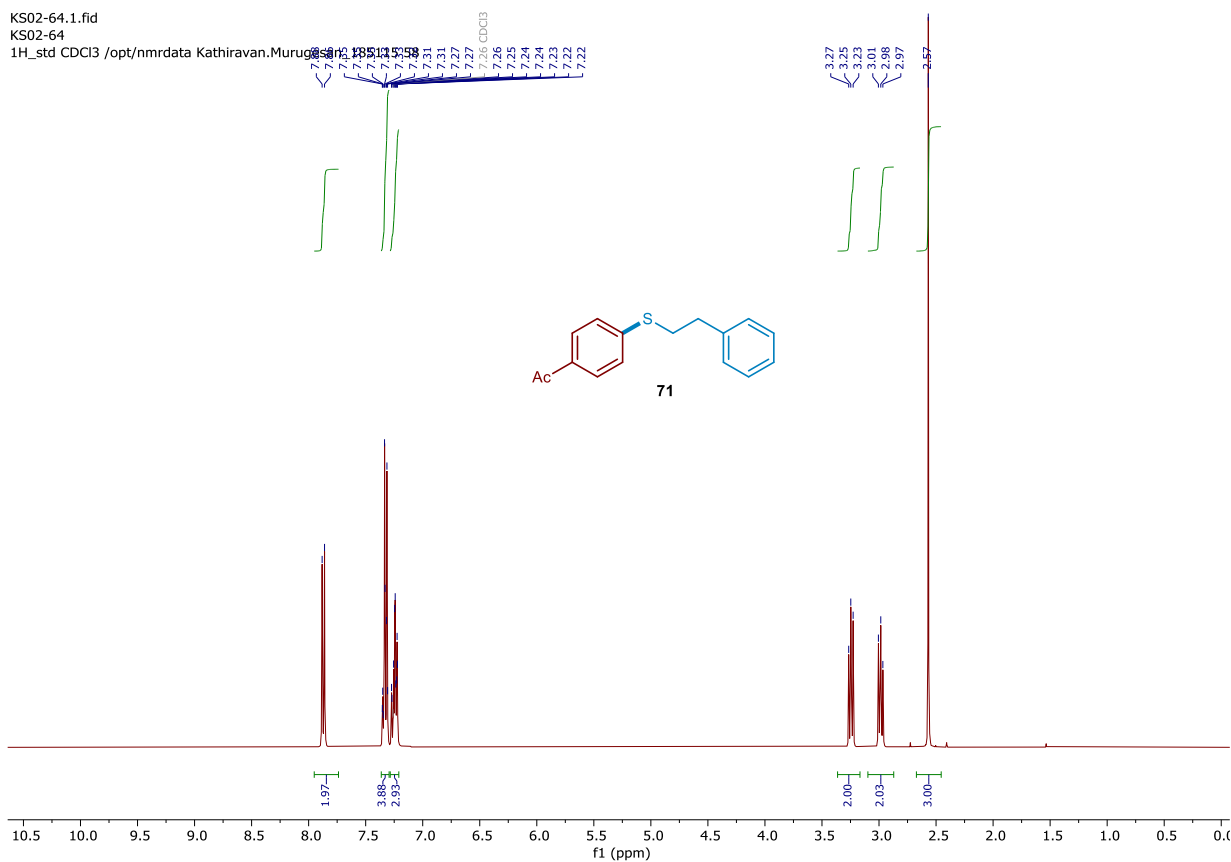
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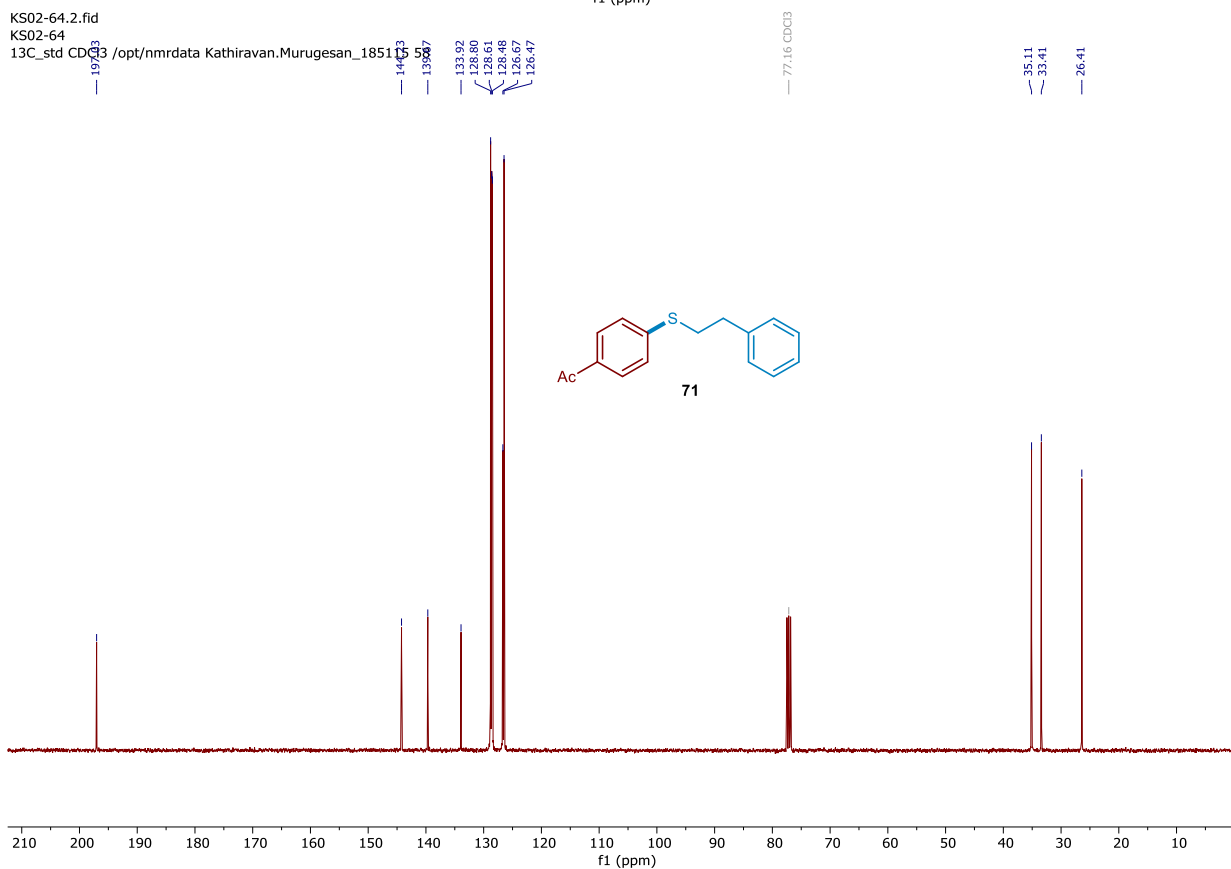
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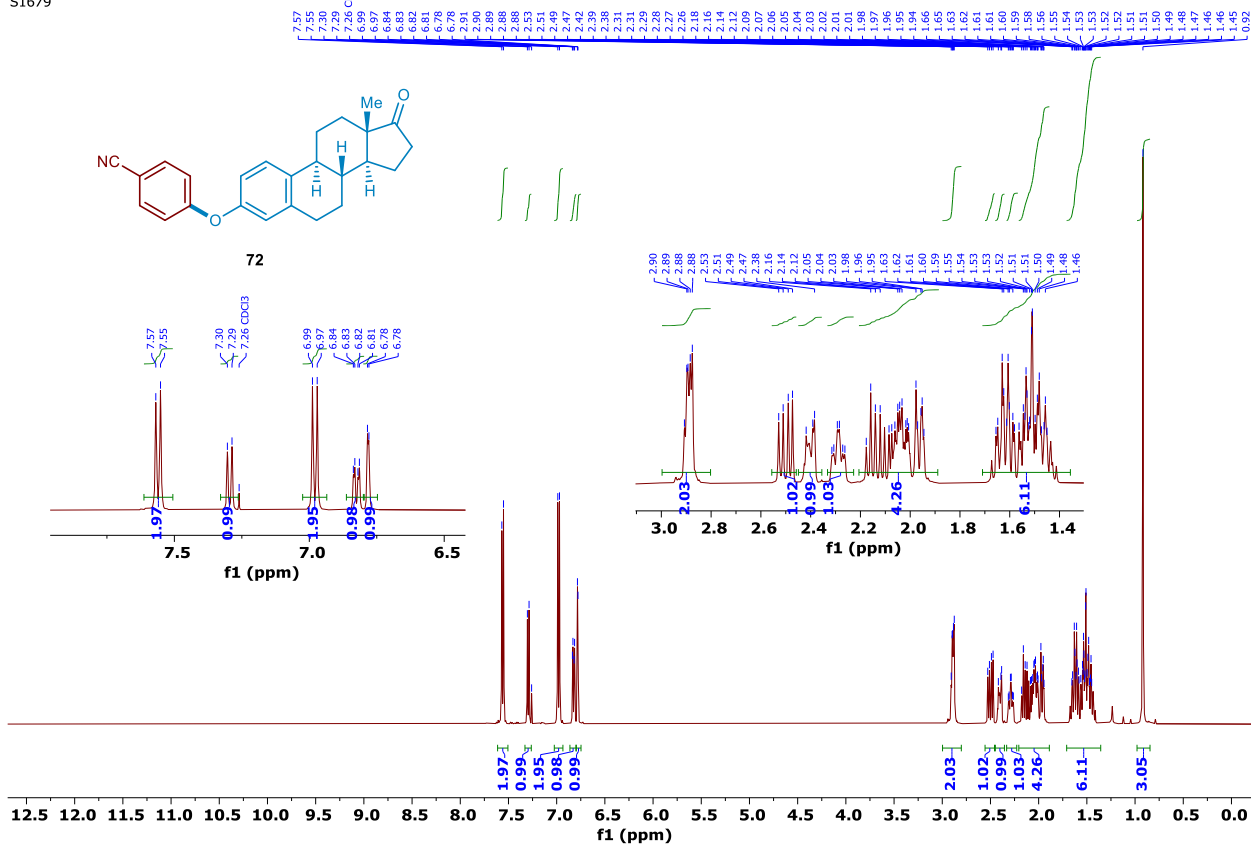


