---- Electronic Supplementary Information ----

A π-conjugated covalent organic framework enables interlocked nickel/photoredox catalysis for light-harvesting cross-coupling reactions

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Section S-I: General Information

All the reactions were performed in oven-dried glassware under a nitrogen atmosphere. Solvents were dried under the standard protocol and were degassed and stored over activated molecular sieves (4 Å). The chemicals were purchased from Sigma Aldrich, Avra Synthesis, TCI, Alfa Aesar, Spectrochem, BLDpharm, and Combi-Blocks and used without further purification unless otherwise mentioned. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F254/0.25 mm) were used. Visualization was accomplished by UV light (254 nm) and an aqueous $KMnO_4$ stain. Kessil lamp (model: PR160L-427 nm) was used for photo-irradiation on the reaction mixture. In the case of an oil-bath heating reaction, the reaction temperatures are disclosed as the bath temperature surrounding the vessel unless otherwise mentioned.

Nuclear magnetic resonance (NMR) spectra were collected using BRUKER (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 471 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{19}F: 376 MHz) instruments. NMR data was taken in the ppm unit and referenced against the solvent residual peaks. Coupling constants (*J*) are reported in Hertz (Hz). Coupling patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sep (septet), dd (doublet of doublet), ddd (doublet of doublet of doublet), td (triplet of doublet), dt (doublet of triplet), tt (triplet of triplet) or m (multiplet).

Gas Chromatography-Mass Spectrometry (GC-MS) was performed on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an DB-5 ms capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific) with helium as the carrier gas.

High-resolution electrospray ionization mass spectrometry (ESI-HRMS) was performed in Bruker micrOTOF-Q II Spectrometer. The samples were prepared simply by dissolved solid or liquid substrates in MeOH or CH_3CN (10^{-3} to 10^{-5} M).

Powder X-ray diffraction (PXRD) data were collected by using a XEUSS system using a Genix micro source from Xenocs operated at 50 kV and 0.6 mA. The Cu Kα radiation (λ = 1.54 Å) was collimated with FOX2D mirror and two pairs of scattering less slits from Xenocs. The 2D patterns were recorded on a Mar345 image plate and processed using Fit2D software. All the measurements have been made in the transmission mode. The sample-to-detector distance calibrated with silver behenate standard is 220.8 mm for PXRD measurement.

Single Crystal X-Ray Diffraction (SCXRD) data for the crystal was collected at 100 K or 293 K on Rigaku (dual, Cu/Mo at zero, Eos) diffractometer using monochromatic CuKα (λ = 1.54184), respectively. Structures were solved by Using Olex2 in the Superflip structure solution program by charge flipping and refined with the least squares minimization SHELXL refinement program. Single crystals of compounds **47**, **48**, **63**, **70** were obtained by slow evaporation of solvent from the methanol solution of the corresponding compounds.

Fourier transform infrared (FT-IR) spectra of the solid samples were recorded on a Bruker Optics ALPHA II spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory. All the data have been reported in the wavenumber (cm^{-1}) scale.

Nitrogen adsorption experiments (0 to 1 bar) were performed using Quantachrome Quadrasorb automatic and Autosorb iQ instrument. The nitrogen adsorption isotherms were collected at 77 K using a liquid nitrogen bath. Before performing gas adsorption experiments, Bpy-sp^2c-COF and Ni@Bpy-sp^2c-COF were degassed at 140°C for 12 hrs under vacuum. Surface areas were calculated using the Brunauer-Emmett-Teller (BET) model applied between P/P_0 values of 0.05 and 0.3 for microporous and mesoporous COFs. Corresponding pore size distributions were calculated using the non-localized density functional theory (NLDFT).

Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TG50 and SDT Q600 TG-DTA analyzer under N_2 atmosphere from 30°C to 900°C along with a ramp rate of 10°C min^{-1}. Before carrying out the TGA, the samples were activated at 100°C for 30 minutes to eliminate the water from the samples.

Scanning Electron Microscopy (SEM) images were obtained using Zeiss SUPRA 55 VP SEM operating at 10 kV using tungsten filament as the electron source. The samples were sputtered with gold (nano-sized film) before the imaging using an SCD 040 Balzers Union sputterer to avoid charging during SEM analyses. The samples were prepared simply by putting a drop of dispersed samples (Bpy-sp^2c-COF and Ni@ Bpy-sp^2c-COF) in isopropanol on a clean piece of Silicon wafer. Elemental mapping of the Bpy-sp^2c-COF and Ni@ Bpy-sp^2c-COF were also recorded using SEM with energy dispersive X-ray spectrometry (EDS). In these cases, samples were prepared by solid sample coating on a non-porous and conductive adhesive carbon strip.

Transmission Electron Microscopy (TEM) images were obtained using UHR FEGTEM, DST-FIST facility of IISER Kolkata at an accelerating voltage of 200 kV. The samples were prepared by direct drop-casting (dispersed in isopropanol) onto copper grids TEM Window (TED PELLA, INC. 200 mesh).

Ultraviolet-Visible Spectroscopy (UV-Vis) of the powder solid samples were measured by JASCO V-670 using a quartz plate holder.

Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) analyzed by the Thermo Scientific instrument (Model no. ThermoiCAP-7400) with Qtegra software. The analytical wavelength for metal detection was selected based on intensity counts and background interference. Operating condition for ICP-OES are given as follow- [Power-1150, Coolant Flow-12 L/min, Auxiliary Flow-0.50 L/min, Nebulizer Flow-0.50 L/min, Additional Flow-0 L/min, Nebulizer gas pressure-210 kPa, Plasma torch- Quartz, Spray chamber- Cyclonic, Carrier gas- Argon].

Photoluminescence Emission (PL) spectra were acquired on a spectrofluorometer Fluoremax X at room temperature. In a screw-capped cuvette, a solid powder sample was dispersed in 2 mL dry acetonitrile and subjected to analysis after degassing for 2 mins.

Time Correlated Single Photon Counting (TCSPC) method is using to collect the data for the time-resolved fluorescence decay. The fluorescence decay and the anisotropy data were measured from a Horiba Jobin Yvon time-resolved spectrometer with a 405 nm diode laser excitation (temporal resolution <70 ps). The raw data of fluorescence decay were fitted by a non-linear least square iteration procedure using IBH DAS6 (version 2.2) software.

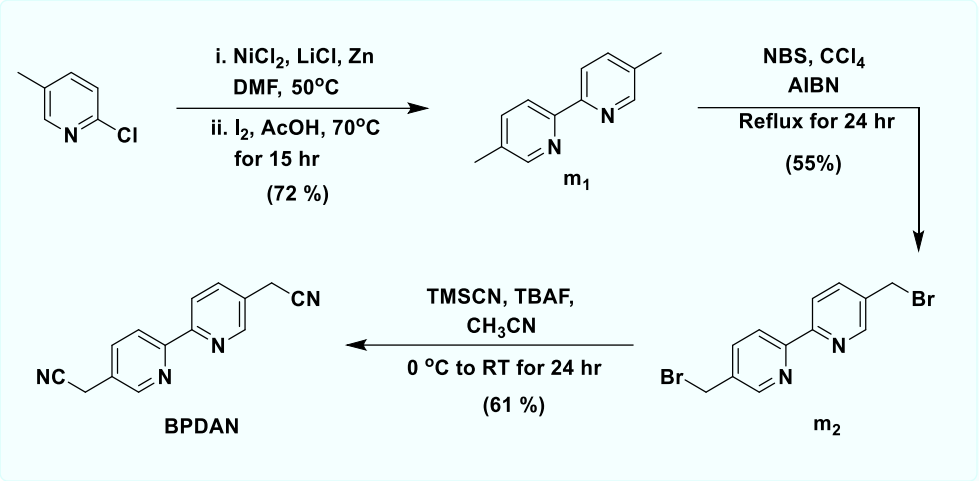
X-ray Photoelectron Spectroscopy (XPS) analysis was carried out using Thermo Scientific's K-Alpha+ spectrometer. The pass energy for the survey scan and the high-resolution scan was maintained at 100 eV and 50 eV, respectively, where the angle between the analyzer and sample surface was 90°. In the case of deconvoluted spectra, first, the spectra were analyzed and fitted by Fityk 1.3.1 software.

Cyclo Voltammetry (CV) experiments were carried out in CHI-660 potentiostat instrument. Model compounds were placed in simple undivided three-electrode cells. Glassy Carbon (GC) (3 mm of diameter) was used as a working electrode, Silver/Silver nitrate (10 mM) as the reference electrode, and Pt wire as a counter electrode. Before each measurement, the working electrode was polished with 0.05 μm alumina paste and rinsed with water/acetone, and finally blow-drying. Degassed acetonitrile and acetonitrile/benzene (1:1) were used as solvents, where tetrabutylammonium hexafluorophosphate ($^{n}Bu_4PF_6$) (0.1 M) acted as a supporting electrolyte. For solid powder samples, first, the sample is coated on carbon paper and air-dried, then subjected to analysis.

Mott-Schottky (MS) experiments were performed after drop casting Bpy-sp^2c-COF and Ni@Bpy-sp^2c-COF samples dispersed in isopropanol onto FTO coated glass. Analysis was performed in 0.2 M aqueous Na_2SO_4 solution using alternating current in the DC bias range from –1 to +1 V versus Ag/AgCl.

Section S-II: Synthesis of Building Blocks

Synthesis of 5,5'bis(cyanomethyl)-2,2'-bipyridine (BPDAN):



BPDAN was prepared by a three-step reaction following previous studies with some modifications.[1]

5,5'-dimethyl-2,2'-bipyridine (m_1)

$NiCl_2$ (0.64 g, 0.5 mmol) and DMF (40 mL) were added to a 100 mL two-neck round-bottom flask. The solution was stirred and heated to 45 °C, and then 2-chloro-5-methylpyridine (2.19 ml, 20 mmol) zinc dust (1.57 g, 12 mmol), and anhydrous LiCl (0.85 g, 10mmol), were added to the solution. The temperature was then raised to 55 °C, and two drops of acetic acid and some grains of iodine crystals were added to the mixture. An immediate rise in temperature and color change to black was observed, indicating the reaction was triggered. The mixture was stirred at 70 °C overnight. After that, the reaction mixture was cooled at room temperature, and 1 N HCl aqueous solution (25 mL) was added to the mixture to consume excess zinc dust. The aqueous ammonia (25%) was added to the reaction mixture to make it alkaline. Then CH_2Cl_2 and water were added to the reaction mixture for workup. The organic layers were collected, dried over anhydrous Na_2CO_3, and concentrated. The crude material was purified by chromatography. **Yield** 0.33 g (72%). Yellowish solid. Column chromatography on silica gel (Eluent: 20-30% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 153.9, 149.6, 137.5, 133.1, 120.4, 18.4.

5,5'-Bis(bromomethyl)-2,2'-bipyridine (m_2)

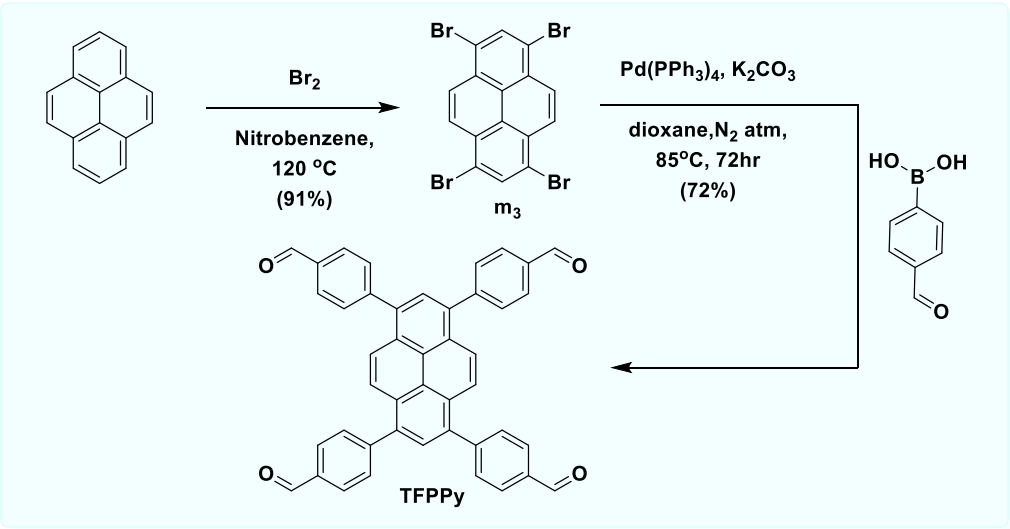
5,5'-dimethyl-2,2'-bipyridine (**m_2**) (1.14 g, 6 mmol) was added in carbontetrachloride (15 ml) in a Schlenk tube and degassed for 20 min, then *N*-bromosuccinimide (NBS) (2.23 g, 12.6

mmol) and AIBN (a pinch) were added to the reaction mixture. Then the tube was sealed under an inert atmosphere. After that, the reaction mixture was refluxed for 20 hr, then cooled the reaction mixture and filtered it. Finally, solvents were removed under reduced pressure to give the crude product. 50 ml methanol was then added to the crude and sonicated for 2 h. A fresh white solid compound remains in the mixture's bottom, which is then filtered out and dried. This residue is used for the next step without further purification. **Yield** 1.12 g (55%). White solid. **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.77 (s, 2H), 8.38 (d, *J* = 8.2 Hz, 2H), 8.05 (dd, *J* = 8.2, 2.3 Hz, 2H), 4.83 (s, 4H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 153.8, 149.5, 138.4, 134.9, 120.7, 30.6.

5,5'bis(cyanomethyl)-2,2'-bipyridine (BPDAN)

In a 25 ml two-neck round-bottom flask 5,5'-Bis(bromomethyl)-2,2'-bipyridine (**m$_2$**) (0.8 g, 2.34 mmol) was added in 10 ml dry CH_3CN under an inert atmosphere. Then TMSCN (0.508 g, 2.92 mmol) was added at room temperature. After that, it was cooled to 0 ^{o}C, and TBAF (1 g, 3.83 mmol) was added and stirred for 15 min at 0 ^{o}C. The reaction mixture was then warmed to room temperature and stirred for 24 h under an inert atmosphere. After that, solvents were removed, and the residue was purified by column chromatography. **Yield** 334 mg (61%). White solid. Column chromatography on silica gel (Eluent: 0.5-1% MeOH in DCM). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.66 (s, 2H), 8.40 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 4.18 (s, 4H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 154.1, 148.8, 137.0, 128.0, 120.6, 118.6, 19.9.

Synthesis of 1,3,6,8 tetra-(4-formylphenyl)pyrene (TFPPy):



TFPPy was synthesized by the following modified reported procedure.[2]

1,3,6,8 tetrabrpmopyrene (m_3)

An oven-dried round-bottom flask charged with pyrene (2g, 9.88 mmol) and 40 ml nitrobenzene was dropwise added bromine (2.24 ml, 4.22 mmol). The reaction mixture was then refluxed for 16 h in an inert atmosphere. It is then cooled to room temperature and filtered before being washed with diethyl ether to yield 1,3,6,8 tetrabrpmopyrine (**m_3**). This residue is used for the next step without further characterization.

1,3,6,8 tetra-(4-formylphenyl)pyrene (TFPPy)

A two-neck round-bottom flask charged with 1,3,6,8-tetrabromopyrene (**m_3**) (1.50 g, 2.89 mmol), 4-formylphenylboronic acid (2.61 g, 17.40 mmol), palladium tetrakis(triphenylphosphine) (0.12 g, 0.10 mmol), and potassium carbonate (2.1 g, 15 mmol) was added dry dioxane (30 mL). Then the mixture was stirred under an inert atmosphere for 72 h at 85 ^{o}C. After that, it was poured into an ice-cold 2 M HCl solution. The resulting yellow solid was filtered and washed three times with 2 M HCl. Later, the residue was repeatedly washed with water and acetone until colorless filtrate came. **TFPPy** was obtained as a bright yellow powder. **Yield** 1.29 g (72%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.16 (s, 4H), 8.18 (s, 4H), 8.09 (s, 10H), 7.86 (s, 8H). Due to the low solubility of this compound in common deuterated solvents, no ^{13}C NMR spectra could be recorded.

Section S-III: Synthesis of Bpy-sp^{2}c-COF and Ni@Bpy-sp^{2}c-COF

Preparation of TpBpy COF Bpy-sp^{2}c-COF and Ni@Bpy-sp^{2}c-COF

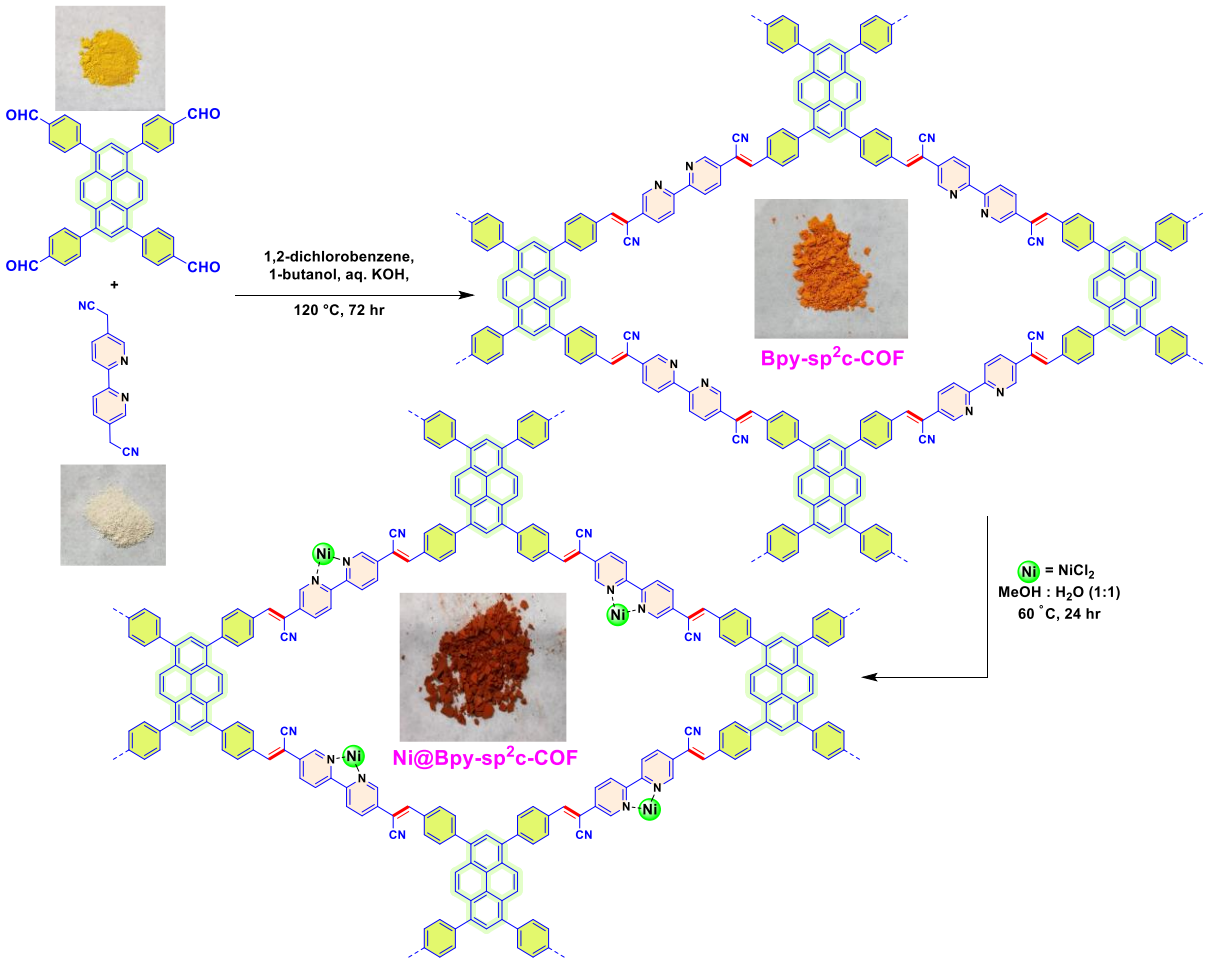


Figure S1: Preparation of Bpy-sp^{2}c-COF and metallation with $NiCl_2$.

Bpy-sp^{2}c-COF was synthesized by the following procedure with some modifications.[3]

An oven-dry sealed tube (10 mL) was charged with TFPPy (14.8 mg, 0.024 mmol) and 5,5'bis(cyanomethyl)-2,2'-bipyridine (11.5 mg, 0.048 mmol), 1,2-dichlorobenze (0.5 mL), 1-butanol (0.5 mL) and aqueous KOH solution (0.1 mL, 4 M). The mixture was ultrasonicated for two minutes, then flash frozen at 77 K (liquid N2 bath), degassed through three freeze-pump-thaw cycles, and sealed under nitrogen using a Schlenk line and vacuum pump. The tube was heated at 120 °C for 96 h. After cooling to room temperature, the residue was washed with HCl (aq. 1 M), water, THF, and methanol three times, respectively. The resulting powder was washed with DMAc, water, and Soxhlet extraction with THF for 2 days. The powder was collected and dried under a vacuum overnight to afford Bpy-sp^2-COF as orange material.

Ni@Bpy-sp^2-COF was prepared by the following method. 50 mg of Bpy-sp^2-COF was treated with 30 mg $NiCl_2$ in 2 mL H_2O-CH_3OH (1:1) mixture. It was further heated at 60 ^oC

and stirred for 24 h. Hereafter, the resulting solid residue was filtered, washed with water and CH_3OH three times each, and dried under vacuum at 120 °C overnight to give the desired Ni@Bpy-sp^2c-COF.

Section S-IV: Characterizations of Materials

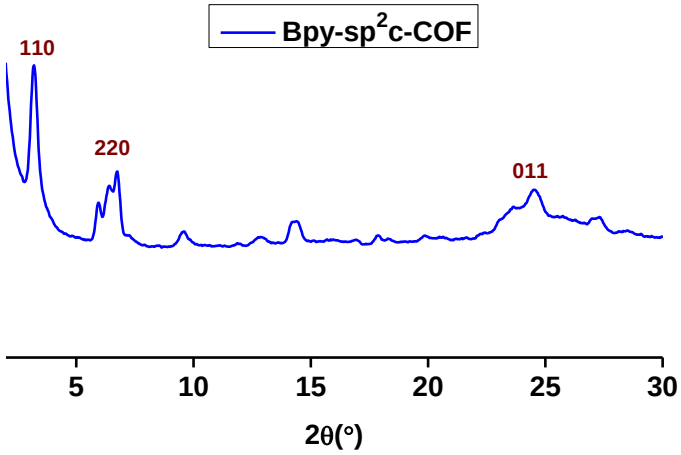


Figure S2: Powder X-ray diffraction data of Bpy-sp^{2}c-COF.[4]

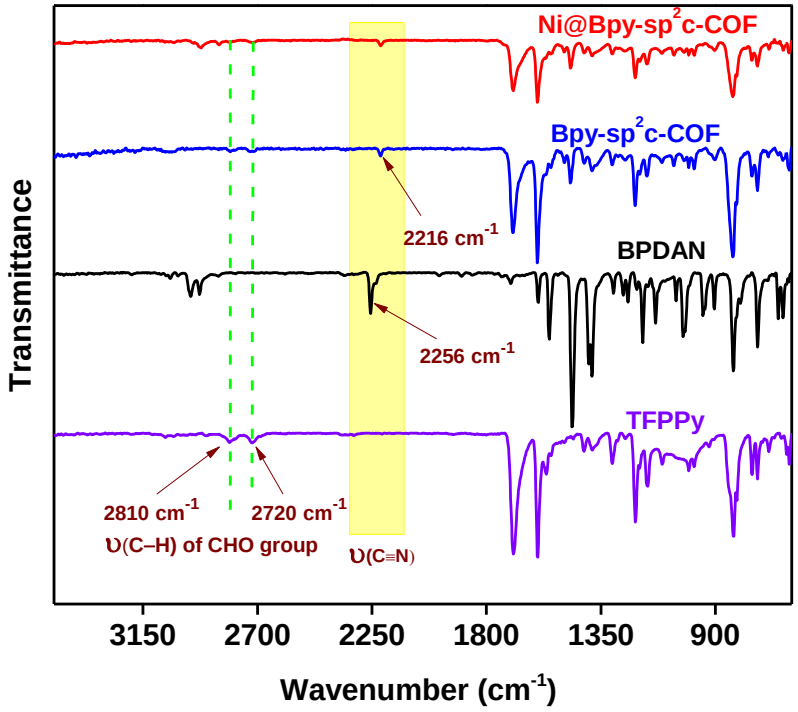


Figure S3: Comparative IR analysis between TFPPy (violet), BPDAN (black), and Bpy-sp^{2}c-COF. (blue) and Ni@Bpy-sp^{2}c-COF. (red).

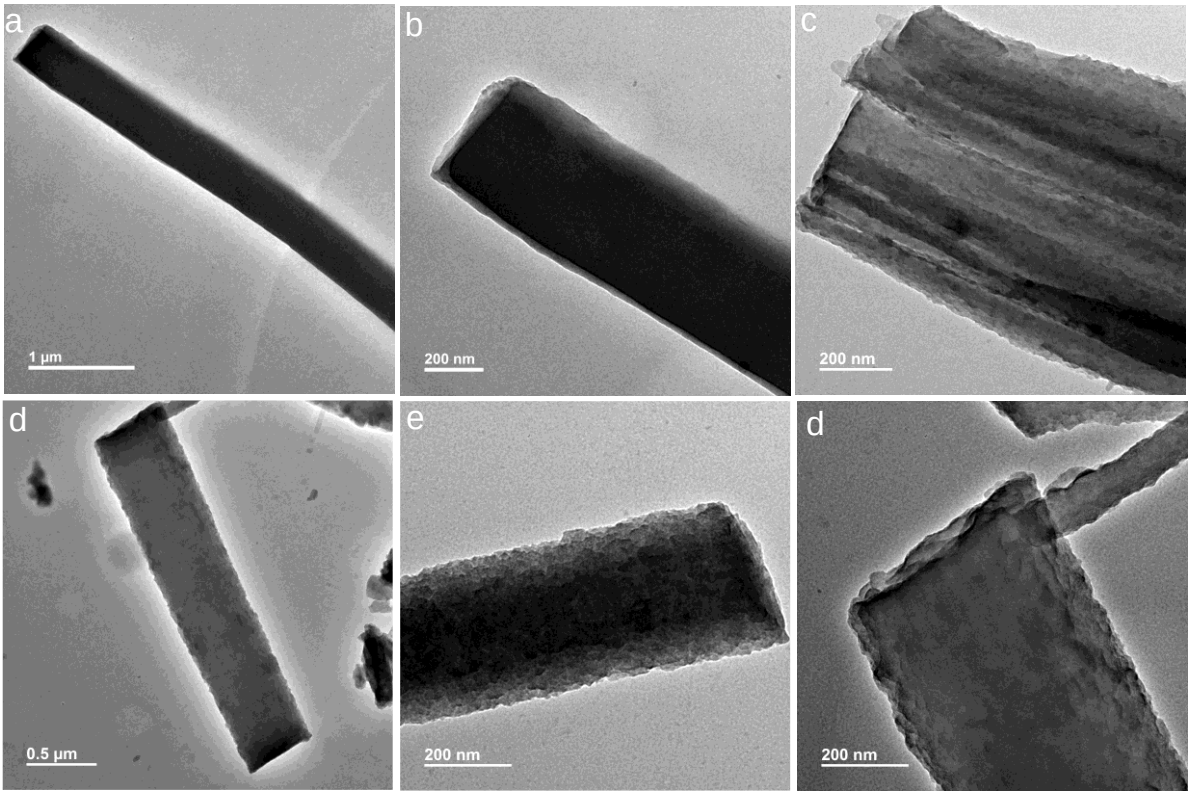


Figure S4: The TEM images of Bpy-sp^{2}c-COF (a,b,c),.and Ni@Bpy-sp^{2}c-COF (d,e,f).

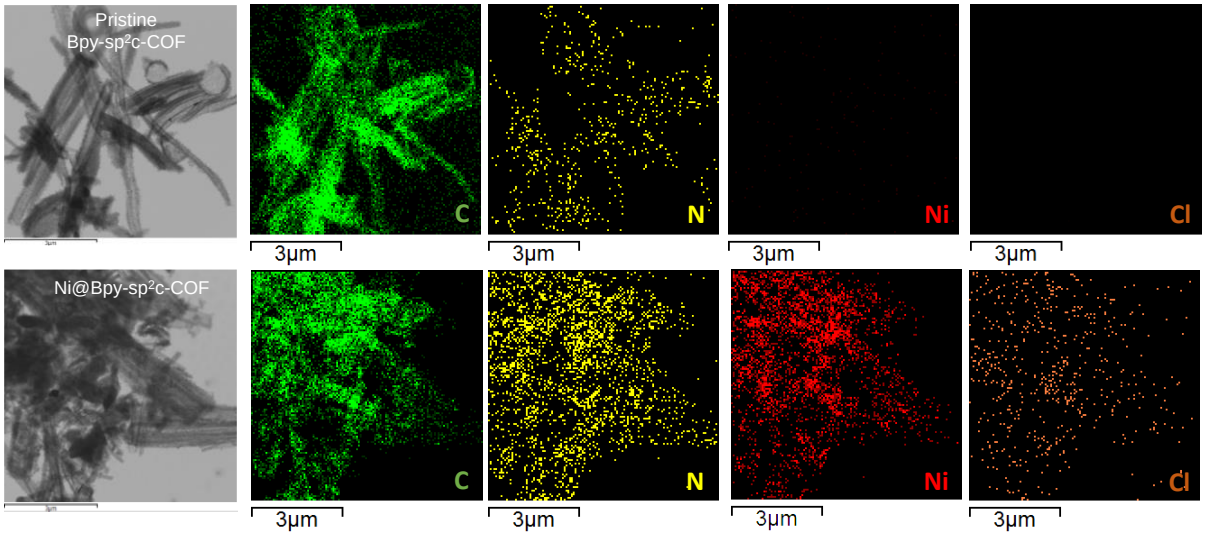


Figure S5: Elemental mapping by TEM-EDX analysis for Bpy-sp^{2}c-COF and Ni@Bpy-sp^{2}c-COF.

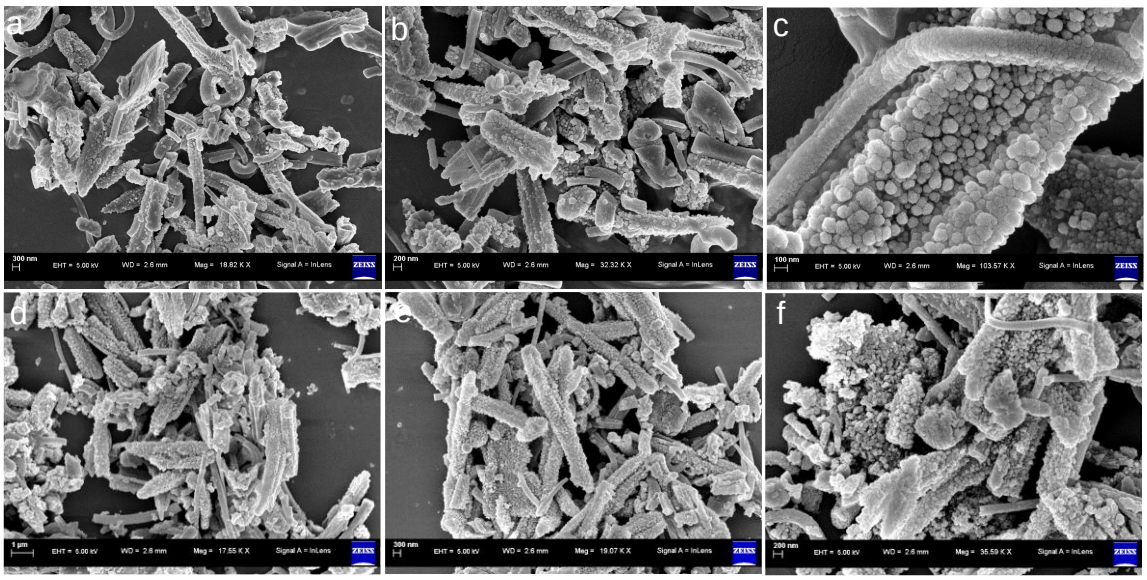


Figure S6: The SEM images of Bpy-sp^{2}c-COF (a,b,c),.and Ni@Bpy-sp^{2}c-COF (d,e,f).

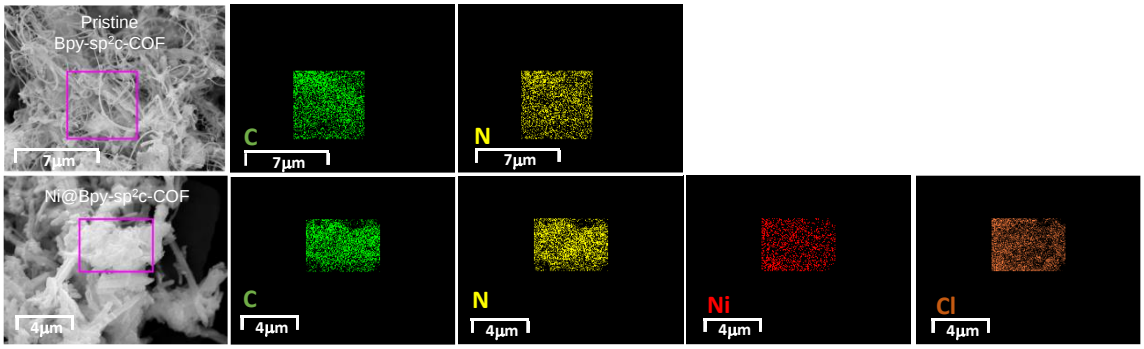


Figure S7: Elemental mapping by SEM-EDX analysis for Bpy-sp^{2}c-COF and Ni@Bpy-sp^{2}c-COF.

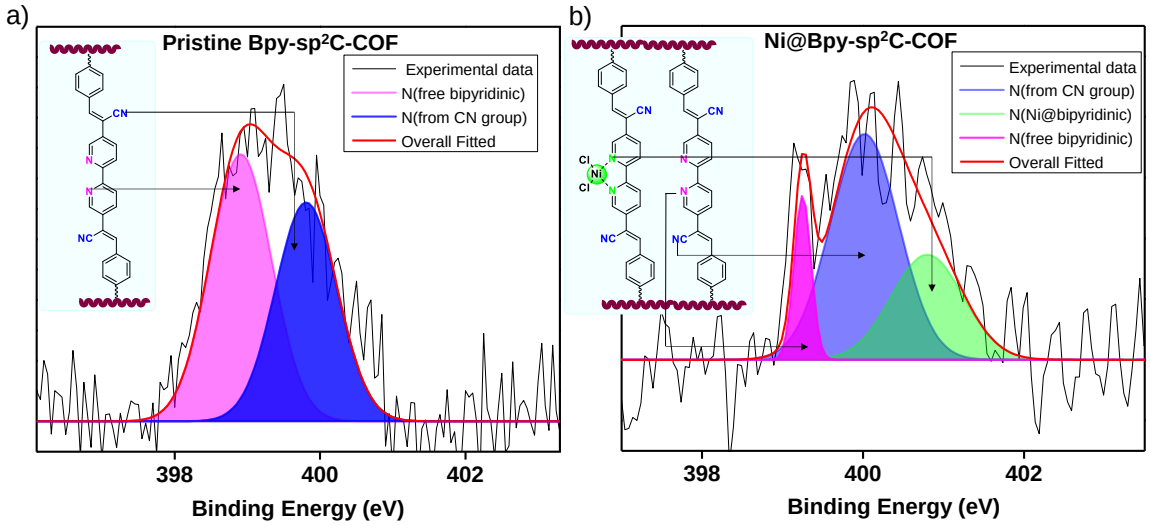


Figure S8: The XPS deconvoluted N1s spectra of (a) Bpy-sp^{2}c-COF, and (b) Ni@Bpy-sp^{2}c-COF. The XPS analysis of the pristine Bpy-sp^{2}c-COF and Ni metal loaded Bpy-sp^{2}c-COF revealed the deconvoluted N1s spectra where the blue area represented N (from nitrile group) contribution, the magenta area represented N (free bipyridine amine) contribution, and green area represented Ni coordinated bipyridine nitrogen contribution.

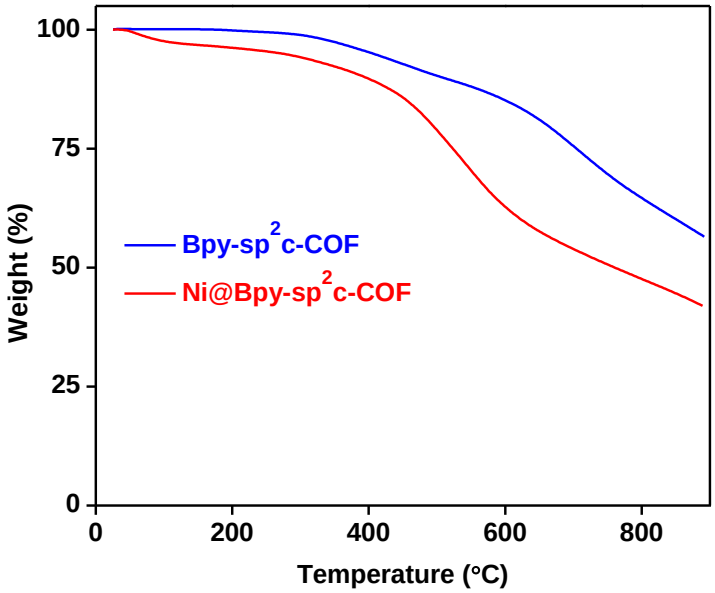
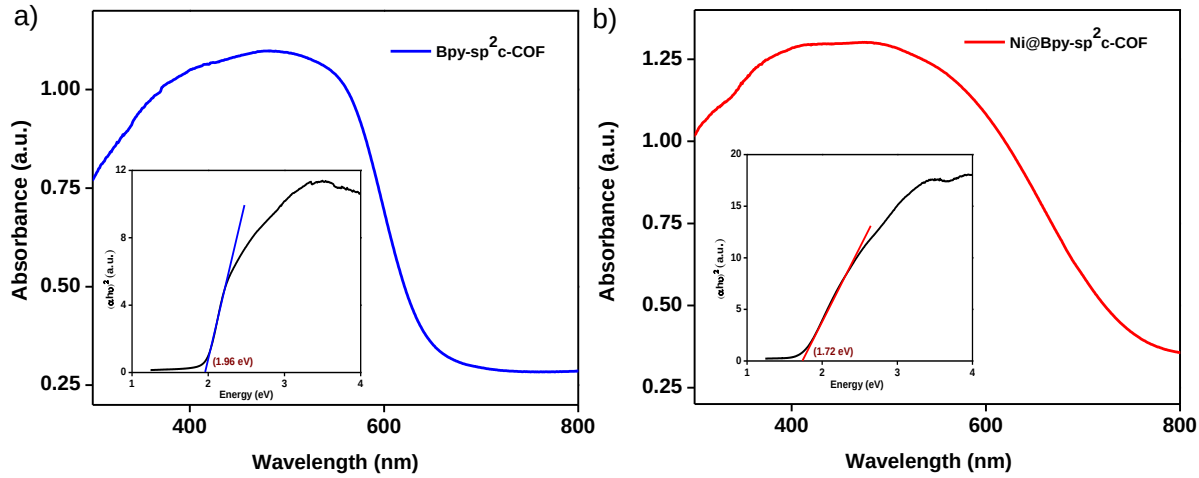


Figure S9: Comparative TGA analysis between Bpy-sp^{2}c-COF (red) and Ni@Bpy-sp^{2}c-COF.



From Tauc Plot; Band Gap Energy Values are ➡ 1.96 eV (Bpy-sp^{2}c-COF) and 1.72 eV (Ni@Bpy-sp^{2}c-COF)

Figure S10: UV-reflectance spectra analysis of a) Bpy-sp^{2}c-COF and b) Ni@Bpy-sp^{2}c-COF Bpy-sp^{2}c-COF. In the inset, band gap energies were calculated from the Tauc plot.

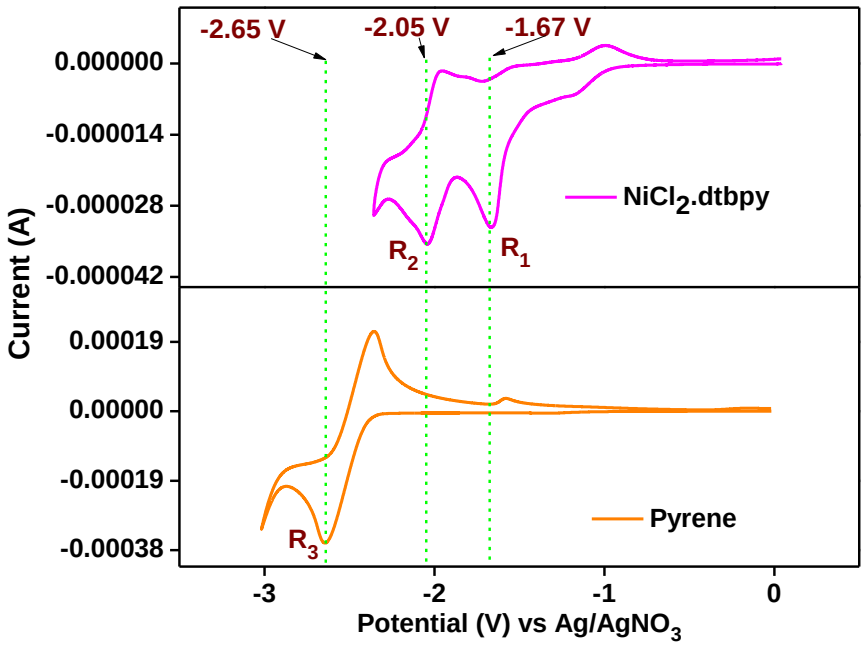


Figure S11a: CV of model compounds; (a) pyrene and (b) Ni(dtbbpy)Cl_2. The CV studies were performed with a conventional three-electrode cell, and the scanning rate was maintained at 100 mV/s and tetrabutylammonium hexafluorophosphate ($^{n}Bu_4PF_6$) (0.1 M) acting as a supporting electrolyte. The CV of Ni(dtbbpy)Cl_2 was measured in degassed acetonitrile, whereas for pyrene, it was acetonitrile/benzene (1:1).

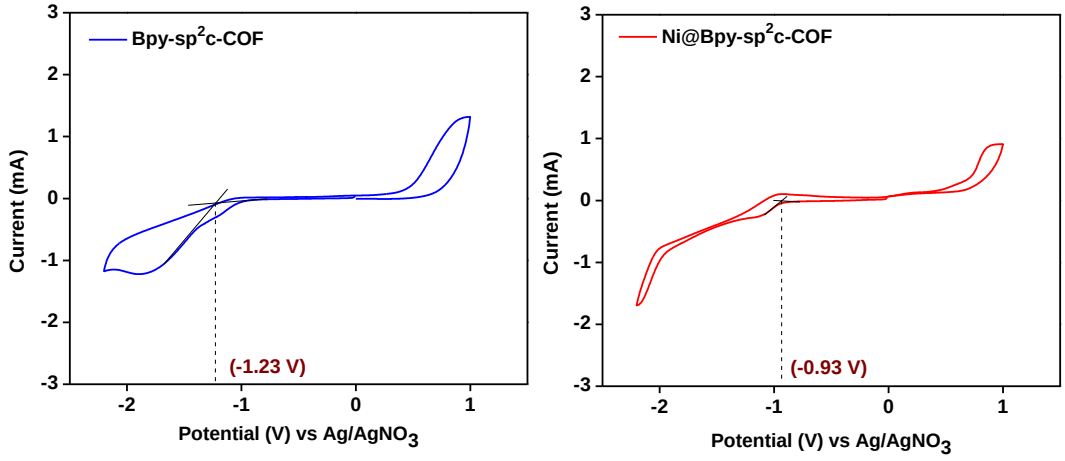


Figure S11b: CV of Bpy-sp^{2}c-COF (left), and Ni@Bpy-sp^{2}c-COF (right).

Table S1: VB and CB Energy calculations from CV.[5]

Solid Material	Reduction potential energy (E_{red})	Conduction band energy [E_{CB}= -e(E_{red} + 4.40)]	Band gap energy (Eg)	Valence band energy [E_{VB} = E_{CB} – Eg]
Bpy-sp^{2}c-COF	-1.23 V	-3.17 eV	1.96 eV	-5.13 eV
Ni@Bpy-sp^{2}c-COF	-0.93V	-3.47 eV	1.72 eV	-5.19 eV

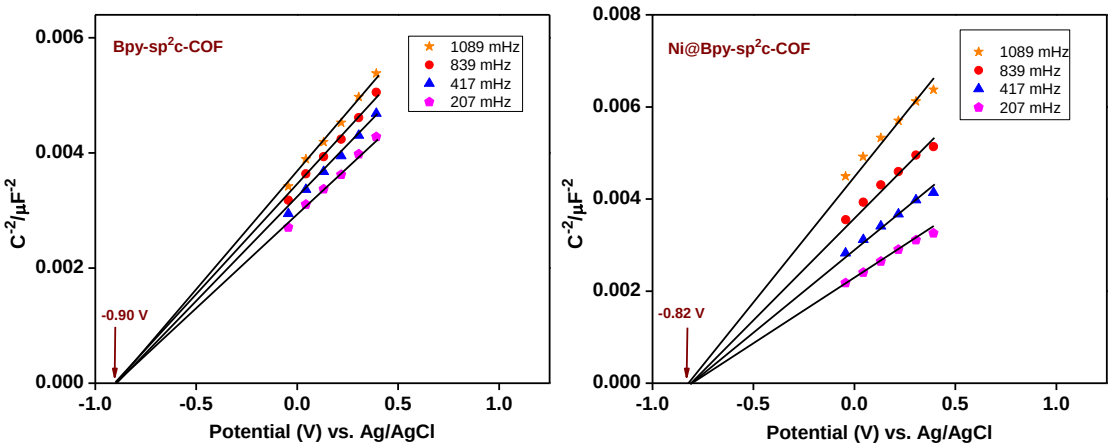


Figure S12: Mott-Schottky analysis of Bpy-sp^{2}c-COF (left), and Ni@Bpy-sp^{2}c-COF (right). From the Mott-Schottky analysis, it was found that the flat band potential position of Bpy-sp^{2}c-COF, and Ni@Bpy-sp^{2}c-COF are –0.90V and –0.82V vs. Ag/AgCl, respectively.

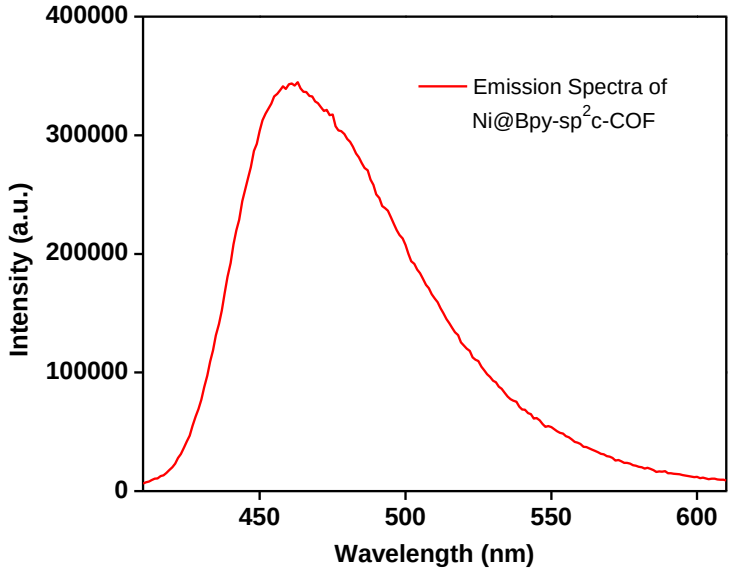
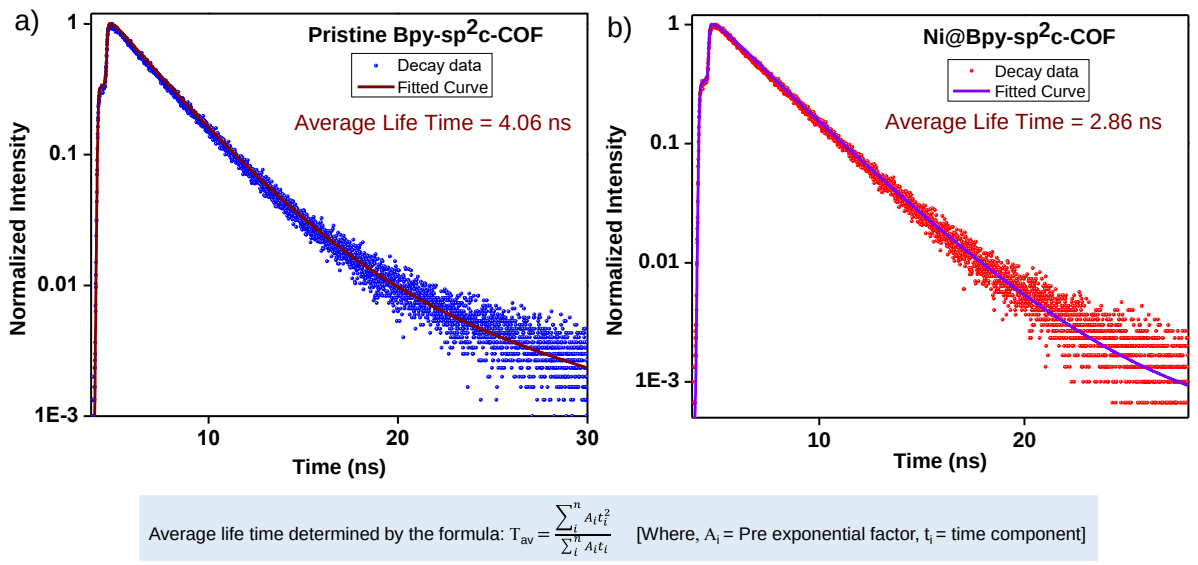


Figure S13: Emission spectra of Ni@Bpy-sp^{2}c-COF in degassed CH_3CN suspension (irradiated at 390 nm).



Average life time determined by the formula: $T_{av} = \frac{\sum_i^n A_i t_i^2}{\sum_i^n A_i t_i}$ [Where, A_i = Pre exponential factor, t_i = time component]

Figure S14: Average life time analysis from fluorescence decay curve; a) Bpy-sp^{2}c-COF, and b) Ni@Bpy-sp^{2}c-COF. The average life time of Bpy-sp^{2}c-COF and Ni@Bpy-sp^{2}c-COF are 4.06 ns and 2.86 ns, respectively.

Photoluminescence quenching analysis

The quencher (dtbbpy)-4-cyanophenylnickel(II) bromide [Ni(ArBr)] was synthesized according to a literature report.[6] Then five different materials were prepared by loading different amounts of Ni(ArBr) in Bpy-sp^{2}c-COF by the following procedure. To five different 2 mL THF dispersions of Bpy-sp^{2}c-COF (10 mg/mL), were added 0.5, 1.0, 1.5, 2.0, or 2.5 mg of Ni(cod)$_2$ inside an argon-filled glove box. The resulting solutions were stirred overnight. 4-Bromobenzonitrile (8 mg) was then added and stirred for 12 h. It was then filtrated to yield a dark brown powder Ni(ArBr)@Bpy-sp^{2}c-COF. The powders were washed by THF several times, and the nickel loadings were determined by ICP-OES analysis as 0.45, 0.83, 1.10, 1.31, and 1.45 wt%, respectively.

Afterward, three sets of quenching experiments were conducted; i) pyrene with Ni(ArBr), ii) Bpy-sp^{2}c-COF with Ni(ArBr), and iii) different Ni-loaded Ni(ArBr)@Bpy-sp^{2}c-COF while exciting 390 nm.