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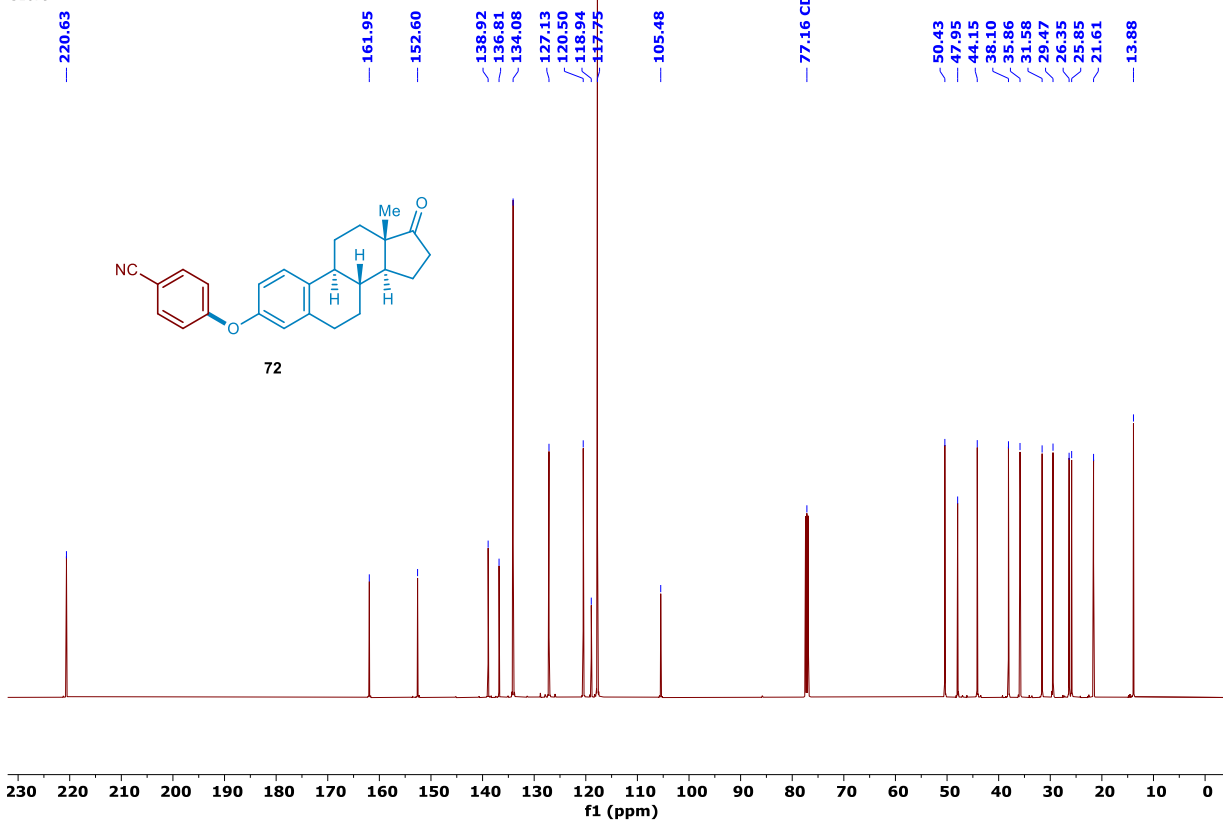
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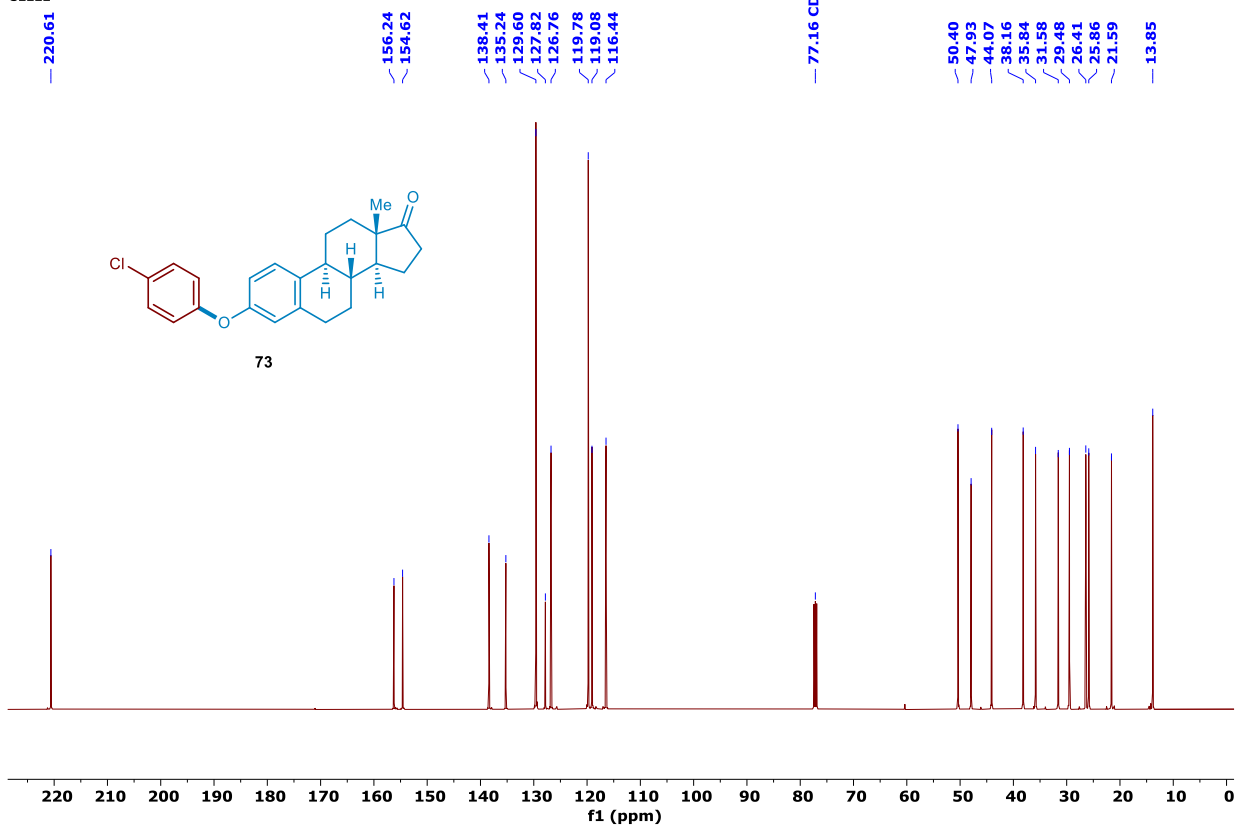


20230209-19-Sagadevan.Arunachalam\_169829-S1679.10.fid  
S1679

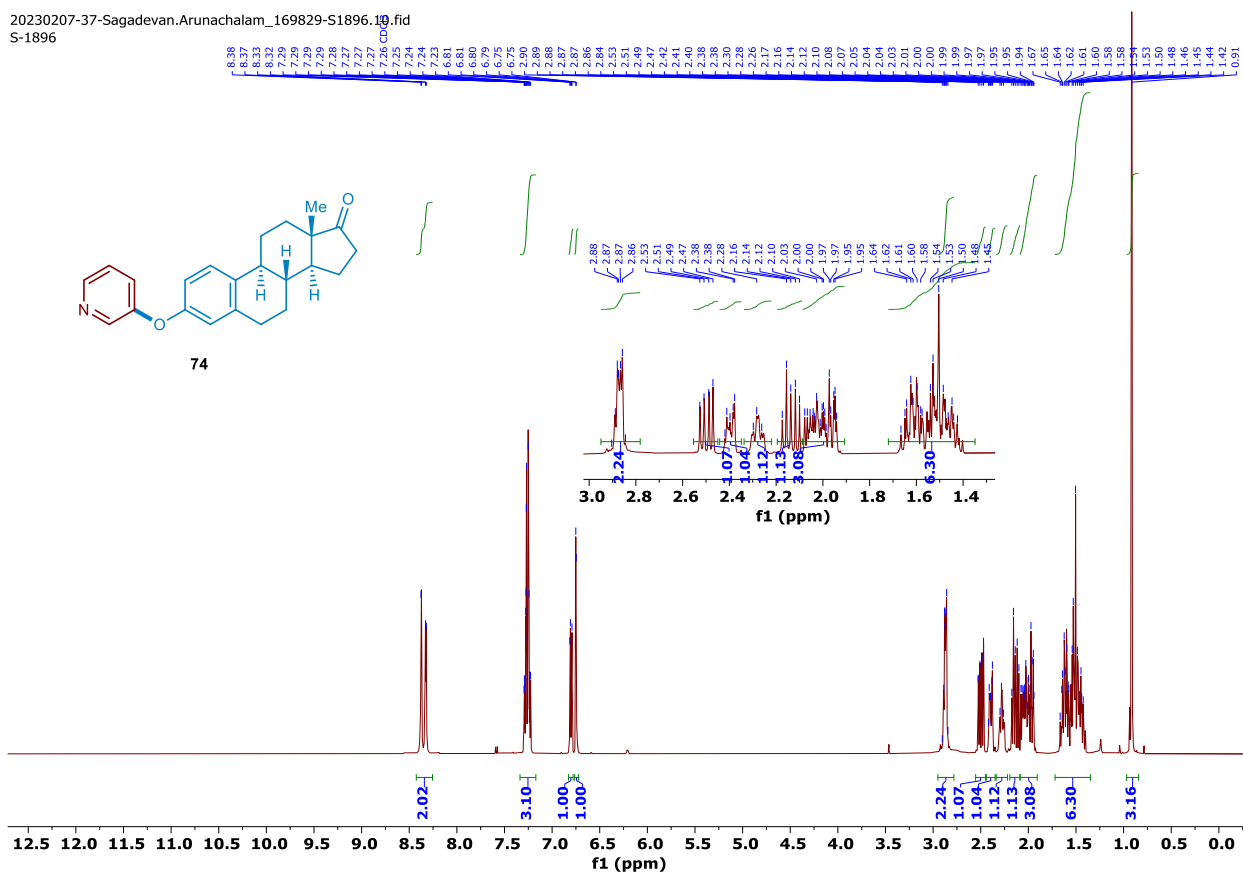


20230209-19-Sagadevan.Arunachalam\_169829-S1679.11.fid  
S1679

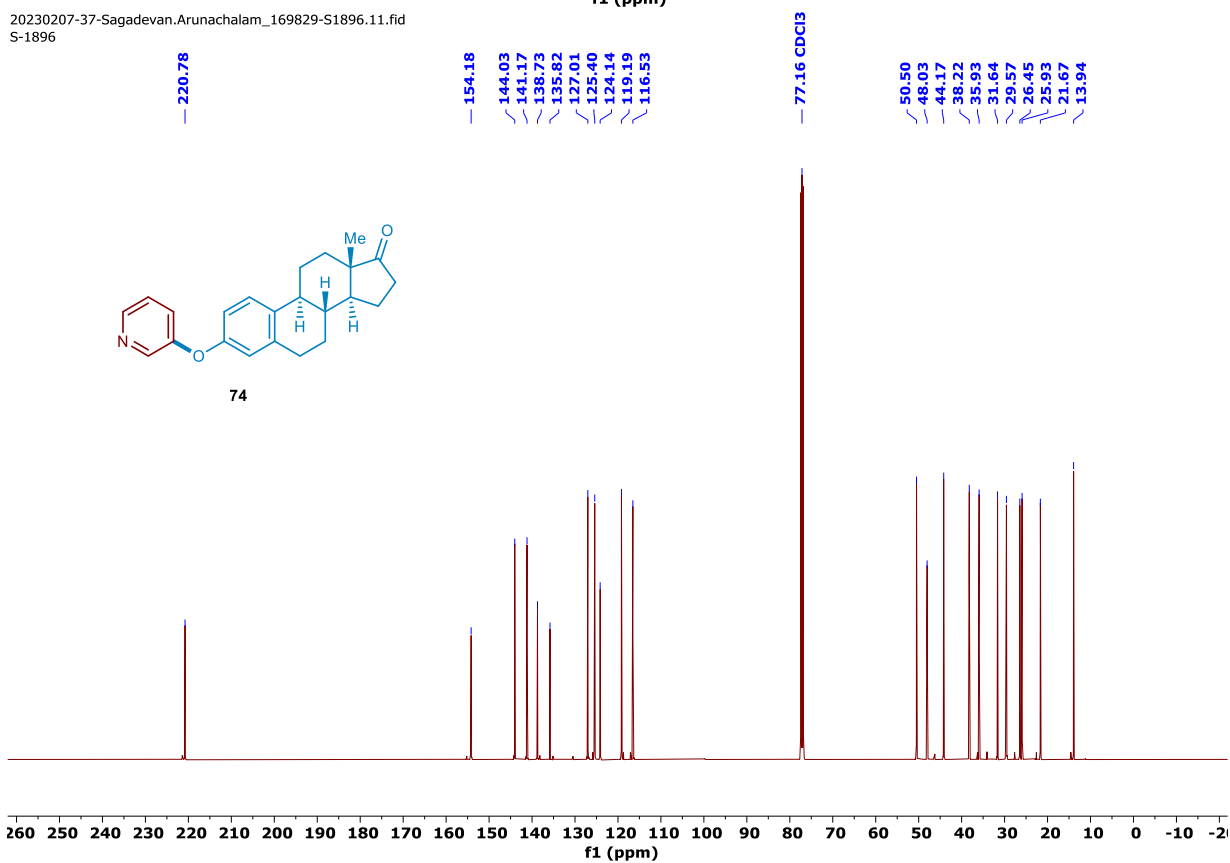


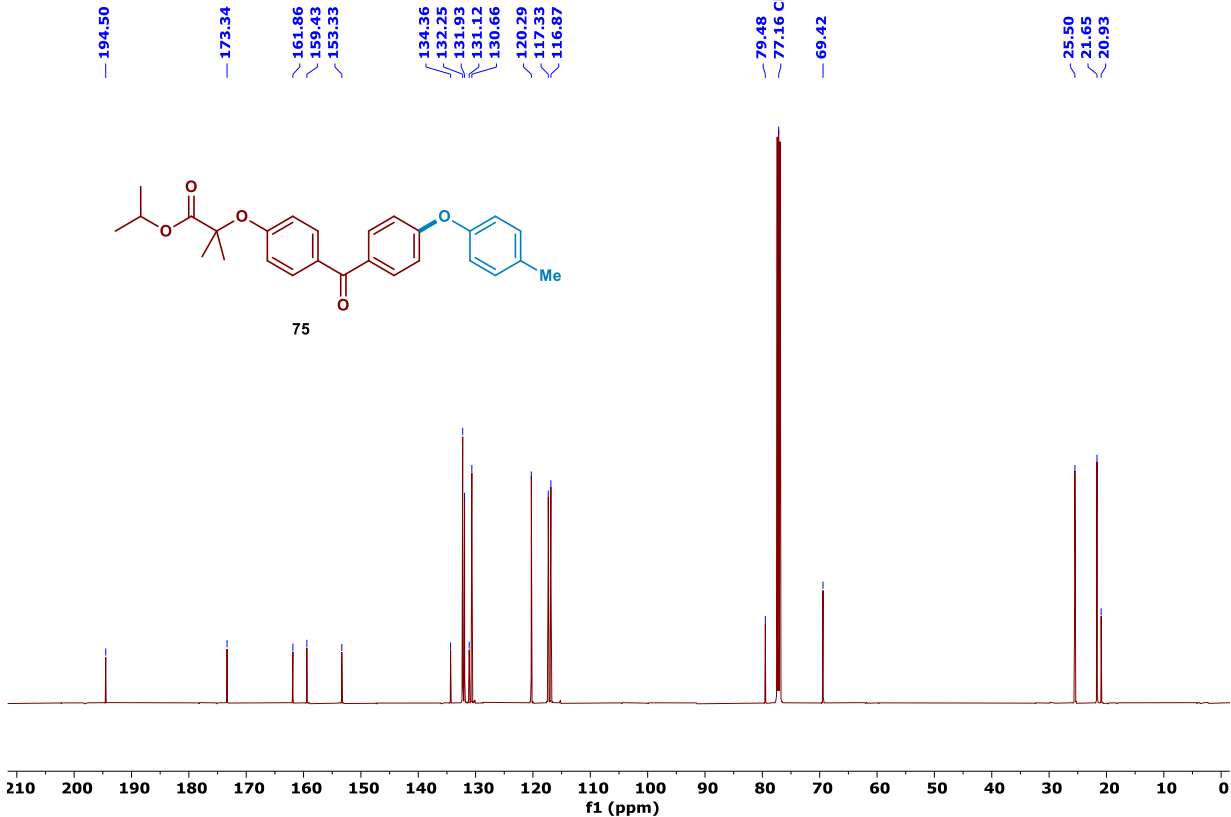