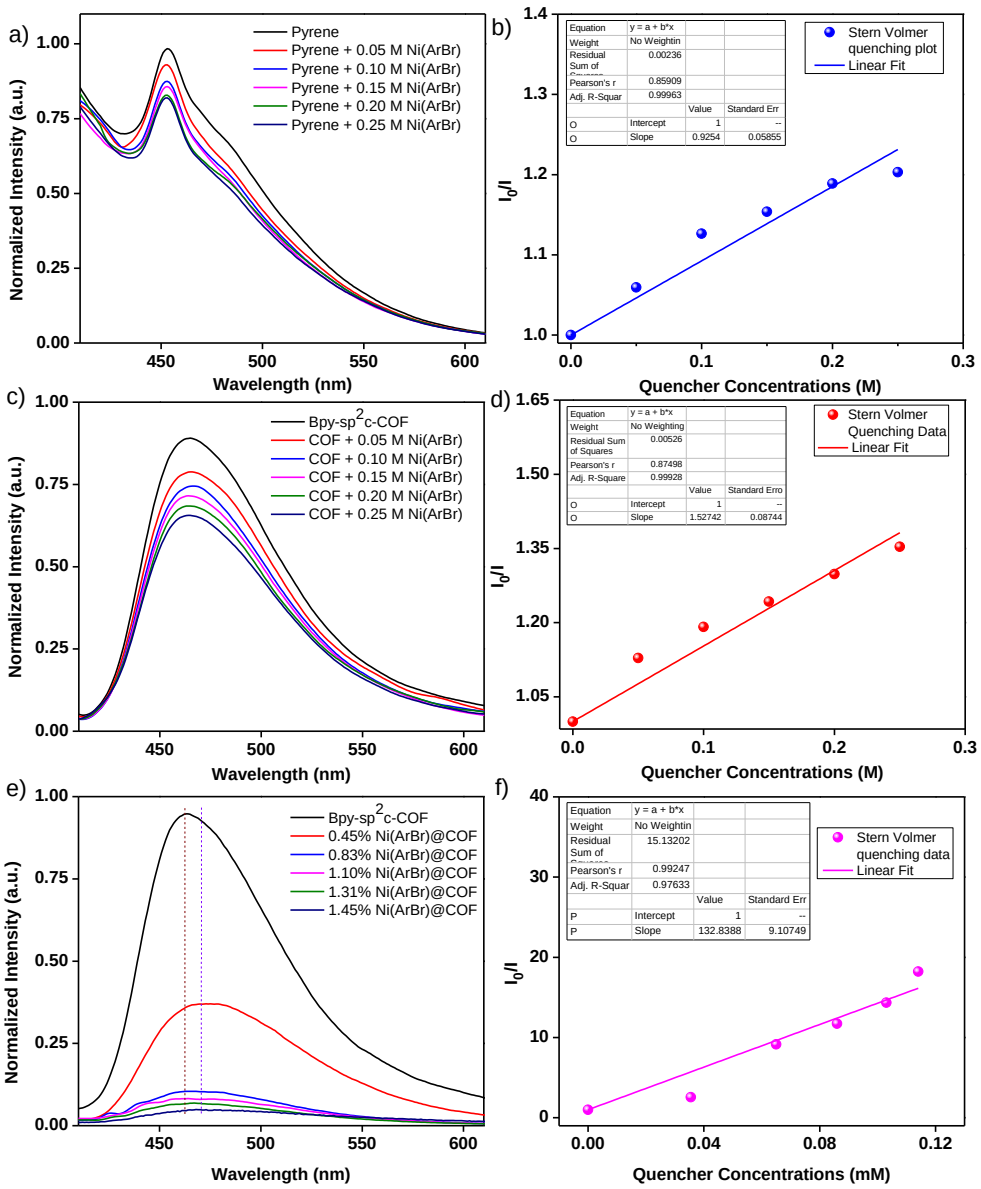


Figure S15: Photoluminescence quenching; a) pyrene with Ni(ArBr), b) Bpy-sp2c-COF with Ni(ArBr), and c) different Ni-loaded Ni(ArBr)@Bpy-sp^{2}c-COF, and d) The Stern Volmer fitted curves are plotted.

The Stern Volmer equation, $(I_0/I) = 1 + K_{sv}[Q]$, is fitted with every quenching experiment. Here, (I_0/I) is the ratio of fluorescence intensity in the absence and the presence of a quencher, K_{sv} and [Q] are the quenching constant and quencher concentration, respectively. $K_{sv} = k_q \times \tau°$, where k_q and $\tau°$ are the quenching rate and lifetime of the photosensitizer, respectively (680 ns and 4.06 ns for pyrene[7] and Bpy-sp^{2}c-COF, respectively). So, the quenching rate k_q is calculated by the equation: $k_q = K_{sv}/\tau°$. The quenching constants are 0.925 M^{-1} [for pyrene with Ni(ArBr)], 1.53 M^{-1} [Bpy-sp^{2}c-COF with Ni(ArBr)], and 1.33 × 10^5 M^{-1} [different Ni-loaded Ni(ArBr)@Bpy-sp^{2}c-COF]. Whereas quenching rates are 1.36 × 10^6 $M^{-1}S^{-1}$, 3.77 × 10^8 $M^{-1}S^{-1}$, and 3.28 × 10^{13} $M^{-1}S^{-1}$, respectively.

Section S-V: Reaction Optimizations and General Procedure for diverse photocatalytic Cross-Coupling Reaction

Reaction Optimizations:

Optimizations for esterification reaction (C–O bond formation)

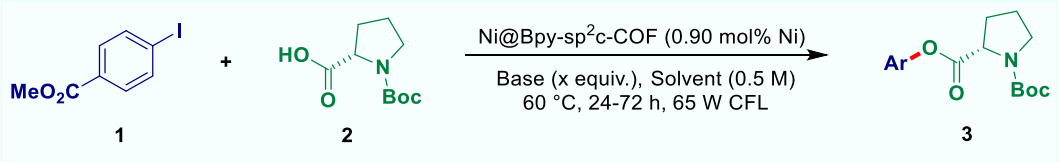


Table S2 (Optimizations)[a]

Entry No.	Solvent (0.5 M)	Base	Base (equiv.)	Time (h)	% Yield of **3**[b]
1	DMF	$^{i}Pr_2NH$	2	24	58
2	Dioxane	$^{i}Pr_2NH$	2	24	trace
3	DMSO	$^{i}Pr_2NH$	2	24	14
4	DMA	$^{i}Pr_2NH$	2	24	23
5	CH_3CN	$^{i}Pr_2NH$	2	24	Trace
6	MeOH	$^{i}Pr_2NH$	2	24	0
7	Hexane	$^{i}Pr_2NH$	2	24	0
8	DMF	Cs_2CO_3	2	24	0
9	DMF	DABCO	2	24	Trace
10	DMF	DBU	2	24	Trace
11	DMF	$^{i}Pr_2NEt$	2	24	Trace
12	DMF	TMG	2	24	51
13	DMF	Pyridine	2	24	0
14	DMF	$Na^{t}BuO$	2	24	42
15	DMF	$K^{t}BuO$	2	24	55
16	DMF	TMPH	2	24	trace
17	DMF	$^{t}BuNH^{i}Pr$	2	24	65
18	DMF	$^{t}BuNH^{i}Pr$	3	24	74
19	**DMF**	**$^{t}BuNH^{i}Pr$**	**3**	**48**	**91(83)**[c]
20	DMF	$^{t}BuNH^{i}Pr$	3	72	92
21	DMF	$^{t}BuNH^{i}Pr$	3	48	58[d]
22	DMF	$^{t}BuNH^{i}Pr$	3	48	76[e]
23	DMF	$^{t}BuNH^{i}Pr$	3	48	90[f]

[a] Reaction conditions: **1** (0.10 mmol), **2** (0.20 mmol), Ni@Bpy-sp^{2}c-COF (0.90 mol% Ni), Base (0.2–0.3 mmol), Solvent (0.5 M), 65W CFL light, 24-72 h. [b] Yield. were determined in gas chromatography by using mesitylene as standard. [c] isolated yield. [d] Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni). [e] Ni@Bpy-sp^{2}c-COF (0.675 mol% Ni). [f] Ni@Bpy-sp^{2}c-COF (1.35 mol% Ni). [DABCO = 1,4-diazabicyclo[2.2.2]octane, DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, TMG = 1,1,3,3-tetramethylguanidine, TMPH = 2,2,6,6-tetramethylpiperidine]

Table S3 (Control Experiments)

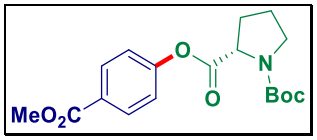
Entry No.	Deviation from standard condition[a]	% Yield of **3**[b]
1	No catalyst	0
2	No light	0
3	No light, heating at 100 °C	24
4	No solvent	0
5	No base	0
6	Catalyst: [0.9 mol% pyrene + 0.9 mol% Ni(dtbbpy)Cl_2]	53
7	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	72
8	Catalyst: [Bpy-sp^2c-COF + 0.9 mol% Ni(dtbbpy)Cl_2]	48
9	Ar-Br (Ar = 4-$MeO_2CC_6H_4$) was used instead of **1**	32[c]
10	Ar-Cl (Ar = 4-$MeO_2CC_6H_4$) was used instead of **1**	Trace
11	In the absence of N_2 atmosphere	0
12	Light source: Blue LED (427 nm) or Green LED (525 nm)	Trace
13	None	91

[a] Standard condition: **1** (0.10 mmol), **2** (0.20 mmol), Ni@Bpy-sp^2c-COF (0.90 mol% Ni), ^{t}BuNH^{i}Pr (0.3 mmol), DMF (0.5 M), 65W CFL light, under N_2 atmosphere 48 h. [b] Yield. were determined in gas chromatography by using mesitylene as standard. [c] Isolated yield.

General procedure for photocatalytic esterification reaction (C–O bond formation)

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl or alkyl iodide (0.10 mmol), acid (0.2 mmol), catalyst Ni@Bpy-sp^2c-COF (2 mg, 0.9 mol% Ni), *t*BuNH*i*Pr (0.3 mmol), and DMF (0.2 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 min. The tube was finally placed in front of a 65 W CFL light (at 4 cm distance) and irradiated for 48 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

1-(tert-butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate (3)[8]



Yield 30.4 mg (0.087 mmol, 87%). White solid. Column chromatography on silica gel (Eluent: 15-30% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.06 (dd, *J* = 11.6,

8.5 Hz, 2H), 7.18 (t, *J* = 9.1 Hz, 2H), 4.56 – 4.42 (m, 1H), 3.91 (d, *J* = 3.6 Hz, 3H), 3.67 – 3.41 (m, 2H), 2.43 – 1.93 (m, 4H), 1.46 (d, *J* = 9.7 Hz, 9H). **^{13}C NMR (126 MHz, CDCl3)** δ (171.3), 171.2, (166.5), 166.3, (154.6), 154.3, 153.8, 131.4, (131.2), 128.0, (127.8), (121.6), 121.3, 80.5, 80.3, (59.3), 59.2, (52.3), (46.8), 46.6, (31.2), 30.1, 28.5, (24.7), 23.9. [Minor rotameric peaks are denoted in parenthesis].

Optimizations for thioetherification reaction (C–S bond formation)

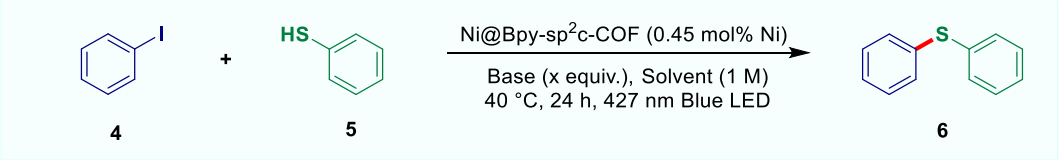


Table S4 (Optimizations)[a]

Entry No.	Solvent (1 M)	Base	Yield of **6**[b]
1	**CH_3CN**	**2,6-Lutidine**	**99 (95)**[c]
2	DMF	2,6-Lutidine	Trace
3	DMA	2,6-Lutidine	12
4	DMSO	2,6-Lutidine	Trace
5	Dioxane	2,6-Lutidine	72
6	THF	2,6-Lutidine	27
7	DCM	2,6-Lutidine	36
8	Hexane	2,6-Lutidine	48
9	CH_3CN	2,4,6-Collidine	14
10	CH_3CN	Pyridine	80
11	CH_3CN	TMG	22
12	CH_3CN	DBU	32
13	CH_3CN	DABCO	43
14	CH_3CN	Cs_2CO_3	62
15	CH_3CN	NEt_3	41
16	CH_3CN	Na^{t}BuO	32
17	CH_3CN	2,6-Lutidine	56[d]
18	CH_3CN	2,6-Lutidine	73[e]

[a] Reaction conditions: **4** (0.10 mmol), **5** (0.15 mmol), Ni@Bpy-sp^{2}c-COF (1 mg, 0.45 mol% Ni), Base (0.2 mmol), Solvent (1 M), 427 nm Blue LED Light 24 h. [b] Yields were determined in gas chromatography by using mesitylene as standard. [c] Isolated yield. [d] Ni@Bpy-sp^{2}c-COF (0.1125 mol% Ni). [e] Ni@Bpy-sp^{2}c-COF (0.225 mol% Ni).

Table S5 (Control Experiments)

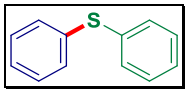
Entry No.	Deviation from standard condition[a]	Yield of **6**[b]
1	No catalyst	0
2	No light	0
3	No solvent	30
4	No base	0
5	Catalyst: [0.45 mol% pyrene + 0.45 mol% Ni(dtbbpy)Cl_2]	Trace
6	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	15
7	Catalyst: [Bpy-sp^2c-COF + 0.45 mol% Ni(dtbbpy)Cl_2]	82
8	Ph-Br used instead of **1**	46[c]
9	Ph-Cl used instead of **1**	Trace
10	None	99

[a] Standard condition: **4** (0.10 mmol), **5** (0.15 mmol), Ni@Bpy-sp^2c-COF (0.45 mol% Ni), 2,6-Lutidine (0.2 mmol), CH_3CN (1 M), 427 nm blue LED light, under N_2 atmosphere, 24 hr. [b] Yields were determined in gas chromatography by using mesitylene as standard.

General procedure for photocatalytic thioetherification reaction

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl iodide (0.10 mmol), thiol (0.15 mmol), catalyst Ni@Bpy-sp^2c-COF (1 mg, 0.45 mol% Ni), 2,6-Lutidine (0.20 mmol), and CH_3CN (0.1 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 min. The tube was finally placed 6 cm away from a 34 W Blue LED (Kessil lamp model: PR160L 427 nm) and irradiated for 24 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

Diphenylsulfane (6)[9]



Yield 17.7 mg (0.095 mmol, 95%). Colorless liquid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.36 – 7.22 (m, 10H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 135.9, 131.1, 129.3, 127.

Optimizations for sulfonation reaction (C–S bond formation)

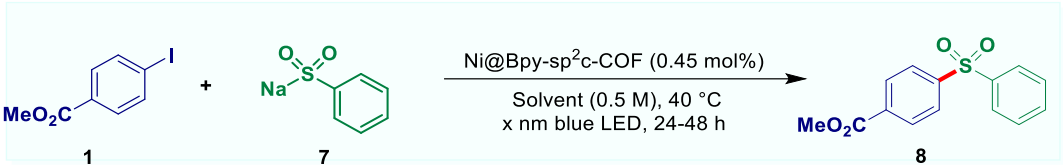


Table S6 (Optimizations)[a]

Entry No.	**7** (equiv.)	Solvent (0.5 M)	Wavelength (nm)	Time (h)	% Yield of **8**[b]
1	2	DMSO	427 nm	24	20
2	2	DMF	427 nm	24	16
3	2	DMA	427 nm	24	Trace
4	3	DMSO	427 nm	24	12
5	2	DMSO	456 nm	24	Trace
6	2	DMSO	467 nm	24	29
7	2	DMSO	390 nm	24	48
8	2	DMSO/Water (9:1)	390 nm	24	51
9	2	DMSO	390 nm	48	28
10	3	DMSO	390 nm	48r	28
11	3	DMSO/Water (9:1)	390 nm	48r	56
12	**3**	**DMSO/Water (9:1)**	**390 nm**	**48**	**94(83[c])**

[a] Reaction conditions: **1** (0.10 mmol), **7** (0.30 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), Solvent (0.5 M), light (390-467 nm), 24-48 h. [b] Yields were determined in gas chromatography by using mesitylene as standard. [c] Isolated yield.

Table S7 (Control Experiments)

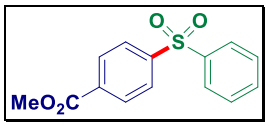
Entry No.	Deviation from standard condition[a]	Yield of **8**[b]
1	No catalyst	7
2	No light	0
3	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	33 (27)[c]
4	Catalyst: [Bpy-sp^2c-COF + 0.45 mol% Ni(dtbbpy)Cl_2]	66[d]
5	Ar-Br (Ar = 4-NCC_6H_4) was used instead of **1**	71[d]
6	Ar-Cl (Ar = 4-NCC_6H_4) was used instead of **1**	Trace
7	None	94

[a] Standard condition: **1** (0.10 mmol), **7** (0.30 mmol), Ni@Bpy-sp^2c-COF (0.45 mol% Ni), DMSO/H_2O (9:1, 0.5 M), 390 nm LED, 48 h. [b] Yields were determined in gas chromatography by using mesitylene as standard. [c] Catalyst: [0.45 mol% pyrene + 0.45 mol% Ni(dtbbpy)Cl_2], [d] isolated yield.

General procedure for photocatalytic sulfonation reaction (C–S bond formation)

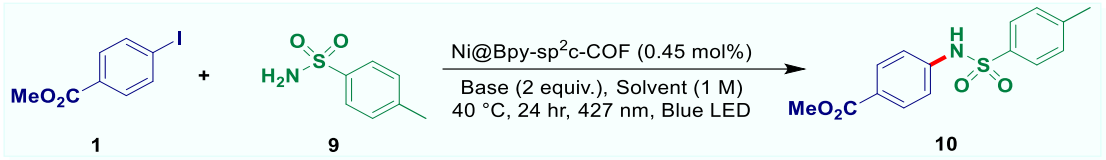
An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl halide (0.10 mmol), benzenesulfinic acid sodium salt (0.3 mmol), catalyst Ni@Bpy-sp^2c-COF (1 mg, 0.45 mol% Ni), and DMSO/ Water (0.2 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 min. The tube was finally placed 6 cm away from a 390 nm light and irradiated for 48 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

Methyl 4-(phenylsulfonyl)benzoate(8)[10]



Yield 26 mg (0.094 mmol, 94%). Yellowish solid. Column chromatography on silica gel (Eluent: 15-25% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 – 8.11 (m, 2H), 8.04 – 7.98 (m, 2H), 7.97 – 7.92 (m, 2H), 7.61 – 7.57 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 3.93 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.6, 145.6, 140.9, 134.4, 133.7, 130.6, 129.6, 128.0, 127.8, 52.8.

Optimizations for sulfonamidation reaction (C–N bond formation)



1 9 10

Table S8 (Optimizations)[a]

Entry No.	Base	Solvent (1 M)	%Yield of **10**[b]
1	NEt_3	CH_3CN	Trace
2	DABCO	CH_3CN	Trace
3	DBU	CH_3CN	Trace
4	**TMG**	**CH_3CN**	**91**(85)[c]
5	TMG	DMF	26
6	TMG	DMA	27
7	TMG	DMSO	Trace

[a] Reaction conditions: **1** (0.20 mmol), **9** (0.10 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), Base (0.2 mmol), Solvent (1 M), 427 nm Blue LED Light, 24 h. [b] Yields were determined by ^{1}H NMR, using 1,3,5-trimethoxybenzene as a standard. [c]Isolated yield.

Table S9 (Control Experiments)

Entry No.	Deviation from standard condition[a]	Yield of **10**[b]
1	No catalyst	0
2	No light	0
3	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	8 (0)[c]
4	Catalyst: [Bpy-sp^{2}c-COF + 0.45 mol% Ni(dtbbpy)Cl_2]	36
5	Ar-Br (Ar = 4-$MeO_2CC_6H_4$) used instead of **1**	52[d]
6	Ar-Cl (Ar = 4-$MeO_2CC_6H_4$) used instead of **1**	20[d]
7	None	91

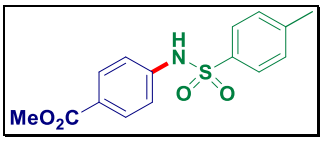
[a] Standard condition: **1** (0.20 mmol), **9** (0.10 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), TMG (0.2 mmol), CH_3CN (1 M), 427 nm Blue LED Light, 24 hr. [b] Yields were determined in ^{1}H NMR, using 1,3,5-trimethoxybenzene as a standard, [c] Catalyst: [0.45 mol% pyrene + 0.45 mol% Ni(dtbbpy)Cl_2], [d] Isolated yield.

General procedure for photocatalytic sulfonamidation reaction

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl halide (**1**, 0.20 mmol), *p*-toluenesulfonamide (**9**, 0.10 mmol), catalyst Ni@Bpy-sp^{2}c-COF (1 mg, 0.45 mol% Ni), TMG (0.20 mmol), and CH_3CN (0.1 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it

was subjected to an ultrasound sonication bath for 2 min. The tube was finally placed 6 cm away from a 34 W Blue LED (Kessil lamp model: PR160L 427 nm) and irradiated for 24 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

Methyl 4-((4-methylphenyl)sulfonamido)benzoate(10)[11]



Yield 25.9 mg (0.085 mmol, 85%). Yellowish Solid. Column chromatography on silica gel (Eluent: 25-35% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.6, 144.5, 141.2, 136, 131.2, 129.9, 127.4, 126.3, 119.2, 52.2, 21.7.

Optimizations for amination reaction (C–N bond formation)

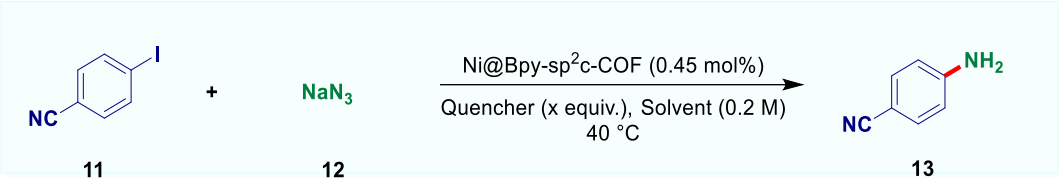


Table S10 (Optimizations)[a]

Entry No.	Quencher	Quencher (equiv.)	Solvent (0.2 M)	Solvent Ratio	Time (h)	% Yield of **13**[b]
1	NEt_3	2	$MeOH/H_2O$	5:3	24	36
2[c]	NEt_3	2	$MeOH/H_2O$	5:3	48	Trace
3[c]	NEt_3	3	$MeOH/H_2O$	5:3	48	Trace
4[c,d]	NEt_3	2	$MeOH/H_2O$	5:3	48	Trace
5[e]	NEt_3	2	$MeOH/H_2O$	5:3	24	Trace
6[f]	NEt_3	2	$MeOH/H_2O$	5:3	24	Trace
7[g]	NEt_3	2	$MeOH/H_2O$	5:3	24	22
8	NEt_3	2	$MeOH/H_2O$	1:1	24	52
9	NEt_3	2	MeOH	-	24	Trace
10	NEt_3	3	MeOH H_2O	5:3	24	56
11	NEt_3	3	$MeOH/H_2O$	1:1	24	36
12	$^{i}Pr_2NH$	2	$MeOH/H_2O$	5:3	24	Trace
13	$^{t}BuNH^{i}Pr$	2	$MeOH/H_2O$	5:3	24	27
14	$^{i}Pr_2NEt$	2	$MeOH/H_2O$	5:3	24	32
15	$N(CH_2CH_2OH)_3$	3	$MeOH/H_2O$	5:3	24	64
16	$N(CH_2CH_2OH)_3$	3	$MeOH/H_2O$	5:3	48	33
17	$N(CH_2CH_2OH)_3$	3	$MeOH/H_2O$	1:1	24	70
18	$N(CH_2CH_2OH)_3$	3	$MeOH/H_2O$	1:1	48	58
19	$N(CH_2CH_2OH)_3$	3	$MeOH/H_2O$	3:5	24	16
20	$N(CH_2CH_2OH)_3$	3	$^{i}PrOH/ H_2O$	1:1	48	15
22	$N(CH_2CH_2OH)_3$	3	$^{t}AmOH/H_2O$	1:1	48	Trace
23[h]	$N(CH_2CH_2OH)_3$	3	$MeOH/H_2O$	1:1	48	Trace
24	**$N(CH_2CH_2OH)_3$**	**3**	**$EtOH/H_2O$**	**1:1**	**48**	**89(93)**[i]

[a] Reaction conditions: **11** (0.10 mmol), **12** (0.50 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), Quencher (x mmol), Solvent (0.2 M), 390-456 nm Blue LED, 24-48 h. [b] Isolated yield, [c] Major presence of by-products, [d] Catalyst (2 mg), [e] Wavelength (390 nm), [f] Wavelength (456 nm), [g] **12** (1 mmol), [h] Solvent (0.5 M), [i] ^{1}H NMR yield by using 1,3,5-Trimethoxybenzene as standard.

Table S11 (Control Experiments)

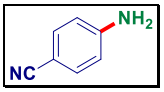
Entry No.	Deviation from standard condition[a]	% Yield of **13**[b]
1	No catalyst	0
2	No light	0
3	Catalyst: [0.45 mol% pyrene + 0.45 mol% Ni(dtbbpy)Cl_2]	17
4	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	19
5	Catalyst: [Bpy-sp^2c-COF + 0.45 mol% Ni(dtbbpy)Cl_2]	32
6	Ar-Br (Ar = 4-NCC_6H_4) used instead of **11**	51
7	Ar-Cl (Ar = 4-NCC_6H_4) used instead of **11**	49
8	None	89

[a] Standard condition: **11** (0.10 mmol), **12** (0.50 mmol), Ni@Bpy-sp^2c-COF (1 mg, 0.45 mol% Ni), TEA (0.3 mmol), EtOH/ H_2O (0.2 M), 427 nm Blue LED Light, 48 hr. [b] Isolated yield.

General procedure for photocatalytic amination reaction

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl halide (0.10 mmol), sodium azide (0.50 mmol), catalyst Ni@Bpy-sp^2c-COF (0.45 mol% Ni), $N(CH_2CH_2OH)_3$ (0.30 mmol), and EtOH/ H_2O (0.5 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 mins. The tube was finally placed 6 cm away from a 34 W Blue LED (Kessil lamp model: PR160L 427 nm) and irradiated for 48 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

4-aminobenzonitrile (13)[12]



Yield 11.0 mg (0.093 mmol, 93%). Yellowish solid. Column chromatography on silica gel (Eluent: 25-35% ethyl acetate in hexane)**.** **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.31 (m, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 4.26 (s, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.7, 133.8, 120.3, 114.4, 99.8.

Optimizations for borylation reaction (C–B bond formation)

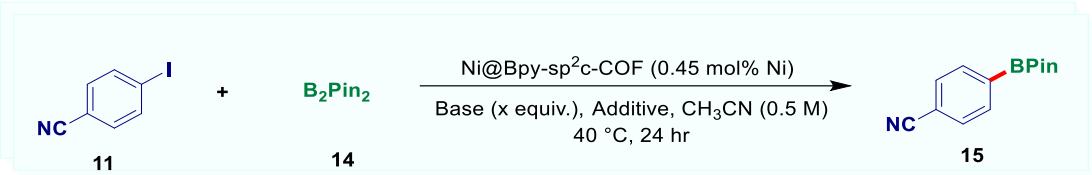


Table S12 (Optimizations)[a]

Entry No.	Base	Additive (20 mol%)	Wavelength (nm)	%Yield of **15**[b]
1	$^{i}Pr_2NH$	Pyridine	390	25
2	$^{i}Pr_2NH$	Pyridine	370	29
3	$^{t}BuNH^{i}Pr$	Pyridine	370	20
4	**$^{i}Pr_2NEt$**	**Pyridine**	**370**	**96 (96)**[c]
5	$^{i}Pr_2NEt$	Pyridine	390	30
6	$^{i}Pr_2NEt$	2,6-Lutidine	370	23

[a] Reaction conditions: **11** (0.10 mmol), **14** (0.30 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), Additive (20 mol%), Base (x mmol), CH_3CN (0.5 M), 370-390 nm LED Light, 24 hr. [b] Yields were determined in gas chromatography by using mesitylene as standard. [c] Isolated yield.

Table S13 (Control Experiments)

Entry No.	Deviation from standard condition[a]	% Yield of **15**[b]
1	No catalyst	17
2	No light	7
3	Without Pyridine	23
4	Catalyst: [0.45 mol% pyrene + 0.45 mol% Ni(dtbbpy)Cl_2]	41
5	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	47
7	Catalyst: [Bpy-sp^{2}c-COF + 0.45 mol% Ni(dtbbpy)Cl_2]	60
8	Ar-Br (Ar = 4-NCC_6H) used instead of **11**	84[c]
9	Ar-Cl (Ar = 4-NCC_6H_4) used instead of **11**	Trace
10	None	96

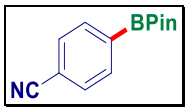
[a] Standard condition: **11** (0.10 mmol), **14** (0.30 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), Pyridine (20 mol%), $^{i}Pr_2NEt$ (0.30 mmol), CH_3CN (0.5 M), 370 nm LED Light, 24 hr. [b] Yields were determined in gas chromatography by using mesitylene as standard, [c] Isolated yield.

General procedure for photocatalytic borylation reaction

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl halide (0.10 mmol), bis(pinacolato)diboron (0.30 mmol), catalyst Ni@Bpy-sp^{2}c-COF (1 mg, 0.45 mol% Ni), pyridine (20 mol%), $^{i}Pr_2NEt$ (0.30 mmol) and CH_3CN (0.2 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 min. The tube

was finally placed 6 cm away from a 370 nm LED light and irradiated for 24 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile(15)[13]



Yield 22.0 mg (0.096 mmol, 96%). White crystalline solid. Column chromatography on silica gel (Eluent: 5-10% ethyl acetate in hexane)**. ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.22, 131.25, 118.97, 114.67, 84.62, 24.98. **^{11}B NMR (161 MHz, $CDCl_3$)** δ 30.5.

Optimizations for Phosphonylation reaction (C–P bond formation)

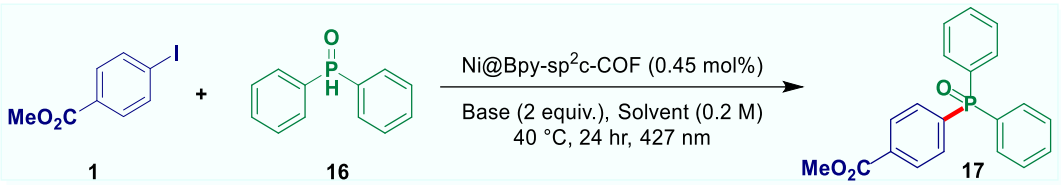


Table S14 (Optimizations)[a]

Entry No.	Base	Solvent	%Yield of **17**[b]
1	Cs_2CO_3	MeOH	14
2	Cs_2CO_3	EtOH	8
3	Cs_2CO_3	^{t}AmOH	Trace
4	Cs_2CO_3	CH_3CN	39
5	Cs_2CO_3	DMF	Trace
6	Cs_2CO_3	DMSO	Trace
7	DBU	CH_3CN	Trace
8	K_2CO_3	CH_3CN	54
10	^{t}BuNH^{i}Pr	CH_3CN	30
11	TMG	CH_3CN	58
14	$^{i}Pr_2NH$	CH_3CN	21
15	$^{i}Pr_2NEt$	CH_3CN	66
16[c]	**$^{i}Pr_2NEt$**	**CH_3CN**	**73 (70)**[d]

[a] Reaction conditions: **1** (0.20 mmol), **16** (0.10 mmol), Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), Base (0.20 mmol), Solvent (0.2 M), 427 nm Blue LED Light, 24 h. [b] Yields were determined in gas chromatography by using mesitylene as standard. [c] Ni@Bpy-sp^{2}c-COF (0.90 mol% Ni), [d] Isolated yield

Table S15 (Control Experiments)

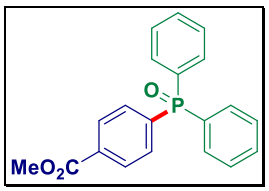
Entry No.	Deviation from standard condition[a]	% Yield of **17**[b]
1	No catalyst	6
2	No light	0
3	Without Base	0
4	Catalyst: [0.9 mol% pyrene + 0.9 mol% Ni(dtbbpy)Cl_2]	61
5	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	86
7	Catalyst: [Bpy-sp^2c-COF + 0.90 mol% Ni(dtbbpy)Cl_2]	51
8	Ar-Br (Ar = 4-NCC_6H_4) used instead of **11**	48[c]
9	Ar-Cl (Ar = 4-NCC_6H_4) used instead of **11**	16[c]
10	CFL light instead of blue LED	15 (39)[c]
11	None	73

[a] Standard condition: **1** (0.20 mmol), **16** (0.10 mmol), Ni@Bpy-sp^2c-COF (0.90 mol% Ni), $^iPr_2NEt$ (0.20 mmol), CH_3CN (0.2 M), 427 nm LED Light, 24 hr. [b] Yields were determined in gas chromatography by using mesitylene as standard, [c] Isolated yield, [d] $^tBuNH^iPr$ used instead of $^iPr_2NEt$.

General procedure for photocatalytic phosphonylation reaction

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with aryl halide (0.20 mmol), diphenylphosphine oxide (0.10 mmol), catalyst Ni@Bpy-sp^2c-COF (0.90 mol% Ni), $^iPr_2NEt$ (0.20 mmol) and CH_3CN (0.5 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 min. The tube was finally placed 6 cm away from a 34 W Blue LED (Kessil lamp model: PR160L 427 nm) and irradiated for 24 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

methyl 4-(diphenylphosphoryl)benzoate (17)[14]



Yield 23.5 mg (0.070 mmol, 70%). White solid. Preparative thin layer chromatography on silica gel (Eluent: 60% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.13 – 8.09 (m, 2H), 7.80 – 7.73 (m, 2H), 7.69 – 7.63 (m, 4H), 7.59 – 7.54 (m, 2H), 7.47 (td, *J* = 7.6, 2.8

Hz, 4H), 3.93 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.4, 137.8 (*J* = 100.8 Hz), 133.3 (*J* = 2.8 Hz), 132.4 (*J* = 2.8 Hz), 132.3 (*J* = 9.9 Hz), 132.2 (*J* = 10.0 Hz), 132.0 (*J* = 105.0 Hz), 129.5 (*J* = 12.1 Hz), 128.8 (*J* = 12.2 Hz), 52.6. **^{31}P NMR (203 MHz, $CDCl_3$)** δ 28.4.

Optimizations for Allylation reaction (C–C bond formation)

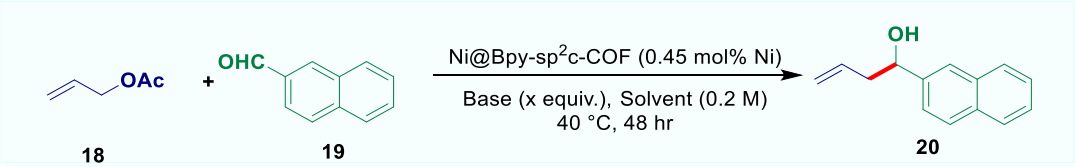


Table S16 (Optimizations)[a]

Entry No.	Quencher	Quencher (equiv.)	Wavelength (nm)	Solvent	Concentration (x M)	Yield of **20**[b]
1	$^{i}Pr_2NEt$	3	427	CH_3CN	0.2	15
2	$^{i}Pr_2NEt$	4	427	CH_3CN	0.2	16
3	NEt_3	3	427	CH_3CN	0.2	Trace
4	$N(CH_2CH_2OH)_3$	3	427	CH_3CN	0.2	Trace
5	$^{t}BuNH^{i}Pr$	3	427	DMF	0.2	Trace
6	$^{i}Pr_2NEt$	3	456	CH_3CN	0.2	Trace
7	$^{i}Pr_2NEt$	3	390	CH_3CN	0.2	Trace
8	**$^{i}Pr_2NEt$**	**4**	**427**	**DMF**	**0.2**	**61(61[c])**
9[d]	$^{i}Pr_2NEt$	4	427	DMF	0.2	13
10	$^{i}Pr_2NEt$	4	427	DMF	0.5	24
11	$^{i}Pr_2NEt$	4	427	DMF	0.1	8
12	$^{i}Pr_2NEt$	5	427	DMF	0.1	20

[a] Reaction conditions: **18** (0.30 mmol), **19** (0.10 mmol), Ni@Bpy-sp2c-COF (1 mg, 0.45 mol% Ni), Quencher (x equiv.), Solvent (y M), 390-456 nm LED Light, 48 h. [b] Yields were determined in gas chromatography by using mesitylene as standard, [c] Isolated yield [d] Allyl acetate (4 equiv.).

Table S17 (Control Experiments)

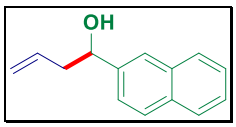
Entry No.	Deviation from standard condition[a]	Yield of **20**[b]
1	No catalyst	Trace
2	No light	0
3	No Quencher	0
4	Catalyst: [0.45 mol% pyrene + 0.45 mol% Ni(dtbbpy)Cl_2]	6
5	Catalyst: [5 mol% pyrene + 5 mol% Ni(dtbbpy)Cl_2]	12
6	Catalyst: [Bpy-sp^2c-COF + 0.45 mol% Ni(dtbbpy)Cl_2]	19
7	None	61

[a] Standard condition: **18** (0.30 mmol), **19** (0.10 mmol), Ni@Bpy-sp2c-COF (0.45 mol% Ni), $^{i}Pr_2NEt$ (0.4 mmol), DMF (0.2 M), 427 nm Blue LED Light, 48 hr. [b] Yields were determined in gas chromatography by using mesitylene as standard.

General procedure for photocatalytic allylation reaction

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with 2-naphthaldehyde (**19**, 0.10 mmol), allyl acetate (**18**, 0.30 mmol), catalyst Ni@Bpy-sp^2c-COF (1 mg, 0.45 mol% Ni), $^{i}Pr_2NEt$ (0.40 mmol), and DMF (0.5 mL). The tube was then purged with N_2 for 1 min and sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 2 min. The tube was finally placed 6 cm away from a 34 W Blue LED (Kessil lamp model: PR160L 427 nm) and irradiated for 48 h. Afterward, the resulting solution was filtered, and the filtrate was concentrated in a vacuum to get the crude product. Finally, the crude product was purified by column chromatography on silica gel.

1-(naphthalen-2-yl)but-3-en-1-ol(20)[15]



Yield 12.1 mg (0.0610 mmol, 61%). Colorless liquid. Column chromatography on silica gel (Eluent: 25-35% ethyl acetate in hexane)**. ^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 – 7.82 (m, 3H), 7.82 – 7.79 (m, 1H), 7.49 (td, *J* = 6.2, 3.2 Hz, 3H), 5.88 – 5.80 (m, 1H), 5.22 – 5.14 (m, 2H), 4.89 (dd, *J* = 7.5, 5.4 Hz, 1H), 2.66 – 2.56 (m, 2H), 2.40 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.4, 134.5, 133.4, 133.1, 128.3, 128.1, 127.8, 126.2, 125.9, 124.6, 124.1, 118.5, 73.5, 43.8.

Section S-VI: Time-Dependent Reaction Profile Analysis for Thioetherification and Mechanistic Studies for Thioetherification and Esterification

Time-dependent experiment 1 (T1)

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with iodobenzene **4** (0.10 mmol), thiophenol **5** (0.15 mmol), catalyst Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni), 2,6-lutidine (0.20 mmol), and CH_3CN (0.1 mL). The tube was then purged with N_2 for 1 min and then sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 5 min. The tube was finally placed 6 cm away from one 34 W Blue LED (427 nm) and irradiated at 40 °C. The reaction progress was tracked by gas chromatography in different hour intervals by using mesitylene as a standard.

Time-dependent experiment 2 (T2)

The reaction procedure was like that of **T1**. The only difference was that catalyst Ni@ Bpy-sp^{2}c-COF was replaced by {Ni(dtbbpy)Cl_2 (0.45 mol%) + [Ir(ppy)$_2$(dtbbpy)]PF_6 (0.45 mol%)} as a catalyst where the amount of metal loading was the same as 1 mg Ni-Ir@TpBpy catalyst.

Time-dependent experiment 3 (T3)

The reaction procedure was like that of **T1**. The only difference was that catalyst Ni@ Bpy-sp^{2}c-COF was replaced by the combination of {Ni(dtbbpy)Cl_2 (0.45 mol%) + pyrene (0.45 mol%} as a catalyst where the amount of metal loading was the same as 1 mg Ni-Ir@TpBpy catalyst.

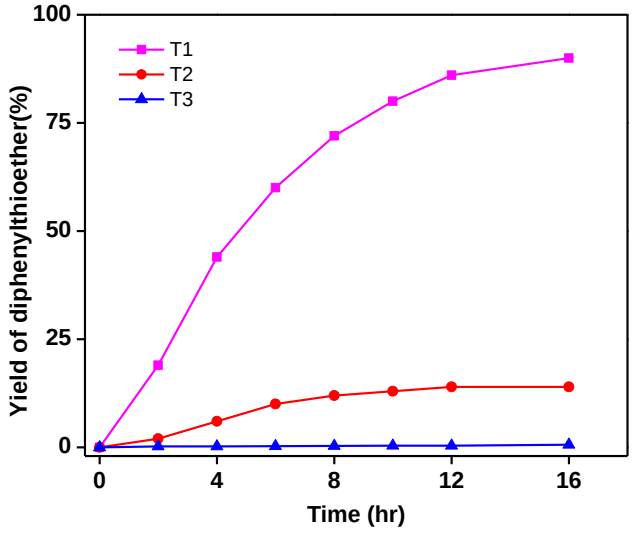


Figure S16: Time dependent reaction profile at condition T1 (magenta), T2 (red) and T3 (blue).

Photoluminescence quenching experiment for the thioetherification reaction.

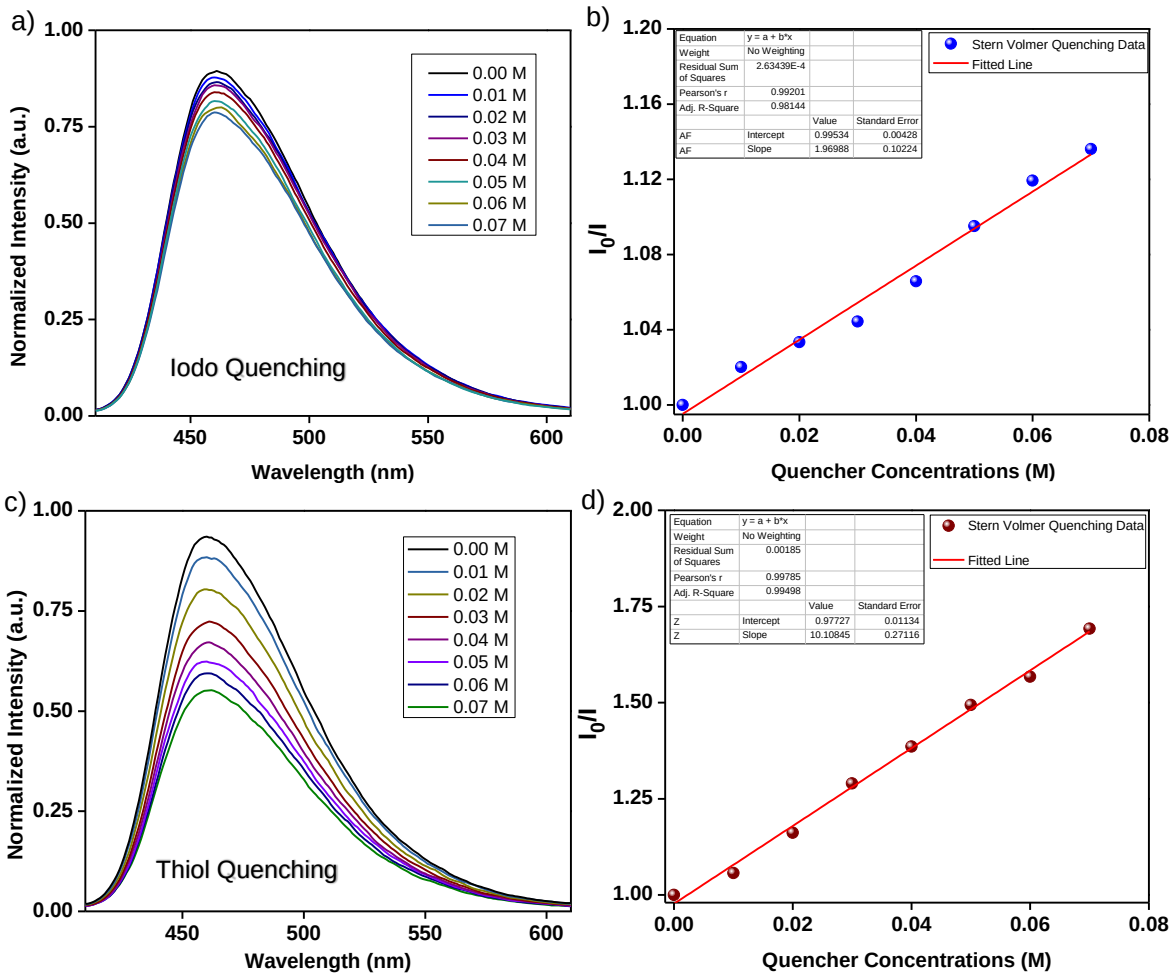
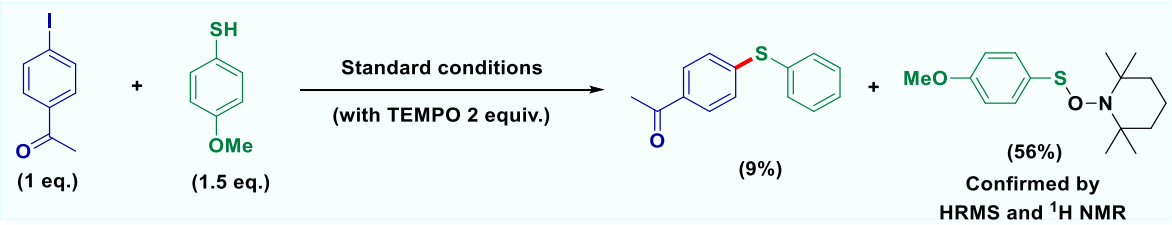


Figure S17a: *Photoluminescence quenching experiments of excited Ni@Bpy-sp^{2}c-COF catalyst in the presence of a) iodobenzene, c) thiophenol and corresponding Stern-Volmer quenching plots are b) and d). respectively.*

We have observed that thiophenol quenches the luminescence at a very high rate K_{sv} = 10.1 M^{-1}, and the quenching rate is almost 5 times higher than for iodobenzene. It suggested a SET mechanism and the existence of radicals.

To further probe the mechanism, we have conducted the reaction in the presence of a well-known radical trapping agent. Indeed, the reaction is quenched in the presence of TEMPO (2 equiv.). Besides, we could isolate and characterize the TEMPO-trapped intermediate via HRMS and ^{1}H NMR.

Radical trapping experiment in the thioetherification reaction:



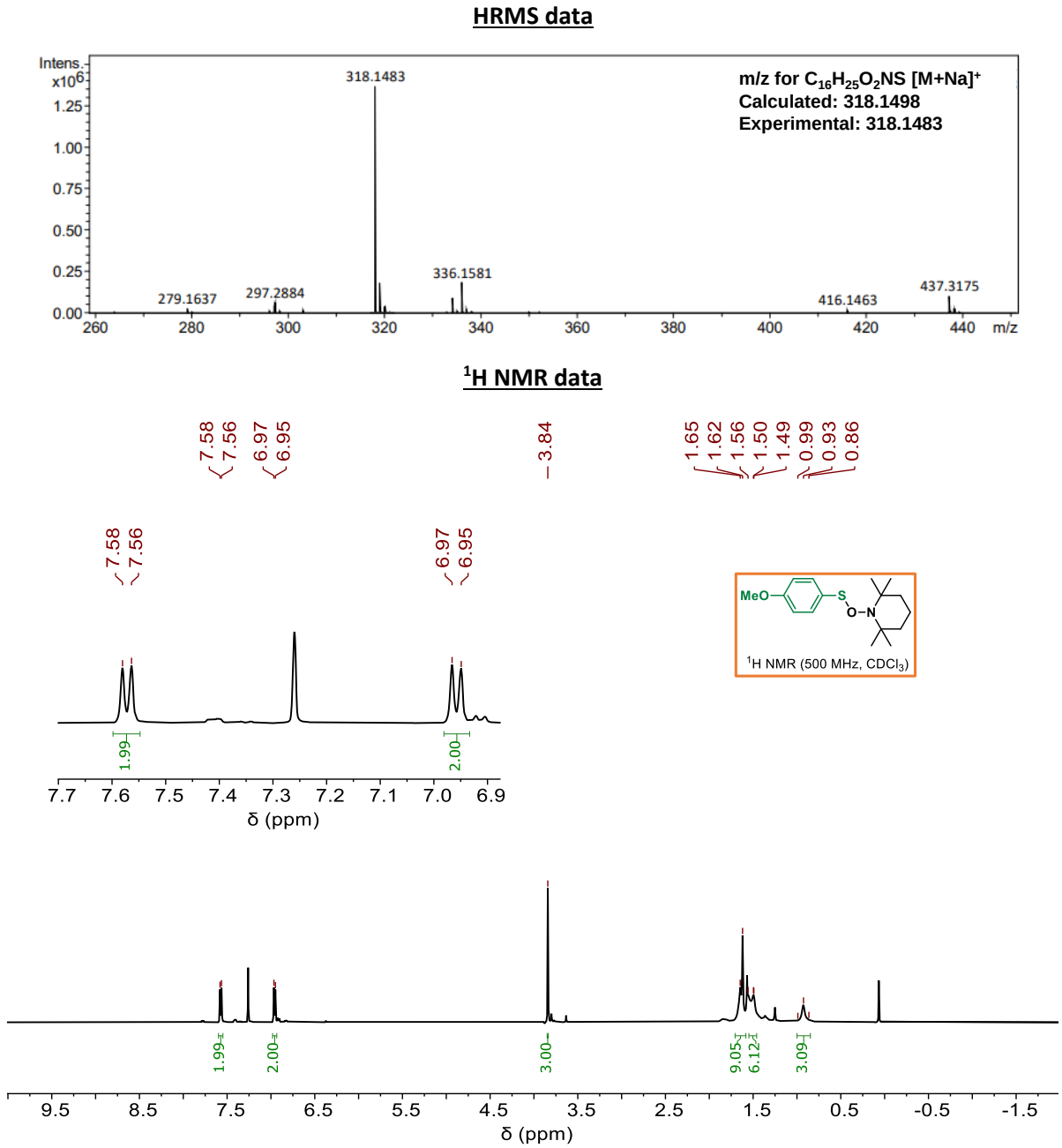


Figure S17b: Confirmation of TEMPO trapped intermediate by HRMS (upper) and ^{1}H NMR (lower) data.

The above quenching experiments and radical trapping control experiment, HRMS, and ^{1}H-NMR data of radical trapped intermediate provide strong evidence for the SET mechanism of thioetherification reaction. Based on the above experiments, we proposed a plausible mechanism for the thioetherifications in Figure S32, Section S-XII.

Photoluminescence quenching experiment for the esterification reaction:

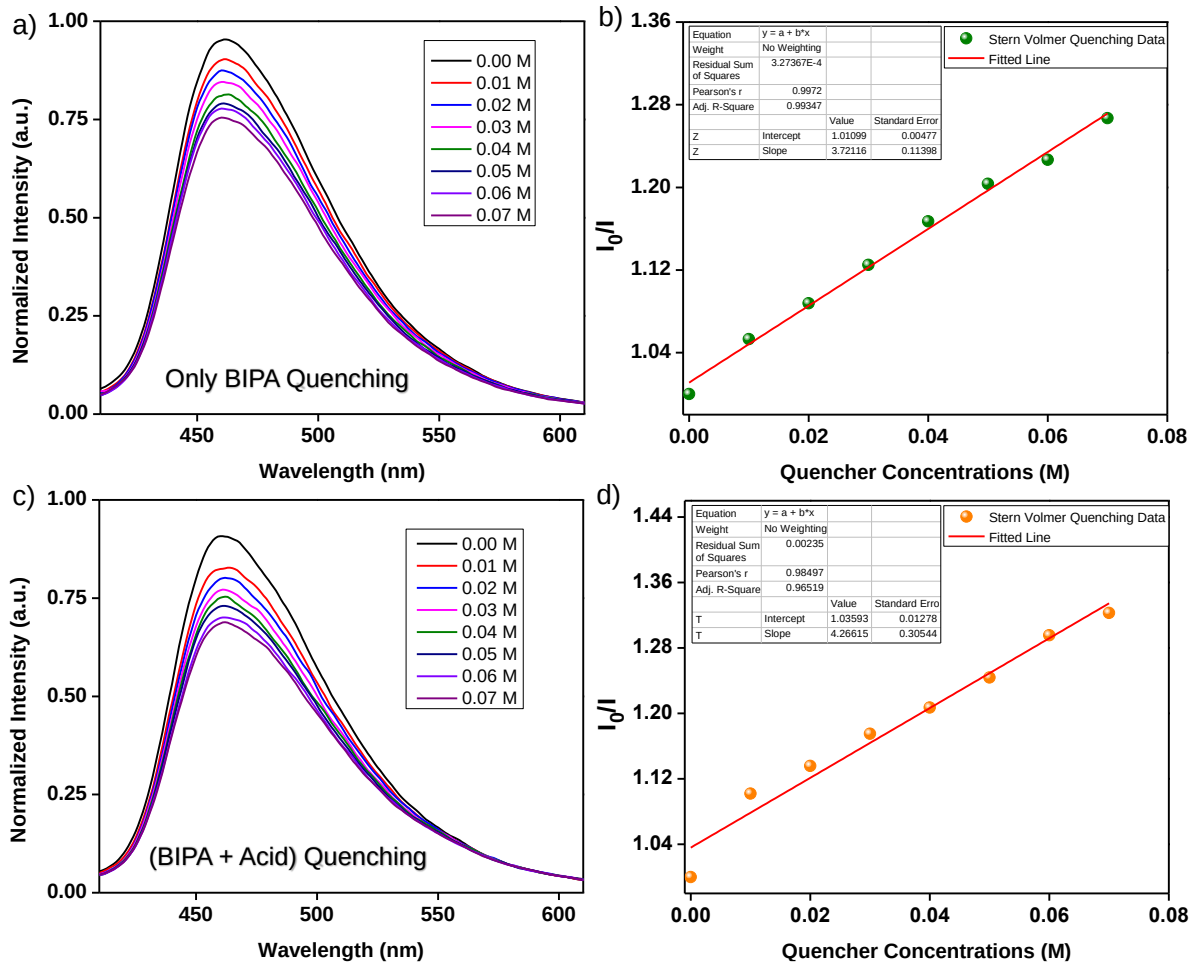
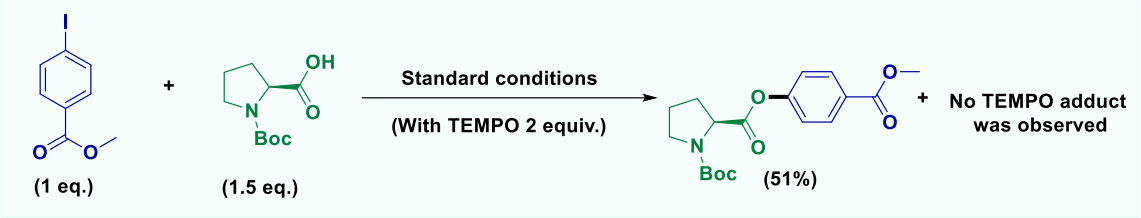


Figure S18: *Photoluminescence quenching experiments of excited Ni@Bpy-sp^{2}c-COF catalyst in the presence of a) BIPA, c) (BIPA + cyclobutanecarboxylic acid), and corresponding Stern-Volmer quenching plots are b) and d) respectively. BIPA = ^{t}BuNH^{i}Pr.*

There are no significant changes in the quenching rate for (BIPA + cyclobutanecarboxylic acid) compared to sole BIPA. This suggested that the SET from the ammonium carboxylate might not be operative under the reaction conditions.

To further get insight into the mechanism, we also performed a radical trapping experiment in the presence of TEMPO. The product is formed in a significant (51%) yield in the presence of TEMPO (2 equiv.). Furthermore, we have not detected any TEMPO adduct via the HRMS analysis of the crude reaction mixture.

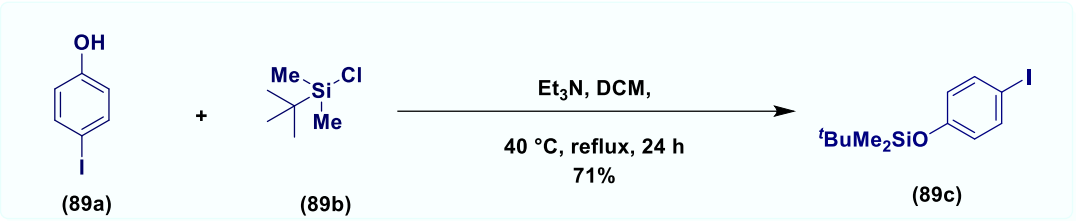
Radical trapping experiment in esterification:



These results point toward an energy transfer rather than a SET mechanistic pathway. The plausible mechanistic pathway is shown below and discussed in Figure S31, Section S-XII. The assumption is further supported by previously reported articles[16] where stoichiometric studies were conducted by a bipyridine (key linker for metal anchoring in Bpy-sp^2c-COF) ligand-based arylnickel(II) complex for reductive elimination.

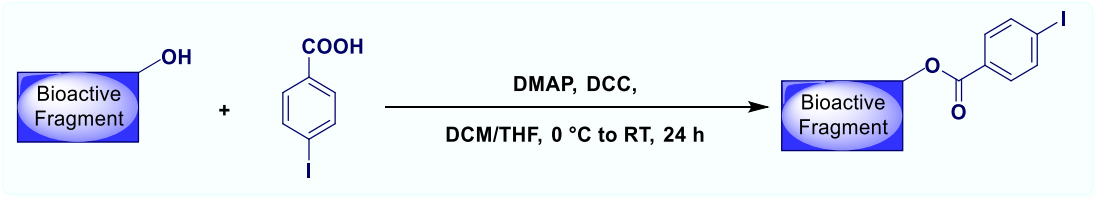
Section S-VII: Starting Material Preparation, Substrate Scopes, and Characterizations Data

Preparation of iodo *tert*-butyl(4-iodophenoxy)dimethylsilane[17]



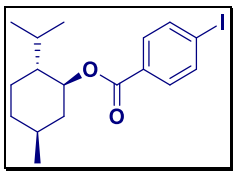
An oven-dried 50 mL round-bottom flask, equipped with a stir bar, was charged with 4-iodophenol (220 g, 1.0 mmol) and anhydrous CH_2Cl_2 (5 mL). Then distilled triethylamine (0.2 mL, 1.4 mmol) and TBDMSCl (150 mg, 1 mmol) were added to the solution. Afterward, this mixture was refluxed with a reflux condenser under an inert atmosphere. After 24 h, the reaction mixture was quenched with HCl (2 M) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were washed with a saturated solution of $NaHCO_3$ and a saturated solution of NaCl until it reached neutrality. The solution was dried over Na_2SO_4 and concentrated under reduced pressure to obtain the crude product. Finally, it was purified by silica gel column chromatography. **Yield** 237.3 mg (0.71 mmol, 71%). Colorless liquid. Column chromatography on silica gel (Eluent: 0-2% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.7 Hz, 2H), 0.98 (s, 9H), 0.19 (s, 6H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.8, 138.4, 122.7, 83.8, 25.8, 18.3, -4.3.

Preparation of iodo derivatives from different bioactive alcohols[18]



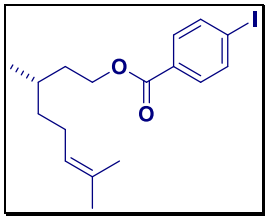
An oven-dried 50 mL round-bottom flask, equipped with a stir bar, was charged with 4-iodobenzoic acid (372 mg, 1.5 mmol), DCC (312 mg, 1.5 mmol), DMAP (24.4 mg, 0.2 mmol), and DCM/ THF (5:1 v/v, 5.0 mL). The mixture was allowed to cool to 0^o C with an ice bath. A solution of bioactive alcohol [(-)-menthol or citronellol or geraniol] (1.0 mmol) in DCM/THF (5:1 v/v, 2.0 mL) was added dropwise to the mixture. The mixture was allowed to warm to room temperature and stirred for 24 h. The solvent was removed by rotary evaporation, and the residue was purified by flash silica gel chromatography.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-iodobenzoate (98c)[19]



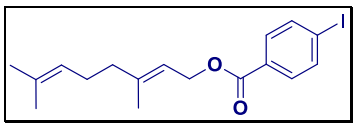
Yield 266 mg (0.69 mmol, 69%). Colorless liquid. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.82 – 7.71 (m, 4H), 4.91 (td, *J* = 10.9, 4.4 Hz, 1H), 2.12 – 2.08 (m, 1H), 1.94 – 1.88 (m, 1H), 1.73 – 1.70 (dt, *J* = 11.9, 2.9 Hz, 2H), 1.57 – 1.50 (m, 2H), 1.16 – 1.04 (m, 2H), 0.91 (dd, *J* = 8.1, 6.7 Hz, 7H), 0.78 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.7, 137.7, 131.1, 130.4, 100.5, 75.3, 47.3, 41.0, 34.4, 31.5, 26.7, 23.8, 22.1, 20.8, 16.7.

(*S*)-3,7-dimethyloct-6-en-1-yl 4-iodobenzoate (99c)



Yield 294 mg (0.76 mmol, 76%). Colorless liquid. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 5.09 (t, *J* = 7.3 Hz, 1H), 4.38 – 4.30 (m, 2H), 2.07 – 1.93 (m, 2H), 1.80 (tt, *J* = 12.9, 5.8 Hz, 1H), 1.68 – 1.53 (m, 8H), 1.39 (ddd, *J* = 15.2, 12.4, 6.0 Hz, 1H), 1.28 – 1.19 (m, 1H), 0.98 – 0.94 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.2, 137.8, 131.5, 131.1, 130.1, 124.6, 100.6, 63.9, 37.1, 35.6, 29.7, 25.8, 25.5, 19.6, 17.8. **IR (ATR/cm^{-1})** 2962.9, 2911.5, 2868.2, 2851.7, 1717.2, 1585.4, 1457.8, 1391.9, 1268.4, 1175.7, 1099.5, 1006.9, 906.0, 846.3. **HRMS (ESI)** m/z calcd. for $C_{11}H_{14}NO_3$ ($[M+Na]^+$) 409.0635, found m/z 409.0663.

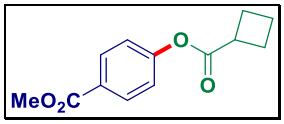
(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-iodobenzoate (100c)[19]



Yield 303.6 mg (0.79 mmol, 79%). Colorless liquid. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.78 – 7.72 (m, 4H), 5.45 (t, *J* = 7.2 Hz, 1H), 5.08 (t, *J* = 6.9 Hz, 1H), 4.82 (d, *J* = 7.1 Hz, 2H), 2.14 – 2.05 (m, 4H), 1.75 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.1, 142.6, 137.7, 131.9, 131.1, 130.0, 123.8, 118.3, 100.6, 62.1, 39.6, 26.3, 25.7, 17.8, 16.6.

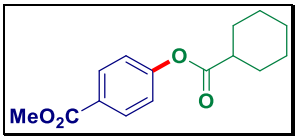
Substrate scopes for esterifications:

Methyl 4-((cyclobutanecarbonyl)oxy)benzoate (21)



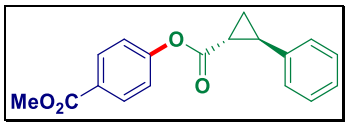
Yield 11.9 mg (0.051 mmol, 51%). Colorless liquid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H), 3.40 (p, *J* = 8.5 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.38 – 2.29 (m, 2H), 2.11 – 1.96 (m, 2H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 173.5, 166.5, 154.7, 131.3, 127.7, 121.7, 52.3, 38.3, 25.4, 18.5. **IR (ATR/cm^{-1})** 2993.8, 2952.6, 2870.3, 1754.3, 1719.3, 1604.0, 1505.1, 1435.1, 1276.6, 1198.3, 1093.3, 1015.1, 761.8. **HRMS (ESI)** m/z calcd. for $C_{13}H_{14}O_4$ ([M+Na]$^+$) 257.0784, found m/z 257.0779.

Methyl 4-((cyclohexanecarbonyl)oxy)benzoate (22)[16b]



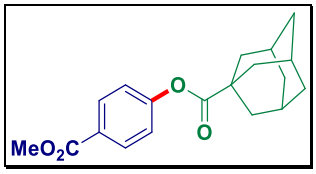
Yield 20.9 mg (0.080 mmol, 80 %). White solid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 6.9 Hz, 2H), 7.14 (d, *J* = 6.9 Hz, 2H), 3.91 (d, *J* = 1.7 Hz, 3H), 2.64 – 2.50 (m, 1H), 2.06 (dd, *J* = 13.1, 4.0 Hz, 2H), 1.82 (dt, *J* = 12.8, 3.8 Hz, 2H), 1.73 – 1.65 (m, 1H), 1.62 – 1.57 (m, 2H), 1.41 – 1.29 (m, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 174.1, 166.5, 154.8, 131.2, 127.6, 121.7, 52.3, 43.4, 29.0, 25.8, 25.5.

Methyl 4-((2-phenylcyclopropane-1-carbonyl)oxy)benzoate (23)



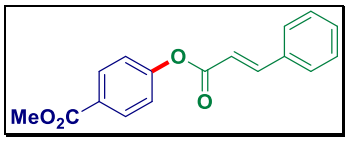
Yield 12.4 mg (0.042 mmol, 42 %). White solid. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.12 – 8.07 (m, 2H), 7.34 (ddd, *J* = 7.8, 5.8, 1.7 Hz, 2H), 7.28 – 7.26 (m, 1H), 7.24 – 7.21 (m, 2H), 7.20 – 7.16 (m, 2H), 3.93 (s, 3H), 2.71 (ddd, *J* = 9.2, 6.7, 4.1 Hz, 1H), 2.16 (ddd, *J* = 8.3, 5.3, 4.2 Hz, 1H), 1.79 (dt, *J* = 9.6, 4.9 Hz, 1H), 1.55 – 1.51 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 171.6, 166.5, 154.5, 139.5, 131.3, 128.8, 127.8, 127.0, 126.4, 121.7, 52.3, 27.5, 24.2, 18.0. **IR (ATR/cm^{-1})** 3063.8, 3037.1, 3012.3, 2958.8, 2919.7, 2849.7, 1721.3, 1599.9, 1433.1, 1400.1, 1260.1, 1093.3, 1011.0. **HRMS (ESI)** m/z calcd. for $C_{18}H_{16}O_4$ ([M+Na]$^+$) 319.0941, found m/z 319.0916.

4-(methoxycarbonyl)phenyl (1s,3s)-adamantane-1-carboxylate (24)[16b]



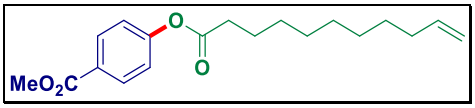
Yield 22.6 mg (0.072 mmol, 72%). White solid. Column chromatography on silica gel (Eluent: 8-10% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.06 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.13 (dd, *J* = 8.8, 2.0 Hz, 2H), 3.91 (s, 3H), 2.11 – 2.07 (m, 3H), 2.06 (s, 6H), 1.80 – 1.75 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.8, 166.5, 155.0, 131.2, 127.6, 121.8, 52.3, 41.3, 38.8, 36.5, 28.0.

Methyl 4-(cinnamoyloxy)benzoate (25)[20]



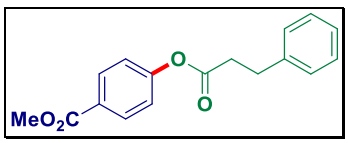
Yield 14.1 mg (0.050 mmol, 50%). White solid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 16.0 Hz, 1H), 7.60 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.27 (d, *J* = 6.5 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.5, 165.0, 154.6, 147.4, 134.2, 131.3, 131.1, 129.2, 128.5, 127.8, 121.8, 117.0, 52.3.

Methyl 4-(undec-10-enoyloxy)benzoate (26)



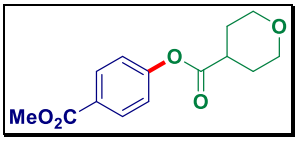
Yield 18.1 mg (0.057 mmol, 57%). Colorless liquid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 5.82 – 5.80 (m, 1H), 5.05 – 4.89 (m, 2H), 3.91 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.06 – 2.03 (m, 2H), 1.78 – 1.72 (m, 2H), 1.40 – 1.30 (m, 10H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.9, 166.5, 154.6, 139.3, 131.3, 127.7, 121.7, 114.3, 52.3, 34.5, 33.9, 29.8, 29.4, 29.3, 29.2, 29.0, 25.0. **IR (ATR/cm^{-1})** 3076.2, 2923.8, 2855.9, 1762.5, 1725.5, 1604.0, 1435.1, 1276.6, 1202.5, 1161.3, 1099.5. **HRMS (ESI)** m/z calcd. for $C_{19}H_{26}O_4$ ($[M+Na]^+$) 341.1723, found m/z 341.1713.

Methyl 4-((3-phenylpropanoyl)oxy)benzoate (27)



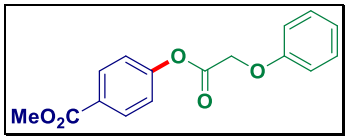
Yield 15 mg (0.053 mmol, 53%). White solid. Column chromatography on silica gel (Eluent: 5-10% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.27 (m, 3H), 7.13 – 7.08 (m, 2H), 3.92 (d, *J* = 0.9 Hz, 3H), 3.09 (t, *J* = 7.7 Hz, 2H), 2.92 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.0, 166.5, 154.4, 140.0, 131.3, 128.8, 128.5, 127.8, 126.7, 121.7, 52.3, 36.1, 31.0. **IR (ATR/cm^{-1})** 2950.6, 2923.8, 2851.7, 1748.1, 1715.2, 1601.9, 1435.1, 1272.5, 1138.6, 1091.3. **HRMS (ESI)** m/z calcd. for $C_{17}H_{16}O_4$ ([M+Na]$^+$) 307.0941, found m/z 307.0922.

4-(methoxycarbonyl)phenyl tetrahydro-2*H*-pyran-4-carboxylate (28)[16b]



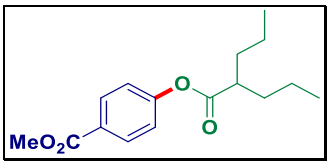
Yield 20.6 mg (0.078 mmol, 78%). White solid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 4.03 (dt, *J* = 11.7, 3.7 Hz, 2H), 3.92 (s, 3H), 3.51 (td, *J* = 11.3, 2.6 Hz, 2H), 2.82 (tt, *J* = 10.9, 4.2 Hz, 1H), 2.03 – 1.88 (m, 4H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.6, 166.4, 154.5, 131.3, 127.9, 121.6, 67.1, 52.4, 40.4, 28.7.

Methyl 4-(2-phenoxyacetoxy)benzoate (29)[20]



Yield 14 mg (0.049 mmol, 49%). White solid. Column chromatography on silica gel (Eluent: 15-20% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.31 (m, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.99 (dt, *J* = 7.7, 1.0 Hz, 2H), 4.90 (s, 2H), 3.92 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.2, 166.3, 157.8, 153.8, 131.4, 129.9, 128.3, 122.3, 121.5, 114.9, 65.5, 52.4.

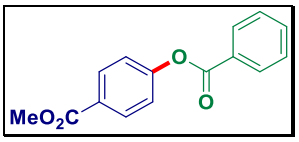
Methyl 4-((2-propylpentanoyl)oxy)benzoate (30)



Yield 17.5 mg (0.063 mmol, 63%). Colorless liquid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H), 2.62 (tt, *J* = 9.1, 5.2 Hz, 1H), 1.79 – 1.71 (m, 2H), 1.58 – 1.52 (m, 2H), 1.47 – 1.39 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 174.6, 166.5, 154.7, 131.3, 127.7, 121.8, 52.3, 45.6, 34.7, 20.8, 14.1. **IR (ATR/cm$^-$**

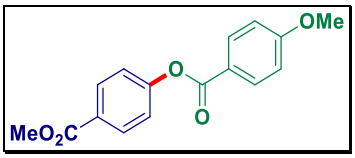
[1]) 2956.8, 2934.1, 2872.3, 1756.3, 1725.5, 1604.0, 1435.1, 1274.5, 1190.1, 1159.2, 1095.4, 759.8. **HRMS (ESI)** m/z calcd. for $C_{16}H_{22}O_4$ ($[M+Na]^+$) 301.1410, found m/z 301.1408.

Methyl 4-(benzoyloxy)benzoate(31)[21]



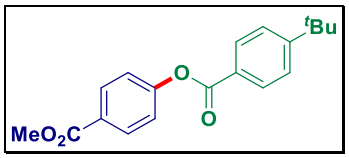
Yield 15.8 mg (0.062 mmol, 62%). White solid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.21 (d, *J* = 7.7 Hz, 2H), 8.13 (d, *J* = 9.0 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 9.1 Hz, 2H), 3.94 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.5, 164.8, 154.8, 134.0, 131.4, 130.4, 129.3, 128.8, 127.9, 121.9, 52.4.

4-(methoxycarbonyl)phenyl 4-methoxybenzoate (32)[22]



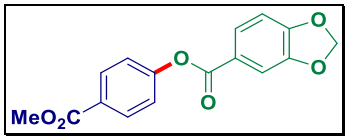
Yield 21.7 mg (0.076 mmol, 76%). White solid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 9.2 Hz, 2H), 3.93 (s, 3H), 3.90 (s, 3H**). ^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.5, 164.5, 164.3, 154.9, 132.5, 131.3, 127.7, 122.0, 121.5, 114.1, 55.7, 52.3.

4-(methoxycarbonyl)phenyl 4-(tert-butyl)benzoate (33)



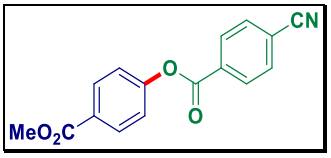
Yield 21.5 mg (0.069 mmol, 69%). White solid. Column chromatography on silica gel (Eluent: 8-10% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.15 (dd, *J* = 8.5, 3.7 Hz, 4H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.5, 164.8, 157.9, 154.9, 131.3, 130.3, 127.8, 126.4, 125.8, 122.0, 52.3, 35.4, 31.2. **IR (ATR/cm^{-1})** 2960.9 2925.9, 2870.3, 2357.6, 1717.2, 1599.9, 1264.2, 1196.3, 1105.7, 1062.5, 1008.9. **HRMS (ESI)** m/z calcd. for $C_{19}H_{20}O_4$ ($[M+Na]^+$) 335.1254, found m/z 335.1245.

4-(methoxycarbonyl)phenyl benzo[d][1,3]dioxole-5-carboxylate (34)



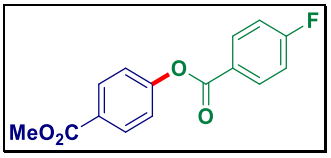
Yield 19.8 mg (0.066 mmol, 66%). White solid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.82 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.60 (d, *J* = 1.7 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 2H), 3.93 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.5, 164.1, 154.8, 152.6, 148.1, 131.3, 127.8, 126.5, 123.1, 121.9, 110.1, 108.4, 102.2, 52.3. **IR (ATR/cm^{-1})** 3067.9, 3002.0, 2954.7, 2917.6, 2845.6, 2802.3, 1731.6, 1713.1, 1604.0, 1492.8, 1435.1, 1268.4, 1210.7, 1159.2, 1103.6, 912.1. **HRMS (ESI)** m/z calcd. for $C_{16}H_{12}O_6$ ($[M+Na]^+$) 323.0526, found m/z 323.0528.

4-(methoxycarbonyl)phenyl 4-cyanobenzoate (35)[21]



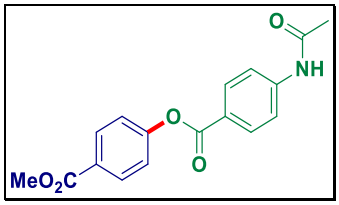
Yield 12.6 mg (0.045 mmol, 45%). White solid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane).**^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.31 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.3, 163.2, 154.2, 133.1, 132.6, 131.5, 130.8, 128.5, 121.7, 117.9, 117.5, 52.4.

4-(methoxycarbonyl)phenyl 4-fluorobenzoate (36)[8]



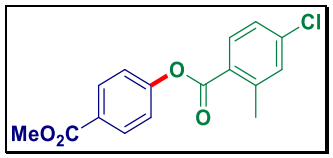
Yield 15.0 mg (0.055 mmol, 55%). White solid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.22 (dd, *J* = 8.7, 5.6 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.20 (t, *J* = 8.4 Hz, 2H), 3.93 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.5 (d, $^{1}J_{C\text{-}F}$ = 255.8 Hz), 166.5, 163.8, 154.6, 133.0 ($^{3}J_{C\text{-}F}$ = 10.1 Hz), 131.4, 128.1, 125.5 ($^{4}J_{C\text{-}F}$ = 3.8 Hz), 121.8, 116.1 ($^{2}J_{C\text{-}F}$ = 22.7 Hz), 52.4. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -103.8 (m, 1F).

4-(methoxycarbonyl)phenyl 4-acetamidobenzoate (37)



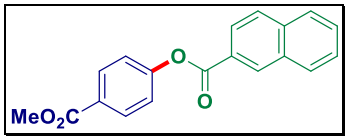
Yield 18.5 mg (0.059 mmol, 59%). Yellow solid. Column chromatography on silica gel (Eluent: 40-50% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.45 (s, 1H), 7.30 (d, *J* = 8.7 Hz, 2H), 3.93 (s, 3H), 2.24 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.6, 166.5, 164.2, 154.8, 143.1, 131.8, 131.4, 127.8, 124.5, 121.9, 119.0, 52.4, 25.0. **IR (ATR/cm^{-1})** 3358.3, 3321.2, 3282.1, 2956.8, 2917.6, 2849.7, 1723.4, 1682.2, 1599.9, 1538.1, 1408.4, 1258.1, 1167.5, 1107.8, 1074.8, 759.8. **HRMS (ESI)** m/z calcd. for $C_{17}H_{15}O_5N$ ($[M+Na]^+$) 336.0842, found m/z 336.0833.

4-(methoxycarbonyl)phenyl 4-chloro-2-methylbenzoate (38)



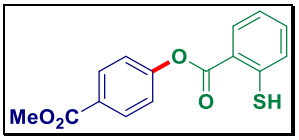
Yield 18.6 mg (0.061 mmol, 61%). White solid. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.12 (t, *J* = 8.0 Hz, 3H), 7.35 – 7.27 (m, 4H), 3.93 (s, 3H), 2.66 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.5, 164.5, 154.5, 143.8, 139.4, 132.8, 132.2, 131.4, 128.0, 126.5, 126.4, 121.9, 52.4, 22.0. **IR (ATR/cm^{-1})** 3076.2, 2956.8, 1739.9, 1717.2, 1599.9, 1562.8, 1505.1, 1441.3, 1410.4, 1291.0, 1241.6, 1202.5, 1161.3, 1101.6, 1037.7, 891.6. **HRMS (ESI)** m/z calcd. for $C_{16}H_{13}ClO_4$ ($[M+Na]^+$) 305.0575, found m/z 305.0593.

4-(methoxycarbonyl)phenyl 2-naphthoate (39)[23]



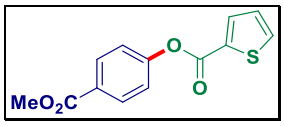
Yield 21.4 mg (0.070 mmol, 70%). White solid. Column chromatography on silica gel (Eluent: 5-10% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.82 (s, 1H), 8.21 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 3.97 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.5, 165.0, 154.9, 136.1, 132.6, 132.3, 131.4, 129.7, 129.0, 128.7, 128.0, 128.0, 127.1, 126.4, 125.5, 122.0, 52.4.

4-(methoxycarbonyl)phenyl 2-mercaptobenzoate (40)



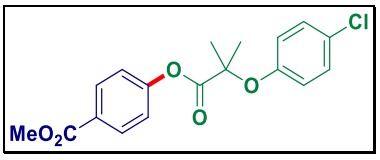
Yield 15.2 mg (0.053 mmol, 53%). Yellow solid. Column chromatography on silica gel (Eluent: 35-45% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.10 – 7.97 (m, 3H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.12 (s, 1H), 3.92 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.7, 141.4, 139.8, 134.1, 132.9, 132.1, 130.7, 130.2, 128.9, 125.5, 52.4. **IR (ATR/cm^{-1})** 2915.6, 2355.5, 1721.3, 1667.8, 1435.1, 1396.0, 1270.4, 1251.9, 1105.7, 1015.1. **HRMS (ESI)** m/z calcd. for $C_{15}H_{12}O_4S$ ([M+Na]$^+$) 311.0344, found m/z 311.0349.

4-(methoxycarbonyl)phenyl thiophene-2-carboxylate(41)



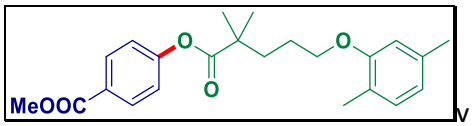
Yield 18.4 mg (0.070 mmol, 70%). White solid. Column chromatography on silica gel (Eluent: 10-12% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.14 – 8.10 (m, 2H), 8.00 (dt, *J* = 3.8, 1.1 Hz, 1H), 7.70 (dt, *J* = 5.0, 1.2 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.19 (ddd, *J* = 5.0, 3.8, 1.1 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 166.5, 160.1, 154.3, 135.2, 134.1, 132.5, 131.4, 128.3, 128.0, 121.8, 52.4. **IR (ATR/cm^{-1})** 3092.6, 2921.7, 2847.6, 1704.9, 1601.9, 1505.1, 1412, 1268.4, 1111.9, 1015.1. **HRMS (ESI)** m/z calcd. for $C_{13}H_{10}O_4S$ ([M+Na]$^+$) 285.0192, found m/z 285.0189.

Methyl 4-((2-(4-chlorophenoxy)-2-methylpropanoyl)oxy)benzoate (42)



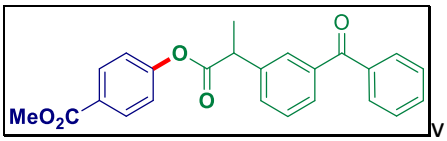
Yield 18.1 mg (0.052 mmol, 52%). Colourless liquid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.09 – 8.05 (m, 2H), 7.27 – 7.23 (m, 2H), 7.10 – 7.07 (m, 2H), 6.91 – 6.88 (m, 2H), 3.91 (s, 3H), 1.74 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 13C NMR (126 MHz, CDCl3) δ 172.3, 166.3, 154.2, 154.0, 131.4, 129.5, 128.3, 127.9, 121.4, 120.7, 79.7, 52.4, 25.4. **IR (ATR/cm^{-1})** 3076.2, 2993.8, 2950.6, 2845.6, 1760.5, 1721.3, 1488.7, 1276.6, 1159.2, 1083.0, 1013.0, 825.7, 757.7. **HRMS (ESI)** m/z calcd. for $C_{18}H_{17}ClO_5$ ([M+Na]$^+$) 371.0657, found m/z 371.0647.

Methyl 4-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)benzoate (43)



Yield 23.5 mg (0.061 mmol, 61%). Colourless liquid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane).**^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 4.02 – 3.97 (m, 2H), 3.92 (s, 3H), 2.31 (s, 3H), 2.18 (s, 3H), 1.39 (s, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 176.0, 166.5, 156.9, 154.8, 136.6, 131.2, 130.5, 127.7, 123.7, 121.7, 120.9, 112.1, 67.8, 52.3, 42.7, 37.2, 25.4, 25.2, 21.5, 15.9. **IR (ATR/cm^{-1})** 2954.7, 2925.9, 2874.4, 1752.2, 1723.4, 1604.0, 1505.1, 1435.1, 1276.6, 1202.5, 1159.2, 1091.3, 1046.0, 805.1, 757.7. **HRMS (ESI)** m/z calcd. for $C_{23}H_{28}O_5$ ([M+Na]$^+$) 407.1829, found m/z 407.1819.

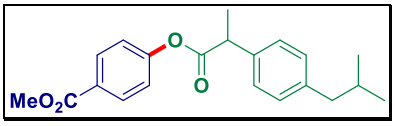
Methyl 4-((2-(3-benzoylphenyl)propanoyl)oxy)benzoate (44)



Yield 22.9 mg (0.059 mmol, 59%). Colourless liquid. Column chromatography on silica gel (Eluent: 25-30% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.85 (s, 1H), 7.81 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.49 (dt, *J* = 13.4, 7.6 Hz, 3H), 7.09 (d, *J* = 8.7 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 1.67 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 196.5, 172.2, 166.4, 154.4, 140.2, 138.3, 137.5, 132.7, 131.6, 131.3, 130.2, 129.5, 129.4, 129.0, 128.5, 127.9, 121.5, 52.3, 45.7, 18.6.

IR (ATR/cm^{-1}) 3065.9, 2987.6, 2950.6, 1754.3, 1717.2, 1659.6, 1601.9, 1435.1, 1274.5, 1198.3, 1107.8, 1066.6. **HRMS (ESI)** m/z calcd. for $C_{24}H_{20}O_5$ ([M+Na]$^+$) 411.1203, found m/z 411.1191.

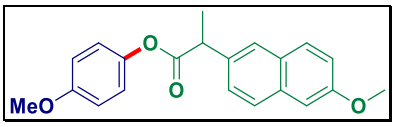
Methyl 4-((2-(4-isobutylphenyl)propanoyl)oxy)benzoate (45)[20]



Yield 16.7 mg (0.049 mmol, 49%). Colourless liquid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 3.95 (q, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.87 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.61 (d, *J*

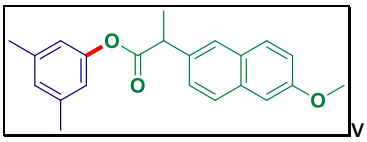
= 7.1 Hz, 4H), 0.91 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.8, 166.5, 154.7, 141.1, 137.0, 131.2, 129.7, 127.7, 127.3, 121.6, 52.3, 45.5, 45.2, 30.3, 22.5, 18.6.

4-methoxyphenyl 2-(6-methoxynaphthalen-2-yl)propanoate (46)



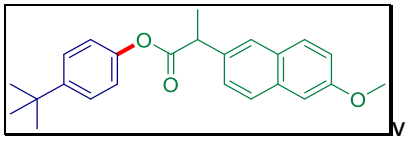
Yield 16.8 mg (0.050 mmol, 50%). White solid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.79 – 7.72 (m, 3H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.13 (m, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 3.77 (s, 3H), 1.69 (dd, *J* = 7.2, 1.7 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 173.7, 157.9, 157.3, 144.5, 135.4, 133.9, 129.5, 129.1, 127.5, 126.3, 126.2, 122.3, 119.2, 114.5, 105.8, 55.7, 55.4, 45.7, 18.7. **IR (ATR/cm^{-1})** 3055.6, 2975.3, 2936.2, 2905.3, 2837.3, 1748.1, 1634.9, 1606.0, 1505.1, 1484.6, 1453.7, 1394.0, 1266.3, 1247.8, 1192.2, 1128.3, 1068.6, 1027.5, 926.6, 889.5, 850.4, 811.3s. **HRMS (ESI)** m/z calcd. for $C_{21}H_{20}O_4$ ([M+Na]$^+$) 359.1254, found m/z 359.1239.

3,5-dimethylphenyl 2-(6-methoxynaphthalen-2-yl)propanoate (47)



Yield 20.7 mg (0.062 mmol, 62%). White solid. Column chromatography on silica gel (Eluent: 1-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.78 – 7.73 (m, 3H), 7.51 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.82 (s, 1H), 6.60 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 2.26 (s, 6H), 1.69 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 173.5, 157.9, 150.9, 139.3, 135.4, 133.9, 129.5, 129.2, 127.6, 127.5, 126.3, 126.3, 119.2, 119.1, 105.8, 55.5, 45.7, 21.3, 18.7. **IR (ATR/cm^{-1})** 2981.5, 2917.6, 2849.7, 1746.0, 1604.0, 1262.2, 1225.1, 1146.9, 1029.5, 854.5, 809.2. **HRMS (ESI)** m/z calcd. for $C_{22}H_{22}O_3$ ([M+Na]$^+$) 357.1461, found m/z 357.1464.

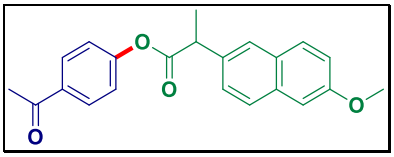
4-(*tert*-butyl)phenyl 2-(6-methoxynaphthalen-2-yl)propanoate (48)



Yield 20.7 mg (0.057 mmol, 57%). White crystalline solid. Column chromatography on silica gel (Eluent: 1-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.75 (dd, *J* = 15.4, 7.6 Hz, 3H), 7.50 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.18 – 7.13 (m, 2H), 6.93 –

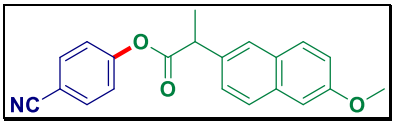
6.88 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 1.69 (d, *J* = 7.2 Hz, 3H), 1.28 (s, 9H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 173.5, 157.9, 148.7, 148.6, 135.4, 133.9, 129.5, 129.1, 127.5, 126.3, 126.3, 120.8, 119.2, 105.8, 55.5, 45.7, 34.6, 31.5, 18.7. **IR (ATR/cm^{-1})** 2958.8, 2925.9, 2853.8, 1746.0, 1604.0, 1484.6, 1457.8, 1208.6, 1169.5, 1144.8, 1027.5, 854.5, 813.3. **HRMS (ESI)** m/z calcd. for $C_{24}H_{26}O_3$ ([M+Na]$^+$) 385.1774, found m/z 385.1772.

4-acetylphenyl 2-(6-methoxynaphthalen-2-yl)propanoate (49)



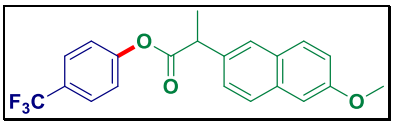
Yield 25.4 mg (0.073 mmol, 73%). Colorless oily liquid. Column chromatography on silica gel (Eluent: 25-40% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.93 (d, *J* = 8.7 Hz, 2H), 7.79 – 7.72 (m, 3H), 7.49 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 2.57 (s, 3H), 1.70 (dd, *J* = 7.2, 1.5 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 197.0, 172.8, 157.9, 154.7, 134.9, 134.0, 130.0, 129.4, 129.1, 127.6, 126.3, 126.1, 121.7, 119.4, 105.8, 55.5, 45.8, 26.7, 18.6. **IR (ATR/cm^{-1})** 3053.5, 2973.2, 2934.1, 2837.3, 1756.2, 1682.2, 1632.8, 1597.8, 1503.1, 1486.6, 1455.7, 1394.0, 1359.0, 1264.2, 1200.4, 1161.3, 1128.3, 1062.5, 1029.5, 959.5, 891.6, 850.4, 809.2. **HRMS (ESI)** m/z calcd. for $C_{22}H_{20}O_4$ ([M+Na]$^+$) 371.1254, found m/z 371.1238.

4-cyanophenyl 2-(6-methoxynaphthalen-2-yl)propanoate (50)



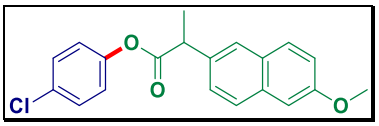
Yield 21.5 mg (0.065 mmol, 65%). Colourless oily liquid. Column chromatography on silica gel (Eluent: 1-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.78 – 7.71 (m, 3H), 7.65 – 7.60 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.20 – 7.10 (m, 4H), 4.14 – 4.07 (m, 1H), 3.93 (s, 3H), 1.70 (d, *J* = 7.6 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.5, 158.1, 154.3, 134.6, 134.1, 133.7, 129.4, 129.1, 127.7, 126.4, 126.0, 122.7, 119.5, 118.3, 109.7, 105.8, 55.5, 45.7, 18.5. **IR (ATR/cm^{-1})** 2923.8, 2851.7, 2229.9, 1756.3, 1601.9, 1505.1, 1206.6, 1165.4, 1124.2, 1066.6, 1029.5, 850.4. **HRMS (ESI)** m/z calcd. for $C_{21}H_{17}NO_3$ ([M+Na]$^+$) 354.1100, found m/z 354.1084.

4-(trifluoromethyl)phenyl 2-(6-methoxynaphthalen-2-yl)propanoate (51)



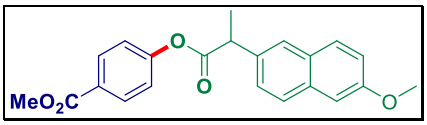
Yield 23.2 mg (0.062 mmol, 62%). Colorless oily liquid. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.78 – 7.73 (m, 3H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.49 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.13 – 7.09 (m, 2H), 4.12 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 1.71 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.8, 158.0, 153.5, 134.8, 134.1, 129.5, 129.1, 128.2 (q, $^{2}J_{C-F}$ = 32.7 Hz), 127.7, 126.8 (q, $^{3}J_{C-F}$ = 3.7 Hz), 126.3, 126.1, 124.0 (q, $^{1}J_{C-F}$ = 272.5 Hz), 122.1, 119.4, 105.8, 55.5, 45.7, 18.5. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -62.2 (s, 3F) **IR (ATR/cm^{-1})** 3059.7, 2936.2, 2847.6, 1758.4, 1606.0, 1321.9, 1163.3, 1120.1, 1058.3, 1015.1, 886.1, 854.5, 804.8. **HRMS (ESI)** m/z calcd. for $C_{21}H_{17}F_3O_3$ ([M+Na]$^+$) 397.1022, found m/z 397.1003.

4-chlorophenyl 2-(6-methoxynaphthalen-2-yl)propanoate (52)



Yield 20.1 mg (0.059 mmol, 59%). White solid. Column chromatography on silica gel (Eluent: 5-10% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.77 – 7.72 (m, 3H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.13 (m, 2H), 6.95 – 6.90 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 1.69 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 173.1, 158.0, 149.4, 135.0, 134.0, 131.3, 129.5, 129.5, 129.1, 127.6, 126.3, 126.1, 122.9, 119.3, 105.8, 55.5, 45.7, 18.6. **IR (ATR/cm^{-1})** 3098.8, 3057.6, 2981.5, 2936.2, 2851.7, 1760.5, 1601.9, 1486.6, 1194.2, 1126.3, 1064.5, 1011.0, 854.5, 817.4. **HRMS (ESI)** m/z calcd. for C20H17ClO$_3$ ([M+Na]$^+$) 363.0758, found m/z 363.0753.

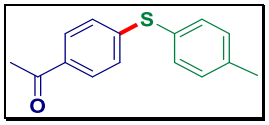
Methyl 4-((2-(6-methoxynaphthalen-2-yl)propanoyl)oxy)benzoate (53)[8]



Yield 30.6 mg (0.084 mmol, 84%). White solid. Column chromatography on silica gel (Eluent: 15-25% ethyl acetate in hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.78 – 7.73 (m, 3H), 7.50 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 1.70 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.8, 166.4, 158.0, 154.6, 134.9, 134.0, 131.2, 129.4, 129.1, 127.8, 127.6, 126.3, 126.1, 121.6, 119.3, 105.8, 55.5, 52.3, 45.7, 18.6.

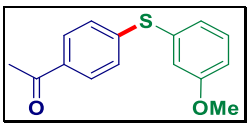
Substrate scopes for thioetherifications:

1-(4-(p-tolylthio)phenyl)ethan-1-one (54)[24]



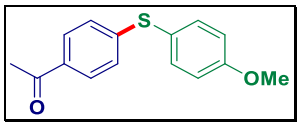
Yield 20.4 mg (0.084 mmol, 84%). Yellow solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 146.1, 139.5, 134.6, 134.3, 130.7, 129.0, 128.1, 126.8, 26.6, 21.4.

1-(4-((3-methoxyphenyl)thio)phenyl)ethan-1-one (55)[25]



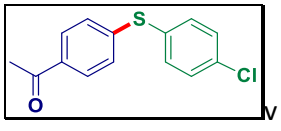
Yield 19.6 mg (0.076 mmol, 76%). Yellow solid. Column chromatography on silica gel (Eluent: 5-10% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 – 7.80 (m, 2H), 7.33 – 7.28 (m, 1H), 7.26 – 7.22 (m, 2H), 7.08 – 7.05 (m, 1H), 7.03 – 7.01 (m, 1H), 6.92 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.79 (s, 3H), 2.55 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.2, 160.5, 144.7, 134.8, 133.4, 130.6, 129.0, 127.9, 125.9, 118.8, 114.8, 55.5, 26.6.

1-(4-((4-methoxyphenyl)thio)phenyl)ethan-1-one (56)[26]



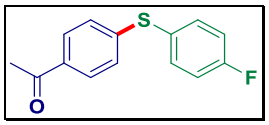
Yield 22.2 mg (0.086 mmol, 86%). White solid. Column chromatography on silica gel (Eluent: 5-10% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.2, 160.8, 147.0, 136.9, 134.0, 128.9, 125.9, 121.5, 115.5, 55.5, 26.5.

1-(4-((4-chlorophenyl)thio)phenyl)ethan-1-one (57)[27]



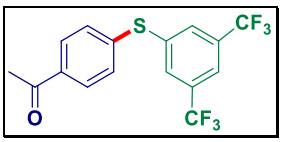
Yield 21.2 mg (0.080 mmol, 80%). White solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.21 (d, *J* = 8.5 Hz, 2H), 2.55 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.1, 144.1, 135.1, 134.9, 131.0, 130.0, 129.1, 127.9, 26.6.

1-(4-((4-fluorophenyl)thio)phenyl)ethan-1-one (58)[27]



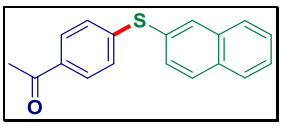
Yield 19.2 mg (0.078 mmol, 78%). Yellow solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 – 7.79 (m, 2H), 7.53 – 7.47 (m, 2H), 7.17 – 7.08 (m, 4H), 2.54 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.2, 163.4 (d, $^{1}J_{C\text{-}F}$ = 249.5 Hz), 145.3, 136.6 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 134.6, 129.0, 127.1(d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 127.0, 117.1 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 26.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.3 (m, 1F).

1-(4-((3,5-bis(trifluoromethyl)phenyl)thio)phenyl)ethan-1-one (59)



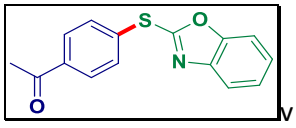
Yield 25.5 mg (0.070 mmol, 70%). Yellowish oil. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.76 (s, 3H), 7.42 (d, *J* = 8.4 Hz, 2H), 2.60 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.0, 139.6, 138.5, 136.7, 132.9 (q, $J_{C\text{-}F}$ = 34.0 Hz), 131.0, 130.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 129.6, 122.9 (q, $J_{C\text{-}F}$ = 273.4 Hz), 121.4 (sep, $J_{C\text{-}F}$ = 3.8 Hz), 26.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.9 (s, 3F). **IR (ATR/cm^{-1})** 3089.1, 2926.1, 2853.9, 1684.3, 1589.6, 1348.7, 1274.5, 1173.6, 1126.3, 1012.7, 954.0, 886.1, 818.2. **HRMS (ESI)** m/z calcd. for $C_{16}H_{10}F_6OS$ ($[M+H]^+$) 365.0429, found m/z 365.0440.

1-(4-(naphthalen-2-ylthio)phenyl)ethan-1-one (60)[27]



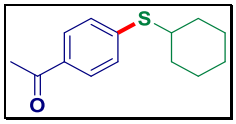
Yield 21.7 mg (0.078 mmol, 78%). White solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 1.8 Hz, 1H), 7.88 – 7.78 (m, 5H), 7.57 – 7.46 (m, 3H), 7.26 – 7.23 (m, 2H), 2.54 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.2, 144.9, 134.7, 134.0, 133.4, 133.1, 130.5, 129.6, 129.5, 129.1, 128.0, 127.9, 127.8, 127.2, 127.0, 26.6.

1-(4-(benzo[d]oxazol-2-ylthio)phenyl)ethan-1-one (61)



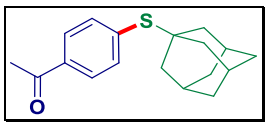
Yield 13.2 mg (0.049 mmol, 49%). Yellowish oil. Column chromatography on silica gel (Eluent: 10-15% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.46 – 7.41 (m, 1H), 7.32 – 7.27 (m, 2H), 2.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.2, 161.7, 151.9, 141.8, 137.5, 133.8, 133.2, 129.3, 124.9, 124.7, 119.4, 110.3, 26.8. **IR (ATR/cm^{-1})** 3061.8, 3002.0, 2962.9, 2921.7, 2851.7, 1682.2, 1589.6, 1499.0, 1449.5, 1396.0, 1356.9, 1256.0, 1235.4, 1124.2, 1087.0, 1013.0, 955.4, 803.0. **HRMS (ESI)** m/z calcd. for $C_{17}H_{23}IO_2$ ($[M+H]^+$) 270.0583, found m/z 270.0596.

1-(4-(cyclohexylthio)phenyl)ethan-1-one (62)[28]



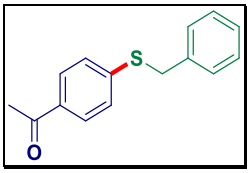
Yield 18.9 mg (0.081 mmol, 81%). White crystalline solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.34 – 3.24 (m, 1H), 2.56 (s, 3H), 2.07 – 1.99 (m, 2H), 1.83 – 1.75 (m, 2H), 1.68 – 1.60 (m, 1H), 1.49 – 1.28 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.3, 143.7, 134.3, 128.8, 128.5, 45.0, 33.2, 26.6, 26.0, 25.8.

1-(4-(((3s,5s,7s)-adamantan-1-yl)thio)phenyl)ethan-1-one (63)



Yield 22.6 mg (0.079 mmol, 79%). White crystalline solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 2.61 (s, 3H), 2.04 – 1.99 (m, 3H), 1.83 (d, *J* = 2.9 Hz, 6H), 1.68 – 1.59 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.9, 137.4, 136.9, 128.1, 49.2, 43.9, 36.2, 30.1, 26.8. **IR (ATR/cm^{-1})** 2899.1, 2847.6, 2357.6, 1678.1, 1587.5, 1350.7, 1251.9, 1037.7, 953.3, 829.8. **HRMS (ESI)** m/z calcd. for $C_{18}H_{22}OS$ ($[M+H]^+$) 287.1464, found m/z 287.1482.

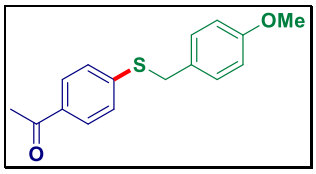
1-(4-(benzylthio)phenyl)ethan-1-one (64)[29]



Yield 15.5 mg (0.064 mmol, 64%). Colorless liquid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.3 Hz,

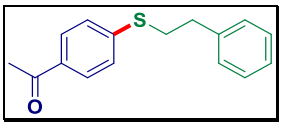
2H), 7.39 (d, *J* = 7.3 Hz, 2H), 7.36 – 7.27 (m, 5H), 4.23 (s, 2H), 2.57 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 197.3, 144.3, 136.3, 134.3, 128.8, 127.6, 127.0, 37.3, 26.5.