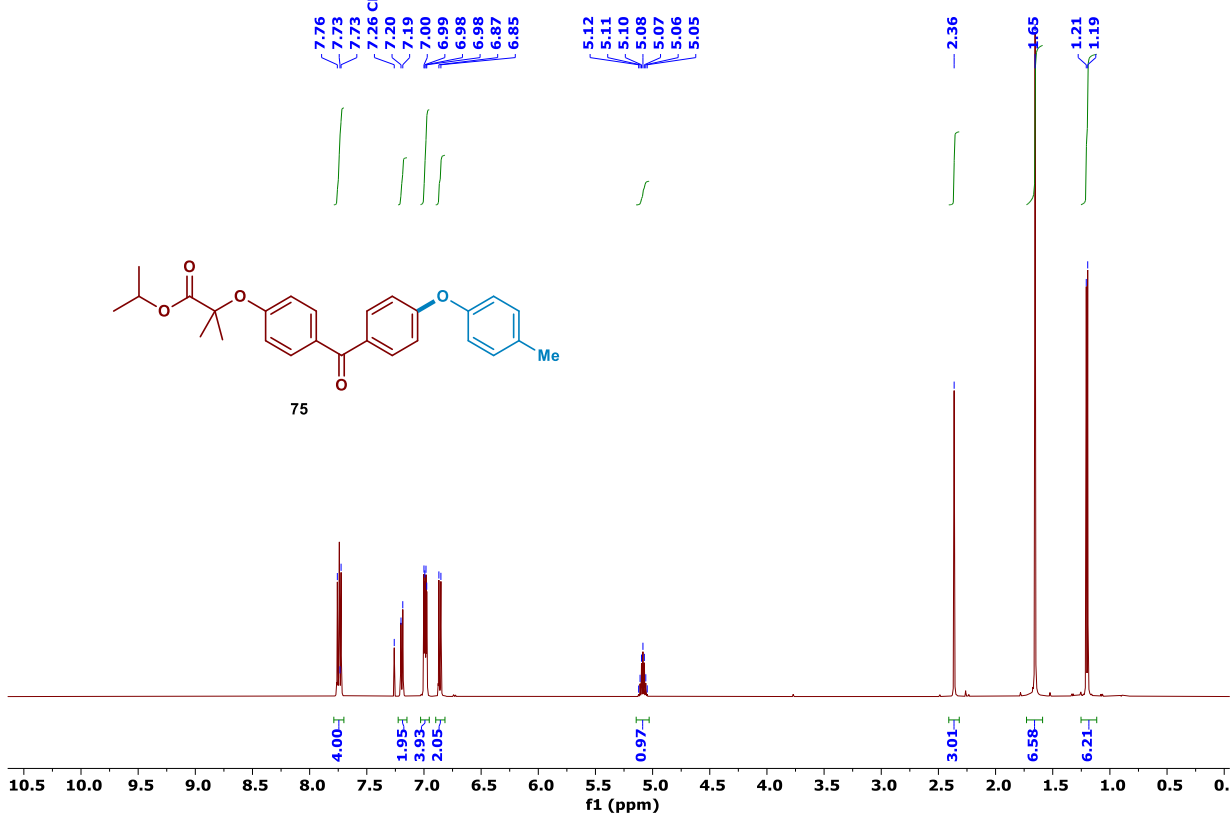


20230207-37-Sagadevan.Arunachalam\_169829-S1896.10.fid  
S-1896

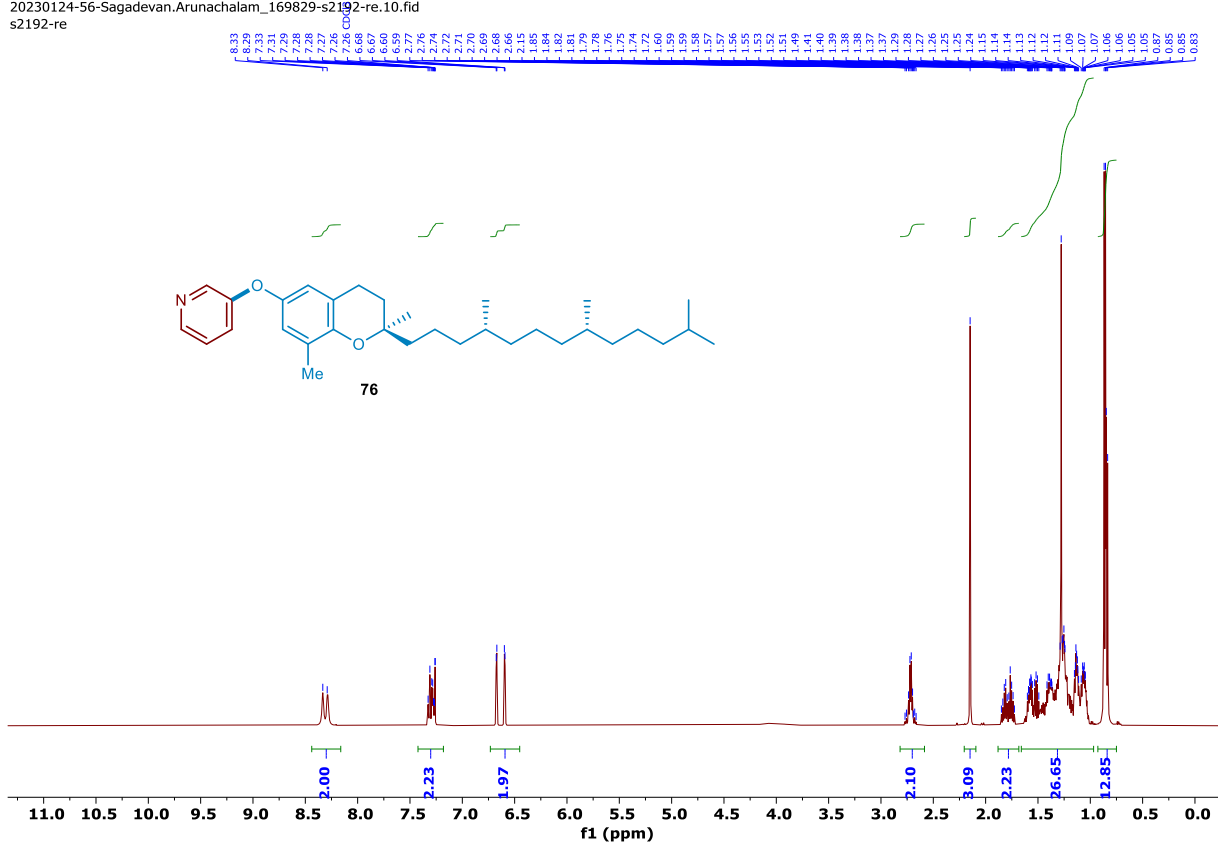


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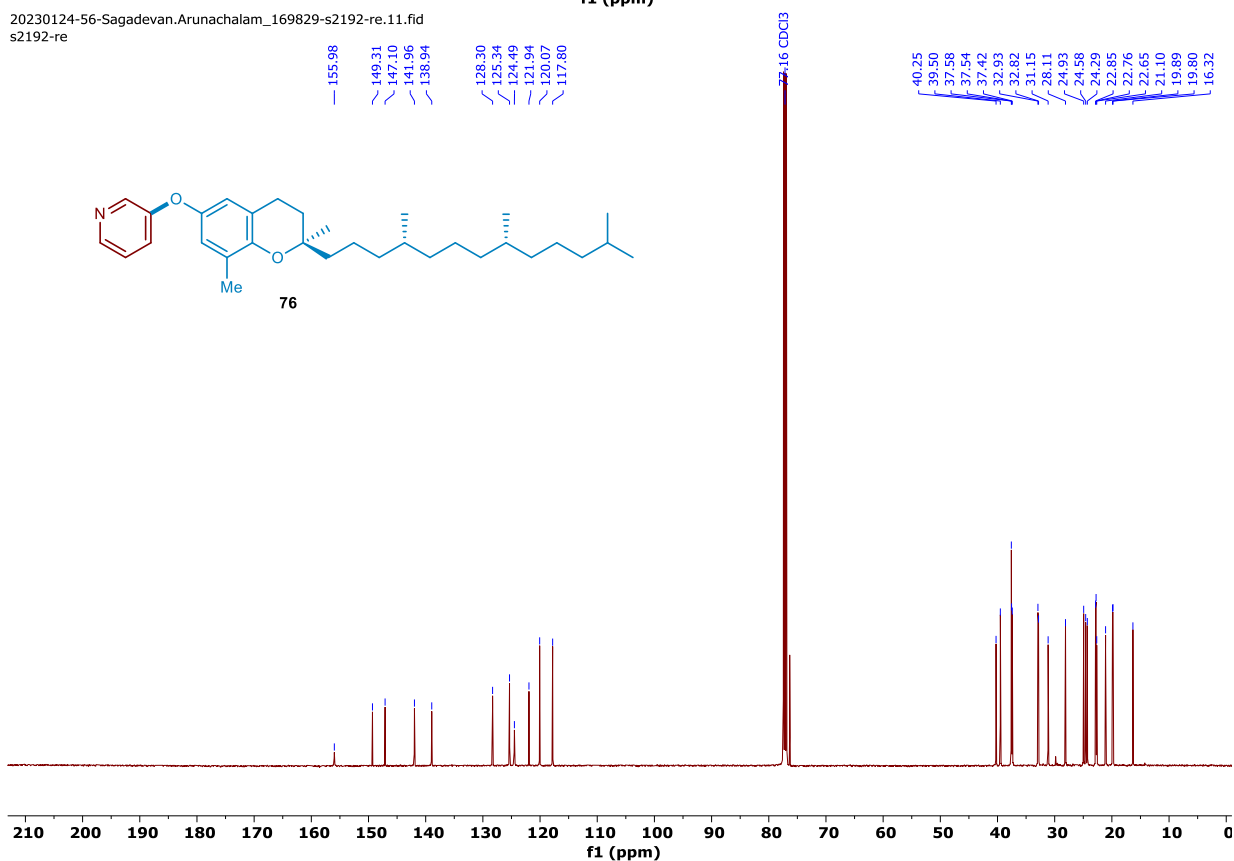




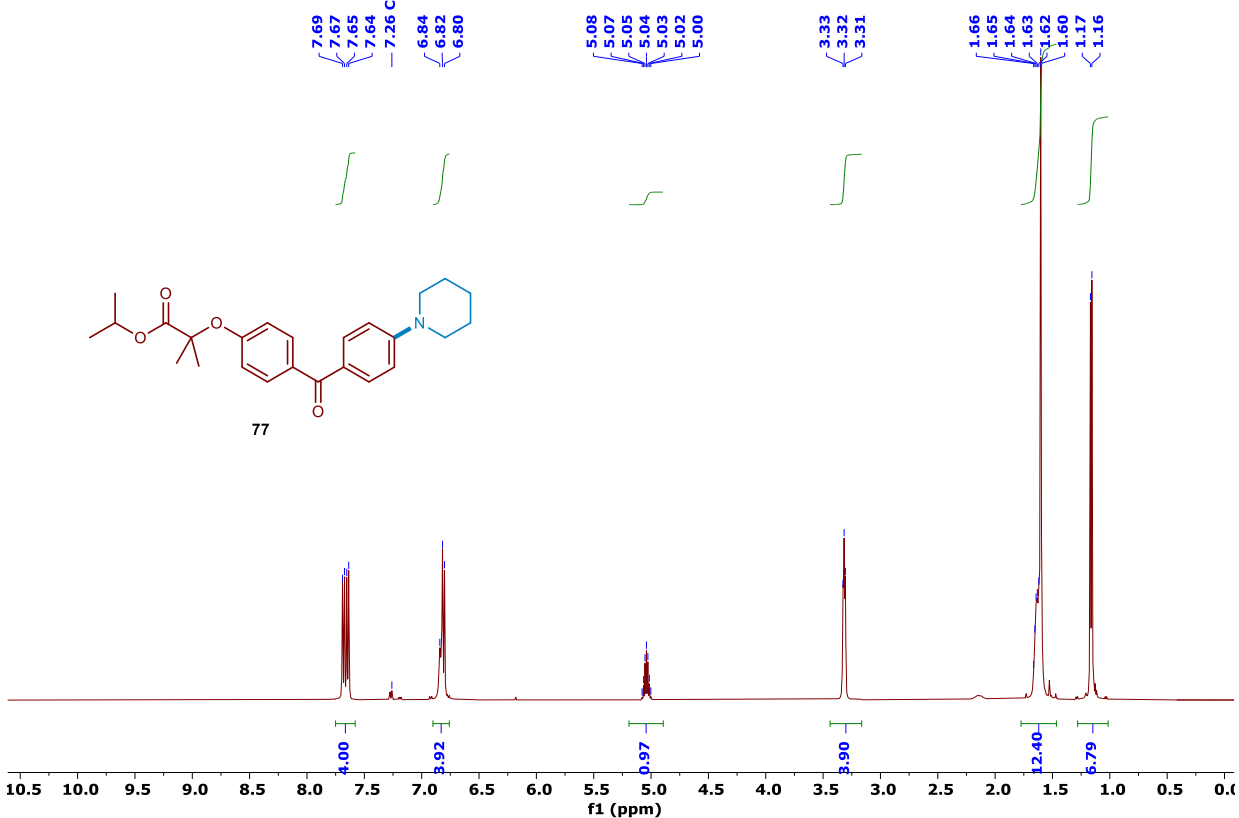
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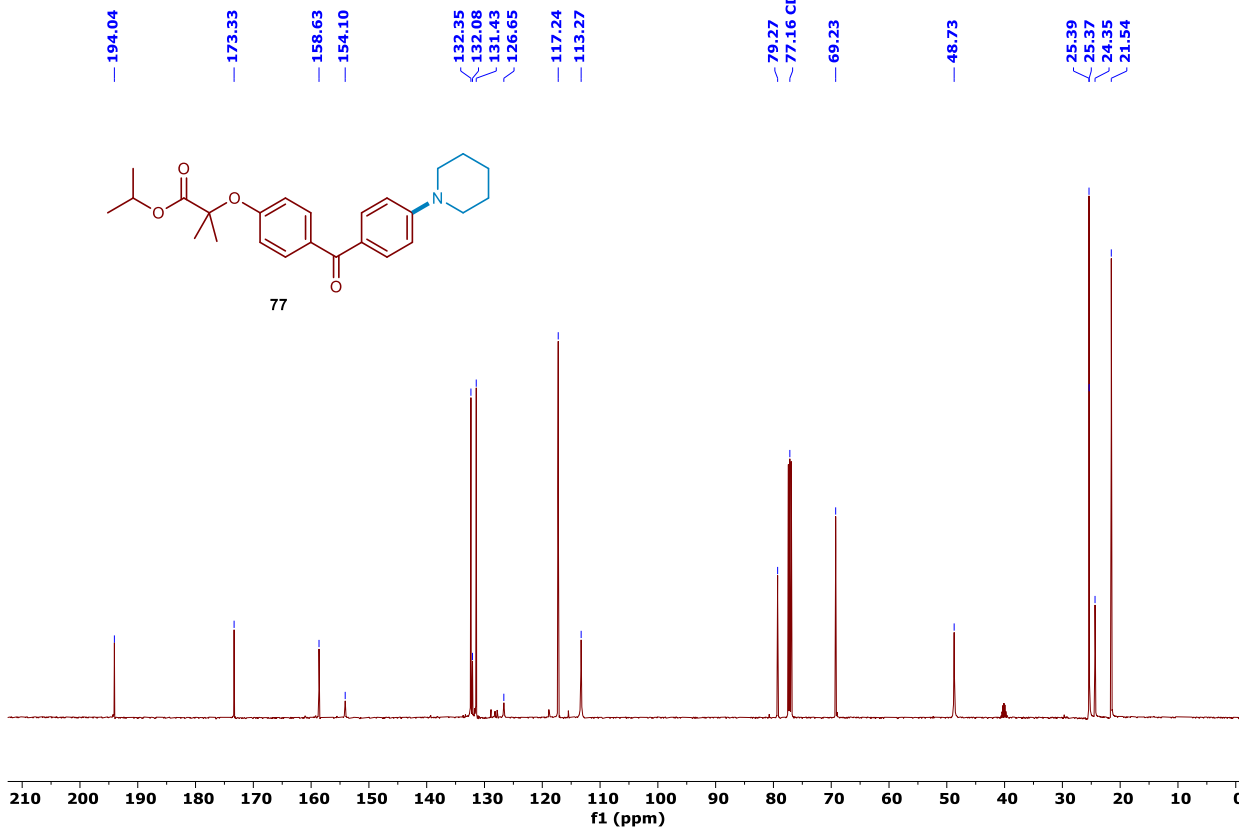
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20230124-58-Sagadevan.Arunachalam\_169829-s2200-re.10.fid  