1-(4-((4-methoxybenzyl)thio)phenyl)ethan-1-one (65)[27]



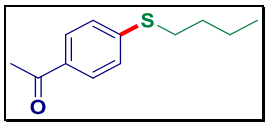
Yield 19.3 mg (0.071 mmol, 71%). Colorless liquid. Column chromatography on silica gel (Eluent: 5-15% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 – 7.80 (m, 2H), 7.34 – 7.26 (m, 4H), 6.86 – 6.82 (m, 2H), 4.17 (s, 2H), 3.79 (s, 3H), 2.55 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 197.4, 159.1, 144.6, 134.2, 130.0, 128.9, 128.2, 127.0, 114.2, 55.4, 36.8, 26.6.

1-(4-(phenethylthio)phenyl)ethan-1-one (66)[30]



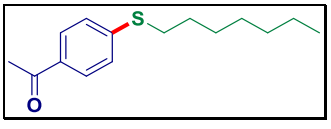
Yield 15.6 mg (0.061 mmol, 61%). Colorless liquid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.29 (m, 4H), 7.26 – 7.19 (m, 3H), 3.27 – 3.22 (m, 2H), 3.01 – 2.95 (m, 2H), 2.57 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 197.3, 144.4, 139.8, 134.1, 129.0, 128.8, 128.6, 126.8, 126.7, 35.3, 33.6, 26.6.

1-(4-(butylthio)phenyl)ethan-1-one (67)[31]



Yield 18.5 mg (0.089 mmol, 89%). Yellowish oil. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.01 – 2.96 (m, 2H), 2.56 (s, 3H), 1.72 – 1.65 (m, 2H), 1.47 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 197.3, 145.1, 133.9, 128.8, 126.4, 31.8, 30.9, 26.5, 22.1, 13.7.

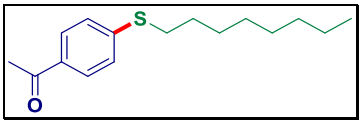
1-(4-(heptylthio)phenyl)ethan-1-one (68)[32]



Yield 22.0 mg (0.088 mmol, 88%). White solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 (d, *J* = 8.5 Hz,

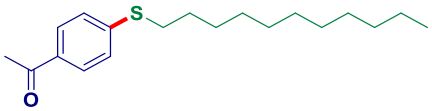
2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.01 – 2.96 (m, 2H), 2.56 (s, 3H), 1.70 (t, *J* = 7.5 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.31 – 1.23 (m, 6H), 0.89 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.8, 128.9, 126.4, 32.1, 31.8, 29.0, 28.9, 28.9, 26.5, 22.7, 14.2.

1-(4-(octylthio)phenyl)ethan-1-one (69)[28]



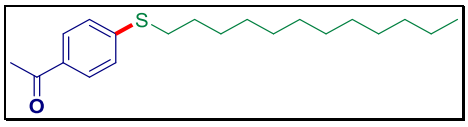
Yield 22.2 mg (0.084 mmol, 84%). White solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.01 – 2.95 (m, 2H), 2.56 (s, 3H), 1.69 (p, *J* = 7.1 Hz, 2H), 1.44 (q, *J* = 7.0 Hz, 2H), 1.32 – 1.24 (m, 8H), 0.89 – 0.85 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.9, 128.9, 126.4, 32.1, 31.9, 29.3, 29.2, 29.0, 28.9, 26.5, 22.8, 14.2.

1-(4-(undecylthio)phenyl)ethan-1-one (70)



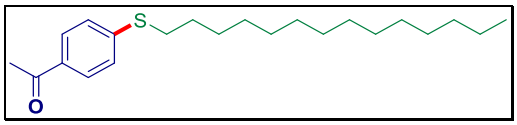
Yield 22.9 mg (0.075 mmol, 75%). White crystalline solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.00 – 2.96 (m, 2H), 2.56 (s, 3H), 1.69 (t, *J* = 7.5 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 2H), 1.30 – 1.26 (m, *J* = 8.5 Hz, 14H), 0.87 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.9, 128.9, 126.4, 32.1, 32.0, 29.7, 29.7, 29.6, 29.4, 29.3, 29.0, 28.9, 26.5, 22.8, 14.2. **IR (ATR/cm^{-1})** 2917.6, 2847.6, 1671.9, 1587.5, 1461.9, 1354.8, 1264.2, 1097.5, 957.4, 815.4. **HRMS (ESI)** m/z calcd. for $C_{19}H_{30}OS$ ($[M+Na]^+$) 329.1910, found m/z 329.1924.

1-(4-(dodecylthio)phenyl)ethan-1-one (71)[33]



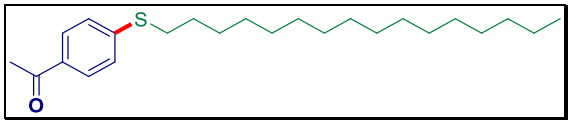
Yield 24.4 mg (0.076 mmol, 76%). White solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 3.01 – 2.94 (m, 2H), 2.56 (s, 3H), 1.69 (p, *J* = 7.3 Hz, 2H), 1.44 (p, *J* = 7.0 Hz, 2H), 1.29 – 1.22 (m, 16H), 0.90 – 0.84 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.9, 128.9, 126.4, 32.1, 32.0, 29.8, 29.7, 29.6, 29.6, 29.5, 29.3, 29.0, 28.9, 26.5, 22.8, 14.2.

1-(4-(tetradecylthio)phenyl)ethan-1-one (72)



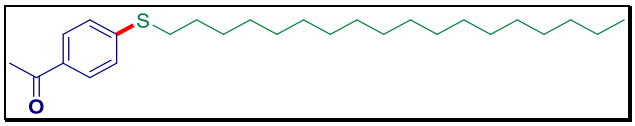
Yield 24.0 mg (0.069 mmol, 69%). White crystalline solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 3.01 – 2.96 (m, 2H), 2.56 (s, 3H), 1. 71 – 1.66 (m, 2H), 1.48 – 1.41 (m, 2H), 1.27 – 1.26 (s, 20H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.9, 128.9, 126.4, 32.2, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 29.0, 28.9, 26.5, 22.8, 14.3. **IR (ATR/cm^{-1})** 2917.6, 2849.7, 1678.1, 1589.6, 1461.9, 1359.0, 1264.2, 1099.5, 963.6, 815.4. **HRMS (ESI)** m/z calcd. for $C_{22}H_{36}OS$ ($[M+Na]^+$) 371.2379, found m/z 371.2387.

1-(4-(hexadecylthio)phenyl)ethan-1-one (73)



Yield 21.5 mg (0.057 mmol, 57%). White crystalline solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 3.00 – 2.95 (m, 2H), 2.83 – 2.82 (m, 4H), 2.56 (s, 3H), 1.69 (p, *J* = 7.4 Hz, 2H), 1.44 (t, *J* = 7.5 Hz, 2H), 1.26 – 1.25 (s, 20H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.9, 128.9, 126.4, 40.4, 39.4, 32.1, 32.0, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.3, 29.0, 28.9, 28.7, 26.6, 22.8, 14.3. **IR (ATR/cm^{-1})** 2952.6, 2917.6, 2874.4, 2847.6, 1678.1, 1589.6, 1472.2, 1461.9, 1361.0, 1266.3, 1192.2, 1099.5, 963.6, 815.4. **HRMS (ESI)** m/z calcd. for $C_{24}H_{40}OS$ ($[M+Na]^+$) 399.2692, found m/z 399.2703.

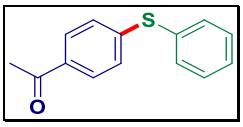
1-(4-(octadecylthio)phenyl)ethan-1-one(74)



Yield 12.5 mg (0.031 mmol, 31%). White crystalline solid. Column chromatography on silica gel (Eluent: 0-1% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.56 (s, 3H), 1.70 (p, J = 7.5 Hz, 2H), 1.48 – 1.41(m, 2H), 1.29 – 1.26 (m, 28H), 0.88 (t, J = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.3, 145.2, 133.9, 128.9, 126.4, 34.2, 32.1, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 28.9, 28.5, 26.5, 24.8, 22.8, 14.2. **IR (ATR/cm^{-1})** 2917.6,

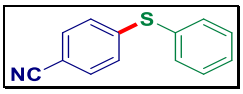
2849.7, 1678.1, 1589.6, 1461.9, 1359.0, 1264.2, 1099.5, 963.6, 815.4. **HRMS (ESI)** m/z calcd. for $C_{26}H_{44}OS$ ([M+H]$^+$) 405.3186, found m/z 405.3200.

1-(4-(phenylthio)phenyl)ethan-1-one (75)[34]



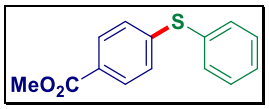
Yield 21.9 mg (0.096 mmol, 96%). Yellow solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.31 – 7.27 (m, 3H), 7.11 (d, *J* = 8.5 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.1, 144.9, 134.6, 133.8, 132.2, 129.7, 128.9, 128.8, 127.5, 26.4.

4-(phenylthio)benzonitrile (76)[35]



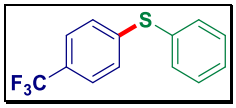
Yield 16.0 mg (0.076 mmol, 76%). White solid. Column chromatography on silica gel (Eluent: 0-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 – 7.40 (m, 7H), 7.18 – 7.13 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.9, 134.6, 132.5, 131.0, 130.0, 129.5, 127.5, 118.9, 108.8.

Methyl 4-(phenylthio)benzoate (77)[36]



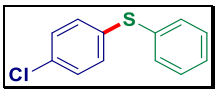
Yield 21.9 mg (0.090 mmol, 90%). White solid. Column chromatography on silica gel (Eluent: 3-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.42 – 7.35 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 144.5, 133.8, 132.5, 130.2, 129.8, 128.8, 127.7, 127.6, 52.2.

Phenyl(4-(trifluoromethyl)phenyl)sulfane (78)[35]



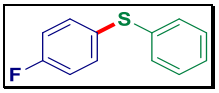
Yield 23.6 mg (0.093 mmol, 93%). Yellow solid. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 – 7.47 (m, 4H), 7.44 – 7.38 (m, 3H), 7.29 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.9, 142.9, 133.5, 132.6, 129.7, 128.5, 128.1 (q, $^2J_{C-F}$ = 33.1 Hz), 125.8 (q, $^3J_{C-F}$ = 3.7 Hz), 124.1 (q, $^1J_{C-F}$ = 272.1 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.3 (s, 3F).

(4-chlorophenyl)(phenyl)sulfane (79)[37]



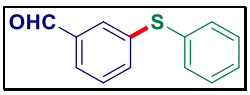
Yield 18.5 mg (0.084, 84%). Colourless oil. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.37 – 7.29 (m, 4H), 7.29 – 7.22 (m, 5H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 135.24, 134.76, 133.11, 132.13, 131.44, 129.44, 129.18, 127.55.

(4-fluorophenyl)(phenyl)sulfane (80)[38]



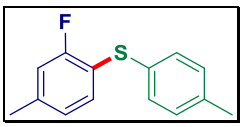
Yield 16.3 mg (0.080 mmol, 80%). Colorless oil. Column chromatography on silica gel (Eluent: 0-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.38 – 7.35 (m, 2H), 7.29 – 7.20 (m, 5H), 7.01 (t, J = 8.7 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.5 (d, $^{1}J_{C\text{-}F}$ = 248.2 Hz), 136.8, 134.2 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 130.3 (d, $^{4}J_{C\text{-}F}$ = 2.52 Hz), 130.1, 129.3, 126.9, 116.5 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz). **^{19}F NMR (376 MHz, CDCl$_3$)** δ -113.9 (m, 1F).

4-(phenylthio)benzaldehyde (81)[39]



Yield 10.1 mg (0.047mmol, 47%). Yellowish oil. Column chromatography on silica gel (Eluent: 3-8% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.93 (s, 1H), 7.77 – 7.68 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 – 7.40 (m, 3H), 7.39 – 7.32 (m, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 191.7, 138.9, 137.2, 135.4, 133.7, 132.6, 130.7, 129.8, 129.7, 128.3, 127.7.

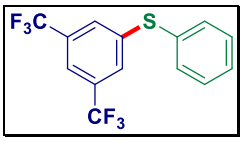
(2-fluoro-4-methylphenyl)(phenyl)sulfane (82)



Yield 16.5 mg (0.071, 71%). Colorless liquid. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.41 – 7.27 (m, 3H), 7.25 – 7.16 (m, 3H), 6.98 – 6.90 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.8 (d, $J_{C\text{-}F}$ = 248.5 Hz), 141.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 135.7, 134.7, 131.4 (d, $J_{C\text{-}F}$ = 69.7 Hz), 129.4 (d, $J_{C\text{-}F}$ = 43.4 Hz), 126.7, 125.7, 118.1 (d, $J_{C\text{-}F}$ = 18.2 Hz), 116.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 21.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -108.9 (m, 1F). **IR (ATR/cm^{-1})** 3016.5, 3055.6, 3002.0, 2919.7, 2851.7, 1608.1, 1581.3, 1474.3, 1437.2, 1387.8, 1266.3, 1177.8, 1155.1, 1083.0, 1023.3,

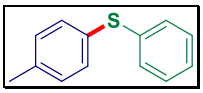
1011.0, 938.9, 813.3. **HRMS (ESI)** m/z calcd. for $C_{13}H_{11}FS$ (M^+) 218.0565, found m/z 218.0563.

(3,5-bis(trifluoromethyl)phenyl)(phenyl)sulfane (83)[40]



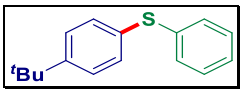
Yield 26.4 mg (0.082mmol, 82%). Colourless oil. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 7.61 (s, 2H), 7.55 – 7.51 (m, 2H), 7.48 – 7.44 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.7, 133.7, 132.3 (q, J_{C-F} = 34.0 Hz), 131.2, 130.0, 129.4, 127.8 (d, J_{C-F} = 2.5 Hz), 123.0 (q, J_{C-F} = 273.4 Hz), 119.6 (sep, J_{C-F} = 3.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.1 (s, 6F).

Phenyl(p-tolyl)sulfane (84)[36]



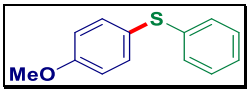
Yield 16.8 mg (0.084 mmol, 84%). Colorless oil. Column chromatography on silica gel (Eluent: 0-2% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$** δ 7.34 – 7.26 (m, 6H), 7.23 – 7.18 (m, 1H), 7.15 (d, J = 7.9 Hz, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.7, 137.3, 132.4, 131.4, 130.2, 130.0, 129.2, 126.5, 21.3.

(4-(tert-butyl)phenyl)(phenyl)sulfane (85)[41]



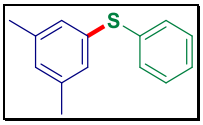
Yield 18.4 mg (0.076 mmol, 76%). Colorless liquid. Column chromatography on silica gel (Eluent: 0-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.20 (m, 9H), 1.32 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 150.7, 136.7, 131.7, 131.6, 130.4, 129.2, 126.7, 126.4, 34.7, 31.4.

(4-methoxyphenyl)(phenyl)sulfane (86)[42]



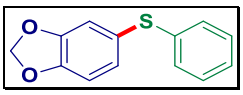
Yield 17.7 mg (0.082 mmol, 82%). Yellowish oil. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, J = 8.8 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.14 (m, 3H), 6.91 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.0, 138.7, 135.5, 129.1, 128.4, 126.0, 124.5, 115.1, 55.5.

(3,5-dimethylphenyl)(phenyl)sulfane (87)[43]



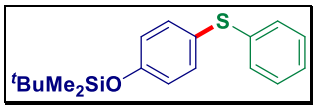
Yield 18.6 mg (0.087mmol, 87%). Colorless oil. Column chromatography on silica gel (Eluent: 0-2% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 7.01 (s, 2H), 6.90 (s, 1H), 2.28 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.9, 136.4, 135.1, 134.8, 130.5, 129.2, 129.1, 126.7, 21.2.

5-(phenylthio)benzo[d][1,3]dioxole (88)[44]



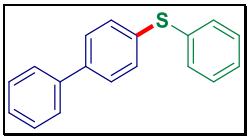
Yield 14.0 mg (0.061 mmol, 61%). Yellowish oil. Column chromatography on silica gel (Eluent: 5-8% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.13 (m, 5H), 6.98 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.96 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 148.5, 148.1, 138.0, 129.2, 129.0, 127.5, 126.4, 126.3, 113.7, 109.1, 101.6.

***Tert*-butyldimethyl(4-(phenylthio)phenoxy)silane (89)**[45]



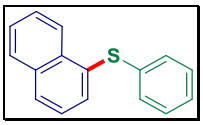
Yield 22.2 mg (0.070 mmol, 70%). Colorless oil. Column chromatography on silica gel (Eluent: 0-2% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 1.00 (s, 9H), 0.22 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 156.1, 138.5, 135.2, 129.1, 128.5, 126.0, 125.3, 121.2, 25.8, 18.3, -4.3.

[1,1'-biphenyl]-4-yl(phenyl)sulfane (90)[35]



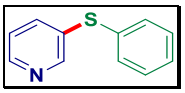
Yield 19.2 mg (0.073 mmol, 73%). White solid. Column chromatography on silica gel (Eluent: 0-2% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 – 7.51 (m, 4H), 7.46 – 7.24 (m, 10H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.4, 140.1, 135.8, 135.0, 131.4, 131.3, 129.4, 128.9, 127.9, 127.6, 127.2, 127.1.

Naphthalen-1-yl(phenyl)sulfane (91)[35]



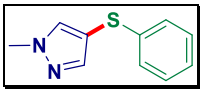
Yield 12.3 mg (0.052 mmol, 52%). Yellowish oil. Column chromatography on silica gel (Eluent: 0-2% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 – 8.36 (m, 1H), 7.91 – 7.85 (m, 2H), 7.68 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.44 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.26 – 7.14 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.0, 134.5, 133.7, 132.7, 131.3, 129.3, 129.2, 129.1, 128.7, 127.1, 126.6, 126.3, 126.0, 125.8.

3-(phenylthio)pyridine (92)[46]



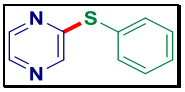
Yield 16.3 mg (0.087 mmol, 87%). Brownish oil. Column chromatography on silica gel (Eluent: 5-15% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 2.4 Hz, 1H), 8.45 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.39 – 7.27 (m, 5H), 7.21 – 7.17 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.1, 147.9, 138.0, 134.0, 133.7, 131.8, 129.6, 127.9, 124.0.

1-methyl-4-(phenylthio)-1H-pyrazole (93)[45]



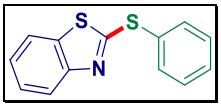
Yield 10.3 mg (0.054 mmol, 54%). Colorless oil. Column chromatography on silica gel (Eluent: 5-15% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (s, 1H), 7.52 (s, 1H), 7.24 – 7.19 (m, 2H), 7.13 – 7.08 (m, 3H), 3.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 144.8, 139.0, 135.3, 129.0, 126.4, 125.4, 107.6, 39.5.

2-(phenylthio)pyrazine(94)[47]



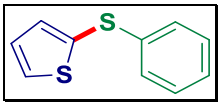
Yield 9 mg (0.048 mmol, 48%). Yellowish oil. Column chromatography on silica gel (Eluent: 5-15% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.32 (t, *J* = 2.1 Hz, 1H), 8.22 (d, *J* = 2.5 Hz, 1H), 8.19 (s, 1H), 7.62 – 7.57 (m, 2H), 7.45 – 7.41 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.7, 143.9, 142.8, 140.2, 135.1, 129.9, 129.7, 129.0.

2-(phenylthio)benzo[d]thiazole (95)[37]



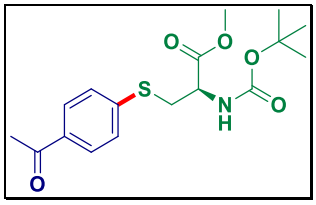
Yield 12.4 mg (0.051 mmol, 51%). White solid. Column chromatography on silica gel (Eluent: 15-20% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.66 (d, *J* = 6.5 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.44 – 7.39 (m, 1H), 7.30 – 7.25 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.9, 153.9, 135.8, 135.6, 135.5, 130.6, 130.0, 126.3, 124.5, 122.0, 120.9.

2-(phenylthio)thiophene (96)[48]



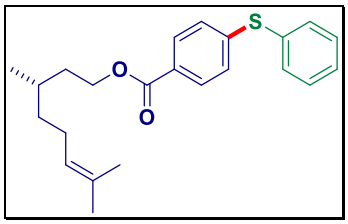
Yield 13.8 mg (0.072 mmol, 72%). Colorless oil. Column chromatography on silica gel (Eluent: 2-5% ethyl acetate in hexane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (dd, *J* = 5.8, 1.5 Hz, 1H), 7.30 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 7.08 (dd, *J* = 5.5, 3.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.8, 136.2, 131.4, 131.3, 129.1, 128.0, 127.3, 126.2.

Methyl *S*-(4-acetylphenyl)-*N*-(*tert*-butoxycarbonyl)-*L*-cysteinate (97)



Yield 28.3 mg (0.080 mmol, 80%). Colorless liquid. Column chromatography on silica gel (Eluent: 2-8% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 5.35 (d, *J* = 8.0 Hz, 1H), 4.61 (d, *J* = 8.2 Hz, 1H), 3.62 (s, 3H), 3.51 – 3.38 (m, 2H), 2.55 (s, 3H), 1.39 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.2, 170.9, 155.1, 142.5, 134.9, 129.0, 128.3, 80.5, 53.4, 52.7, 35.6, 28.4, 26.6. **IR (ATR/cm^{-1})** 3354.1, 2977.3, 2927.9, 2849.7, 1713.1, 1682.2, 1589.6, 1505.1, 1359.0, 1262.2, 1157.2. **HRMS (ESI)** m/z calcd. for $C_{17}H_{23}O_5NS$ ($[M+Na]^+$) 376.1189, found m/z 376.1170.

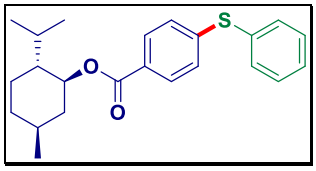
(*S*)-3,7-dimethyloct-6-en-1-yl 4-(phenylthio)benzoate (98)



Yield 28.7 mg (0.078 mmol, 78%). Colorless liquid. Column chromatography on silica gel (Eluent: 0-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.41 – 7.35 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.10 – 5.07 (m, 1H),

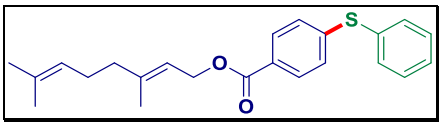
4.37 – 4.29 (m, 2H), 2.06 – 1.93 (m, 2H), 1.80 – 1.77 (m, 1H), 1.66 (d, *J* = 1.5 Hz, 3H), 1.60 – 1.52 (m, 5H), 1.43 – 1.35 (m, 1H), 1.26 – 1.19 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.4, 144.3, 133.7, 132.7, 131.5, 130.2, 129.8, 128.7, 128.1, 127.8, 124.7, 63.6, 37.1, 35.6, 29.7, 25.8, 25.5, 19.6, 17.8. **IR (ATR/cm^{-1})** 3057.6, 2967.0, 2917.6, 2853.8, 1715.2, 1593.7, 1474.3, 1439.3, 1400.1, 1377.5, 1357.4, 1266.3, 1177.8, 1103.6, 1013.0, 928.6, 846.3. **HRMS (ESI)** m/z calcd. for $C_{23}H_{28}O_2S$ ($[M+H]^+$) 369.1883, found m/z 369.1877.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-(phenylthio)benzoate (99)[49]



Yield 25.4 mg (0.069 mmol, 69%). White solid. Column chromatography on silica gel (Eluent: 0-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.93 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 – 2.11 (m, 1H), 1.96 – 1.90 (m, 1H), 1.78 – 1.71 (m, 2H), 1.65 – 1.51 (m, 3H), 1.17 – 1.06 (m, 2H), 0.94 (dd, *J* = 9.5, 6.7 Hz, 7H), 0.81 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.8, 144.1, 133.7, 132.8, 130.2, 129.7, 128.7, 128.4, 127.9, 75.0, 47.4, 41.1, 34.4, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7.

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-(phenylthio)benzoate (100)



Yield 27.9 mg (0.076 mmol, 76%). Colorless liquid. Column chromatography on silica gel (Eluent: 0-5% ethyl acetate in hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.48 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.47 – 5.44 (m, 1H), 5.11 – 5.08 (m, 1H), 4.81 (dd, *J* = 14.7, 7.2 Hz, 2H), 2.19 – 2.05 (m, 4H), 1.76 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 2.2 Hz, 3H), 1.61 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.4, 144.2, 142.6, 133.7, 132.8, 132.0, 130.3, 129.7, 128.7, 128.1, 127.9, 123.9, 118.5, 62.0, 39.7, 26.4, 25.8, 17.8, 16.7 **IR (ATR/cm^{-1})** 2960.9, 2923.8, 2853.8, 1715.2, 1593.7, 1266.3, 1105.7. **HRMS (ESI)** m/z calcd. for $C_{23}H_{26}O_2S$ ($[M+Na]^+$) 389.1546, found m/z 389.1534.

Section S-VIII: Crystal Data for Few Newly Formed Products

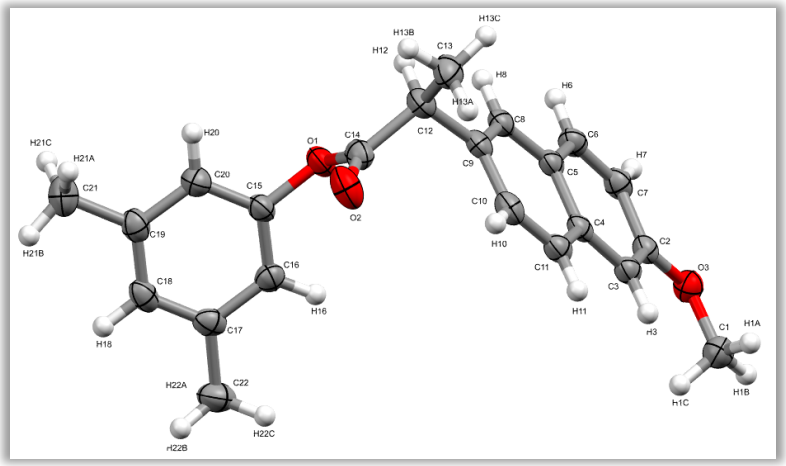


Figure S19: Molecular structure of **47** (ORTEP view, 50% probability ellipsoids).

Table S18: Crystal data and structure refinement for compound 47 (CCDC No. *2216734)*

Identification code	KKUKA076_auto_1
Empirical formula	$C_{44}H_{44}O_6$
Formula weight	668.79
Temperature/K	100.1(5)
Crystal system	triclinic
Space group	P-1
a/Å	5.70840(10)
b/Å	12.2516(2)
c/Å	25.4722(4)
α/°	88.8970(10)
β/°	89.8080(10)
γ/°	83.7420(10)
Volume/Å^3	1770.51(5)
Z	2
ρ_{calc}g/cm^3	1.255
μ/mm^{-1}	0.656
F(000)	712.0
Crystal size/mm^3	0.1 × 0.03 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	3.47 to 136.398
Index ranges	$-5 \le h \le 6$, $-14 \le k \le 14$, $-30 \le l \le 30$
Reflections collected	30578
Independent reflections	6348 [R_{int} = 0.0647, R_{sigma} = 0.0332]
Data/restraints/parameters	6348/0/459
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0481, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0523, wR_2 = 0.1264
Largest diff. peak/hole / e Å^{-3}	0.42/-0.24

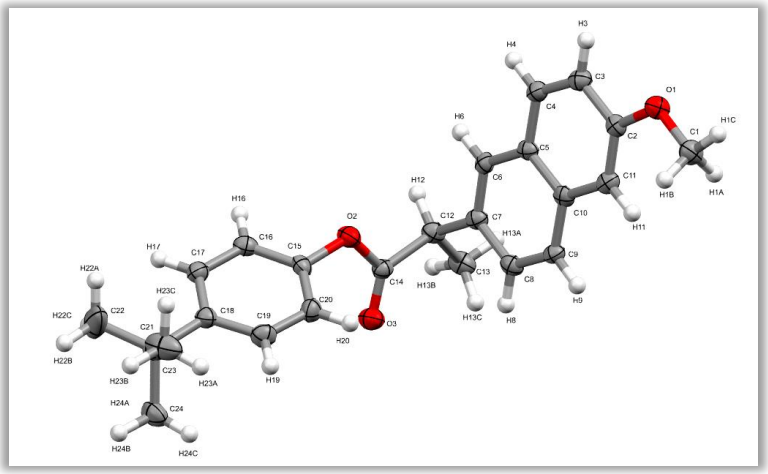


Figure S20: Molecular structure of **48** (ORTEP view, 50% probability ellipsoids).

Table S19: Crystal data and structure refinement for compound 48 (CCDC No. *2216737*)

Identification code	KKU-066_auto_1
Empirical formula	$C_{24}H_{26}O_3$
Formula weight	362.45
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	11.1315(4)
b/Å	16.4750(6)
c/Å	10.7131(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1964.69(12)
Z	4
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.628
F(000)	776.0
Crystal size/mm^3	0.05 × 0.05 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.364 to 137.308
Index ranges	$-13 \leq h \leq 13$, $-18 \leq k \leq 19$, $-12 \leq l \leq 12$
Reflections collected	10964
Independent reflections	3144 [R_{int} = 0.0695, R_{sigma} = 0.0444]
Data/restraints/parameters	3144/1/249
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0482, wR_2 = 0.1261
Final R indexes [all data]	R_1 = 0.0556, wR_2 = 0.1418
Largest diff. peak/hole / e Å^{-3}	0.20/-0.27

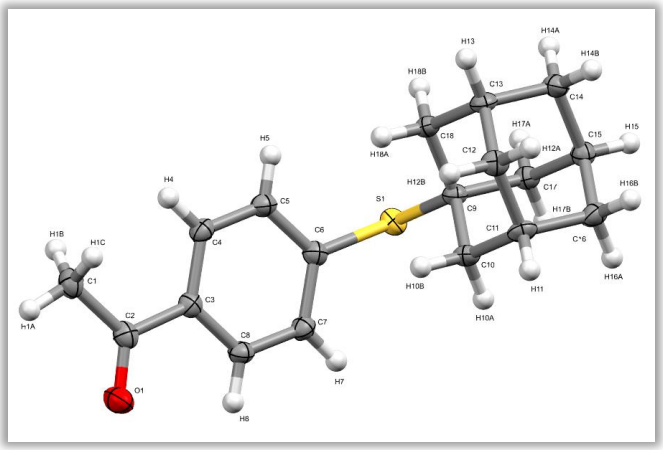


Figure S21: Molecular structure of **63** (ORTEP view, 50% probability ellipsoids).

Table S20: Crystal data and structure refinement for 63 (CCDC No. *2216735*)

Identification code	AYJ-ADASH_1
Empirical formula	$C_{18}H_{22}OS$
Formula weight	286.41
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.46020(10)
b/Å	10.5870(2)
c/Å	11.9686(3)
α/°	69.336(2)
β/°	76.155(2)
γ/°	85.5380(10)
Volume/Å^3	743.65(3)
Z	2
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	1.857
F(000)	308.0
Crystal size/mm^3	0.12 × 0.04 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.106 to 136.666
Index ranges	-6 ≤ h ≤ 7, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	12139
Independent reflections	2656 [R_{int} = 0.0529, R_{sigma} = 0.0327]
Data/restraints/parameters	2656/0/182
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0894
Final R indexes [all data]	R_1 = 0.0354, wR_2 = 0.0914
Largest diff. peak/hole / e Å^{-3}	0.21/-0.24

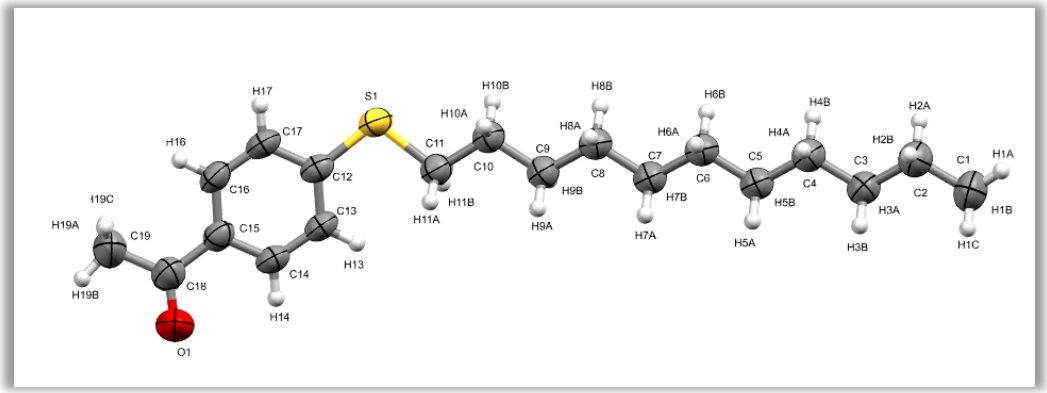
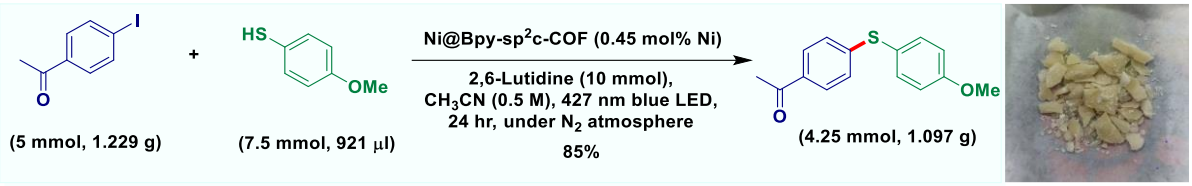


Figure S22: Molecular structure of **70** (ORTEP view, 50% probability ellipsoids).

Table S21: Crystal data and structure refinement for 70 (CCDC No. *2216257*)

Identification code	SEK117_1
Empirical formula	$C_{19}H_{30}OS$
Formula weight	306.49
Temperature/K	298.5(7)
Crystal system	monoclinic
Space group	Cc
a/Å	44.2057(9)
b/Å	7.38100(10)
c/Å	5.60640(10)
α/°	90
β/°	92.306(2)
γ/°	90
Volume/Å^3	1827.79(6)
Z	4
ρ_{calc}g/cm^3	1.114
μ/mm^{-1}	1.532
F(000)	672.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4 to 136.106
Index ranges	$-52 \leq h \leq 49$, $-8 \leq k \leq 8$, $-5 \leq l \leq 6$
Reflections collected	10076
Independent reflections	2467 [R_{int} = 0.0267, R_{sigma} = 0.0133]
Data/restraints/parameters	2467/2/192
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0347, wR_2 = 0.0998
Final R indexes [all data]	R_1 = 0.0350, wR_2 = 0.1001
Largest diff. peak/hole / e Å^{-3}	0.13/-0.13
Flack parameter	0.078(15)

Section S-IX: Gram scale synthesis



An oven-dried 50 mL Schlenk tube with a magnetic stir bar was charged with 1-(4-iodophenyl)ethan-1-one (1.23 g, 5 mmol), 4-methoxythiophenol (921 µl, 7.5 mmol), catalyst Ni@Bpy-sp^{2}c-COF (50 mg, 0.0225 mmol Ni), 2,6-Lutidine (1158 µl, 10 mmol), and CH_3CN (5 mL). The tube was then purged with N_2 for 1 min and then sealed with a glass stopper and Teflon. Then it was subjected to an ultrasound sonication bath for 1 min. The tube was finally placed between four 34 W Blue LED (427 nm), separated by ~6 cm from the tube, and irradiated for 24 h. A cooling fan is used from the upper sides of the handmade reaction chamber to control the temperature. Afterward, the resulting solution was filtered and concentrated. The crude product was further purified by column chromatography on silica gel (Eluent: 2-8% ethyl acetate in hexane). **Yield** 1.10 g (85%).

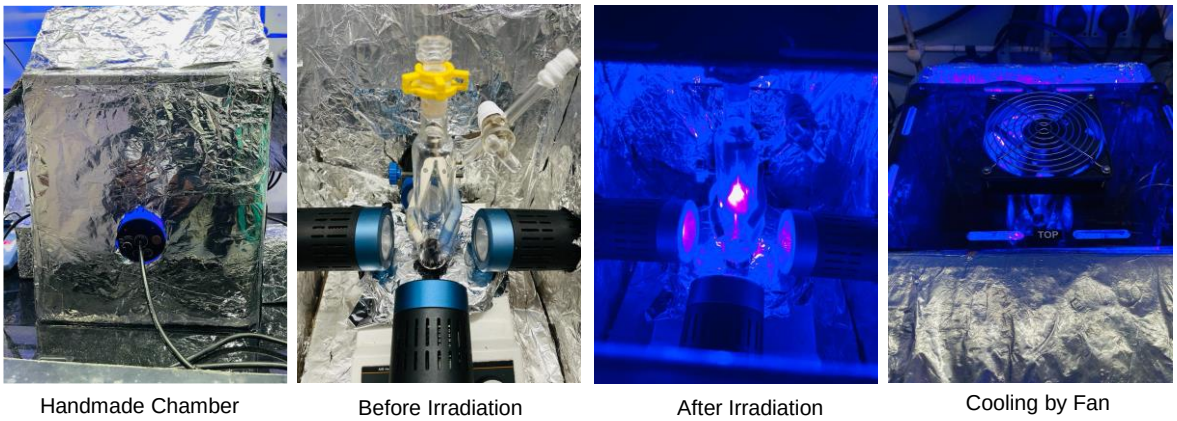


Figure S23: Set up for gram scale synthesis.

Section S-X: Recyclability Experiments

An oven-dried 15 mL sealed tube with a magnetic stir bar was charged with **4** (0.10 mmol), **5** (0.15 mmol), catalyst Ni@Bpy-sp^{2}c-COF (4 mg), 2,6-Lutidine (0.20 mmol), and CH_3CN (0.1 mL). The tube was then purged with N_2 for 1 min and then sealed with a plastic screw cap containing a Teflon-lined silicone septum. Then it was subjected to an ultrasound sonication bath for 5 min. The tube was finally placed 6 cm away from one 34 W Blue LED (427 nm) and irradiated at room temperature for 24 h. Afterward, the solution was settled at room temperature for a few hours. Then the upper filtrate part was taken to measure the yield of **6** by GC-MS analysis. After analyzing the yield, the lower residue portion was washed with EtOAc, and the filtrate part was removed carefully, keeping the residue in the tube. The washing step is repeated three times, and then the residue part is dried well and used for the next cycle. The reaction was recycled for up to 6 th cycles. The yields of **6** are given as follows.

No. of cycle	1	2	3	4	5	6
% Yield of 6	99	96	97	95	91	85

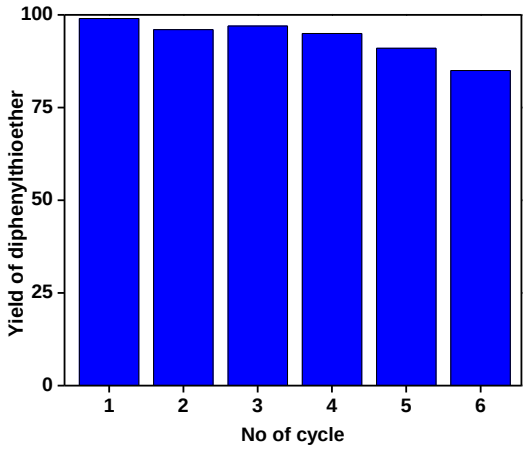


Figure S24: Recyclability of Ni@Bpy-sp^{2}c-COF catalyst in thioetherification reaction. From ICP-OES analysis, it was measured that after 6th cycle, the leaching of Ni was 0.21%.

Section S-XI: After Catalysis Material Characterizations

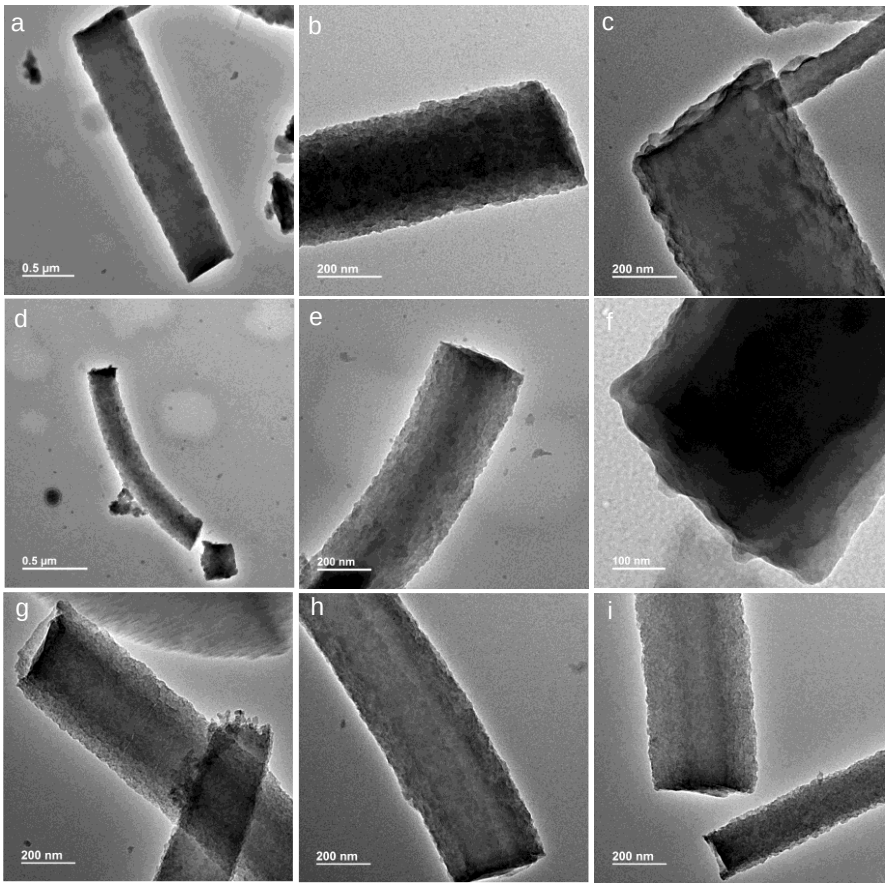


Figure S25: TEM images of Ni@Bpy-sp^{2}c-COF; (a, b, c) before catalysis, (d, e, f) after thioetherification catalysis, and (g, h, i) after esterification catalysis.

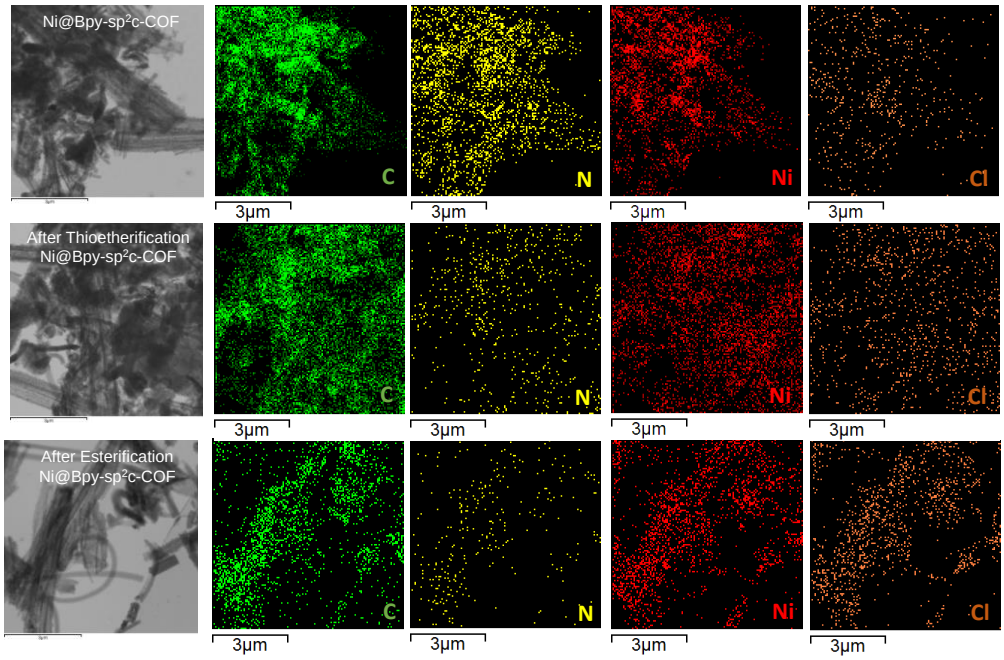


Figure S26: TEM-EDX analysis of Ni@Bpy-sp^{2}c-COF; before catalysis (upper), after thioetherification catalysis (middle), and after esterification catalysis (bottom).

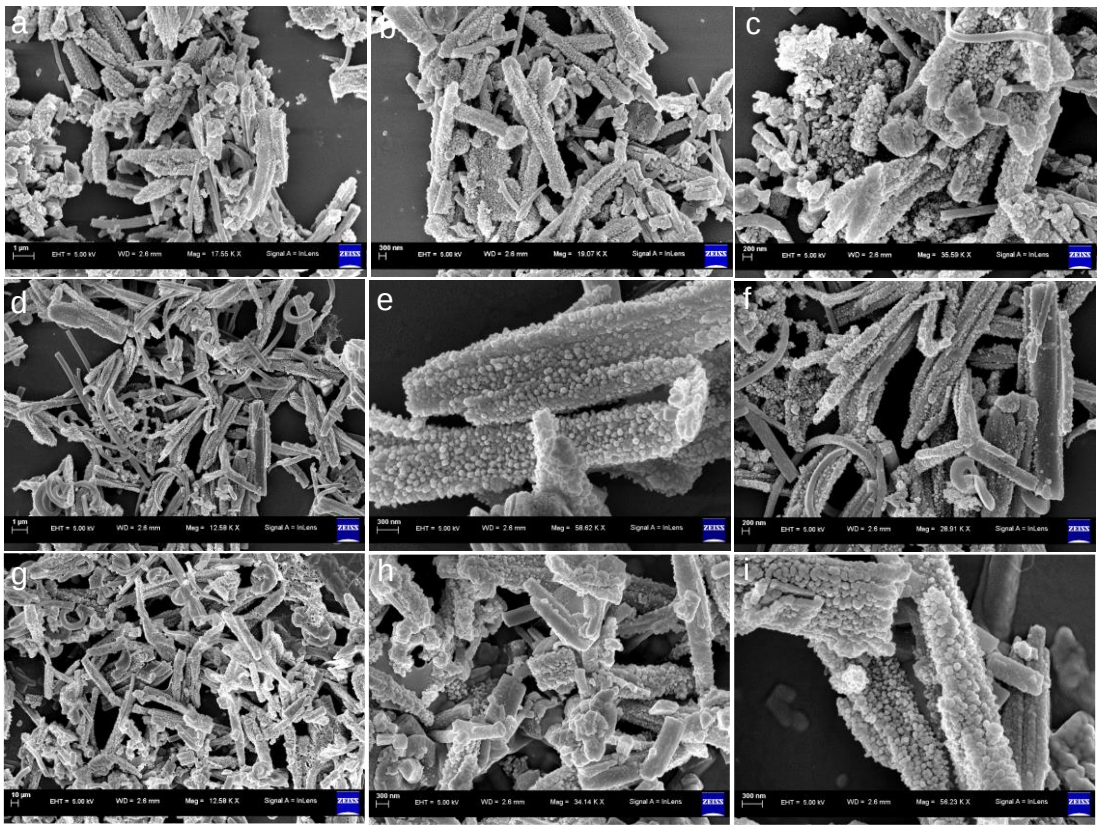


Figure S27: SEM images of Ni@Bpy-sp^{2}c-COF; (a, b, c) before catalysis, (d, e, f) after thioetherification catalysis, and (g, h, i) after esterification catalysis.

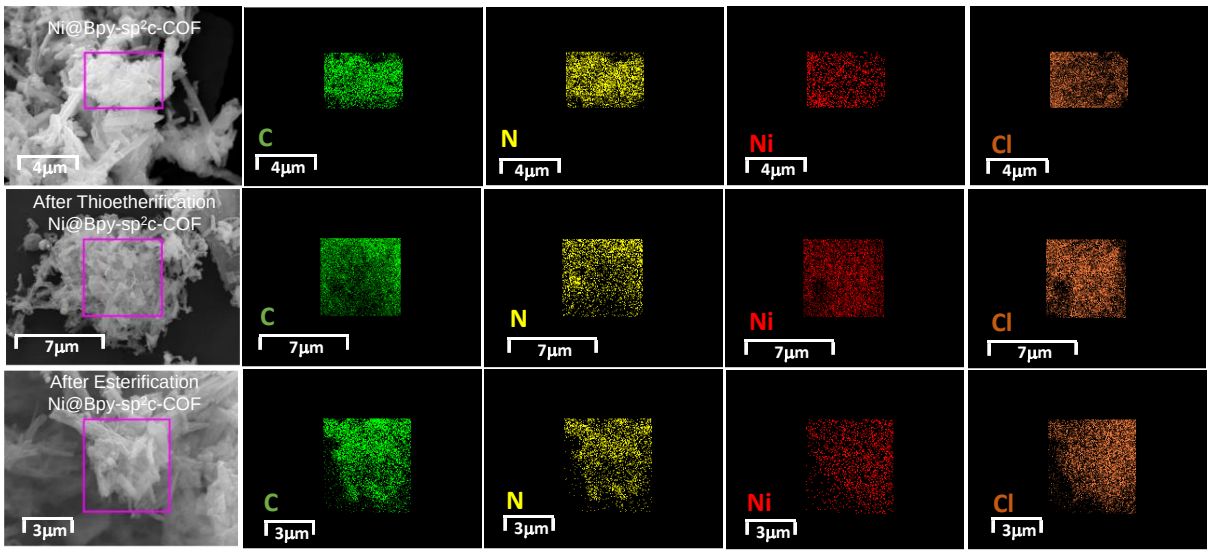


Figure S28: SEM-EDX analysis of Ni@Bpy-sp^{2}c-COF; before catalysis (upper), after thioetherification catalysis (middle), and after esterification catalysis.

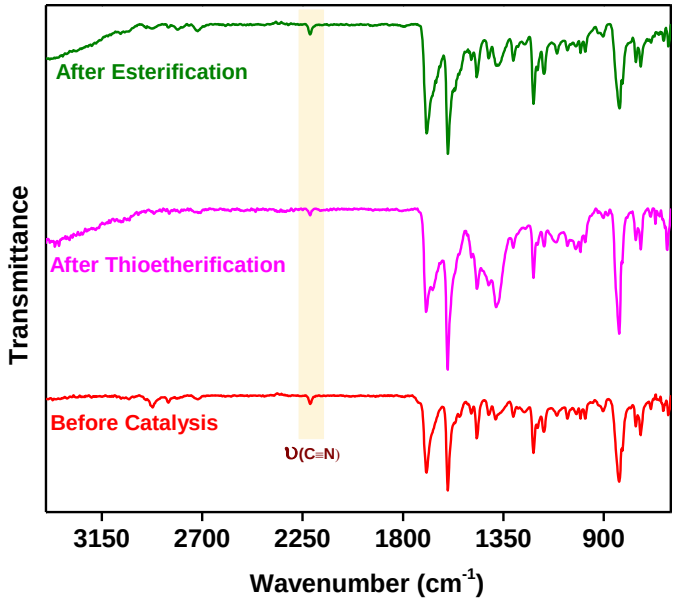


Figure S29: Comparative IR analysis of Ni@Bpy-sp^{2}c-COF; before catalysis (red), after thioetherification (magenta), and after esterification (olive).