s2200-re

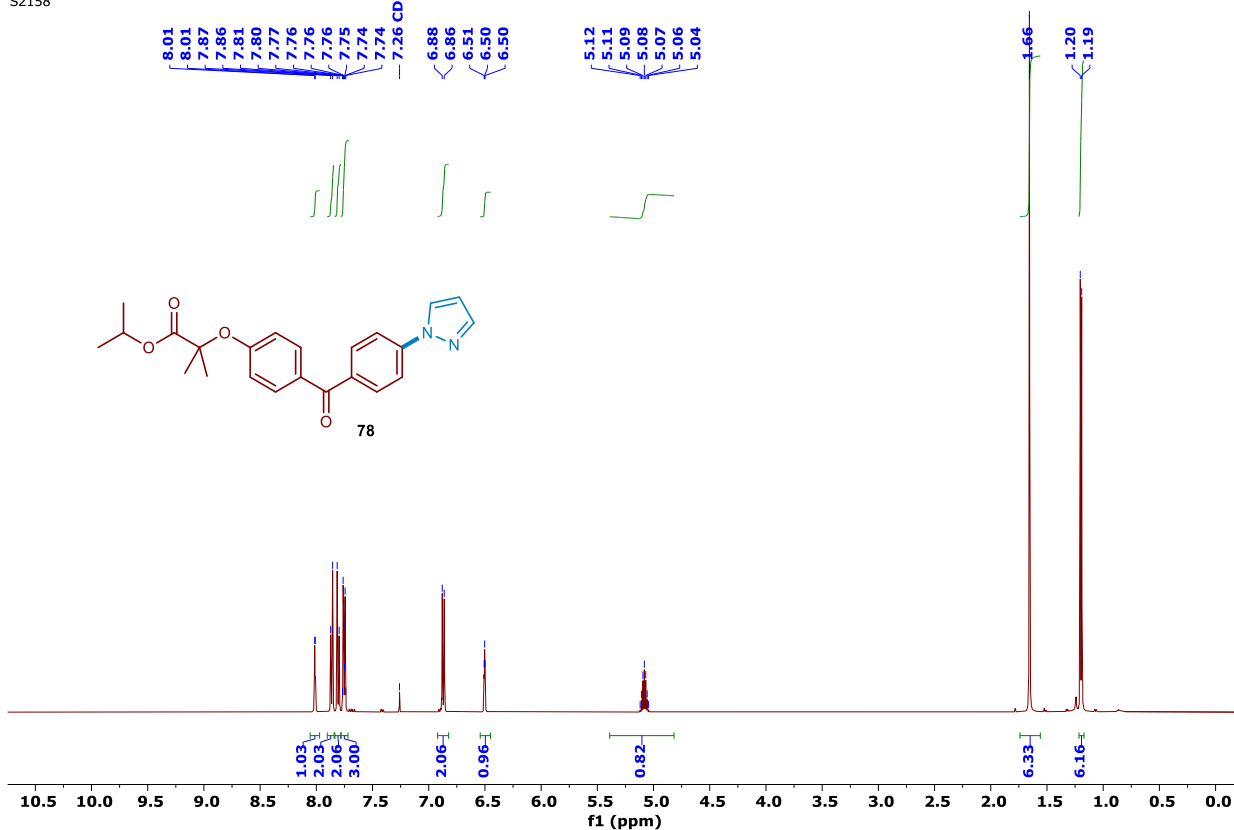


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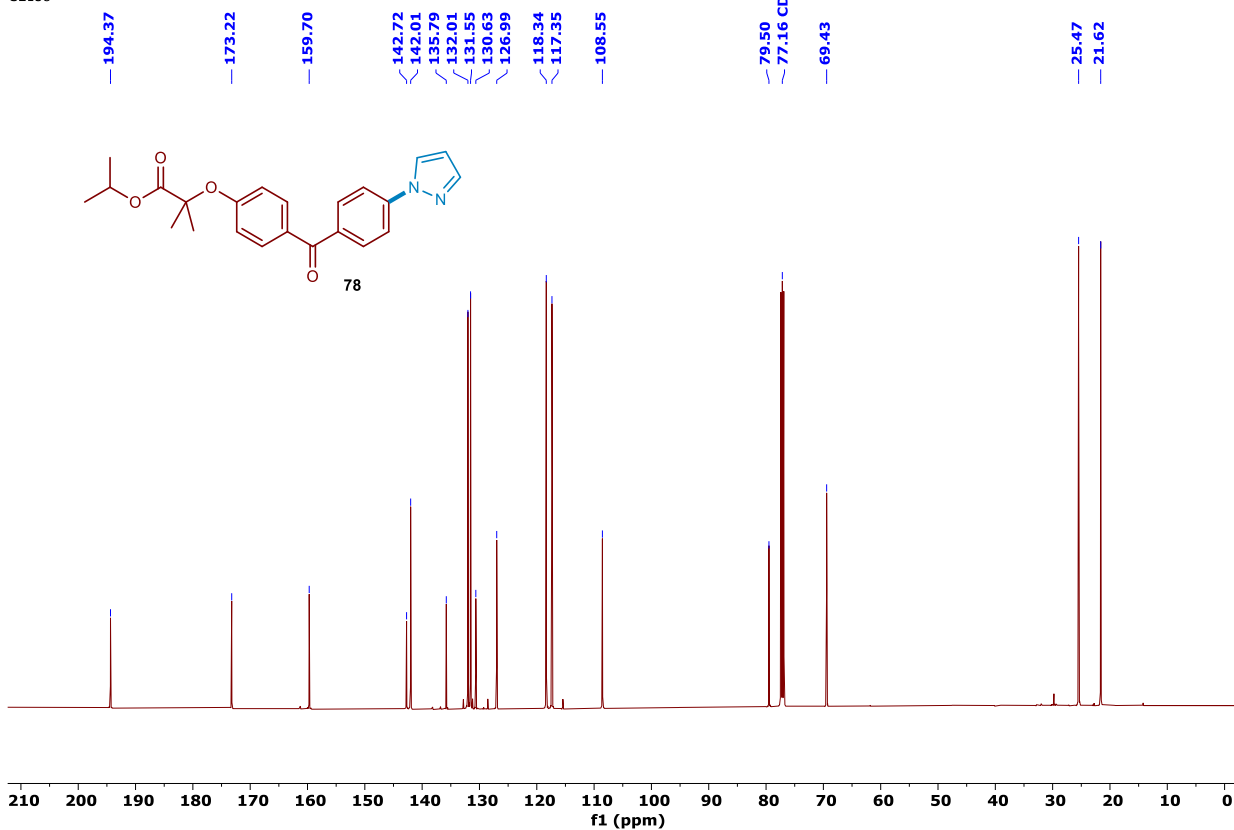




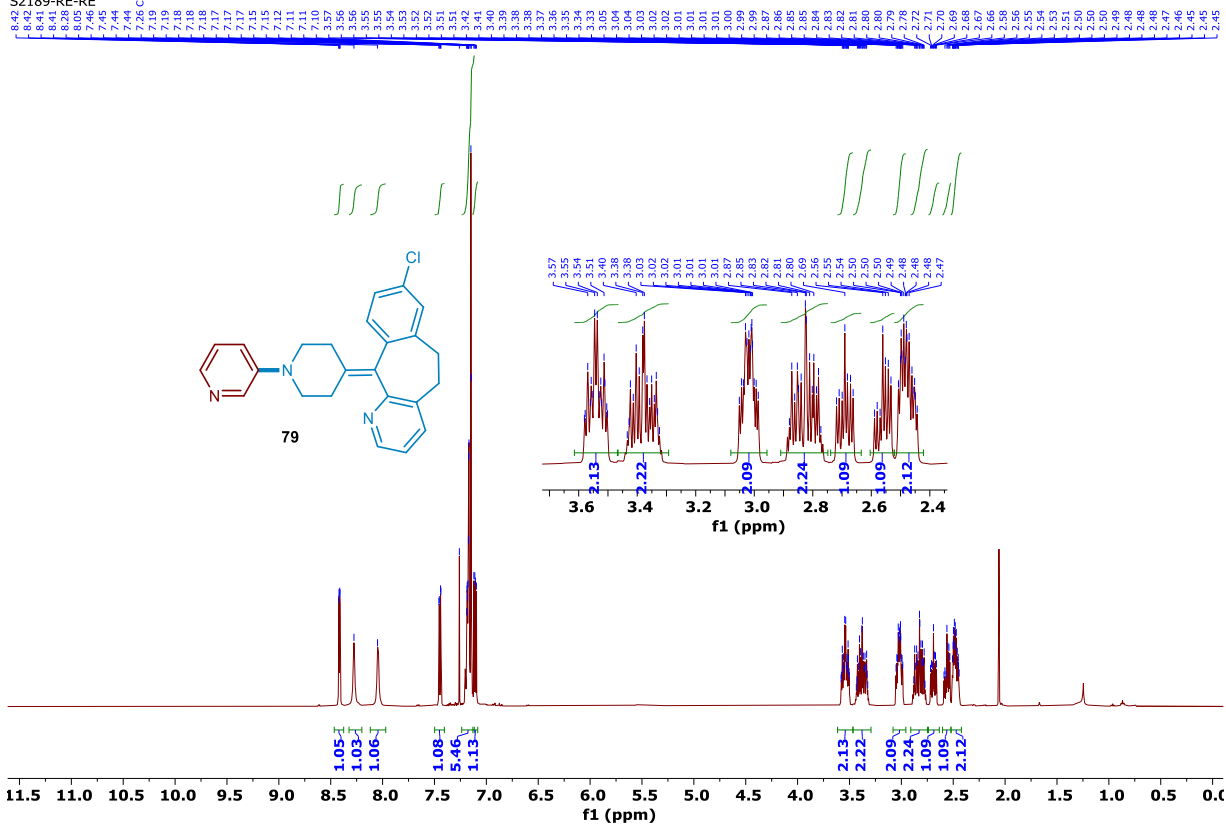
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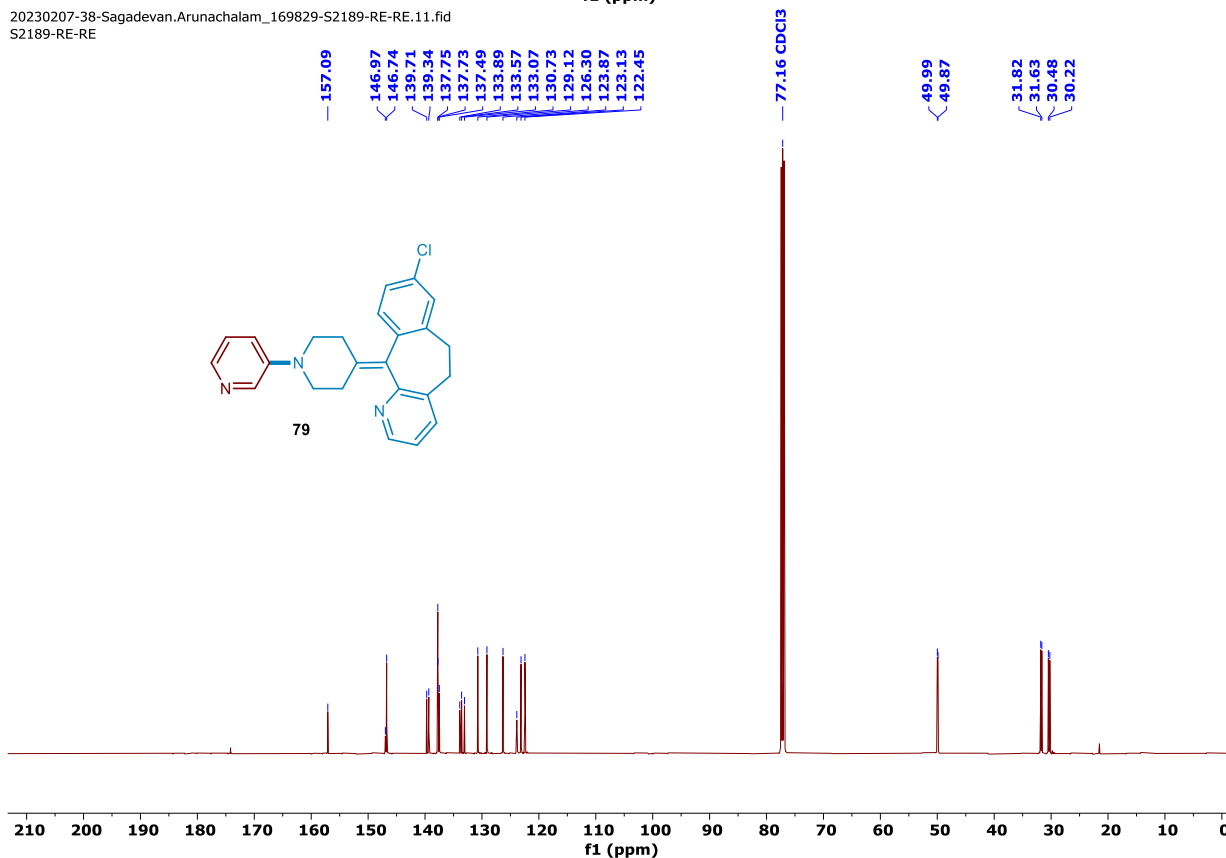
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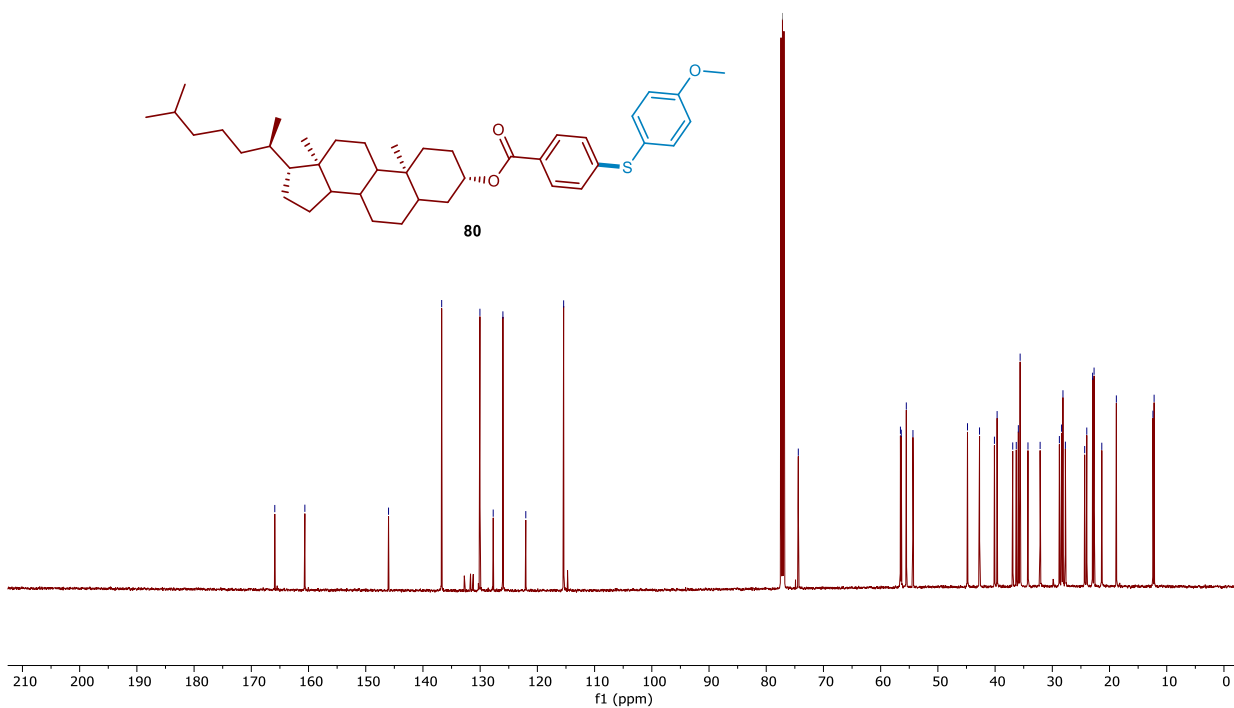
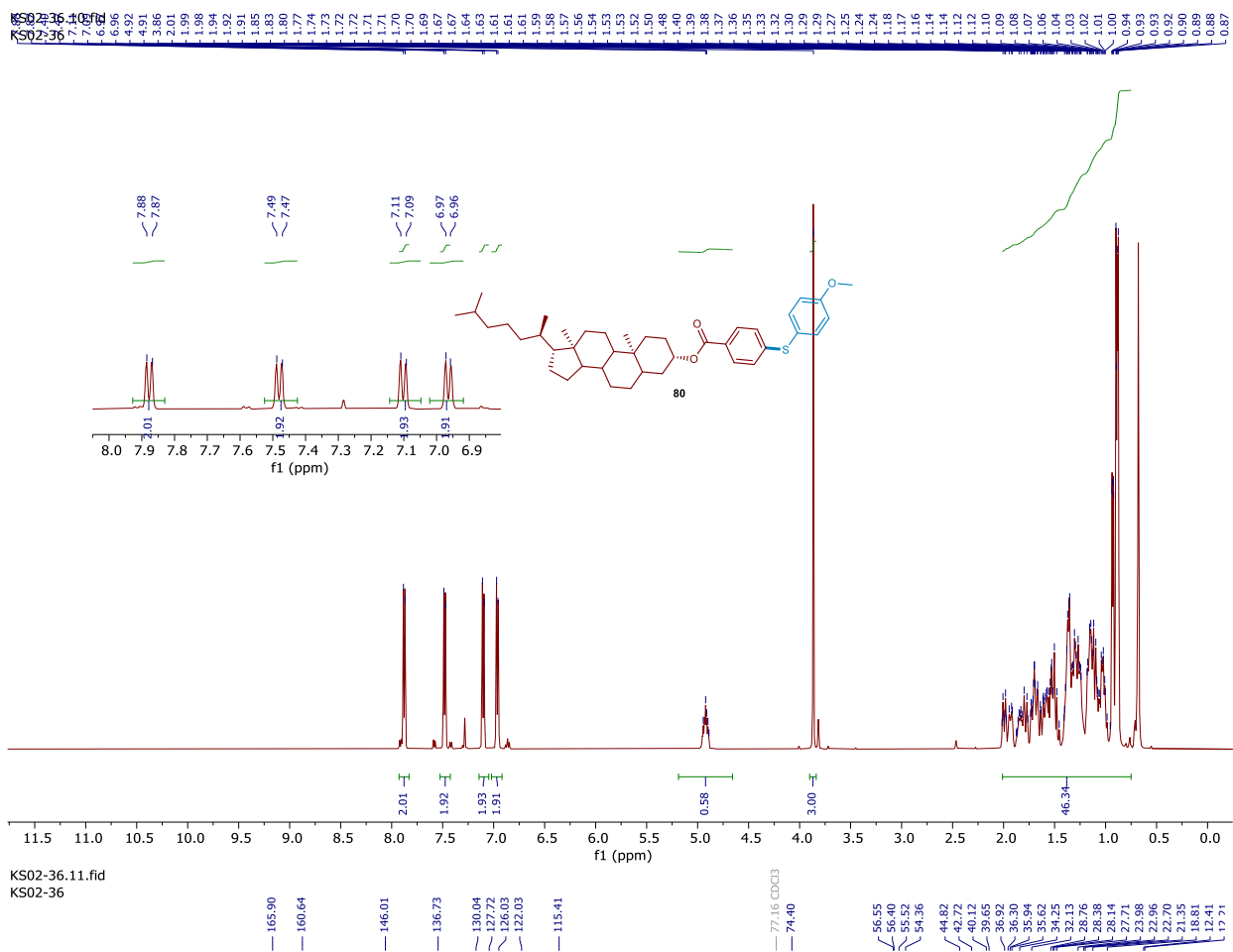