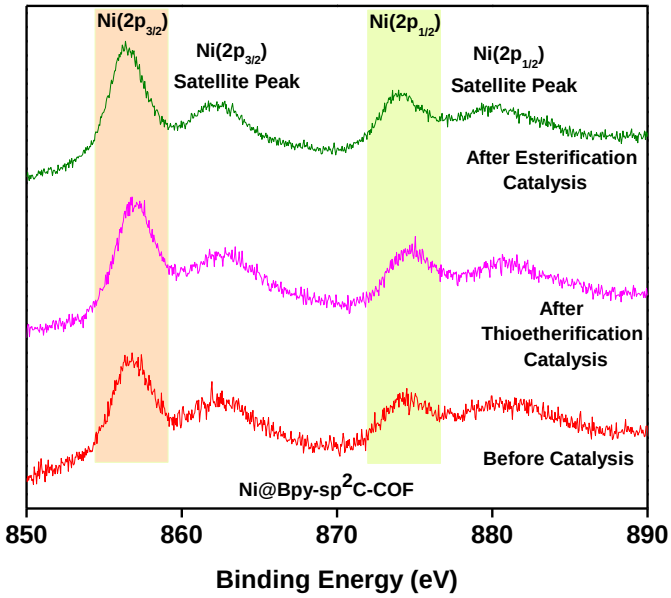


Figure S30: Comparative XPS analysis of Ni@Bpy-sp^{2}c-COF; before catalysis (red), after thioetherification (magenta), and after esterification (olive).

Section S-XII: Plausible Mechanistic Pathway

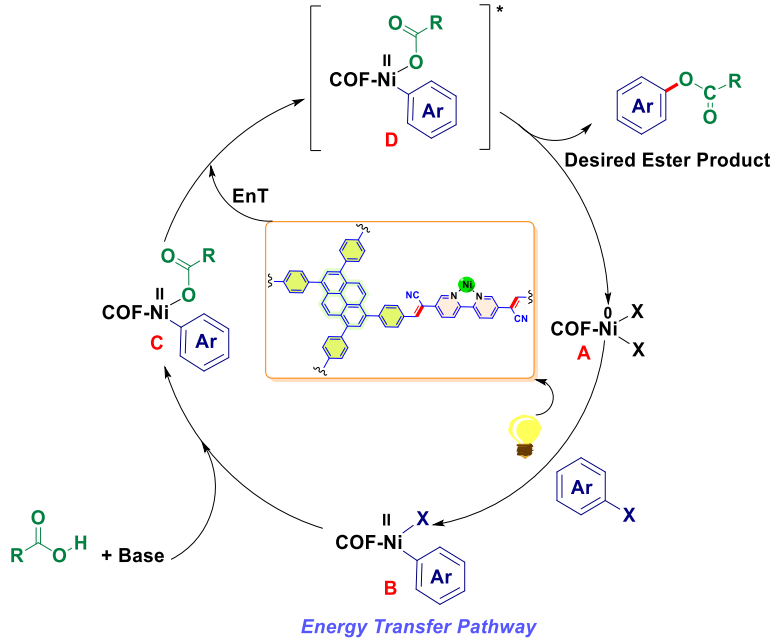


Figure S31: Plausible mechanism for esterification reaction.[16b]

Two successive reductive quenching would convert Ni@Bpy-sp^{2}c-COF to intermediate **A**. The oxidative addition with organic halide, followed by ligand exchange with the carboxylate nucleophile, would yield intermediate **C**. At the same time, visible light irradiation of the COF backbone produces a long-lived excited state. At this juncture, energy transfer can occur to form the excited state intermediate **D** while simultaneously regenerating the ground state of COF. The resulting excited intermediate **D** then undergoes reductive elimination to generate the desired ester and completes the catalytic cycle.

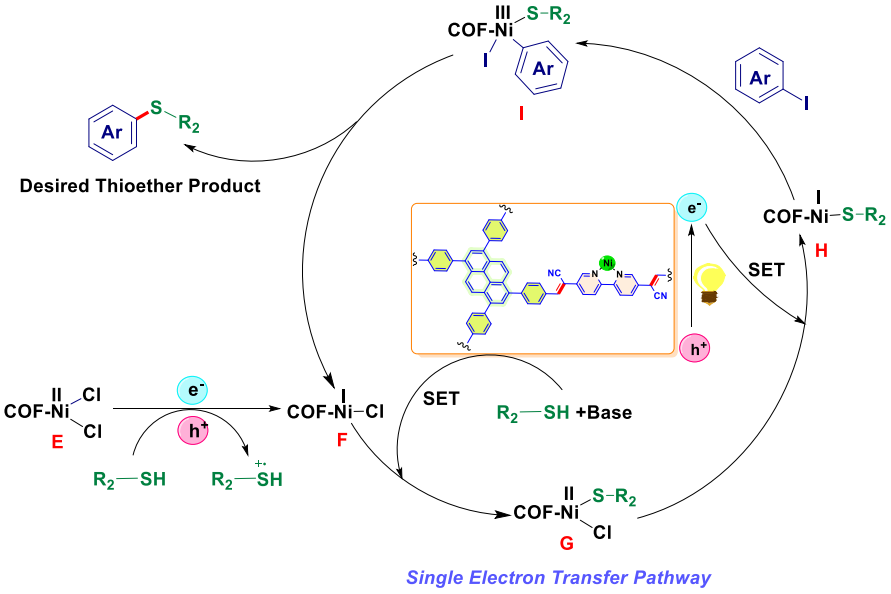


Figure S32: Plausible mechanism for thioetherifications reaction.[50]

In this Bpy-sp^{2}c-COF barring dual-catalytic process, the photosensitive Bpy-sp^{2}c-COF cycle and Ni cycles are connected via radical and electron transfers. Upon Blue-light irradiation, photosensitive Bpy-sp^{2}c-COF induced a higher excited state Bpy-sp^{2}c-COF*, followed by reductive quenching of photoexcited Bpy-sp^{2}c-COF* by single electron transfer (SET), which generates the radical thiol cation R-SH$^{\bullet+}$. The thiol-radical cation is deprotonated in the presence of a base, and the thiol radical R-S$^{\bullet}$ is generated. A radical trapping generated a Ni^{II}-sulfide intermediate **G**. The single electron reduction yields intermediate **H** that undergoes an oxidative addition with aryl iodide to produce a Ni^{III}-intermediate **I**. Finally, a reductive elimination process delivers the desired C-S cross-coupled product, regenerating the catalyst.

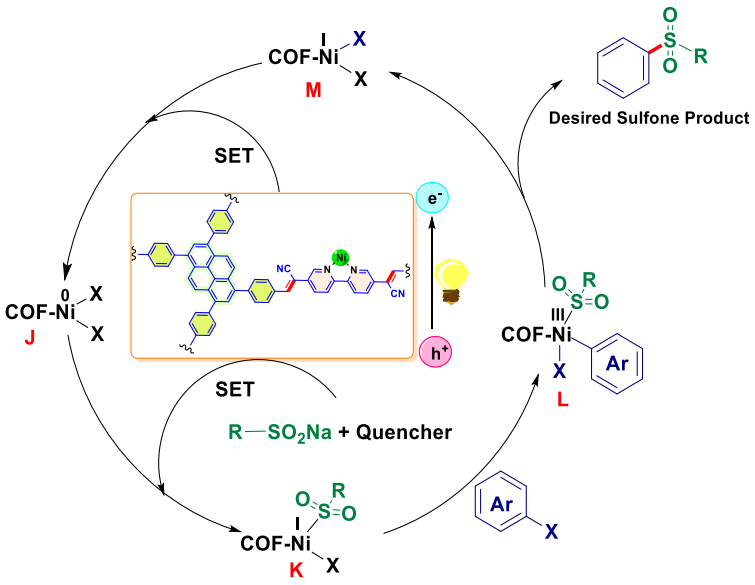


Figure S33: Plausible mechanism for sulfonation.[10]

The catalytic cycle of sulfonation reaction under light irradiation is initiated by an electron transfer from the COF backbone to the nickel center, resulting in [Ni^0(COF)]X$_2$ (**J**) as active catalyst species. Again, the single electron transfer happened in the presence of sulfonate and quencher, leading to the formation of intermediate **K**. It further participated in oxidative addition with aryl halide to form Ni^{III}-intermediate **L** followed by reductive elimination to intermediate **M**. As a result, the aryl sulfone product is formed as our desired one. Simultaneously the Ni^I catalyst species is regenerated, which can be used further in the next catalytic cycle.

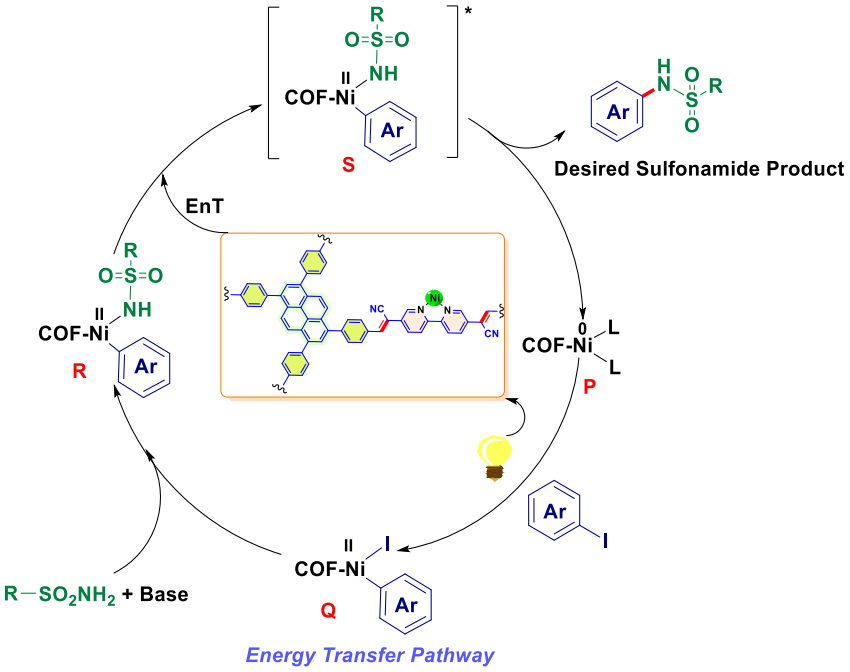


Figure S34: Plausible mechanism for sulfonamidation.[51]

Like the esterification mechanism, the sulfonamidation catalytic cycle goes *via* an energy transfer mechanism. At first, the Ni^0-intermediate **P** reacts with the Aryl halide substrate *via* oxidative addition to form intermediate **Q.** Transmetalation with the Aryl sulfonamide in the presence of a base, followed by reductive elimination stimulated *via* energy transfer, gives the desired C-N coupled product. Simultaneously, the transmetalation process yields the reactive intermediate **P** to participate in the next catalytic cycle.

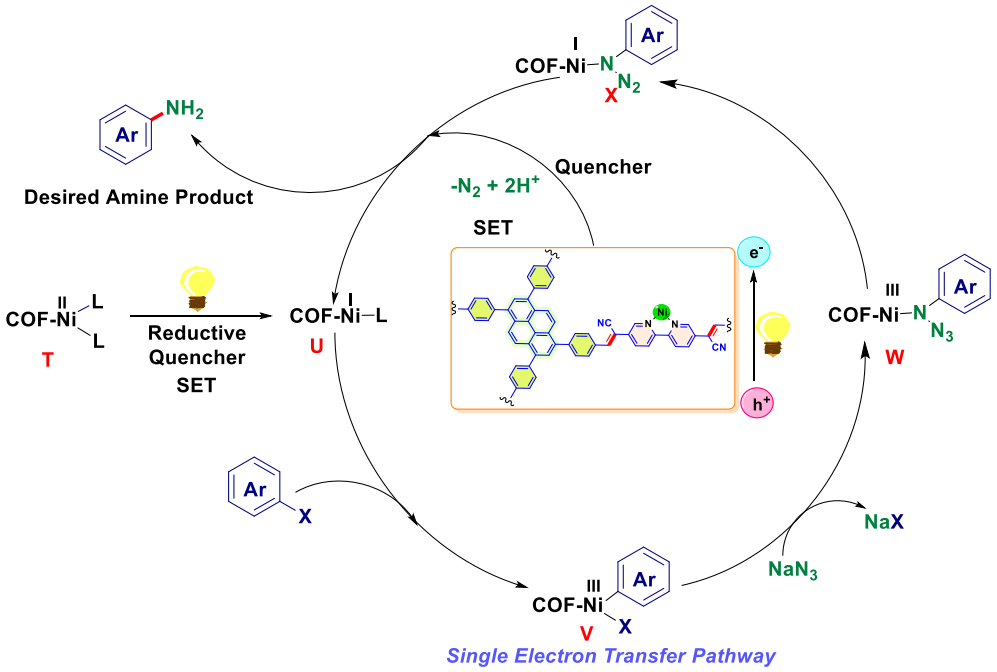


Figure S35: Plausible mechanism for amination.[12]

The proposed mechanism of the interlocked Ni/photoredox catalyzed amination reaction suggests the single electron transfer pathway initiated *via* photoexcited electron-hole pair generation in the COF backbone upon light irradiation. The electron donation can quench the generated hole from the quencher. In contrast, the electron is utilized to reduce the Ni(I) species (**U**) that undergoes oxidative addition (transformed to the intermediate **V**), followed by a transmetalation mechanism to form the species **W.** Simultaneously, via nitrogen evolution and proton donation from the oxidized quencher, the desired Amine is formed, regenerating the Ni(I) catalyst species **U**.

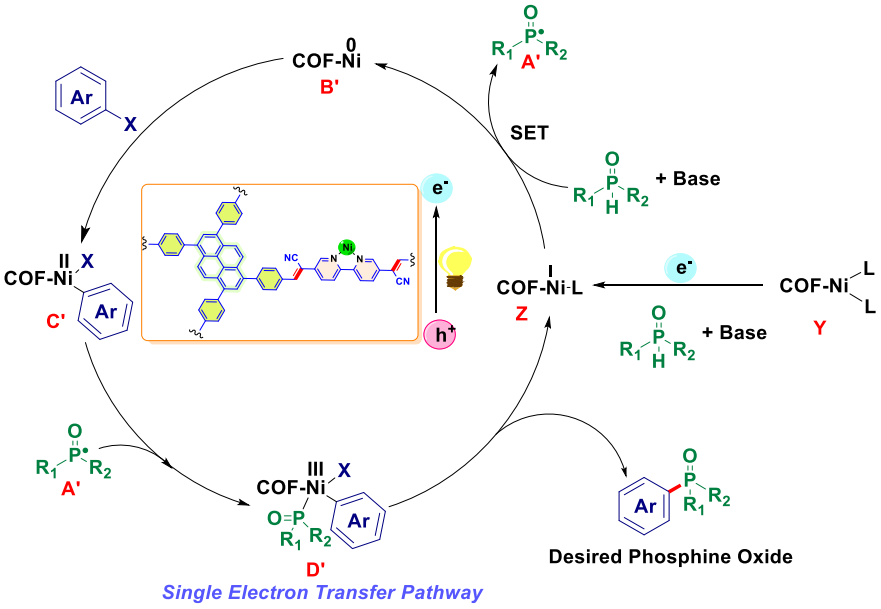


Figure S36: Plausible mechanism for phosphonylation.[14]

The reduction of Ni(II) species (**Y**) *via* an electron transfer from the COF backbone generates the active catalyst Ni(I) species (**Z**)**,** which starts the phosphonylation catalytic cycle. The cycle continues with a single electron transfer process from the diphenylphosphine oxide substrate to the Ni(I) complex (**Z**), forming P-centred radical species (**A'**) concurrently. The cycle then advances via well-known oxidative addition to **B'**, giving **C'**, which, *via* SET mechanism with previously formed P-centred radical species (**A'**), offers **D'**. The reductive elimination step from species **D'** generates the desired product phosphine oxide and returns the species **Z'**, which can take part in the next catalytic cycle.

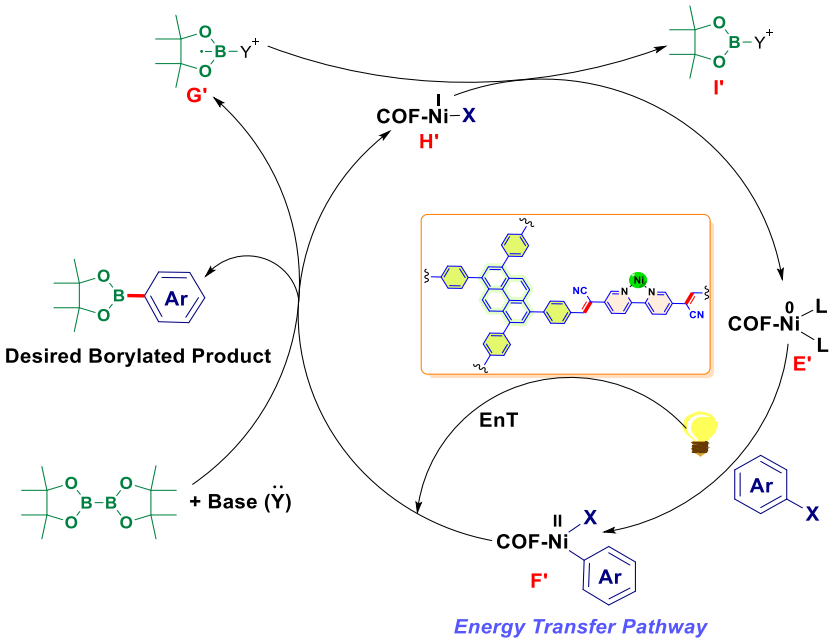


Figure S37: Plausible mechanism for borylation.[52]

The borylation catalytic cycle drives *via* a possible energy transfer mechanism. At first, Ni(0) species **E'** reacts with the aryl halide substrate *via* oxidative addition to form species **F'.** Transmetalation with the B_2Pin_2 in the presence of a base (Y) stimulated via energy transfer followed by reductive elimination gives the desired Borylated product. Simultaneously, in the transmetalation process, species **G'** is formed *via* electron transfer to **H'**. As a result, the intermediate **I'** is formed and returns the original catalyst species **E'** that can take part in the next catalytic cycle.

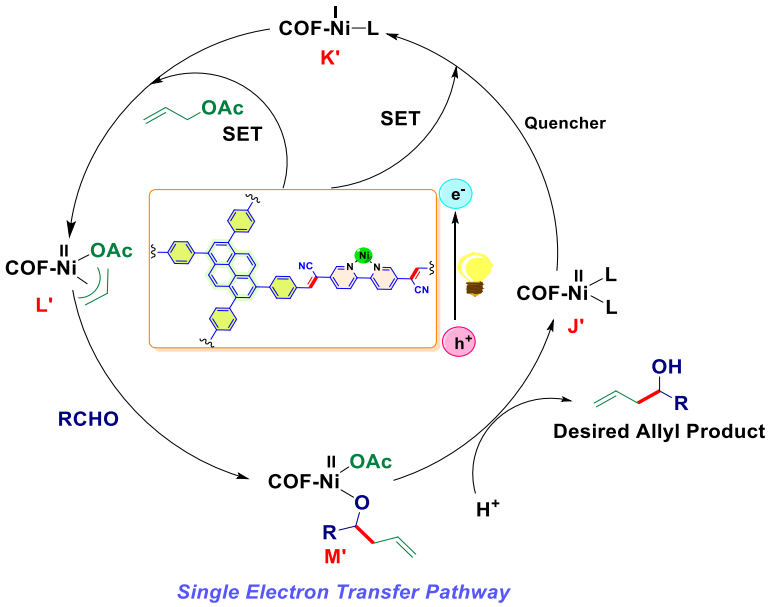


Figure S38: Plausible mechanism for allylation.[15]

The catalytic cycle of Ni@Bpy-sp^{2}c-COF catalyzed allylation reaction under light irradiation is initiated by the single electron transfer (SET) from the COF backbone to the nickel center (**J'**), resulting in **K'** as active catalyst species. This photoexcited COF backbone can further reduce species **K'** to form [Ni^{II}(η3-allyl)(OAc)] complex (**L'**) by reacting with allyl acetate through oxidative addition. The proton developed via deprotonation of oxidized quencher protonates species **M'** formed by adding the aldehyde species**,** generating homoallylic alcohol as our desired product. Simultaneously the Ni^{II} catalyst species (**J'**) is regenerated, and the catalytic cycle continues.

Section S-XIII: Comparison of the State-of-the-Art of Photocatalytic Cross-Coupling Reactions and This Work

A comparison table demonstrating the state-of-the-art for Ni@Bpy-sp^{2}c-COF-catalyzed eight different cross-coupling reactions is listed below. The thermal reactions are not compared due to the heterogeneity of the discussions.

Esterification (C–O bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Science* **2017**, *355*, 380-385	1 mol% $Ir(ppy)_3$, 5 mol% $NiBr_2$•diglyme, 5 mol% dtbbpy	62-95	➢ Ir-metal based photocatalyst ➢ External ligand is required ➢ No reusability of Ir/Ni-catalyst ➢ High Ni-loading ➢ Possibility of Ni-black formation
2	*Org. Chem. Front.*, **2019**, *6*, 2353-2359	20 mol% thioxanthen-9-one (as photosensitizer), 5 mol% $NiBr_2$, 6 mol% dtbbpy	32-93	➢ Very high dosage of a PS ➢ High Ni-loading ➢ Possibility of Ni-black formation ➢ No reusability of both catalysts
3	*Chem. Commun.* **2020**, *56*, 8273 – 8276	2 mol% boron-based PC, 5 mol% $NiBr_2$•diglyme, 5 mol% dtbbpy	44-93	➢ Organophotosensitizer used ➢ No reusability of both catalysts ➢ Possibility of Ni-black formation
4	*J. Am. Chem. Soc.* **2022**, *144*, 19592−19602	5 mol% $Pd(dba)_2$ or $Pd(TFA)_2$, 5-10 mol% Acridinium-phosphine based ligand	38-98	➢ Elite acridinium-phosphine-based ligand, which acts as PC ➢ High dosage of Pd-catalyst ➢ No reusability of the catalyst
5	*Chem* **2022**, *8*, 2419-2431	10 mol% $NiCl_2$•DME, 10 mol% 4-phenyl-2-(pyridin-2-yl)quinoline (PPQN) based ligand	55	➢ Photoactive ligand ➢ High dosage of Ni ➢ No reusability of the catalyst
6	*Angew. Chem. Int. Ed.* **2022**, *61*, *e202211433*	5 mol% $NiCl_2$•glyme, 5 mol% Czbpy (carbazole-bipyridine based)	49-92	➢ High dosage of Ni catalyst ➢ Ni was introduced as like homogeneous ➢ Sophisticated carbazole-bipyridine-based external ligand, which acts as PC
7	*Nat. Commun.* ***2019***, *10*, 2843-2852	5 mol% $CsPbBr_3$ as PC, 5 mol% $NiCl_2$•dtbbpy	70-85	➢ Perovskite as PC ➢ Non-reusable catalyst ➢ High dosage of Ni-catalyst ➢ Limited substrate scopes
8	*Angew. Chem. Int. Ed.* **2018**, *57*, 3488 –3492	3.33 mg/mmol carbon-nitride based photosensitizer CN-OA-m, 10 mol% $NiCl_2$•glyme or $Ni(OAc)_2$•$4H_2O$, 10 mol% dtbbpy	5-94	➢ Heterogeneous reusable photosensitizer ➢ Ni-catalyst as like homogeneous and have no reusability ➢ High dosage Ni-catalyst
9	*ChemCatChem* **2022**, *14*, *e202200477*	2.7* 10^{-4} CdSe@CdS, 30 mol% $NiCl_2$•DME, 45 mol% dtbbpy	8-96	➢ Heterogeneous reusable photosensitizer ➢ Very high dosage Ni-catalyst

				➢ Ni-catalyst as like homogeneous and have no reusability
10	***This work***	Ni@Bpy-sp^{2}c-COF (0.90 mol% Ni content)	42-86	➢ No external ligand ➢ Bpy-sp^{2}c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ A low dosage of catalyst ➢ Excellent substrate diversity ➢ No Ni-black formation ➢ Applications in late-stage functionalization of bioactive molecules
Thioetherification (C–S bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Org. Lett.* **2016**, *18*, 876−879	2 mol% $[Ru(bpy)_3](PF_6)_2$, 5 mol% $NiCl_2$•diglyme, 5 mol% dtbbpy	52-98	➢ Ru-based photosensitizer ➢ High dosage of catalyst ➢ No reusability of Ru/Ni-catalyst ➢ Alkylsilicate used for desired hydrogen atom transfer (HAT) from thiol
2	*J. Am. Chem. Soc.* **2016**, *138*, 1760−1763	2 mol% Ir[dF(CF_3)(ppy)]$_2$(dtbbpy)PF_6, 5 mol% $NiCl_2$•glyme, 5 mol% dtbbpy	62-95	➢ Ir-based photosensitizer ➢ High dosage of catalyst ➢ No reusability of Ir/Ni-catalyst ➢ Possibility of Ni-black formation
3	*Chem. Eur. J.* **2017**, *23*, 1 – 8	0.2 mol% 3,7-(4-biphenyl)-1-naphthalene-10-phenoxazine, 5 mol% $NiCl_2$•glyme, 5 mol% dtbbpy	64-98	➢ Organophotosensitizer used ➢ No reusability of PS ➢ High dosage of non-reusable Ni-catalyst ➢ Possibility of Ni-black formation
4	*Angew. Chem. Int. Ed.* **2017**, *56*, 874 –879	1 mol% [*fac*-Ir(ppy)$_3$], stoichiometric $CsCO_3$ base	52-94	➢ Ir-based photosensitizer ➢ No reusability of the catalyst ➢ Stoichiometric inorganic base
5	*Angew. Chem. Int. Ed.* **2018**, *130*, 14286 – 14290	0.02 mol% Zr_2-Ir-Ni MOF as catalyst	60-98	➢ MOF-based Ir/Ni decorated dual catalyst ➢ Metal decorated building block for MOF formation ➢ Reusable catalyst ➢ No heterocyclic iodide/thiol showed as a substrate
6	*J. Am. Chem. Soc.* **2019**, *141*, 15767−15772	0.05 mol% Hf_2-Ir-Ni MOF as catalyst	91-98	➢ Metal decorated building block for MOF formation ➢ Reusable catalyst ➢ Limited substrate scopes
7	*Angew. Chem. Int. Ed.* **2021**, *60*, 10820-10827	2 mol% Ace-COF-Ni	5-94	➢ COF backbone acts as a photosensitizer as well as a metal anchoring ligand ➢ Reusability of the whole

				catalyst ➢ High dosage Ni-catalyst ➢ No heterocyclic iodo/thiol substrate scope
8	*Chem. Eur. J.* **2023**, *29*, *e202202967*	Acr^2-Tf-Bpy^1 COF (3 mg), 4 mol% $NiCl_2$.glyme	98	➢ Heterogeneous reusable PS ➢ COF as a heterogenous ligand as well as a photosensitizer ➢ Ni-catalyst as like homogeneous and have no reusability
9	***This work***	Ni@Bpy-sp^2c-COF (0.45 mol% Ni content)	31-95	➢ No external ligand ➢ Bpy-sp^2c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ Low catalyst loading ➢ Excellent substrate diversity ➢ No Ni-black formation ➢ Applications in late-stage functionalization of bioactive molecules
Sulfonation (C–S bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Angew. Chem. Int. Ed.* **2018**, *57*, 1371 –1375	1 mol% Ir-catalyst, 10 mol% $NiCl_2$.glyme, 10 mol% dtbbpy	32-94	➢ Ir-based photosensitizer ➢ High dosage of catalyst ➢ No reusability of Ir/Ni-catalyst ➢ External ligand required
2	*Chem. Sci.*, **2018**, *9*, 3186–3191	2 mol% $[Ru(bpy)_3](PF_6)_2$, 2.5 mol% $[Ni(Phen)(H_2O)_4]Cl_2$, 5 mol% dtbbpy	33-86	➢ Ru-based photosensitizer ➢ High dosage of Ru/Ni-catalyst ➢ No reusability of Ru/Ni-catalyst
3	*Chem. Eur. J.* **2020**, *26*, 3484 – 3488	20 mol% Hantzsch Ester, 150 mol% $CsCO_3$	39-95	➢ Hantzsch ester as catalyst ➢ No reusability of the catalyst ➢ Stoichiometric inorganic base ➢ Electron donor-acceptor complex needs to form between Hantzsch ester and aryl sulfonate
4	*Org. Chem. Front.*, **2022**, *9*, 1437–1444	20 mol% 2-chloro-thioxanthen-9-one (Cl-TXO), 10 mol% $NiBr_2$•$3H_2O$, 12 mol% dtbbpy	47-91	➢ Xanthone based Organophotosensitizer ➢ High dosage of Ni-catalyst ➢ No reusability of catalysts ➢ External ligand used
5	*Chem* **2022**, *8*, 2419-2431	10 mol% $NiCl_2$•DME, 10 mol% 4-phenyl-2-(pyridin-2-yl)quinoline (PPQN) based ligand	62	➢ Photoactive ligand ➢ No additional photosensitizer ➢ High dosage of Ni ➢ No reusability of the catalyst
6	*Chem. Sci.*, **2021**, *12*, 6323-6332	Boron carbonnitride (BCN) as photosensitizer	40-93	➢ Semiconducting material BCN as a photosensitizer ➢ Reusable photosensitizer ➢ Reusable catalyst

				➢ Limited scope for sulfonation
7	*Angew. Chem. Int. Ed.* **2022**, *61*, *e202211433*	5 mol% $NiCl_2$•glyme, 5 mol% Czbpy (carbazole-bipyridine based)	49-92	➢ High dosage of Ni catalyst ➢ Ni was introduced as like homogeneous ➢ Sophisticated carbazole-bipyridine-based external ligand, which acts as PS
8	*Chem. Eur. J.* **2023**, *29*, *e202202967*	Acr^2-Tf-Bpy^1 COF (3 mg), 4 mol% $NiCl_2$.glyme	55	➢ Heterogeneous reusable photosensitizer ➢ COF as a heterogenous ligand and photosensitizer ➢ Ni-catalyst as like homogeneous and have no reusability
9	***This work***	Ni@Bpy-sp^2c-COF (0.45 mol% Ni content)	83	➢ No external ligand ➢ Bpy-sp^2c-COF acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ Low catalyst loading ➢ No Ni-black formation
Sulfonamidation (C–N bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Science* **2016**, *353*, 279-283	0.02 mol% $Ir[dF(CF_3)(ppy)]_2(dtbbpy)PF_6$ photosensitizer, 5 mol% $NiCl_2$•DME catalyst	72	➢ Ir-based photosensitizer ➢ High dosage of Ni-catalyst ➢ No reusability of Ir/Ni-catalyst ➢ Possibility of Ni-black formation
2	*Angew. Chem. Int. Ed.* **2018**, *57*, 3488 –3492	0.05 mol% $[Ir(ppy)_2(dtbbpy)]PF_6$ or $[Ir(ppy)_2(bpy)]PF_6$ photosensitizer, 5 mol% $NiCl_2$•glyme, ligand free or 1 mol% dtbbpy	55-99	➢ Ir-based photosensitizer ➢ High dosage of Ni-catalyst ➢ No reusability of Ir/Ni-catalyst ➢ Possibility of Ni-black formation
3	*Org. Lett.* **2019**, *21*, 2740−2744	0.15-1 mol% $[Ir(ppy)_2(dtbbpy)]PF_6$ photosensitizer, 0.20-5 mol% [Ni (dtbbpy]Br_2,	25-99	➢ Ir-based photosensitizer ➢ High dosage of Ni-catalyst ➢ No reusability of Ir/Ni-catalyst ➢ Possibility of Ni-black formation
4	*Angew. Chem. Int. Ed.* **2022**, *61*, *e202211433*	5 mol% $NiCl_2$•glyme, 5 mol% Czbpy (carbazole-bipyridine based)	61-89	➢ High dosage of Ni catalyst ➢ Ni is introduced as homogeneous ➢ Sophisticated carbazole-bipyridine-based external ligand, which acts as PS
5	***This work***	Ni@Bpy-sp^2c-COF (0.45 mol% Ni content)	85	➢ No external ligand ➢ Bpy-sp^2c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ Low catalyst loading

				➢ No Ni-black formation
Amination (C–N bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Chem* **2022**, *8*, 2419-2431	10 mol% $NiCl_2$•DME, 10 mol% 4-phenyl-2-(pyridin-2-yl)quinoline (PPQN) based ligand	56	➢ Photoactive ligand ➢ High dosage of Ni ➢ No reusability of the catalyst
2	*Angew. Chem.* **2022**, *134*, *e202203176.*	Ni-mpg-CN_x (~ 3 mol% Ni content)	26-87	➢ Carbon nitride as photosensitizer as well as heterogeneous ligand ➢ High dosage of catalyst ➢ Low turnover number (TON) ➢ The leaching of Ni is high ➢ Possibility of Ni black formation
3	***This work***	Ni@Bpy-sp^2c-COF (0.45 mol% Ni content)	89	➢ No external ligand ➢ Bpy-sp^2c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ The leaching of Ni is very low ➢ Low catalyst loading ➢ No Ni-black formation
Borylation (C–B bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Chem. Sci.*, **2016**, *7, 3676–3680*	300 W Hg-lamp	15-90	➢ High energy UV light ➢ Possibility of undesired side reactions
2	*Org. Lett.* **2016**, *18,* 5248−5251	1 mol% [fac-Ir$(ppy)_3$]	55-89	➢ Ir-based photosensitizer ➢ No reusability of Ir-catalyst
3	*Org. Lett.* **2019**, *21,* 9950−9953	5 mol% 3,7-di-([1,1′-biphenyl]-4-yl)-10-(4-(trifluoromethyl)phenyl) -10Hphenoxazine	40-83	➢ Organophotosensitizer used ➢ No reusability of PS ➢ High dosage of photosensitizer
4	***This work***	Ni@Bpy-sp^2c-COF (0.45 mol% Ni content)	96	➢ No external ligand ➢ Visible-light-mediated reaction ➢ Bpy-sp^2c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable
Phosphonylation (C–P bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Chem. Eur. J.* **2015**, *21,* 4962 – 4965	5 mol% $[Ru(bpy)_3Cl_2]$•$6H_2O$, 2 mol% $[Ni(COD)_2]$, 2 mol% dtbbpy	39-91	➢ Ru-based photosensitizer ➢ External bipyridine-based ligand is needed ➢ High dosage of Ru-catalyst

				➢ No reusability of Ru/Ni-catalyst
2	*Org. Lett.* **2021**, *23,* 160−165	20 mol% thioxanthen-9-one thioxanthone, 10 mol% $NiBr_2$, 12 mol% dtbbpy	51-92	➢ Organophotosensitizer used ➢ High dosage of catalyst ➢ No reusability of photosensitizer and Ni-catalyst ➢ High dosage of catalyst
3	*Chem* **2022**, *8*, 2419-2431	10 mol% $NiCl_2$•DME, 10 mol% 4-phenyl-2-(pyridin-2-yl)quinoline (PPQN) based ligand	51	➢ Photoactive ligand ➢ High dosage of Ni ➢ No reusability of the catalyst
4	*Dalton Trans.*, **2020**, *49*, 17147–17151	Black TiO_2 NPs (3.0 mg), 10 mol% $NiCl_2$•glyme, 10 mol% dtbbpy	71-93	➢ TiO_2 NPs as a photosensitizer ➢ Ni is introduced as like homogeneous ➢ High dosage of Ni catalyst ➢ External ligand is required
5	***This work***	Ni@Bpy-sp^2c-COF (0.45 mol% Ni content)	70	➢ No external ligand ➢ Bpy-sp^2c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ Low catalyst loading ➢ No Ni-black formation
Allylation (C–C bond formation)				
Entry	**References**	**Catalyst system**	**Yield (%)**	**Remarks**
1	*Chem. Commun.*, **2019**, *55*, 6838--6841	5 mol% $[Ru(bpy)_3Cl_2]$•$6H_2O$, 10 mol% $[NiBr_2(glyme)]$, 15 mol% *o*-phenanthroline	38-97	➢ Ru-based photosensitizer ➢ External phenanthroline-based ligands ➢ Very high dosage of Ru and Ni-catalyst ➢ No reusability of Ru/Ni-catalyst
2	*Adv. Synth. Catal.* **2021**, *363*, 1105 – 1111	2 mol% $[Ir(ppy)_2(dtbbpy)]PF_6$ photosensitizer, 10 mol% $CoBr_2$, 10 mol% dtbbpy	30-85	➢ Ir-based photosensitizer ➢ External bipyridine-based ligand is required ➢ High dosage of catalyst ➢ No reusability of Ir/Co-catalyst
3	*ACS Catal.* **2021**, *11*, 2992−2998	1 mol% $[Ir(ppy)_2(dtbbpy)]PF_6$ photosensitizer, 10 mol% $CoSO_4$•H_2SO_4, 10 mol% dtbbpy	24-89	➢ Ir-based photosensitizer ➢ External bipyridine-based ligand is required ➢ High dosage of catalyst ➢ No reusability of Ir/Co-catalyst
4	*Angew. Chem.* **2022**, *134*, *e202114981*	5 mol% 2,4,6-tris(diphenylamino)-5-fluoroisophthalonitrile, 10 mol% $NiCl_2$(glyme), 15 mol% IndaBOX chiral ligand, 200 mol% Hantzsch's ester	30-94	➢ High-dosage of photosensitizer ➢ Very high dosage of Ni-catalyst and expensive ligand ➢ No reusability of photosensitizer and Ni-catalyst
5	*Chem* **2022**, *8*, 2419-2431	10 mol% $NiCl_2$•DME, 10 mol% 4-phenyl-2-	51	➢ Photoactive ligand ➢ High dosage of Ni

		(pyridin-2-yl)quinoline (PPQN) based ligand		➢ No reusability of the catalyst
6	***This work***	Ni@Bpy-sp^{2}c-COF (0.45 mol% Ni content)	61	➢ No external ligand ➢ Bpy-sp^{2}c-COF itself acts as a heterogeneous ligand as well as a photosensitizer ➢ The whole catalyst can be reusable ➢ Low catalyst loading ➢ No Ni-black formation

Section S-XIV: References

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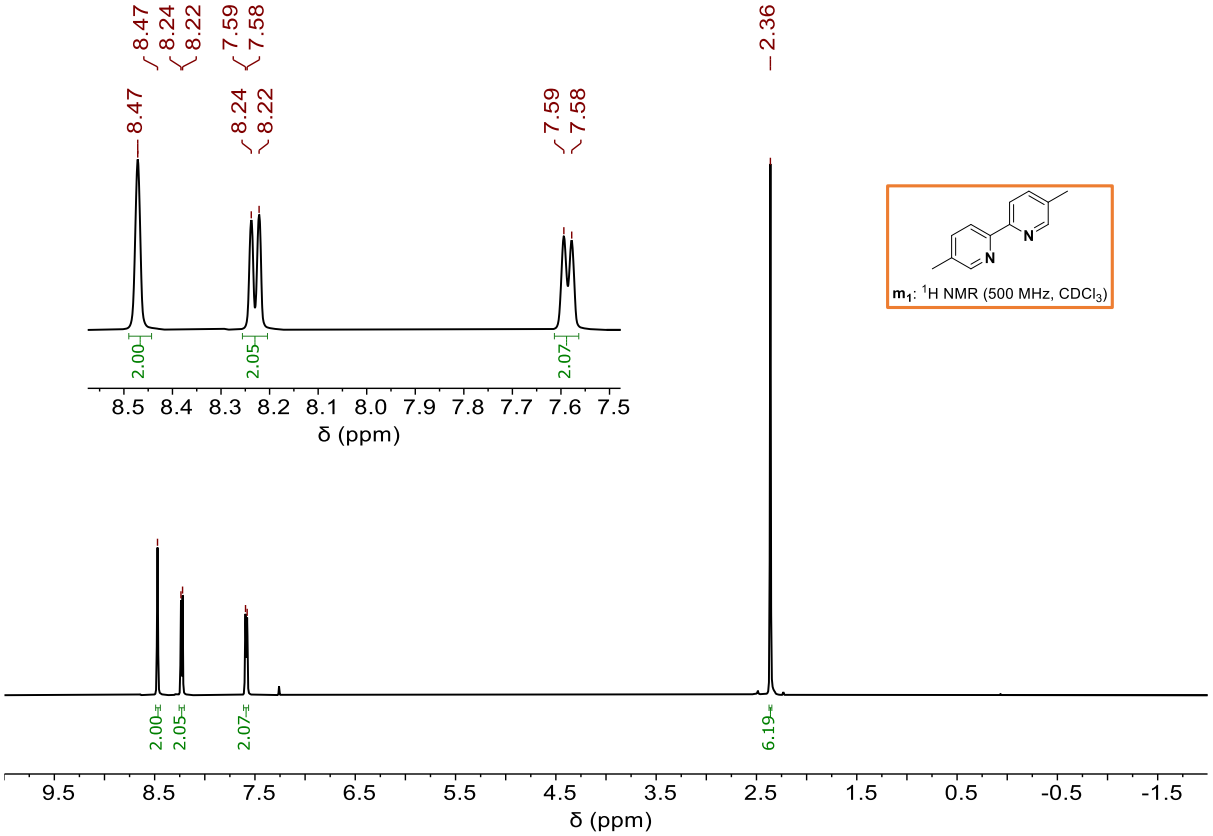
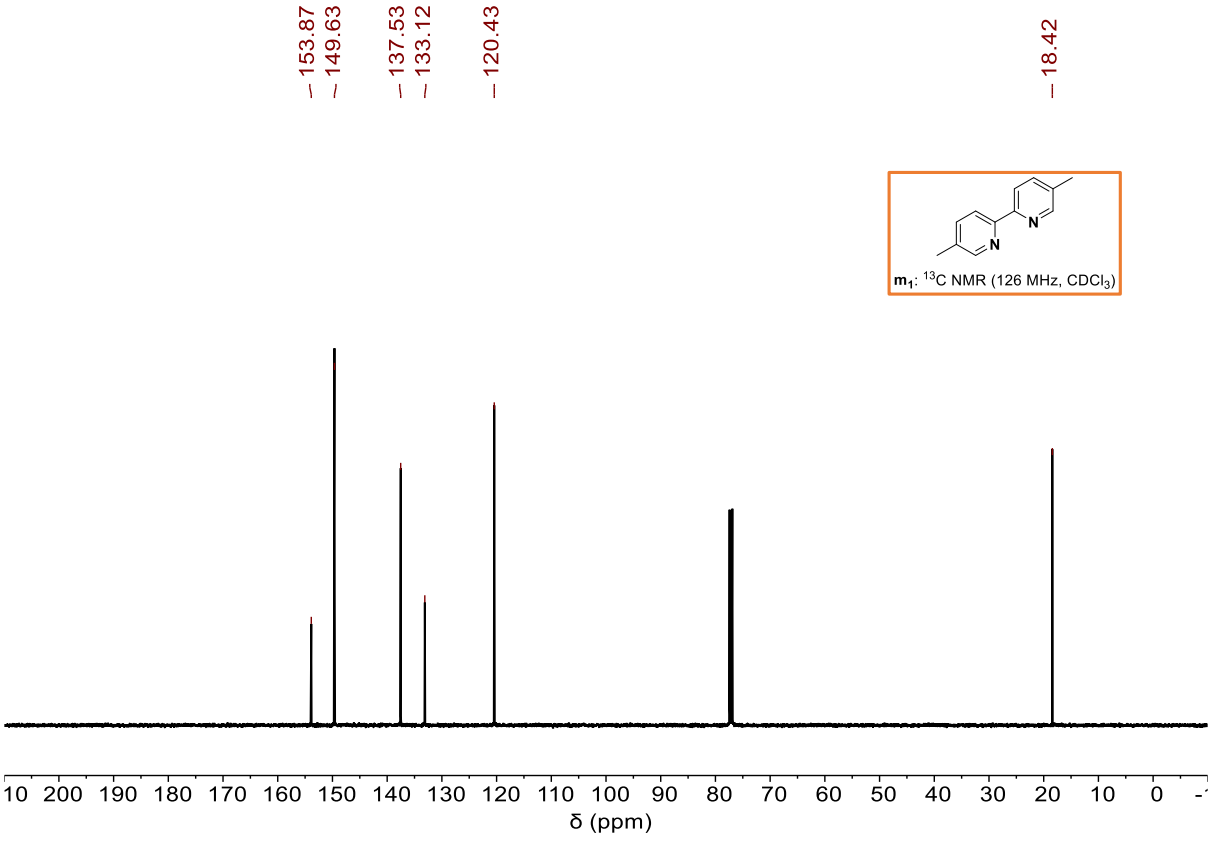
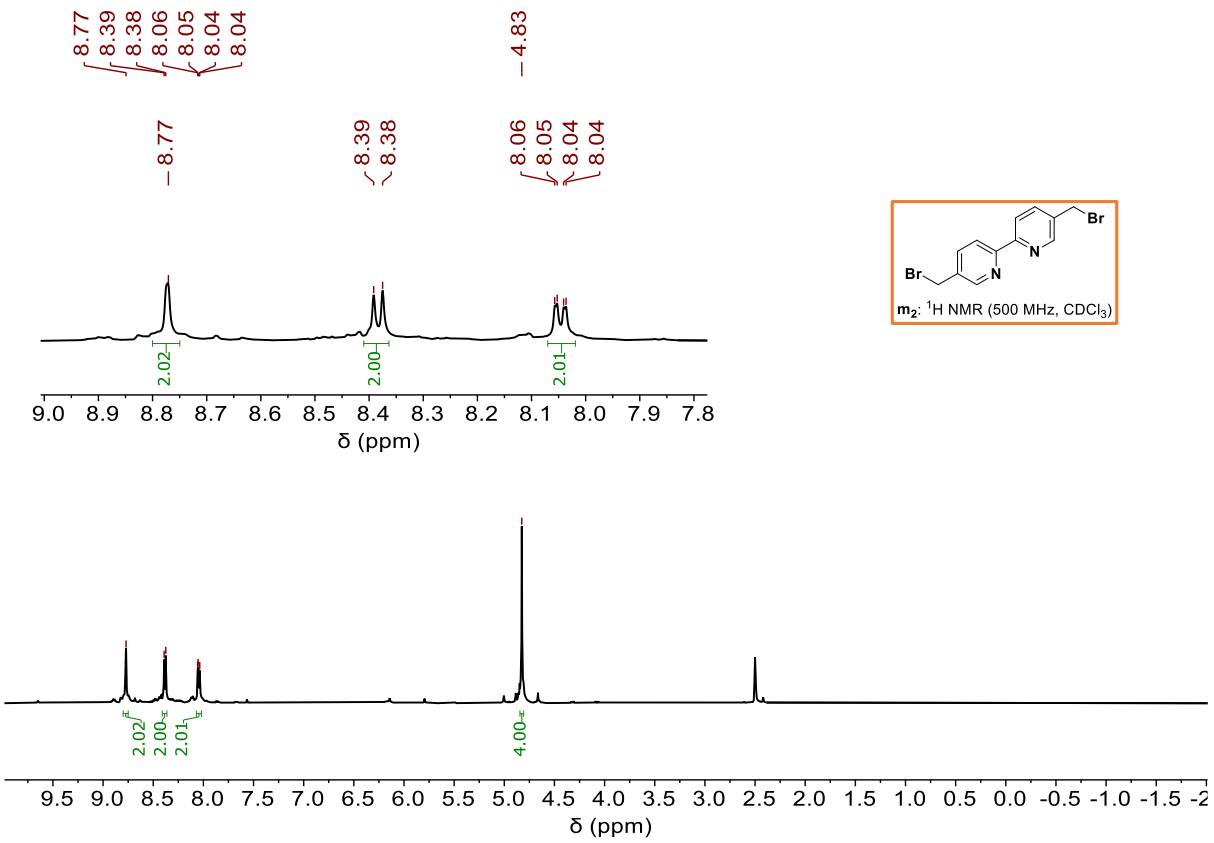
Section S-XV: Copies of ^{1}H, ^{13}C, ^{11}B, ^{31}P and ^{19}F NMR Spectra

NMR Copies for Building Blocks



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8.39
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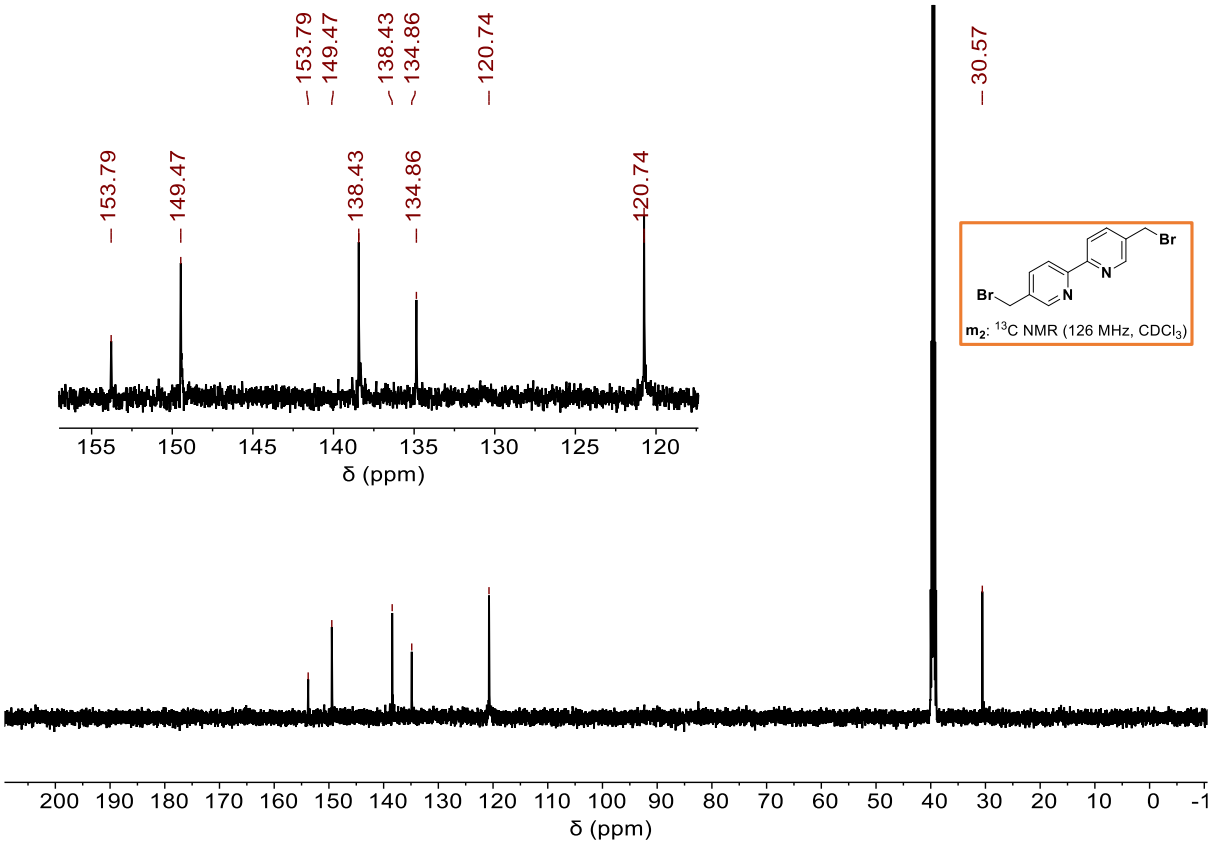
8.06
8.05
8.04
8.04
4.83
2.02
2.00
2.01
δ (ppm)
Br
N
Br
N
m2: 1H NMR (500 MHz, CDCl3)
4.00
δ (ppm)


153.79
149.47
138.43
134.86
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30.57
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Br
N
Br
N
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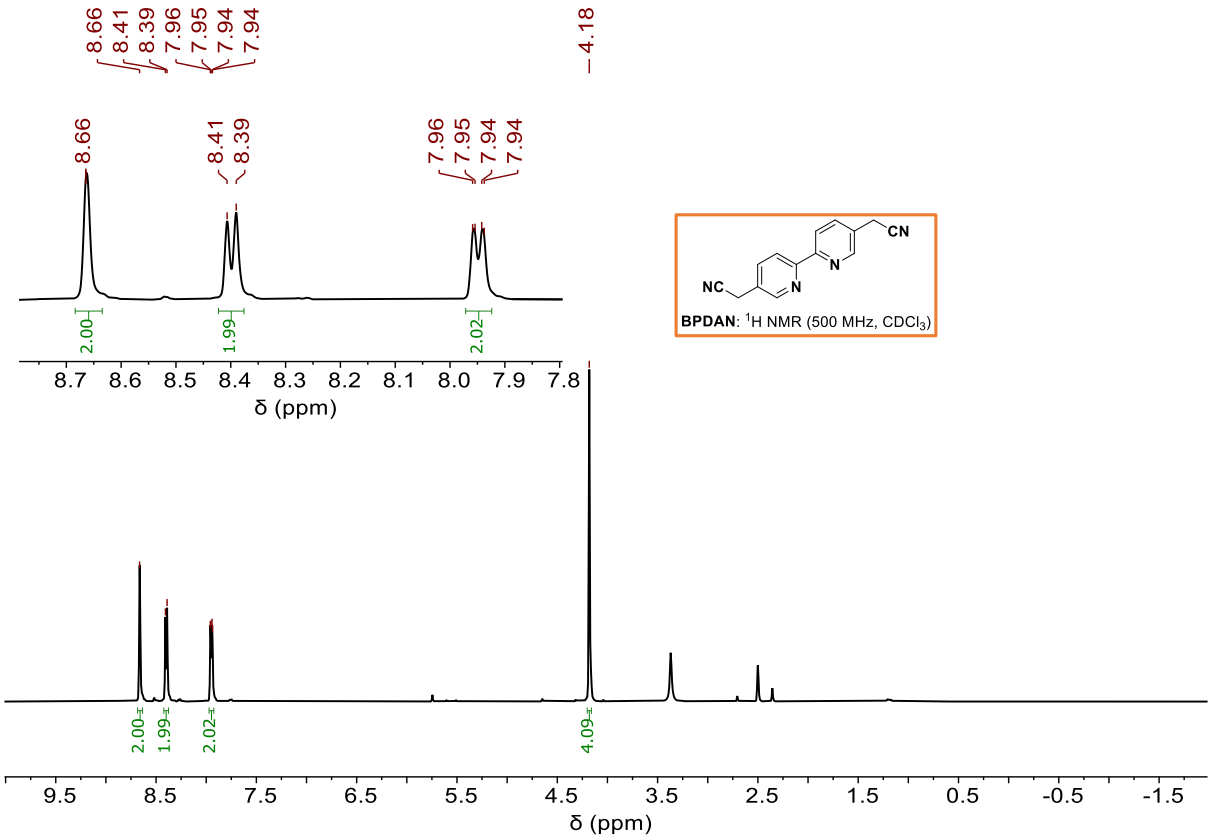
δ (ppm)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8.41
8.39
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7.95
7.94
7.94
4.18
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1.99
2.02
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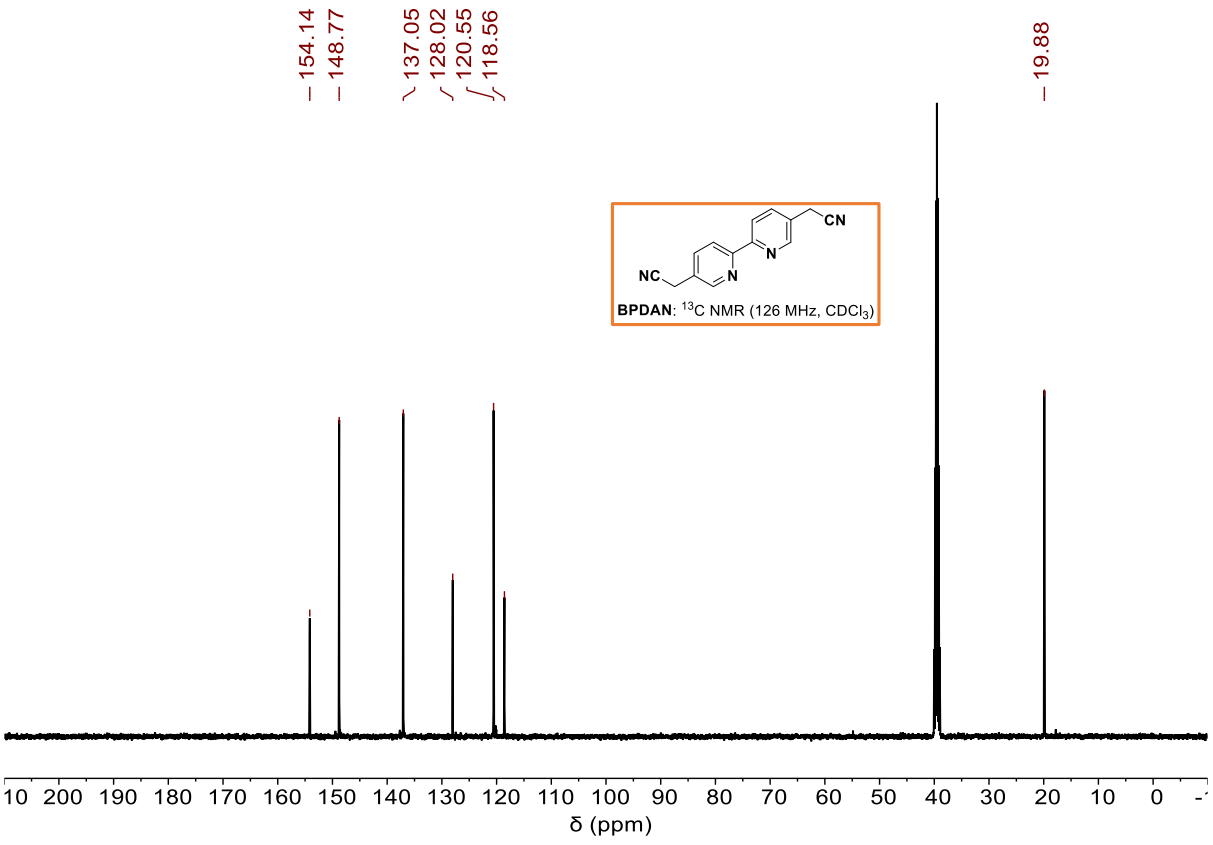
δ (ppm)
CN
NC
N
BPDAN: ^{1}H NMR (500 MHz, CDCl$_3$)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NC
N
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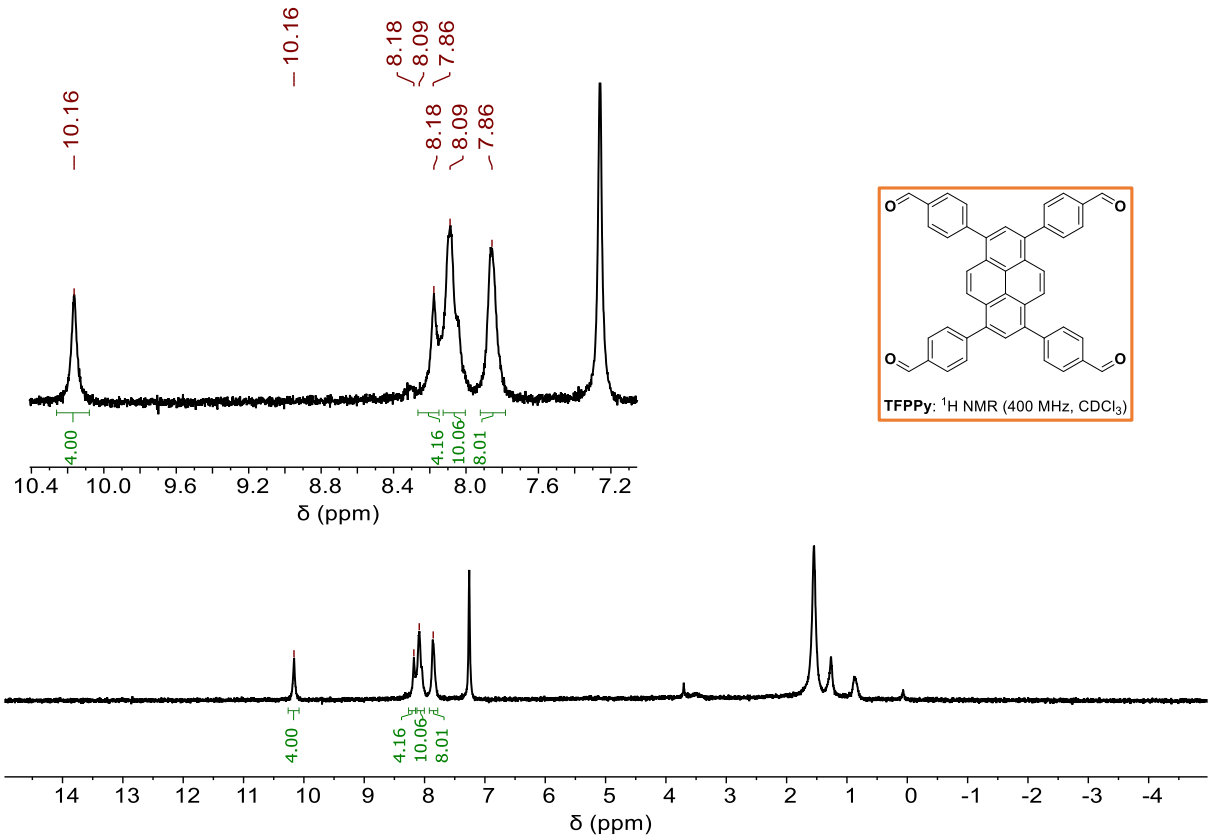
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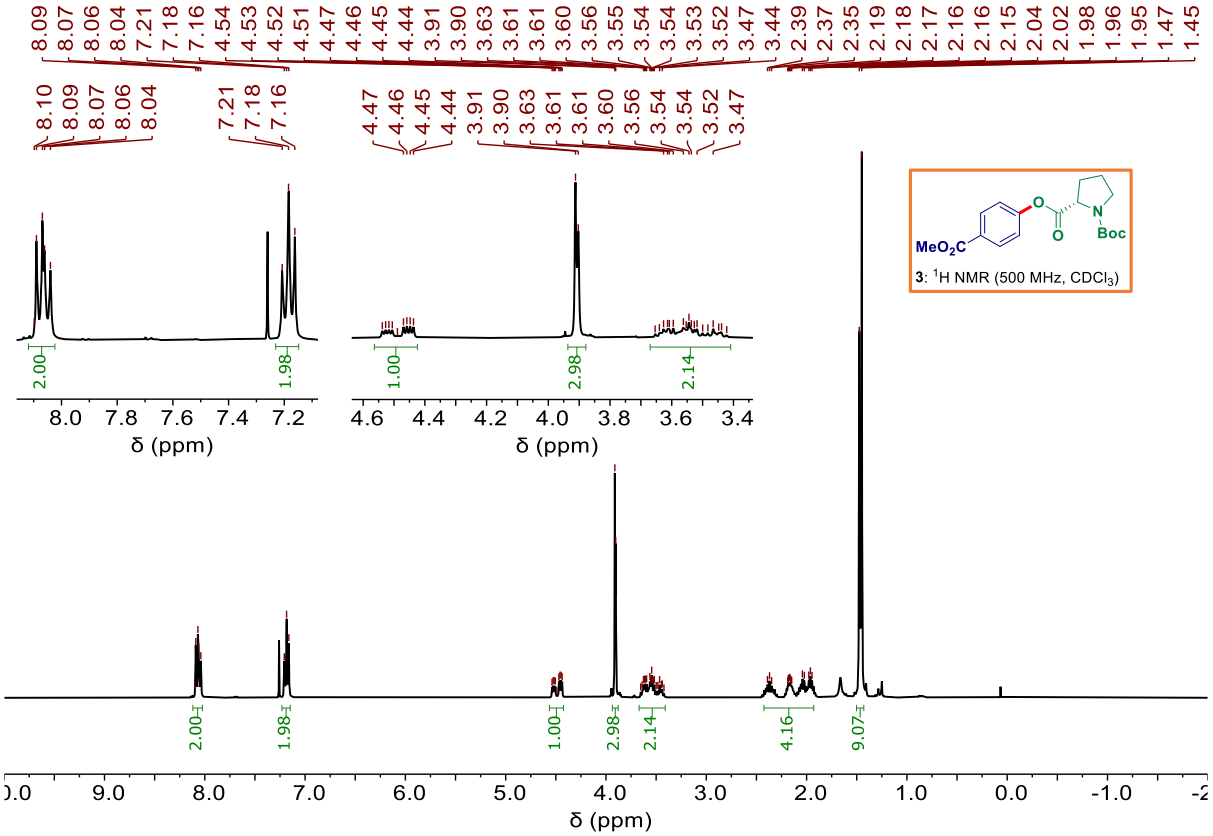
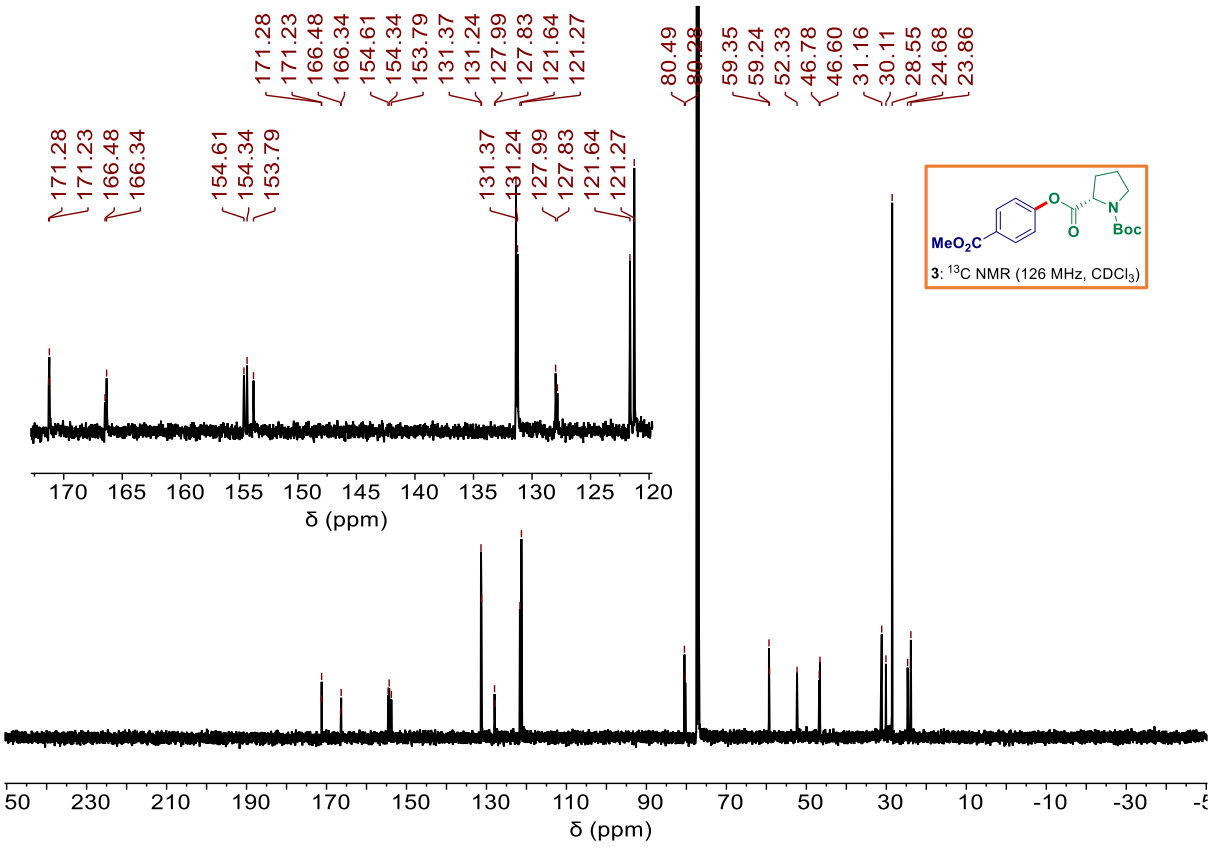
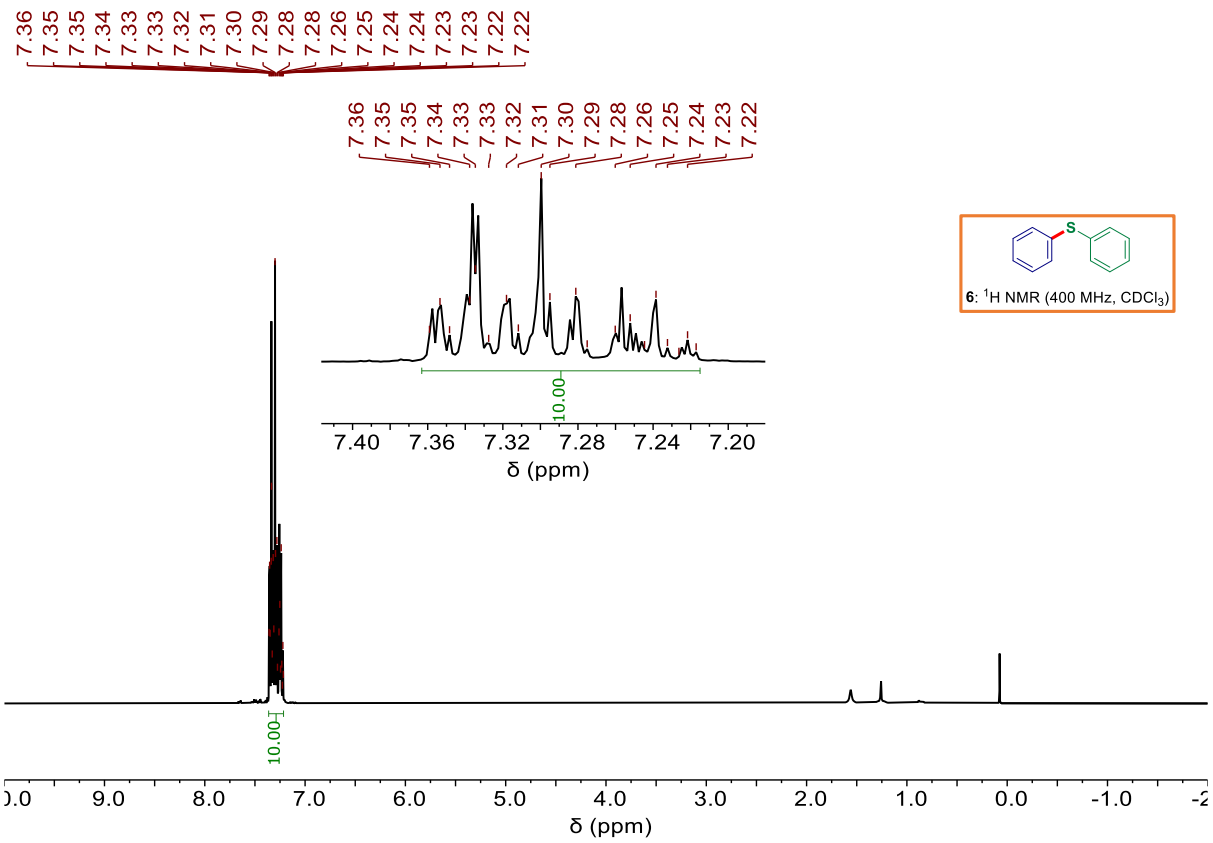
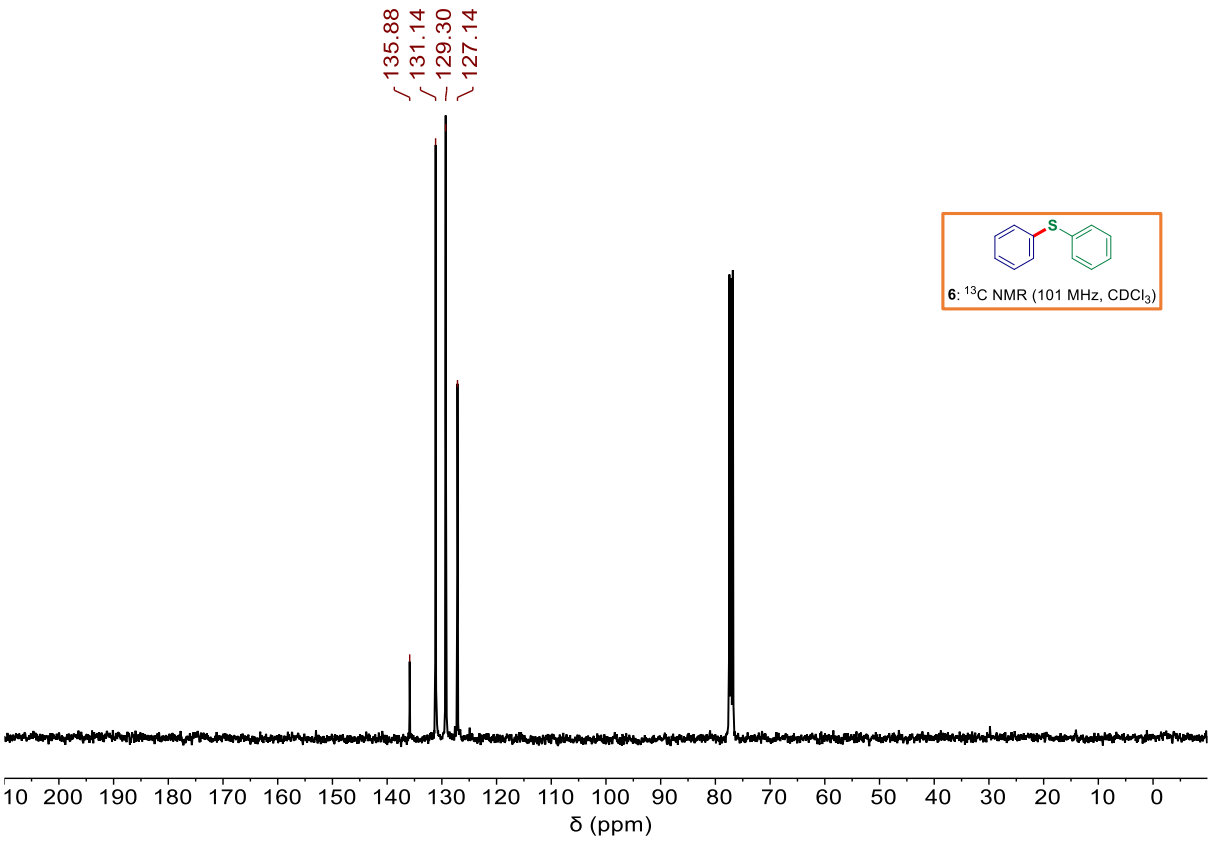
NMR Copies for Diverse Model Cross-Coupled Products






7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.28 7.28 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.22
7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.28 7.26 7.25 7.24 7.23 7.22
10.00
7.40 7.36 7.32 7.28 7.24 7.20
δ (ppm)
6: 1H NMR (400 MHz, CDCl3)
10.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)


135.88
131.14
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127.14
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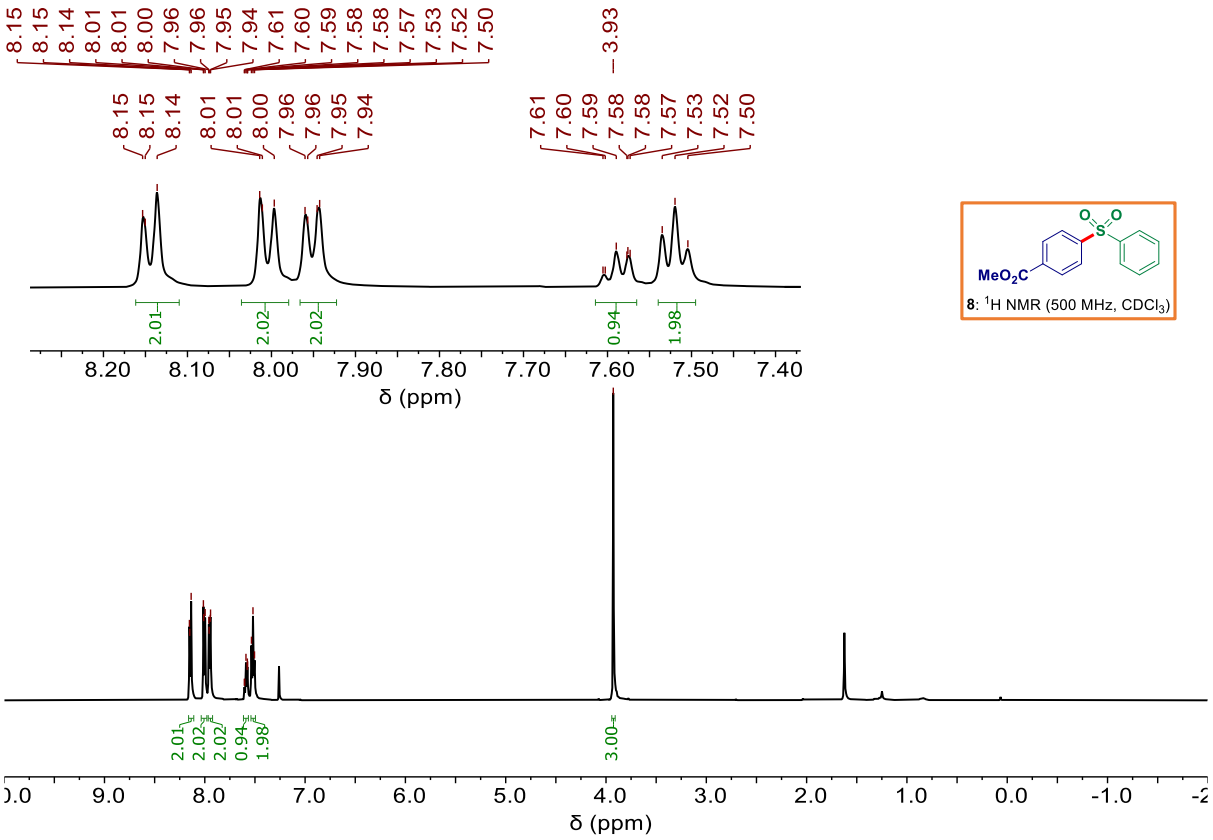
δ (ppm)


8.15
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8.14
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8.01
8.00
7.96
7.96
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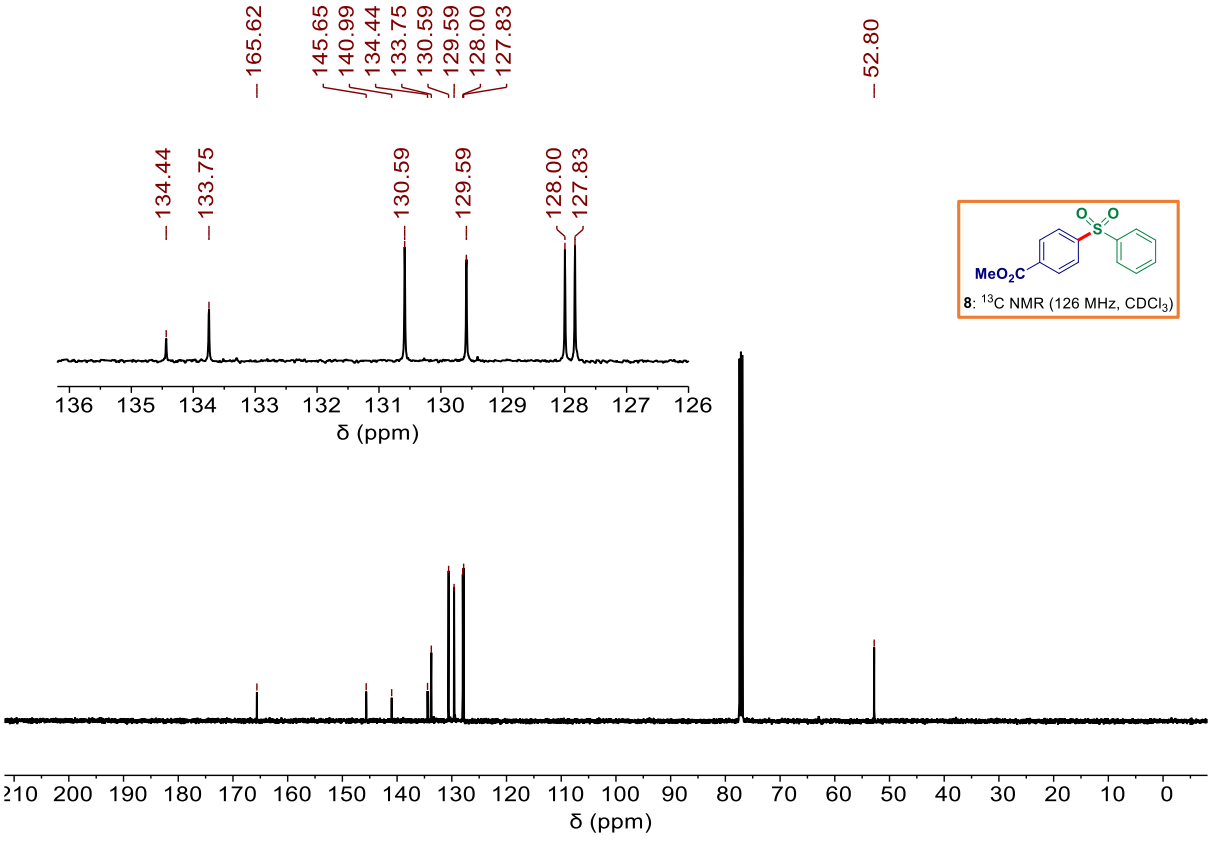
7.94
7.61
7.60
7.59
7.58
7.58
7.57
7.53
7.52
7.50
3.93
2.01
2.02
2.02
0.94
1.98
3.00
δ (ppm)
MeO2C
8: 1H NMR (500 MHz, CDCl3)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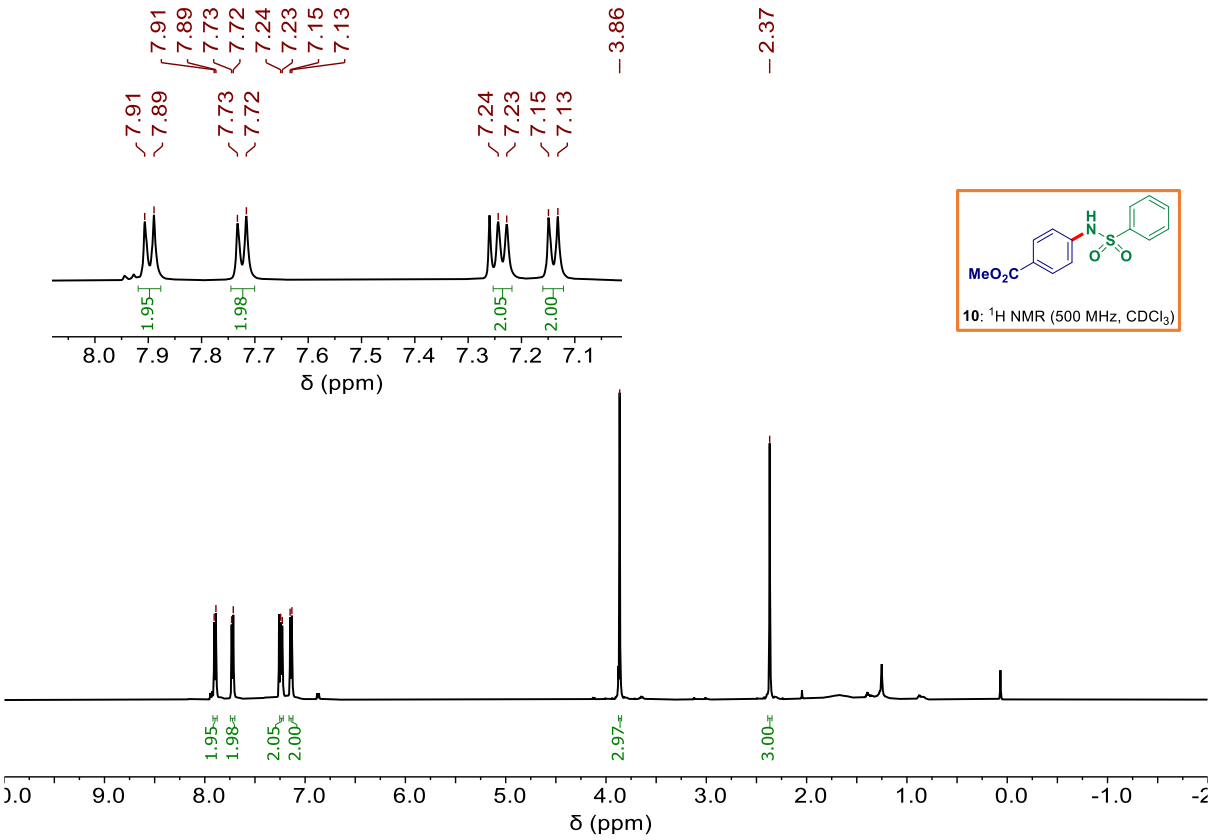
52.80
δ (ppm)
MeO2C
8: 13C NMR (126 MHz, CDCl3)


7.91
7.89
7.73
7.72
7.24
7.23
7.15
7.13
3.86
2.37
1.95
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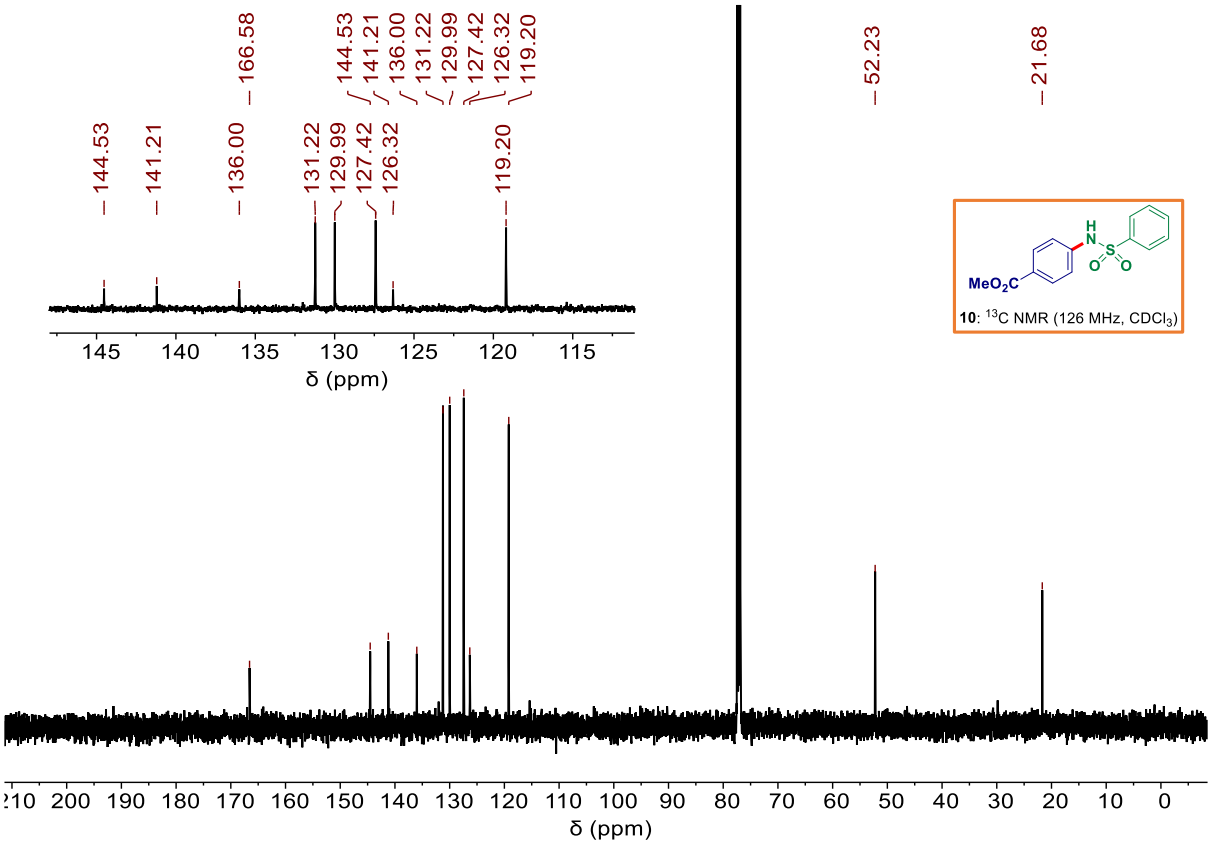
2.05
2.00
2.97
3.00
δ (ppm)
MeO2C
10: 1H NMR (500 MHz, CDCl3)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136.00
131.22
129.99
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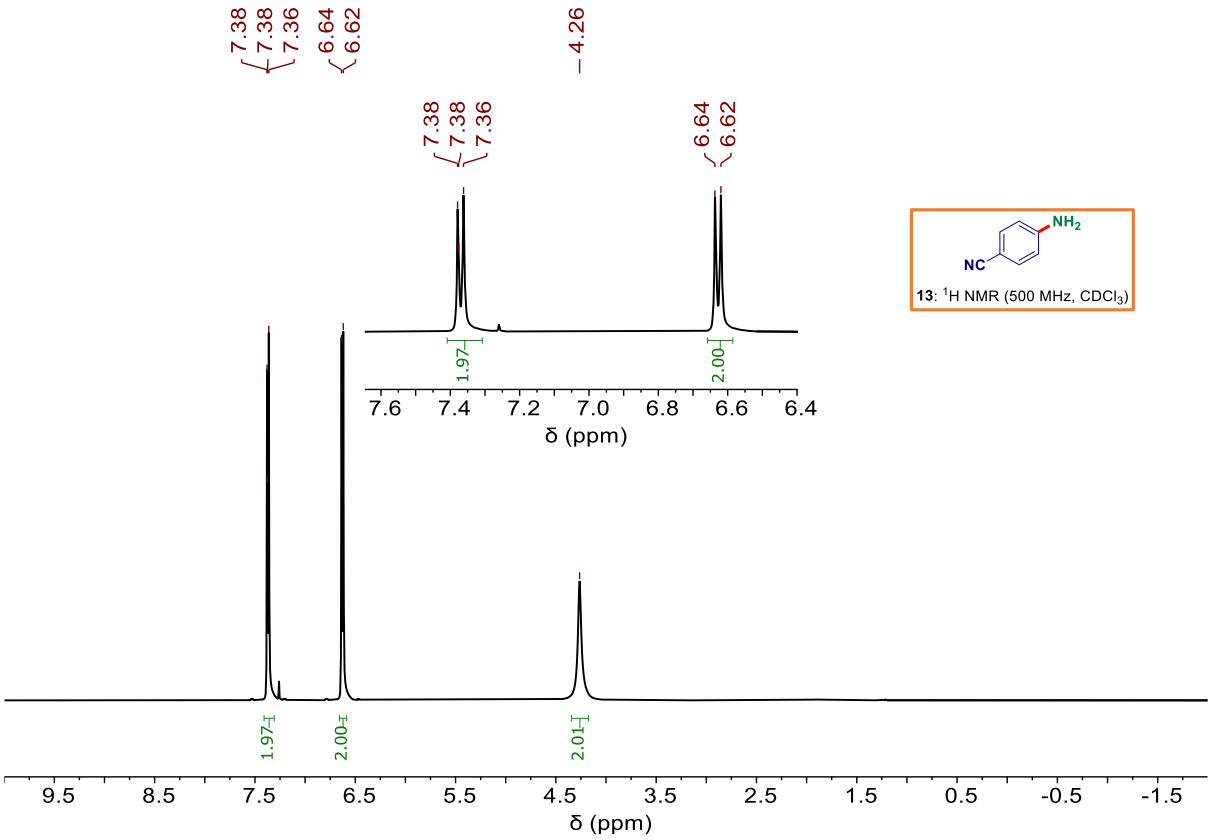
126.32
119.20
52.23
21.68
δ (ppm)
MeO2C
10: 13C NMR (126 MHz, CDCl3)


7.38
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1.97
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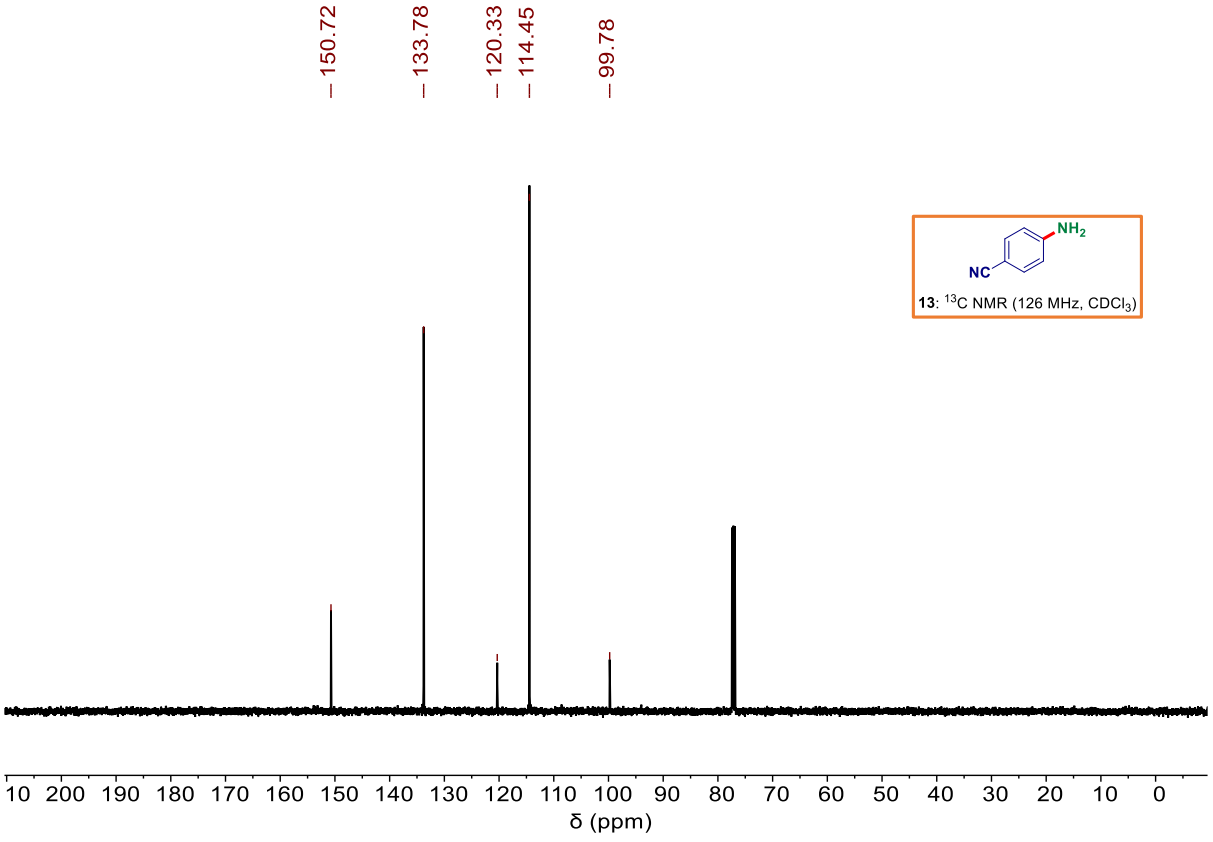
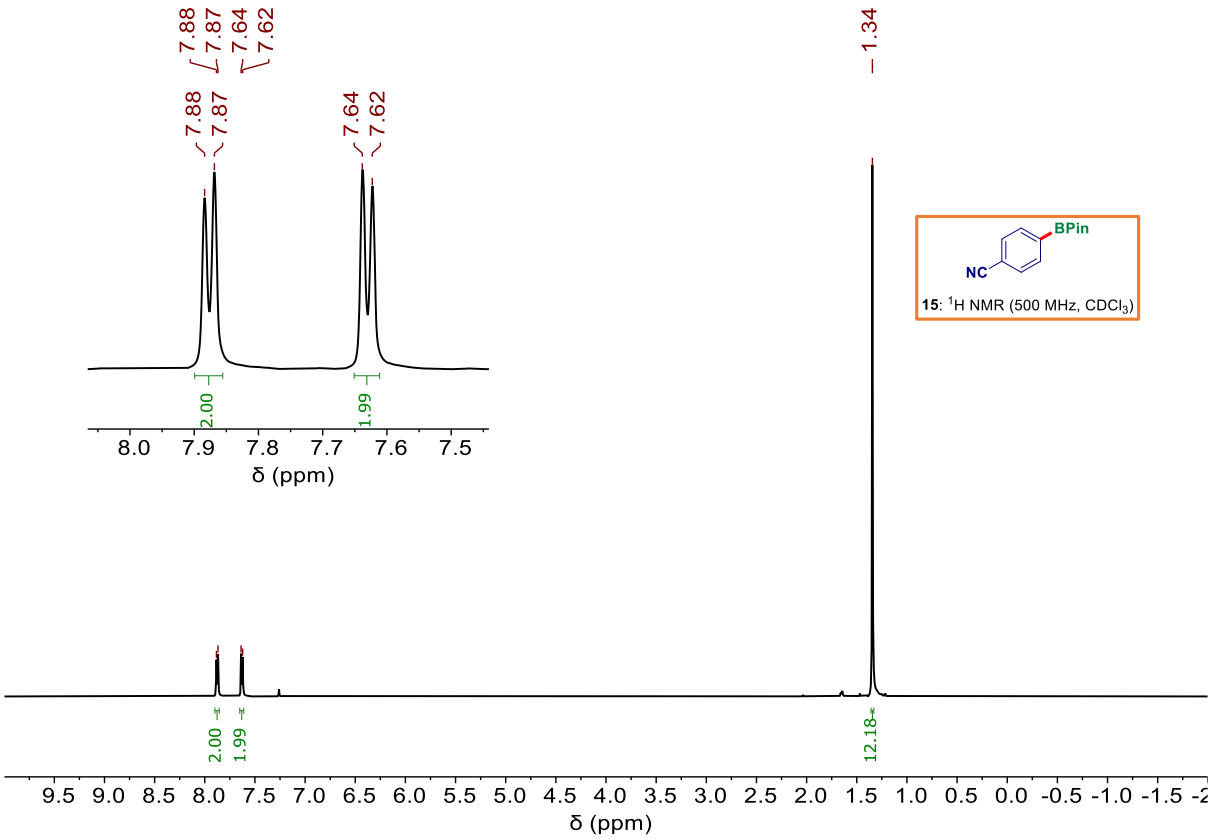
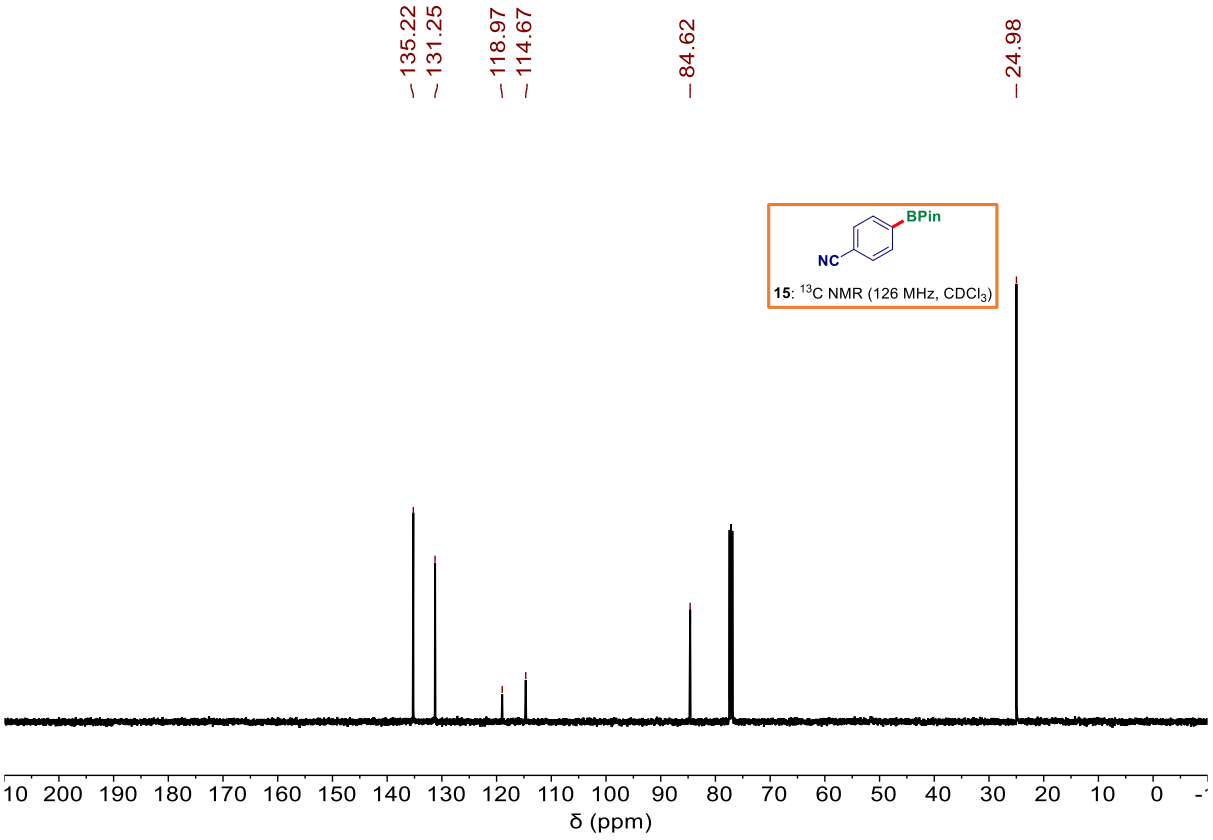
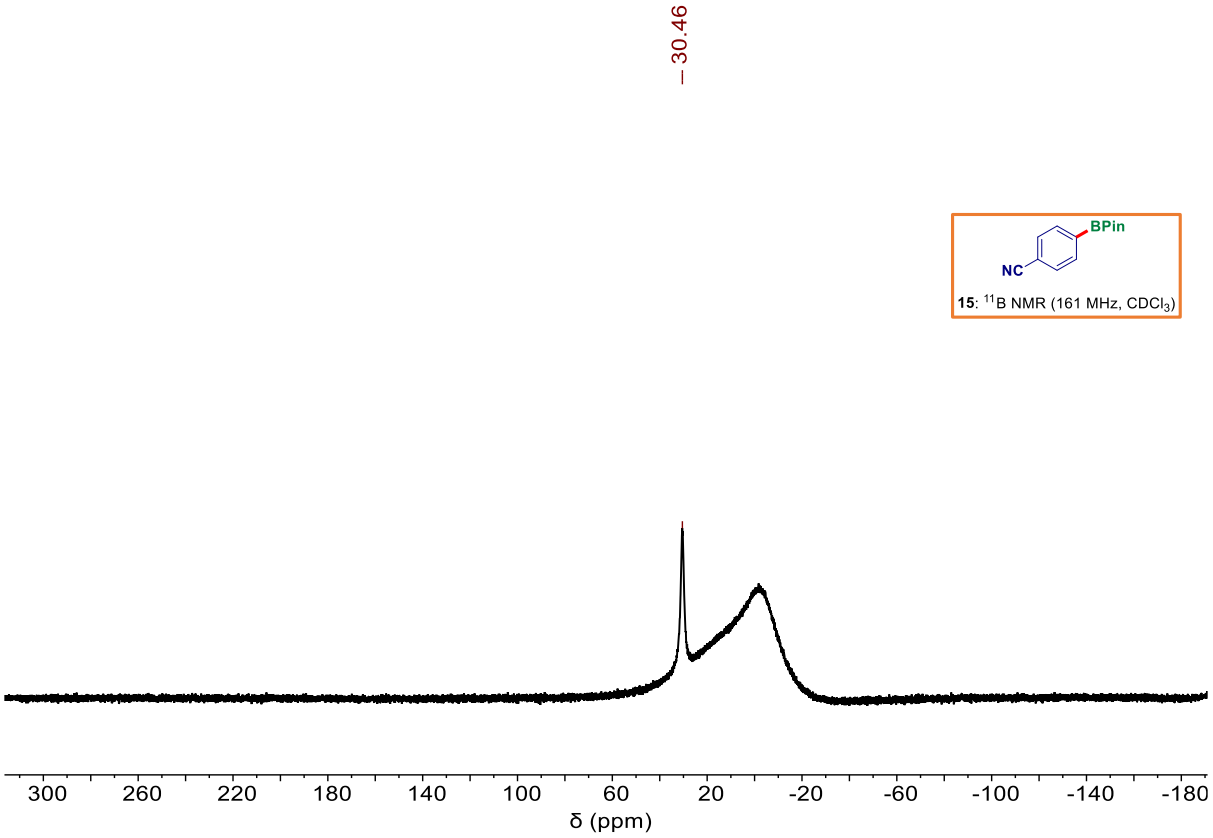
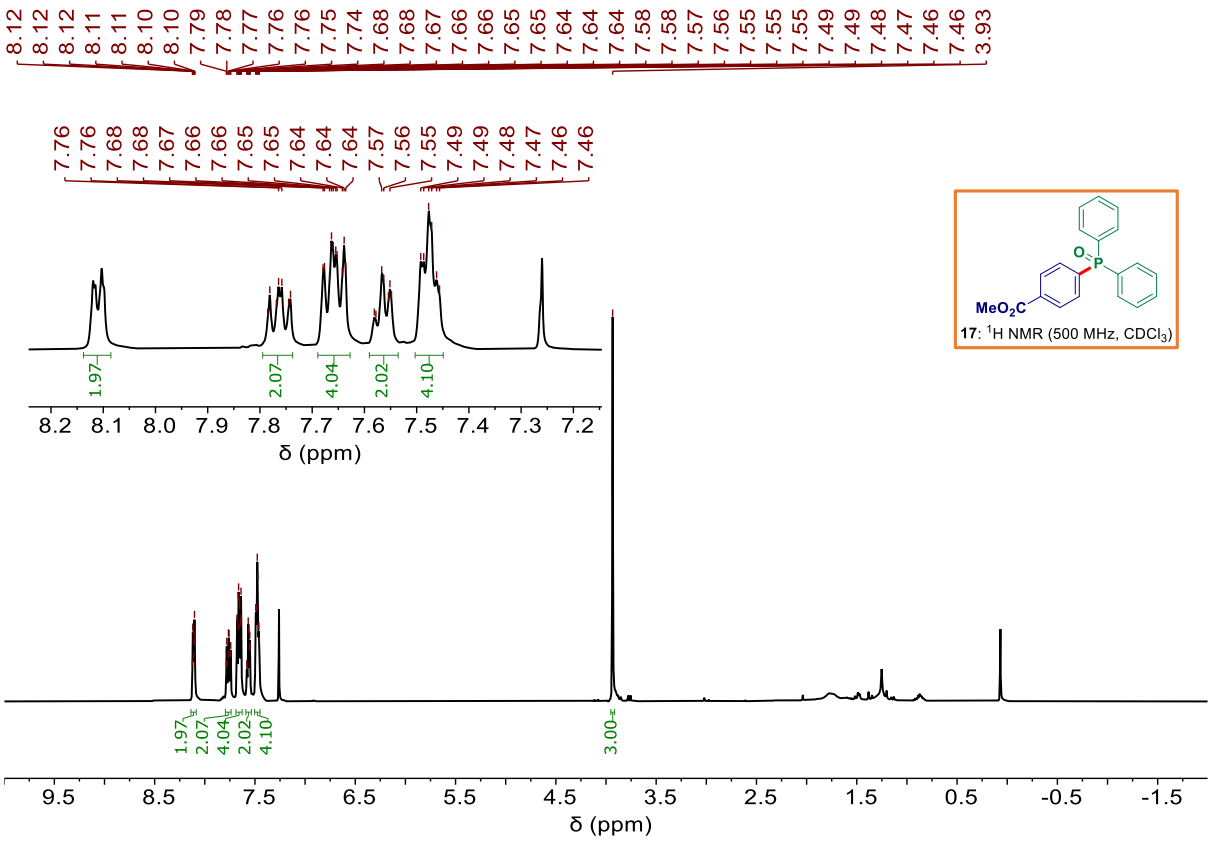
2.01
δ (ppm)
NH2
NC
13: 1H NMR (500 MHz, CDCl3)