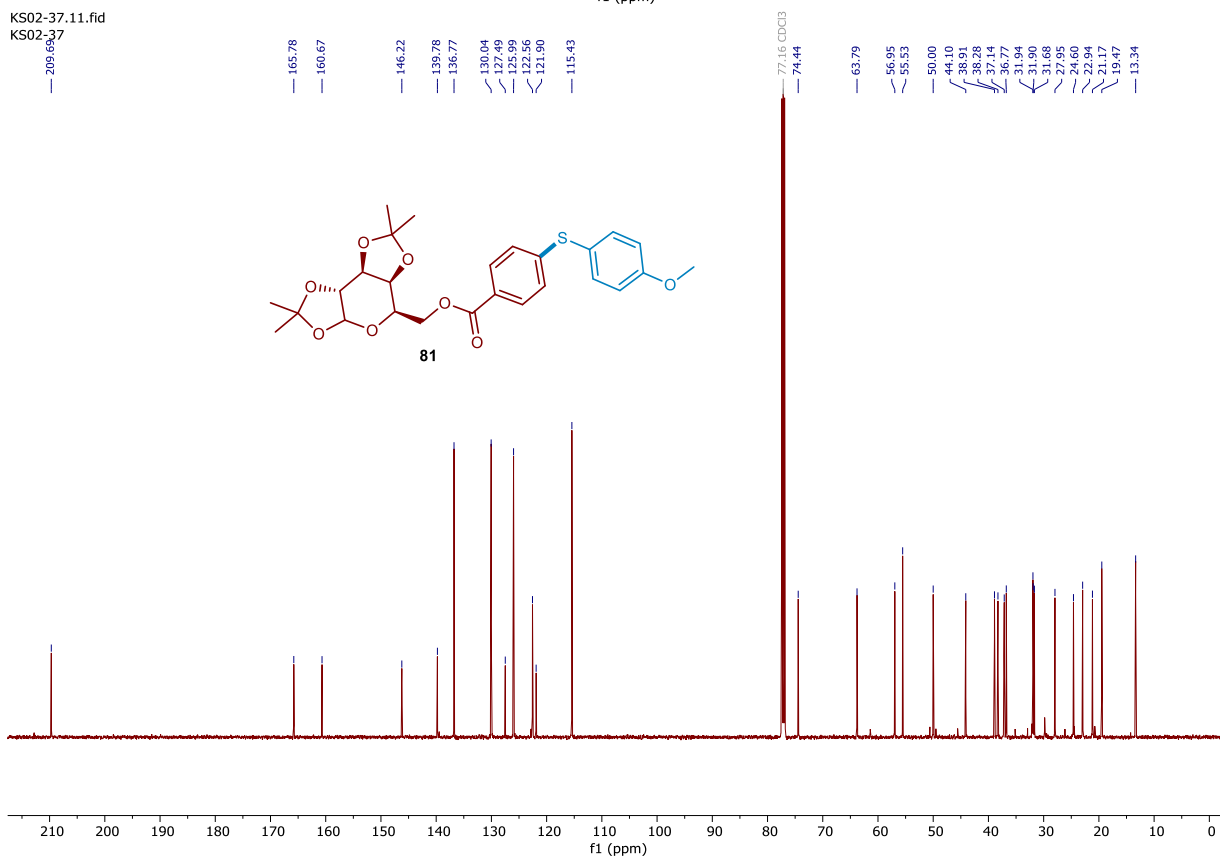
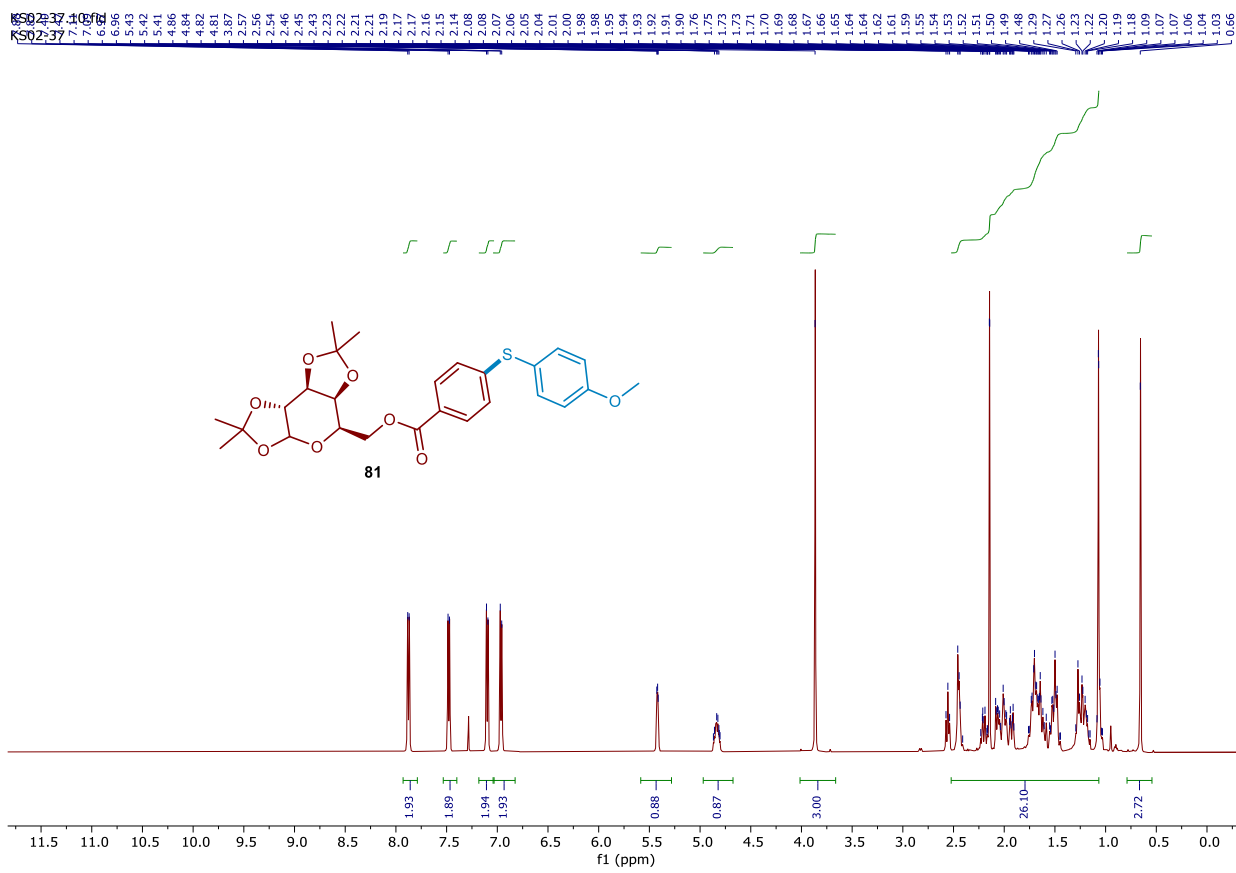
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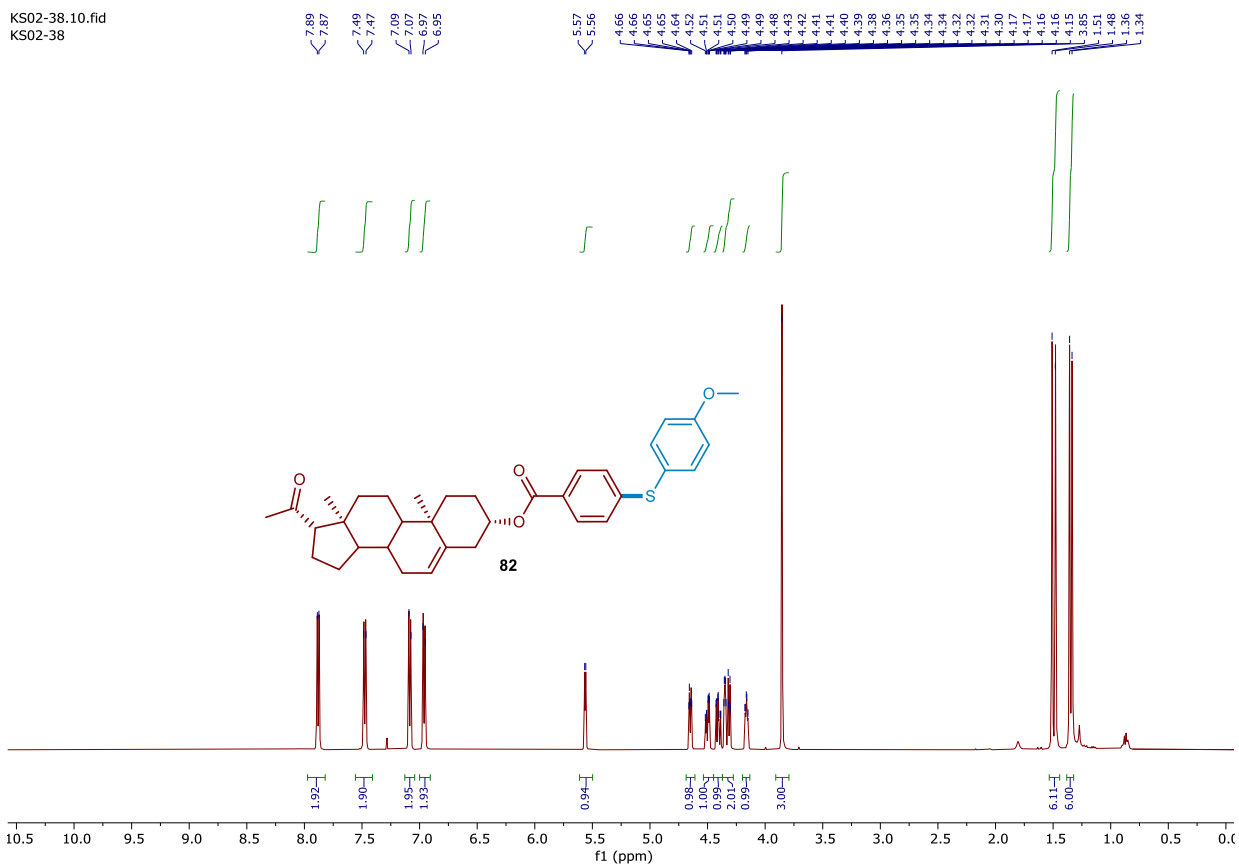
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