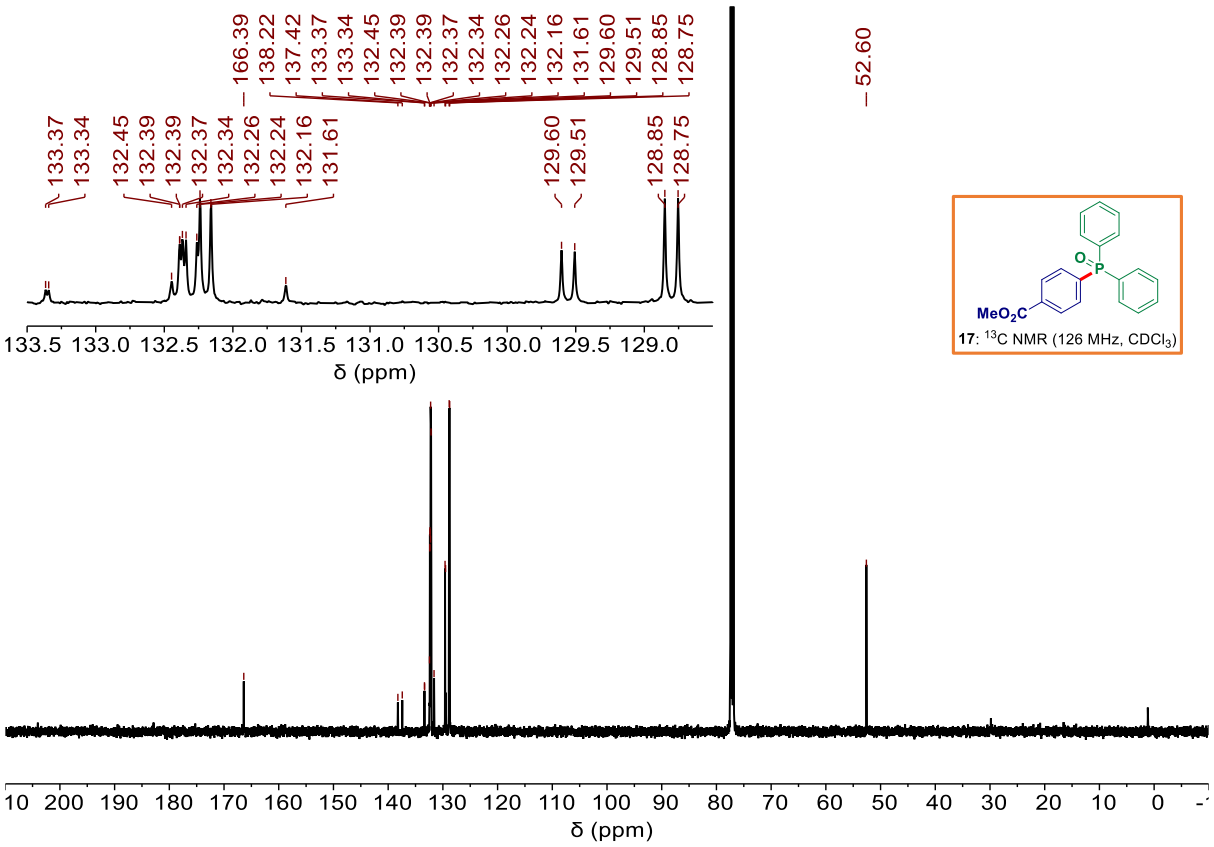

150.72
133.78
120.33
114.45
99.78
δ (ppm)
NH2
NC
13: 13C NMR (126 MHz, CDCl3)

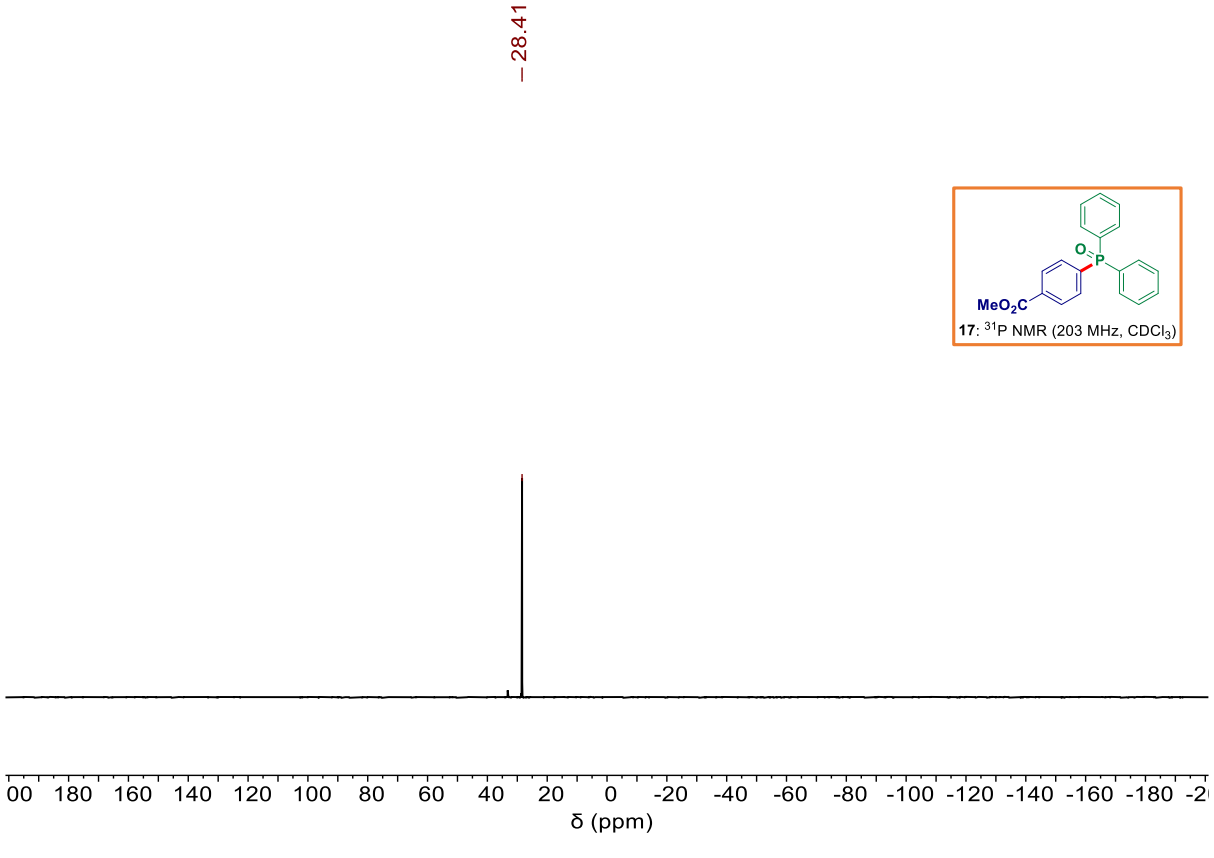

7.88
7.87
7.64
7.62
1.34
BPin
NC
15: 1H NMR (500 MHz, CDCl3)
2.00
1.99
12.18
δ (ppm)

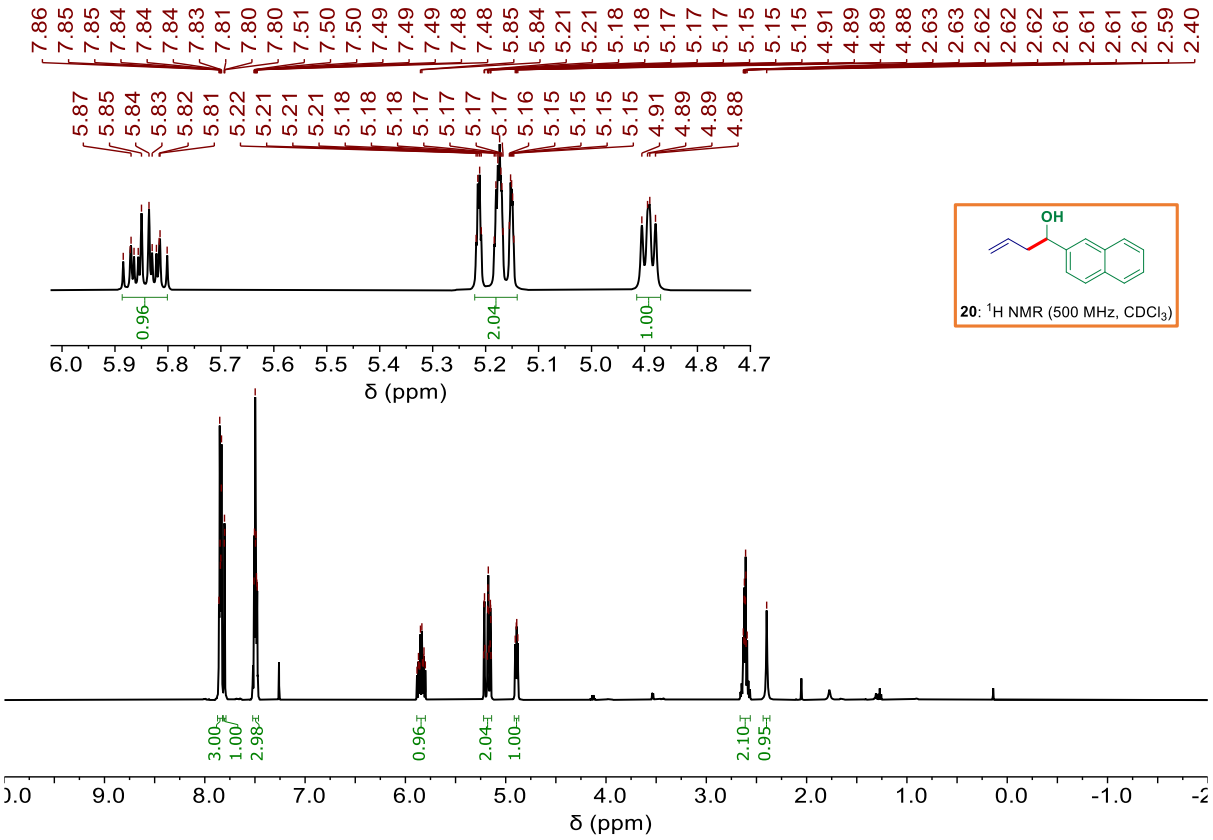

135.22
131.25
118.97
114.67
84.62
24.98
BPin
NC
15: 13C NMR (126 MHz, CDCl3)
δ (ppm)

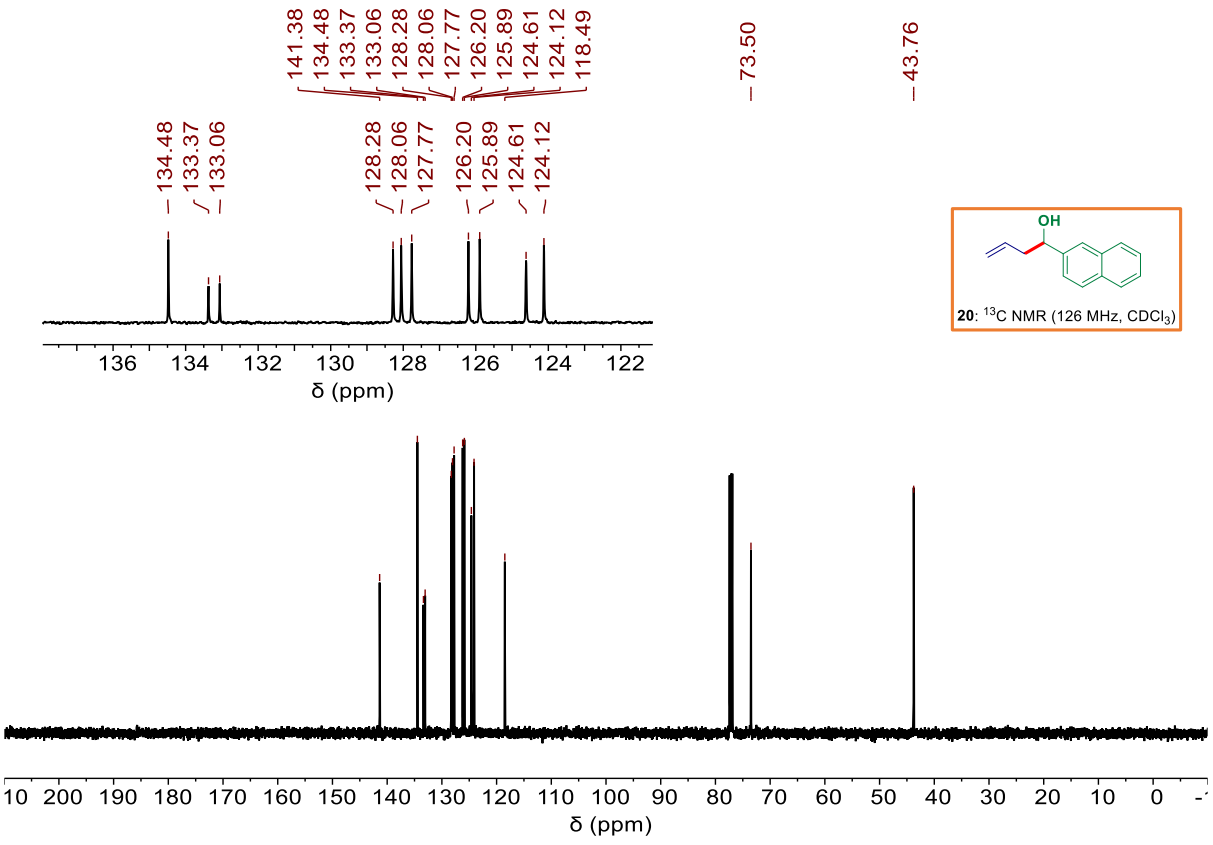

30.46
BPin
NC
15: 11B NMR (161 MHz, CDCl3)
300 260 220 180 140 100 60 20 -20 -60 -100 -140 -180
δ (ppm)


8.12 8.12 8.12 8.11 8.11 8.10 8.10 7.79 7.78 7.77 7.76 7.76 7.75 7.74 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.64 7.64 7.64 7.58 7.58 7.57 7.56 7.55 7.55 7.55 7.49 7.49 7.48 7.47 7.46 7.46 3.93
7.76 7.76 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.64 7.64 7.64 7.57 7.56 7.55 7.49 7.49 7.48 7.47 7.46 7.46
1.97 2.07 4.04 2.02 4.10
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
δ (ppm)
O
P
MeO2C
17: 1H NMR (500 MHz, CDCl3)
1.97 2.07 4.04 2.02 4.10 3.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)

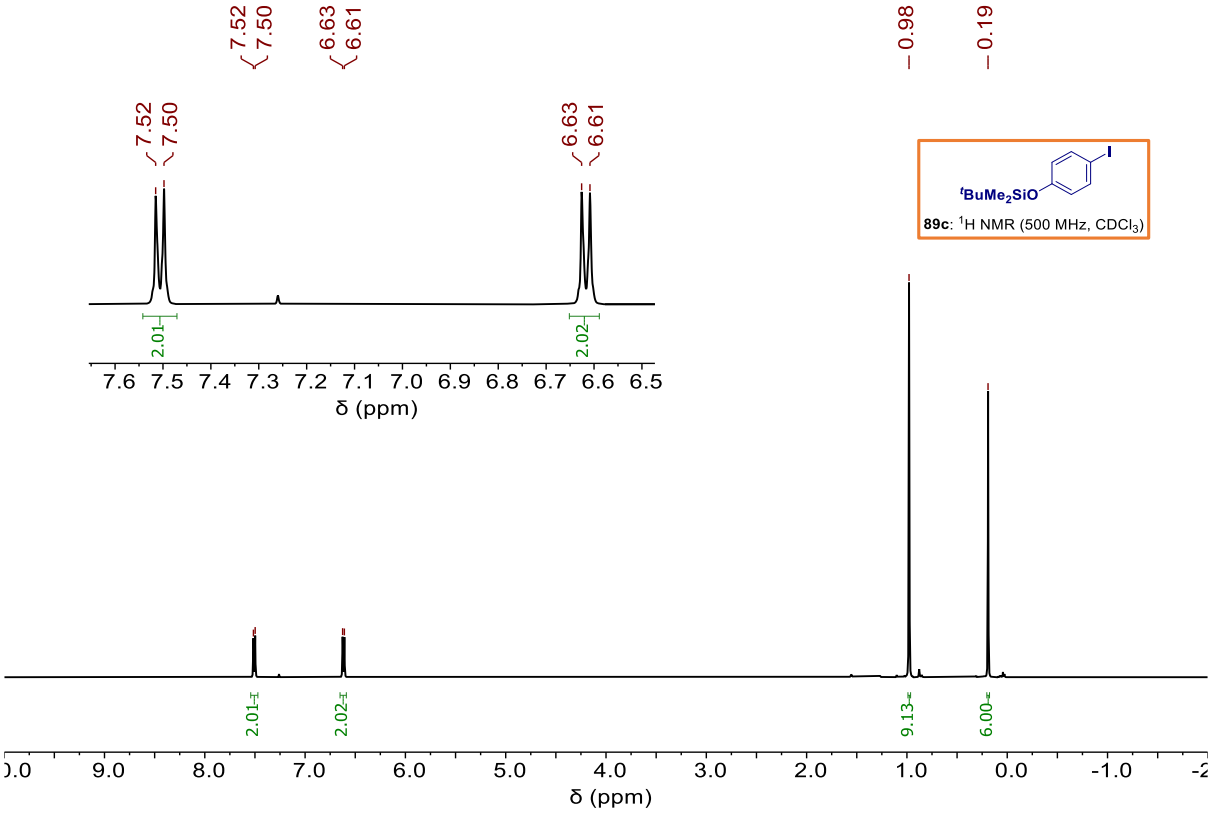

166.39
138.22
137.42
133.37
133.34
132.45
132.39
132.39
132.37
132.34
132.26
132.24
132.16
131.61
129.60
129.51
128.85
128.75
52.60
133.37
133.34
132.45
132.39
132.39
132.37
132.34
132.26
132.24
132.16
131.61
129.60
129.51
128.85
128.75
133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0
δ (ppm)
MeO2C
17: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

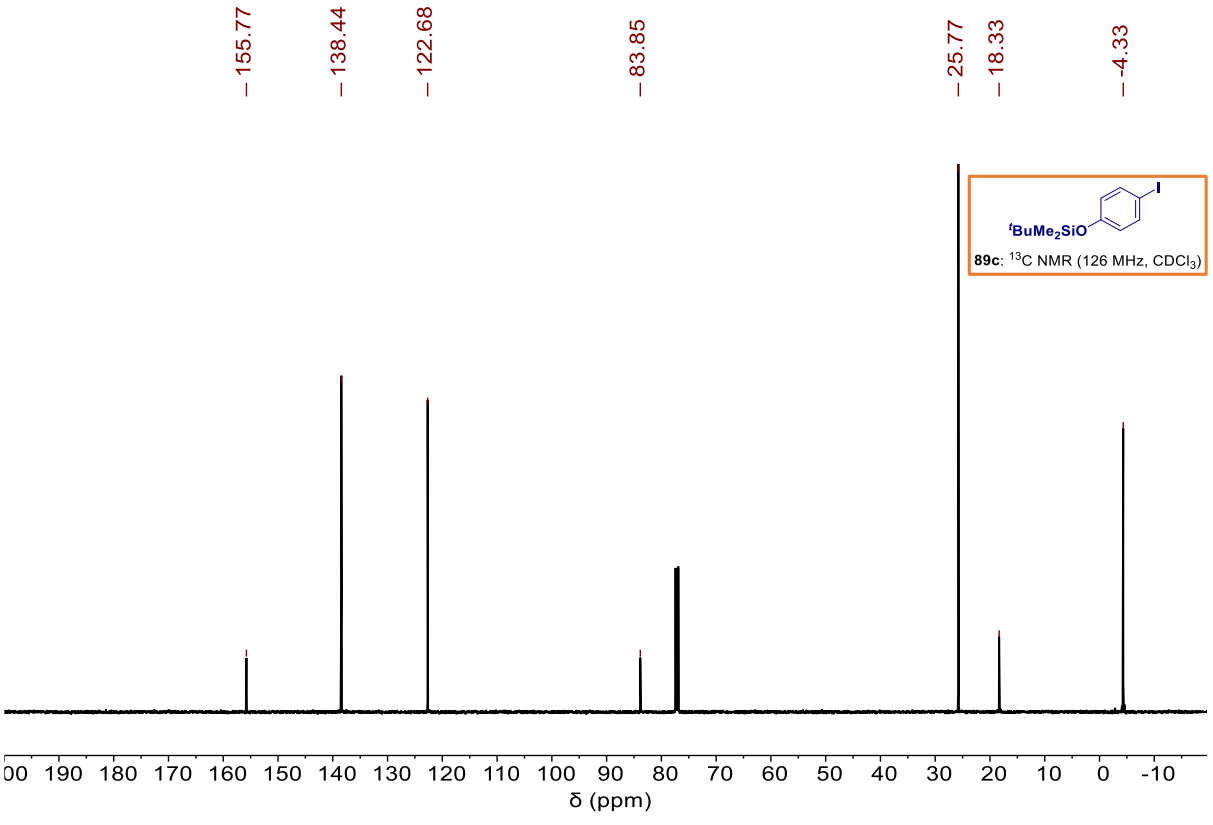

28.41
MeO2C
17: 31P NMR (203 MHz, CDCl3)
00 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
δ (ppm)

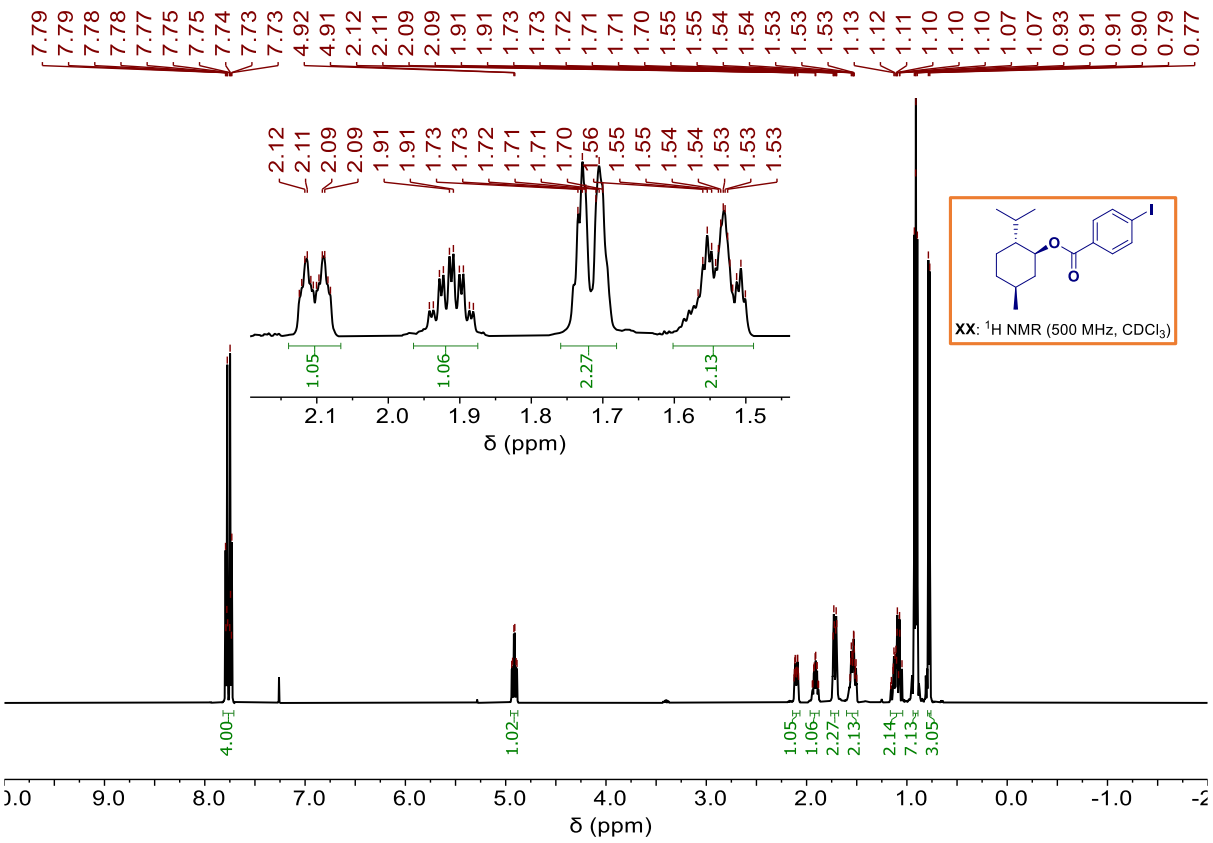

7.86 7.85 7.85 7.84 7.84 7.84 7.83 7.81 7.80 7.80 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.48 5.85 5.84 5.21 5.21 5.18 5.18 5.17 5.17 5.17 5.15 5.15 5.15 4.91 4.89 4.89 4.88 2.63 2.63 2.62 2.62 2.62 2.61 2.61 2.61 2.61 2.59 2.40
5.87 5.85 5.84 5.83 5.82 5.81 5.22 5.21 5.21 5.21 5.18 5.18 5.18 5.17 5.17 5.17 5.17 5.16 5.15 5.15 5.15 5.15 4.91 4.89 4.89 4.88
0.96 2.04 1.00
6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7
δ (ppm)
OH
20: 1H NMR (500 MHz, CDCl3)
3.00 1.00 2.98 0.96 2.04 1.00 2.10 0.95
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

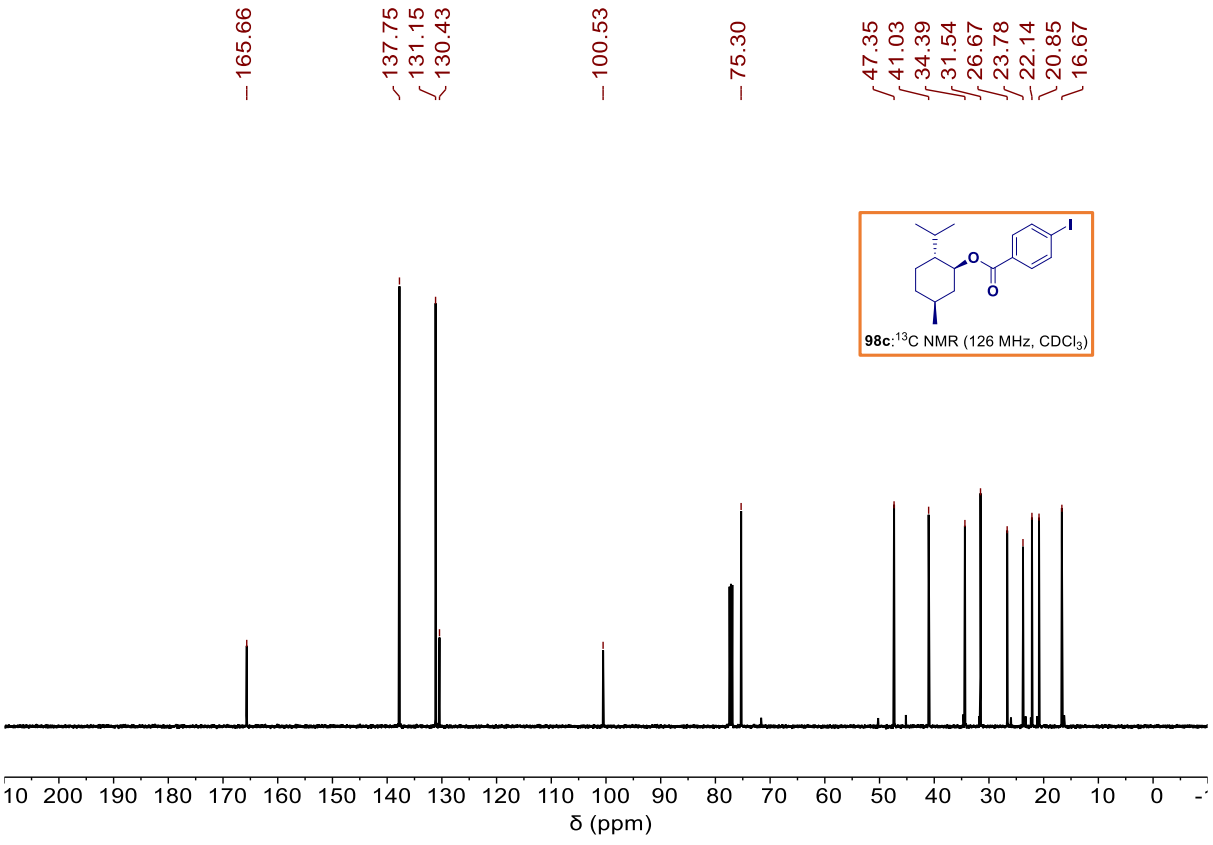

141.38 134.48 133.37 133.06 128.28 128.06 127.77 126.20 125.89 124.61 124.12 118.49
73.50
43.76
134.48 133.37 133.06 128.28 128.06 127.77 126.20 125.89 124.61 124.12
136 134 132 130 128 126 124 122
δ (ppm)
OH
20: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

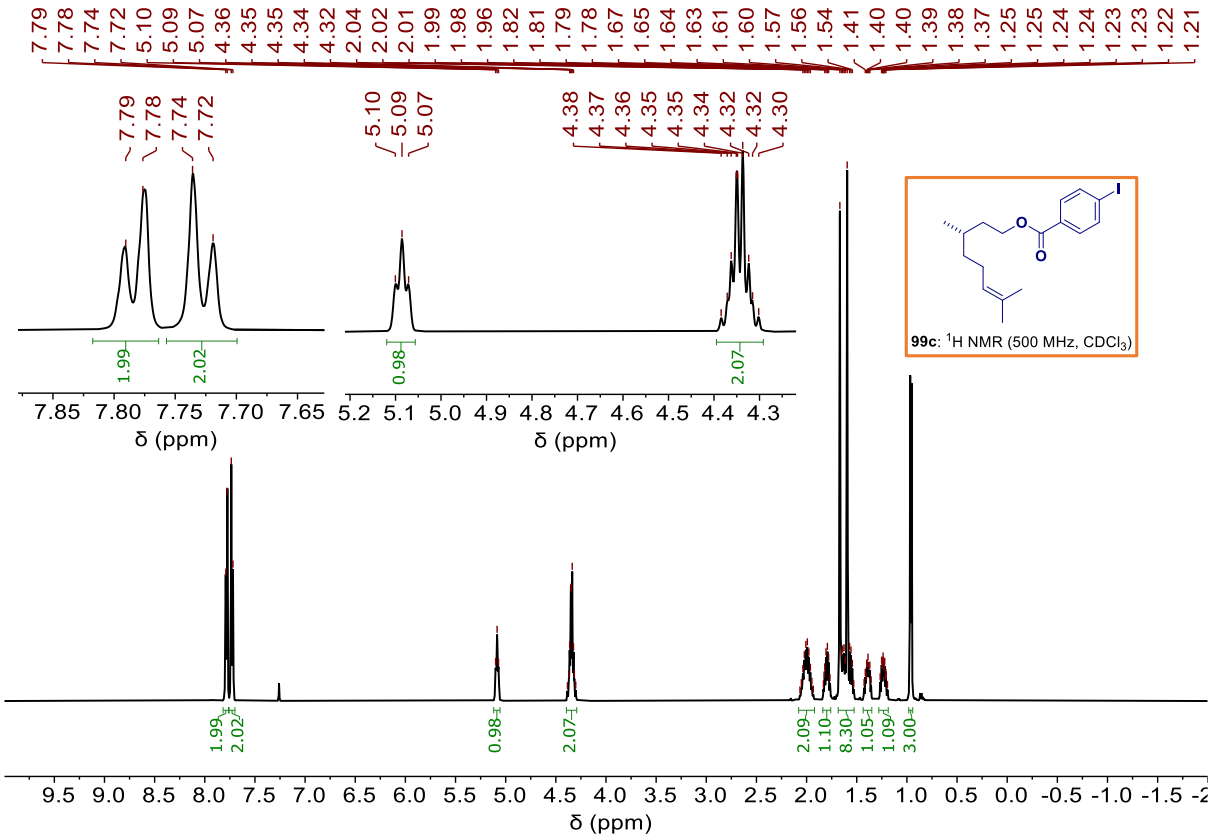
NMR Copies for Iodo derivatives of Bioactive Molecules

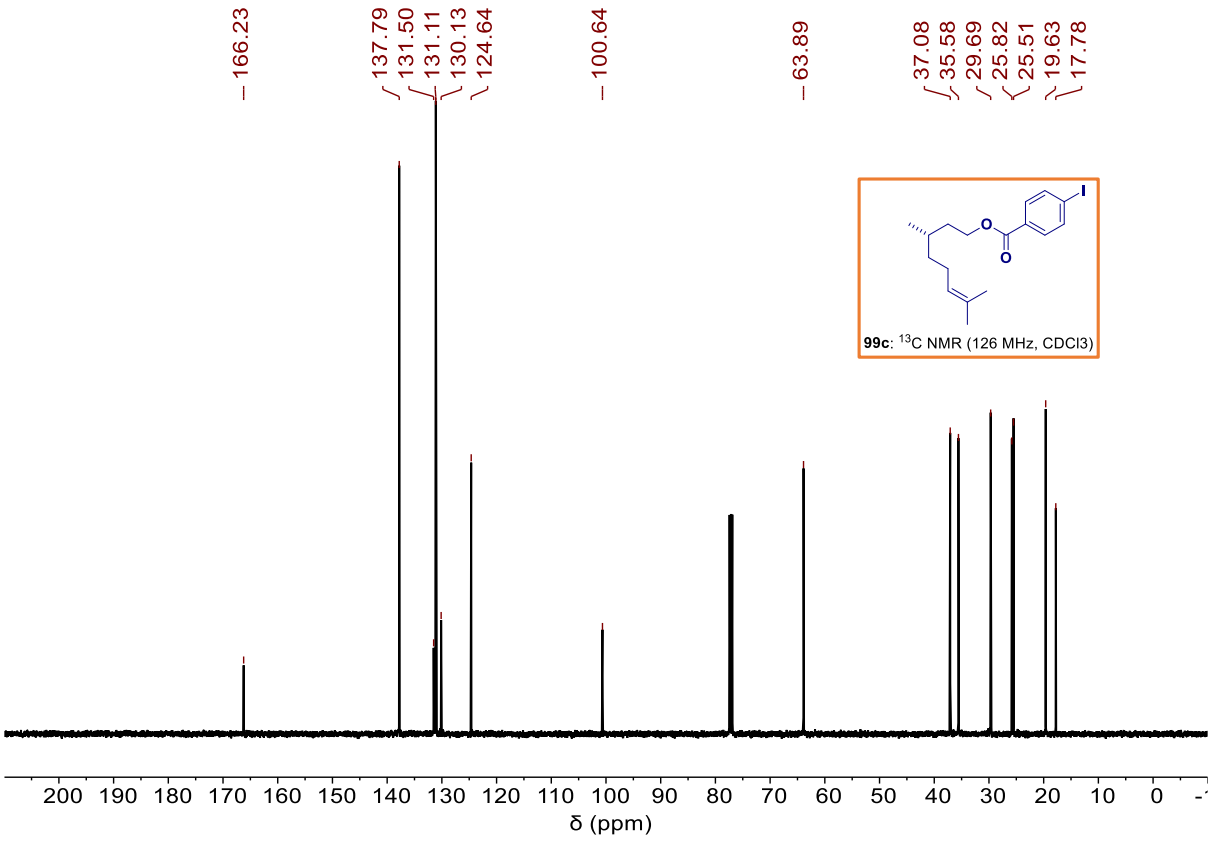


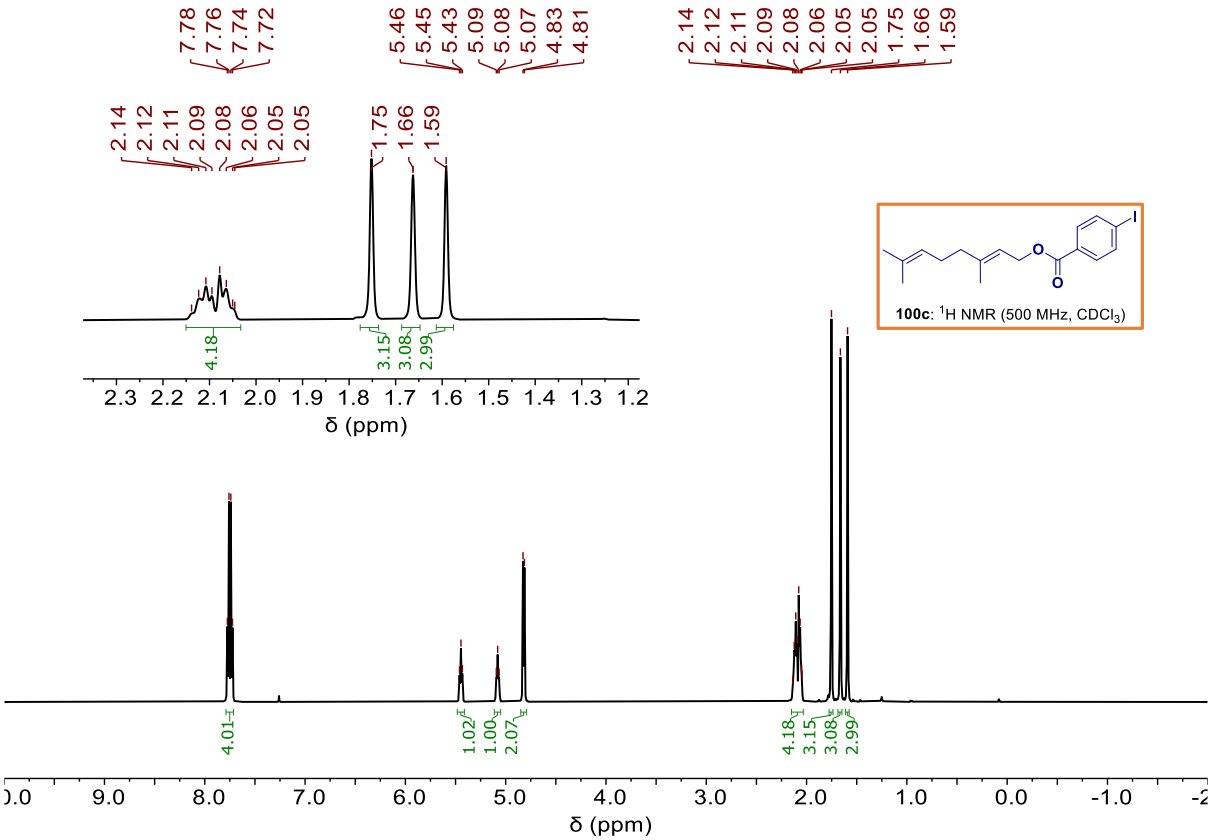


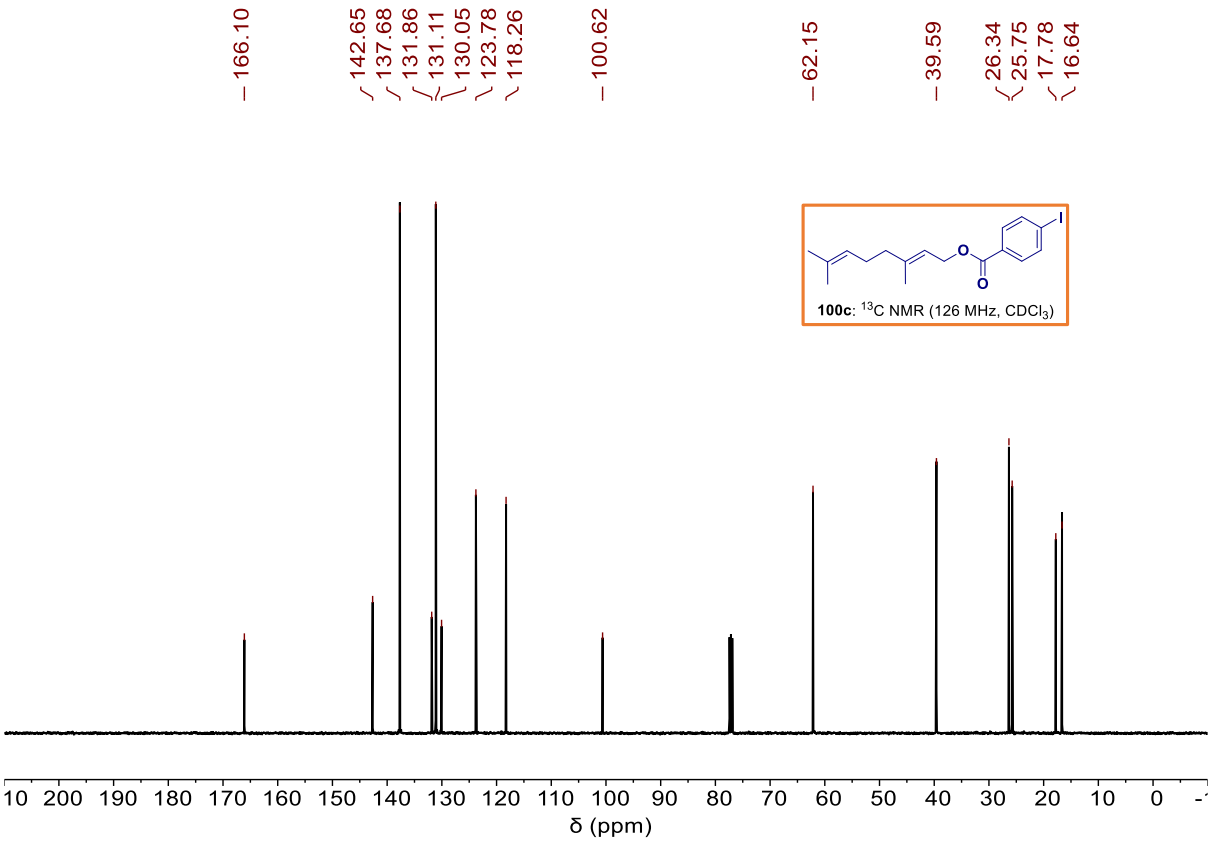

7.79 7.79 7.78 7.78 7.77 7.75 7.75 7.74 7.73 7.73 4.92 4.91 2.12 2.11 2.09 2.09 1.91 1.91 1.73 1.73 1.72 1.71 1.71 1.70 1.55 1.55 1.54 1.54 1.53 1.53 1.53 1.13 1.12 1.11 1.10 1.10 1.10 1.07 1.07 0.93 0.91 0.91 0.90 0.79 0.77
2.12 2.11 2.09 2.09 1.91 1.91 1.73 1.73 1.72 1.71 1.71 1.70 1.56 1.55 1.55 1.54 1.54 1.53 1.53 1.53
1.05 1.06 2.27 2.13
2.1 2.0 1.9 1.8 1.7 1.6 1.5
δ (ppm)
XX: ^{1}H NMR (500 MHz, CDCl$_3$)
4.00 1.02 1.05 1.06 2.27 2.13 2.14 7.13 3.05
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)


165.66
137.75 131.15 130.43
100.53
75.30
47.35 41.03 34.39 31.54 26.67 23.78 22.14 20.85 16.67
98c: ^{13}C NMR (126 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

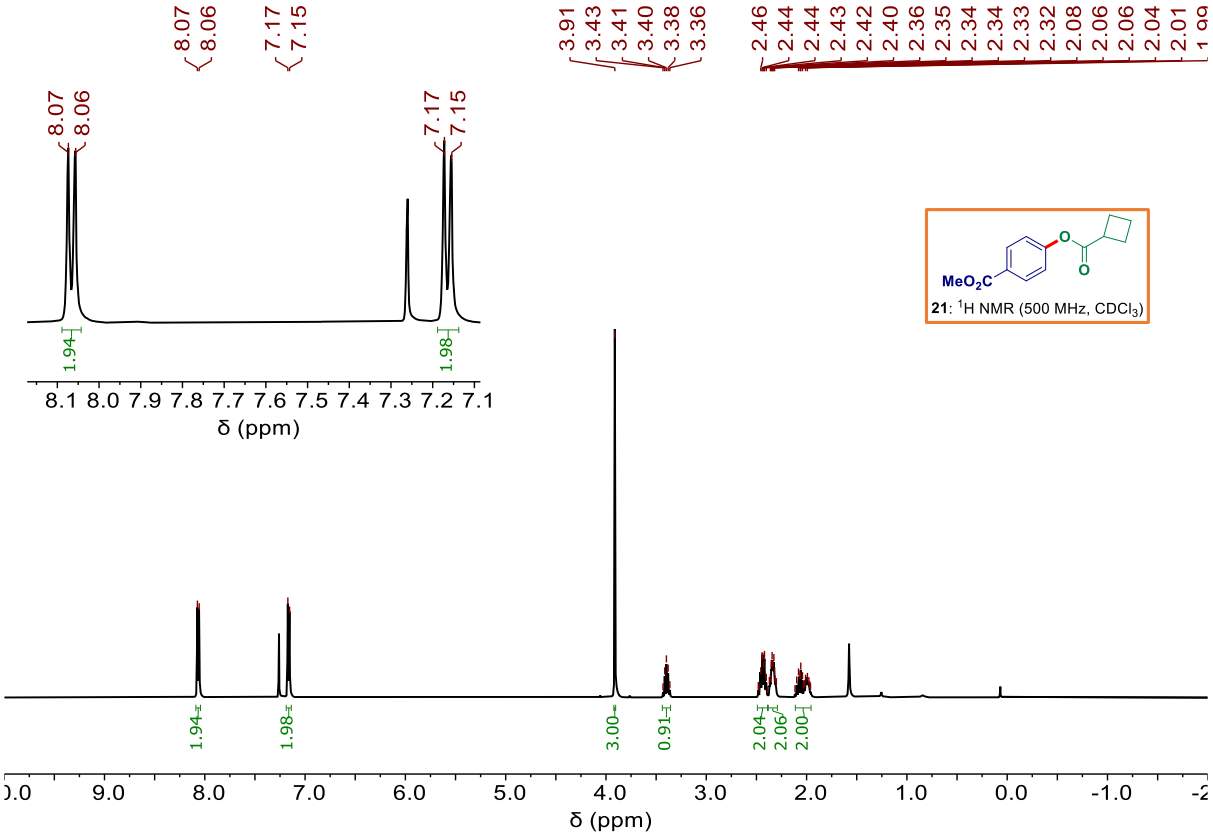

7.79 7.78 7.74 7.72 5.10 5.09 5.07 4.36 4.35 4.35 4.34 4.32 2.04 2.02 2.01 1.99 1.98 1.96 1.82 1.81 1.79 1.78 1.67 1.65 1.64 1.63 1.61 1.60 1.57 1.56 1.54 1.41 1.40 1.40 1.39 1.38 1.37 1.25 1.25 1.24 1.24 1.23 1.23 1.22 1.21
δ (ppm)
99c: 1H NMR (500 MHz, CDCl3)

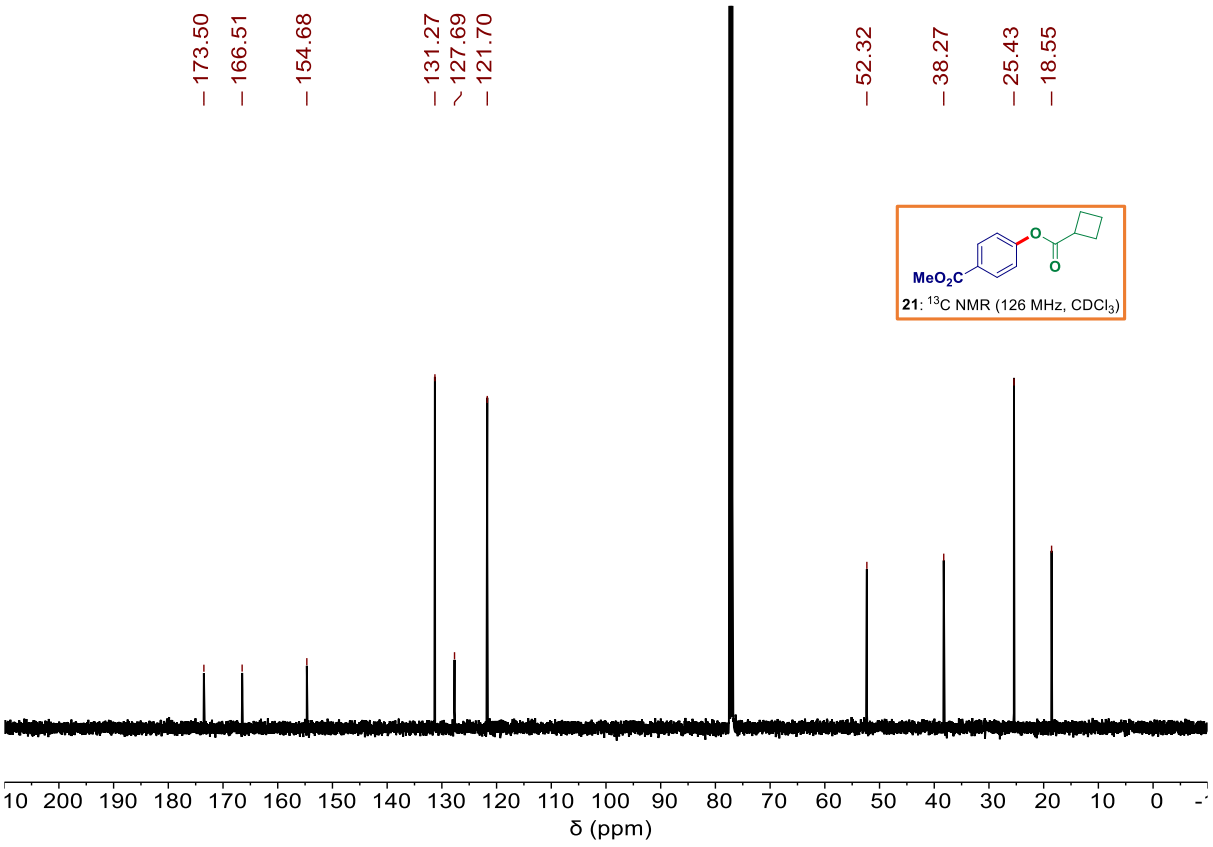

166.23 137.79 131.50 131.11 130.13 124.64 100.64 63.89 37.08 35.58 29.69 25.82 25.51 19.63 17.78
δ (ppm)
99c: 13C NMR (126 MHz, CDCl3)

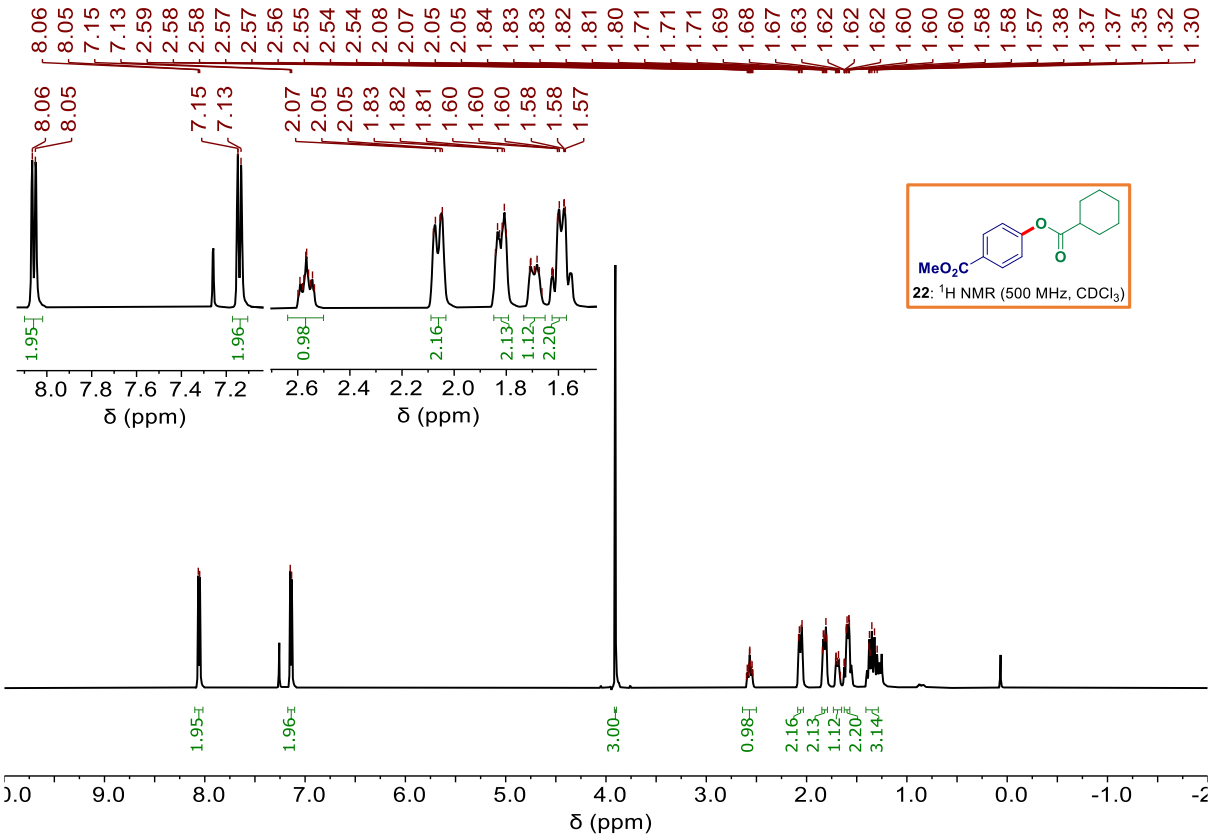

7.78
7.76
7.74
7.72
5.46
5.45
5.43
5.09
5.08
5.07
4.83
4.81
2.14
2.12
2.11
2.09
2.08
2.06
2.05
2.05
1.75
1.66
1.59
4.18
3.15
3.08
2.99
δ (ppm)
4.01
1.02
1.00
2.07
4.18
3.15
3.08
2.99
δ (ppm)
100c: 1H NMR (500 MHz, CDCl3)

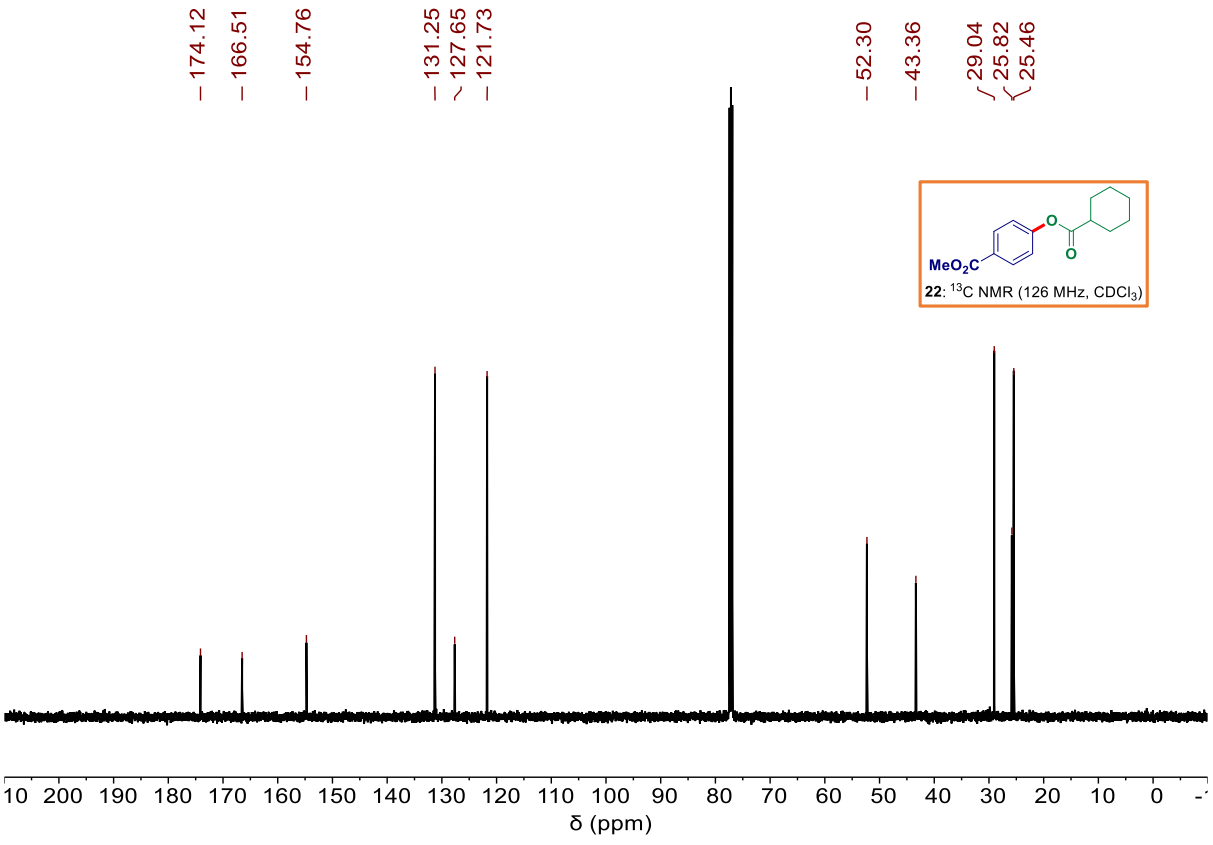

166.10
142.65
137.68
131.86
131.11
130.05
123.78
118.26
100.62
62.15
39.59
26.34
25.75
17.78
16.64
δ (ppm)
100c: 13C NMR (126 MHz, CDCl3)

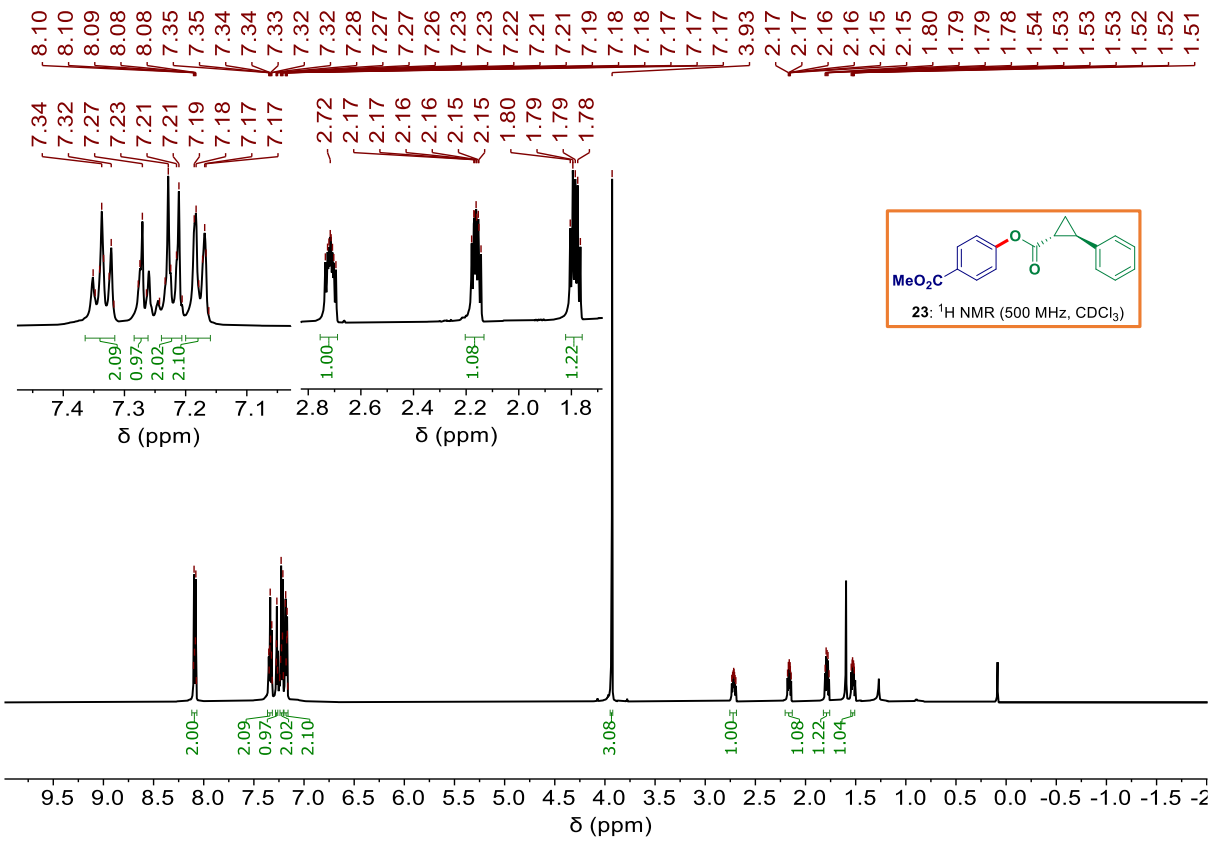
NMR Copies for Ester Substrate Scopes

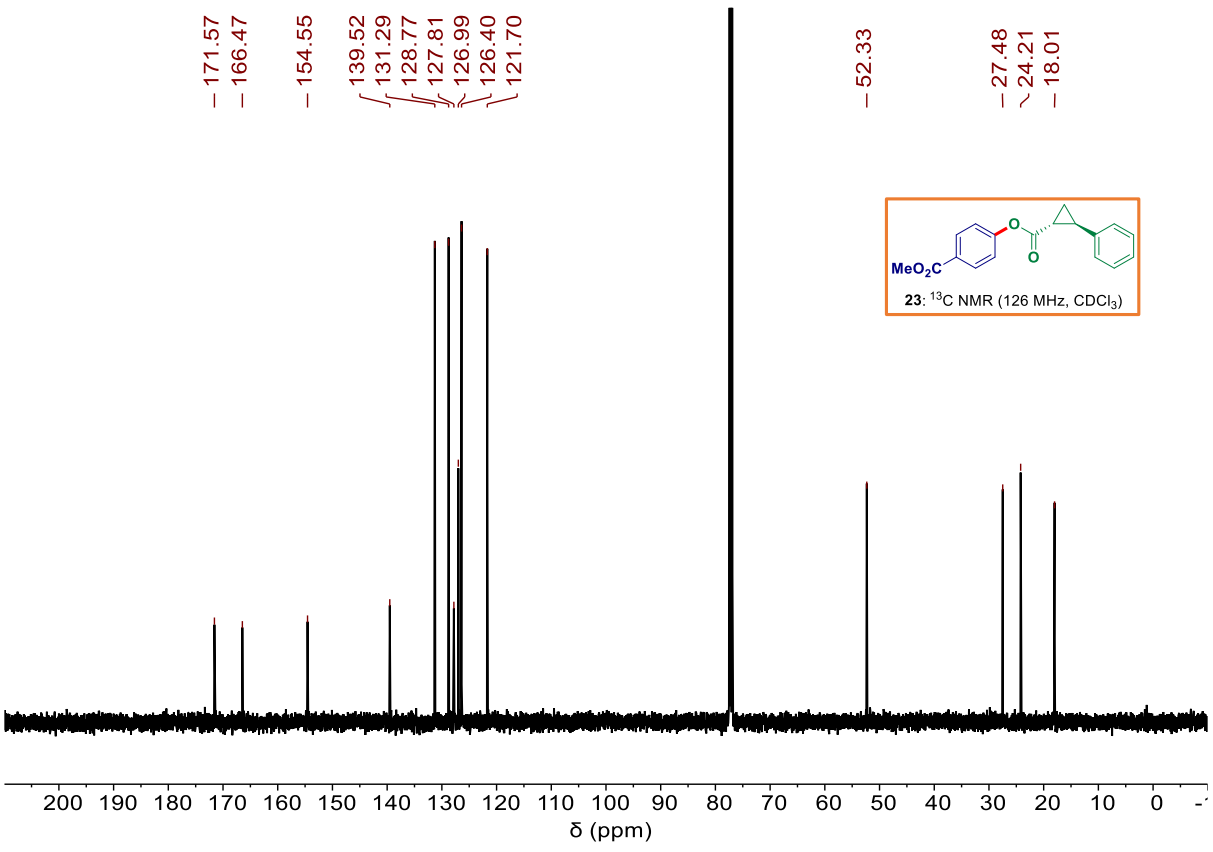


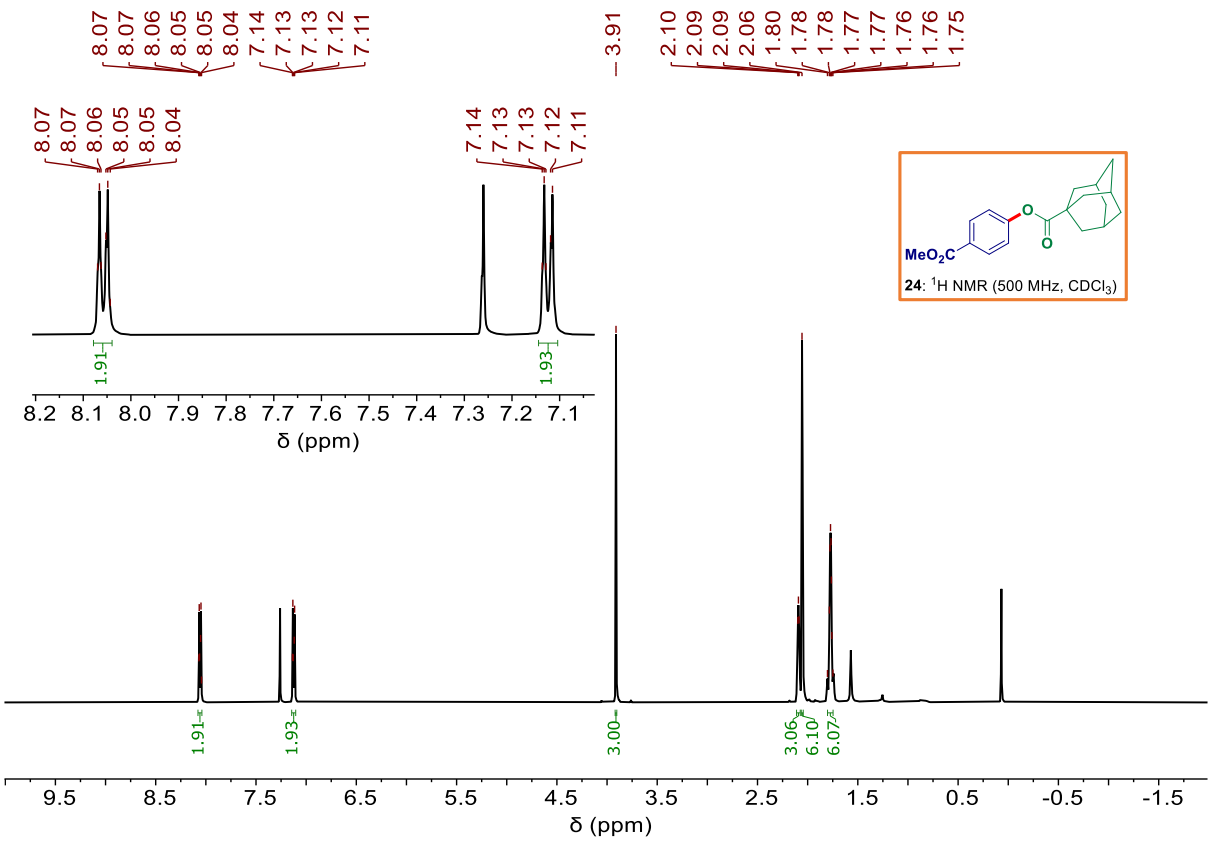


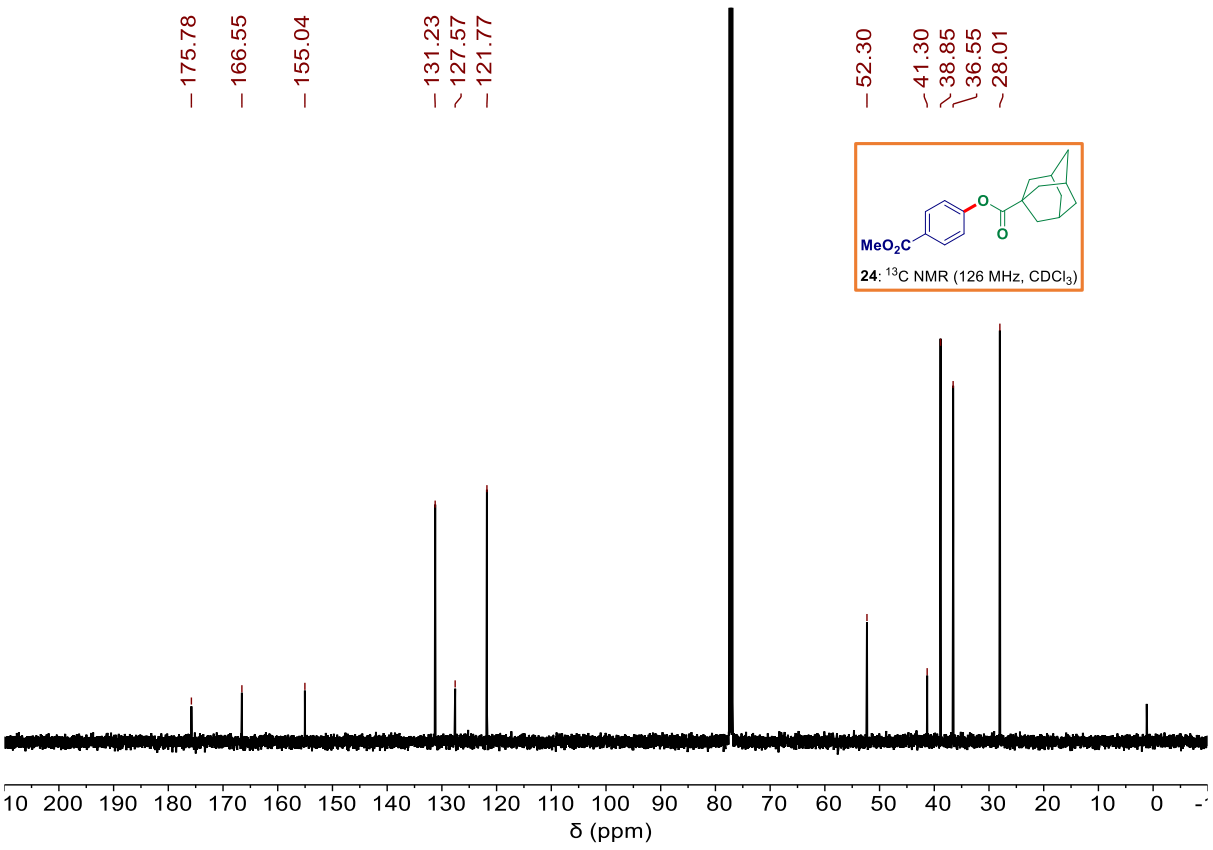

8.06 8.05 7.15 7.13 2.59 2.58 2.58 2.57 2.57 2.56 2.55 2.54 2.54 2.08 2.07 2.05 2.05 1.84 1.83 1.83 1.82 1.81 1.80 1.71 1.71 1.71 1.69 1.68 1.67 1.63 1.62 1.62 1.62 1.60 1.60 1.60 1.58 1.58 1.57 1.38 1.37 1.37 1.35 1.32 1.30
δ (ppm)
MeO2C
22: 1H NMR (500 MHz, CDCl3)

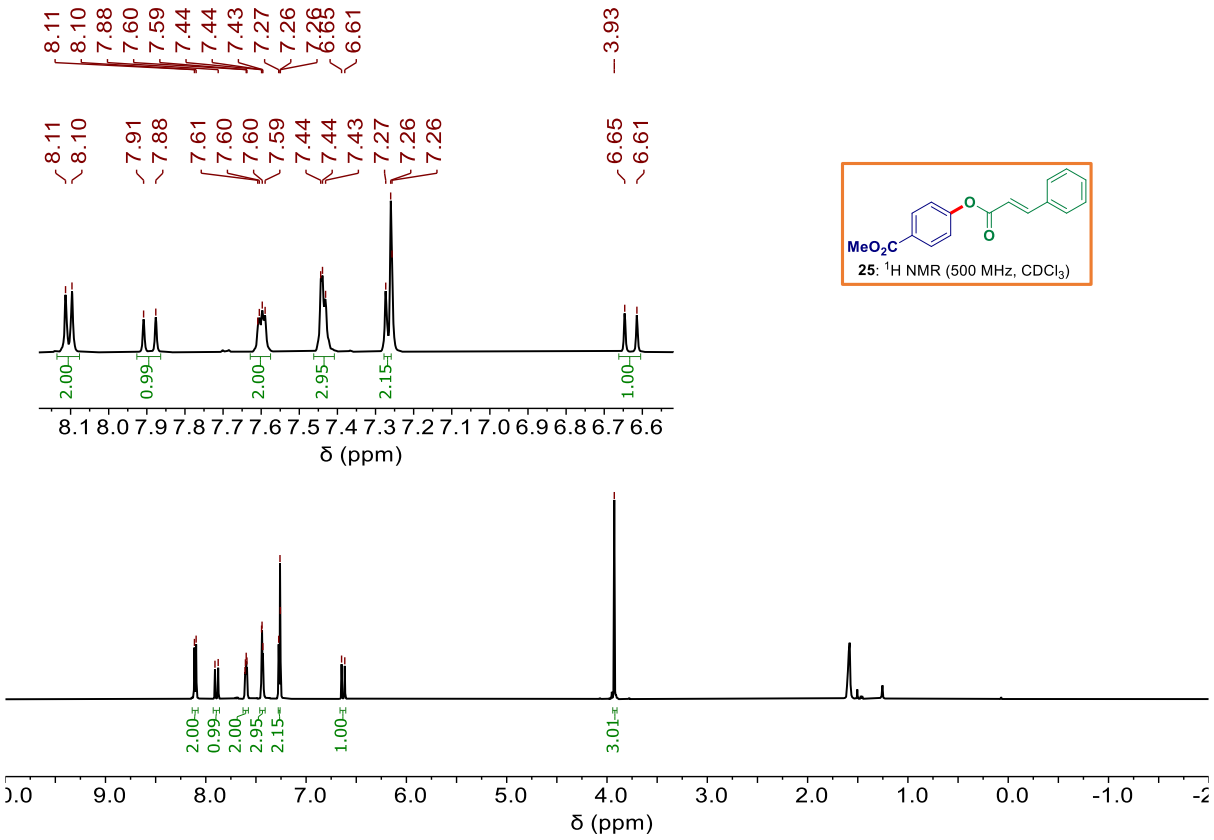

174.12 166.51 154.76 131.25 127.65 121.73 52.30 43.36 29.04 25.82 25.46
δ (ppm)
MeO2C
22: 13C NMR (126 MHz, CDCl3)

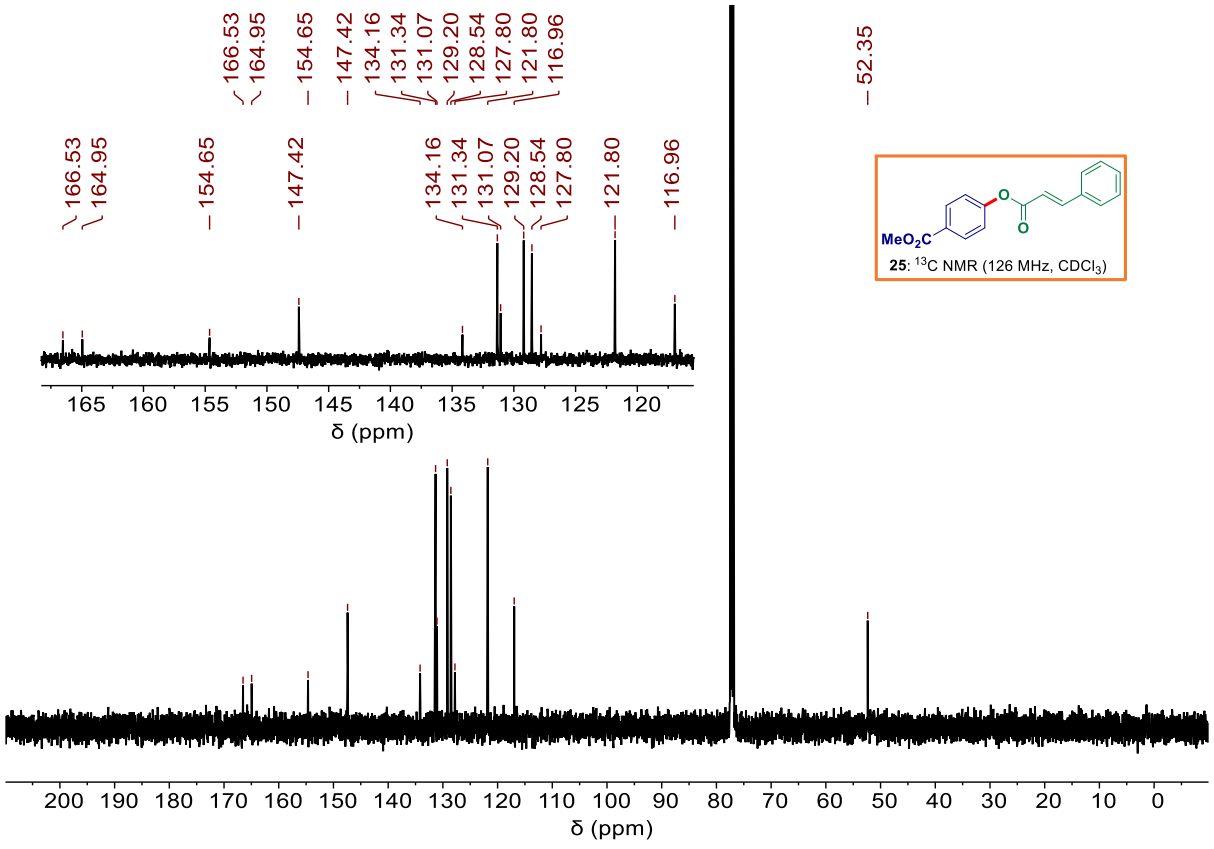

δ (ppm)
23: ^{1}H NMR (500 MHz, $CDCl_3$)

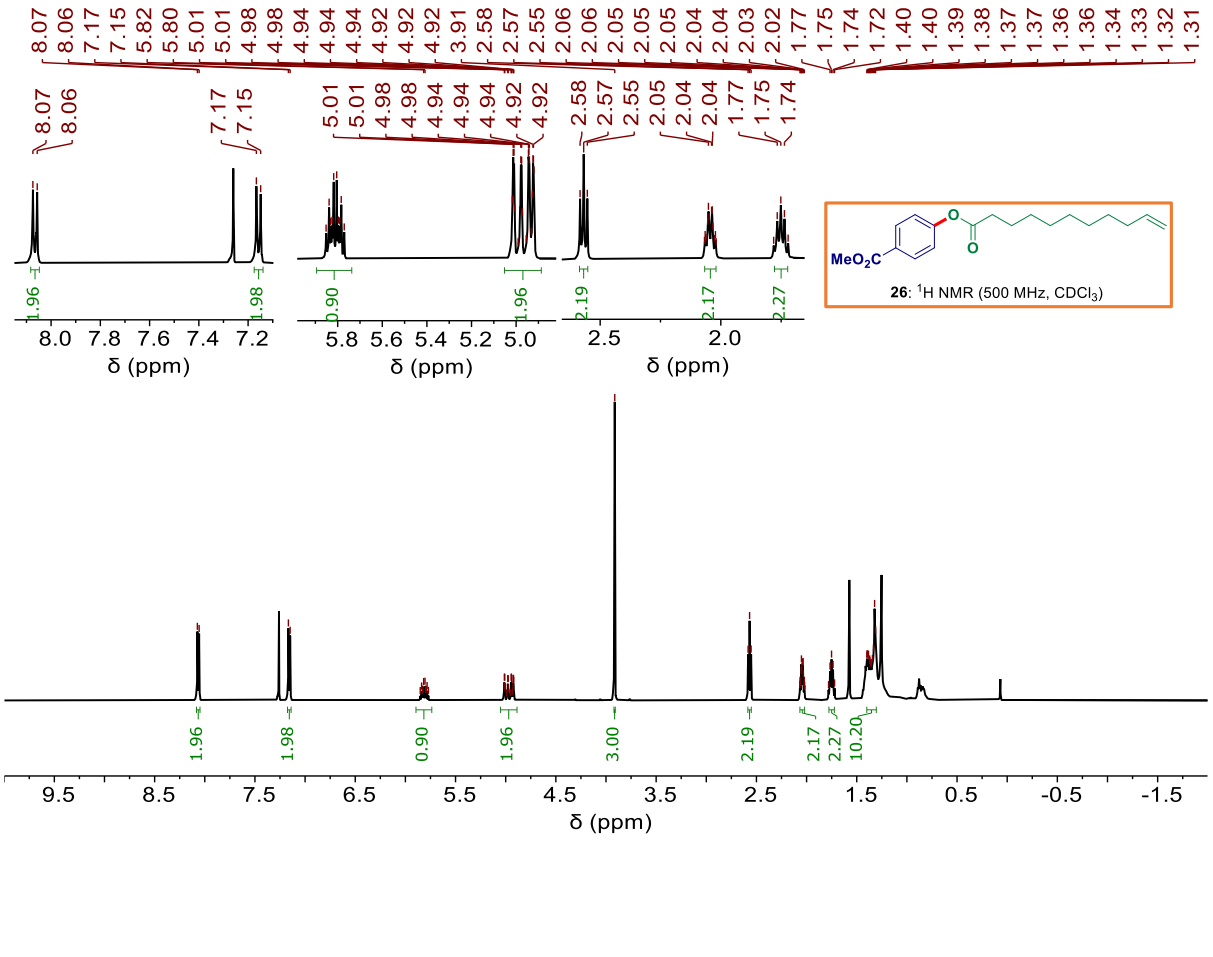

δ (ppm)
23: ^{13}C NMR (126 MHz, $CDCl_3$)

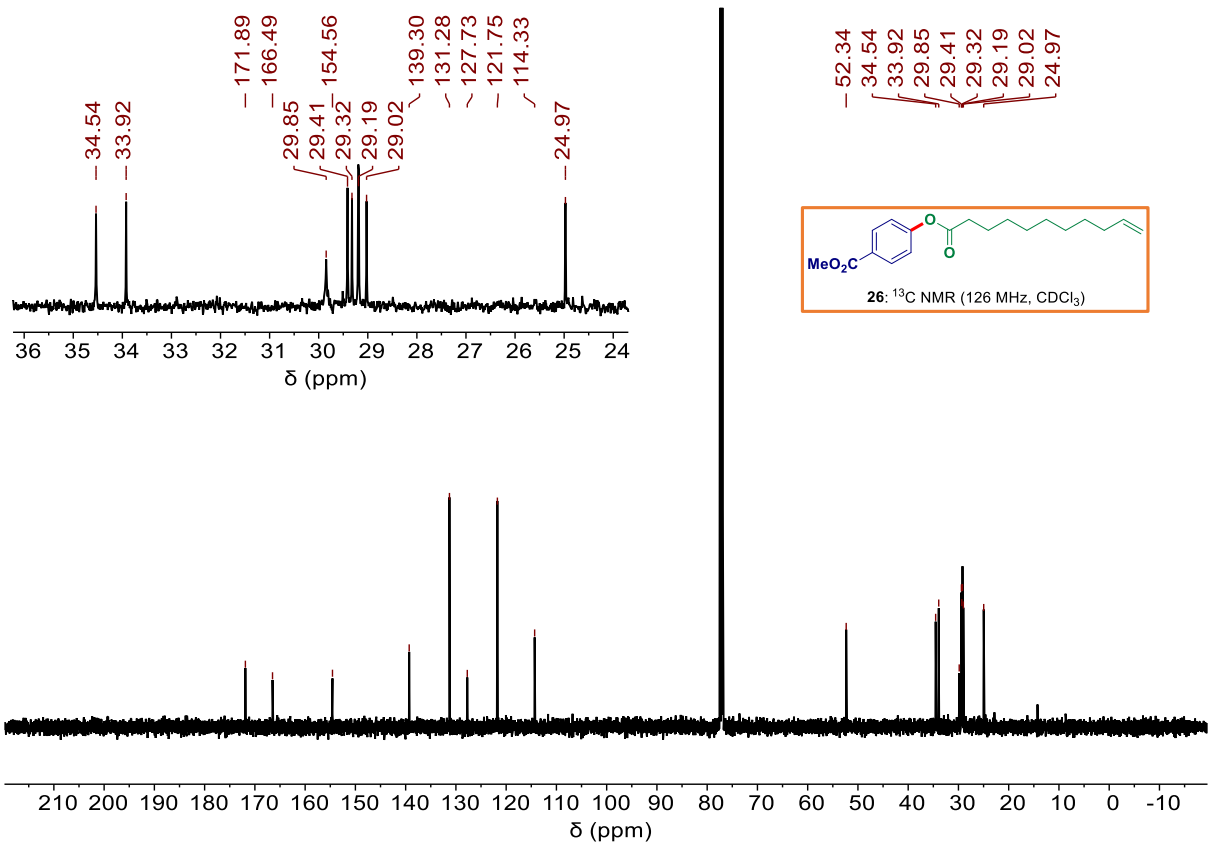

8.07
8.07
8.06
8.05
8.05
8.04
7.14
7.13
7.13
7.12
7.11
3.91
2.10
2.09
2.09
2.06
1.80
1.78
1.78
1.77
1.77
1.76
1.76
1.75
1.91
1.93
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
δ (ppm)
MeO2C
O
O
24: 1H NMR (500 MHz, CDCl3)
1.91
1.93
3.00
3.06
6.10
6.07
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)

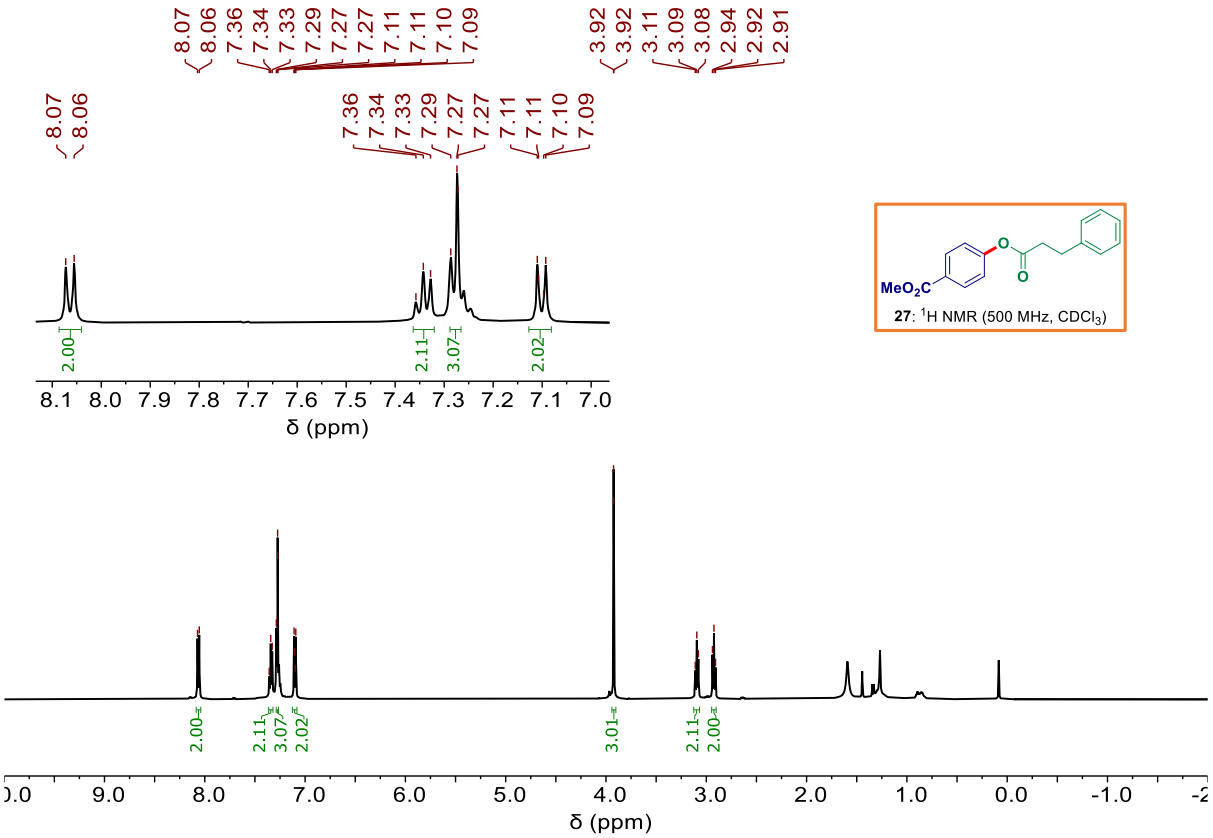

175.78
166.55
155.04
131.23
127.57
121.77
52.30
41.30
38.85
36.55
28.01
MeO2C
O
O
24: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

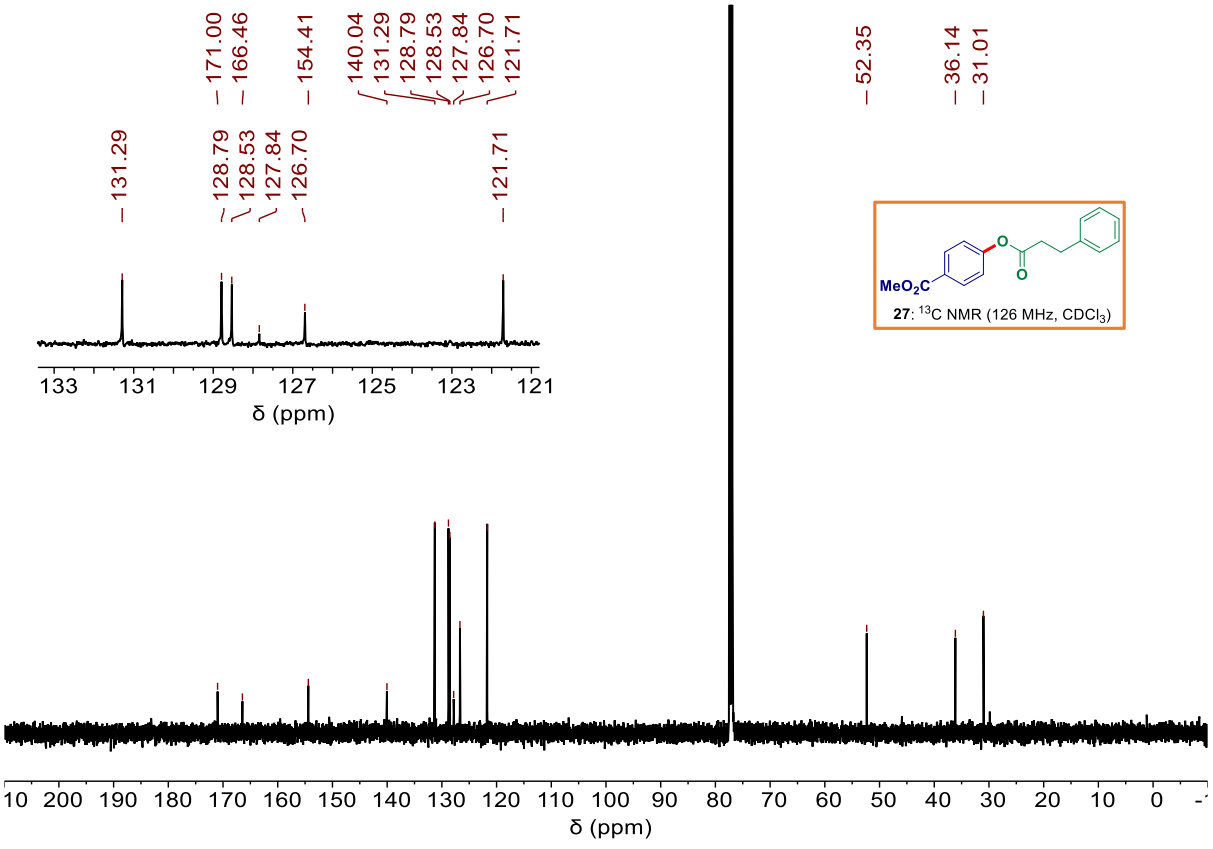

8.11
8.10
7.88
7.60
7.59
7.44
7.44
7.43
7.27
7.26
6.65
6.61
3.93
7.91
7.61
7.60
7.60
7.59
7.44
7.44
7.43
7.27
7.26
7.26
6.65
6.61
2.00
0.99
2.00
2.95
2.15
1.00
δ (ppm)
MeO2C
25: 1H NMR (500 MHz, CDCl3)
3.01
δ (ppm)

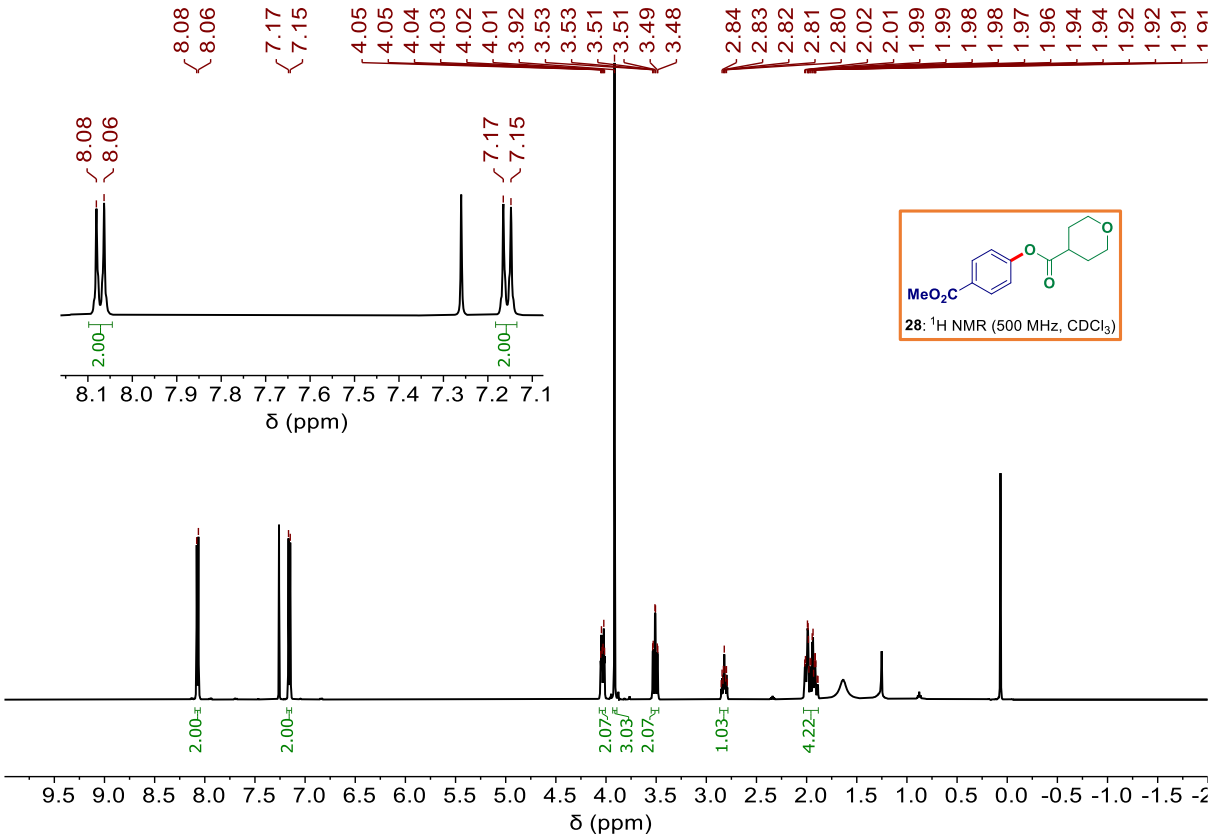

166.53
164.95
154.65
147.42
134.16
131.34
131.07
129.20
128.54
127.80
121.80
116.96
52.35
δ (ppm)
MeO2C
25: 13C NMR (126 MHz, CDCl3)
δ (ppm)

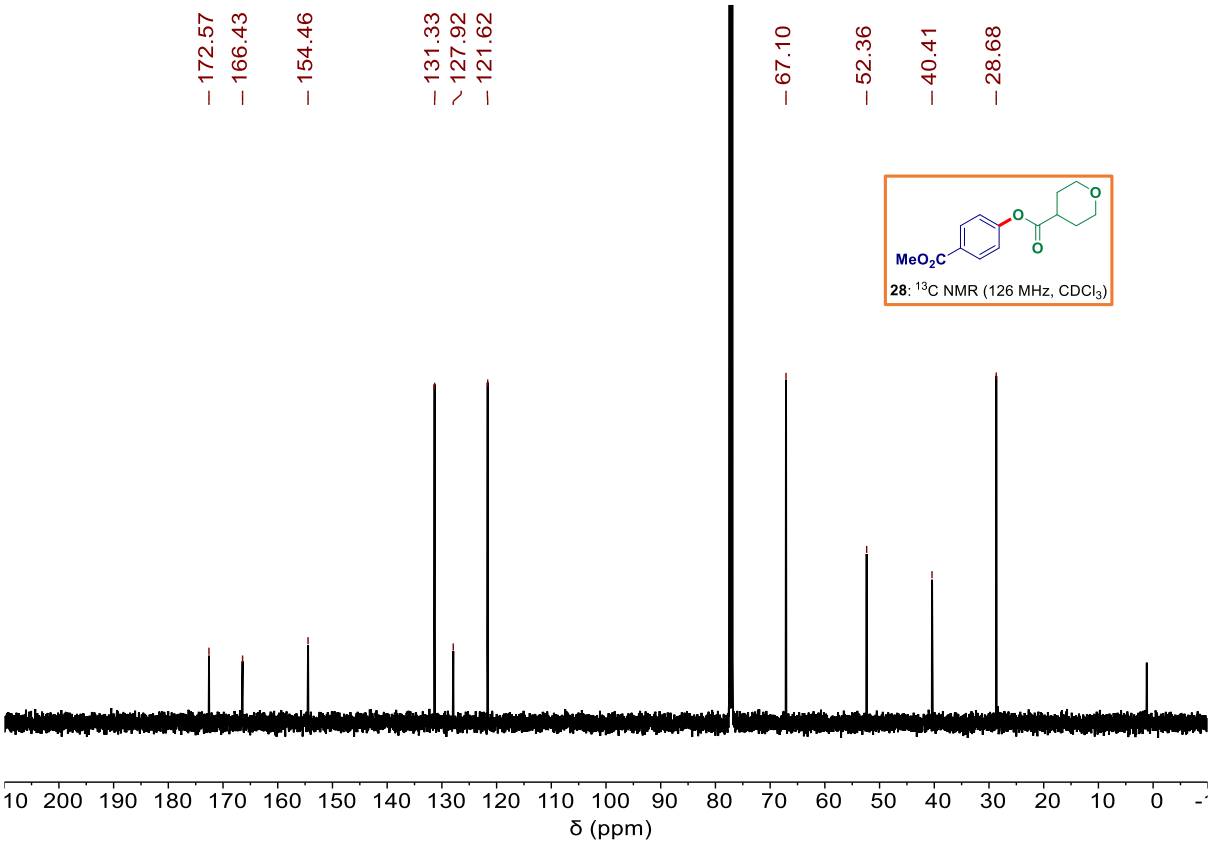

8.07 8.06 7.17 7.15 5.82 5.80 5.01 5.01 4.98 4.98 4.94 4.94 4.94 4.92 4.92 4.92 3.91 2.58 2.57 2.55 2.06 2.06 2.05 2.05 2.05 2.04 2.04 2.03 2.02 1.77 1.75 1.74 1.72 1.40 1.40 1.39 1.38 1.37 1.37 1.36 1.36 1.34 1.33 1.32 1.31
1.96 1.98 0.90 1.96 2.19 2.17 2.27 10.20 3.00
δ (ppm)
MeO2C
26: 1H NMR (500 MHz, CDCl3)

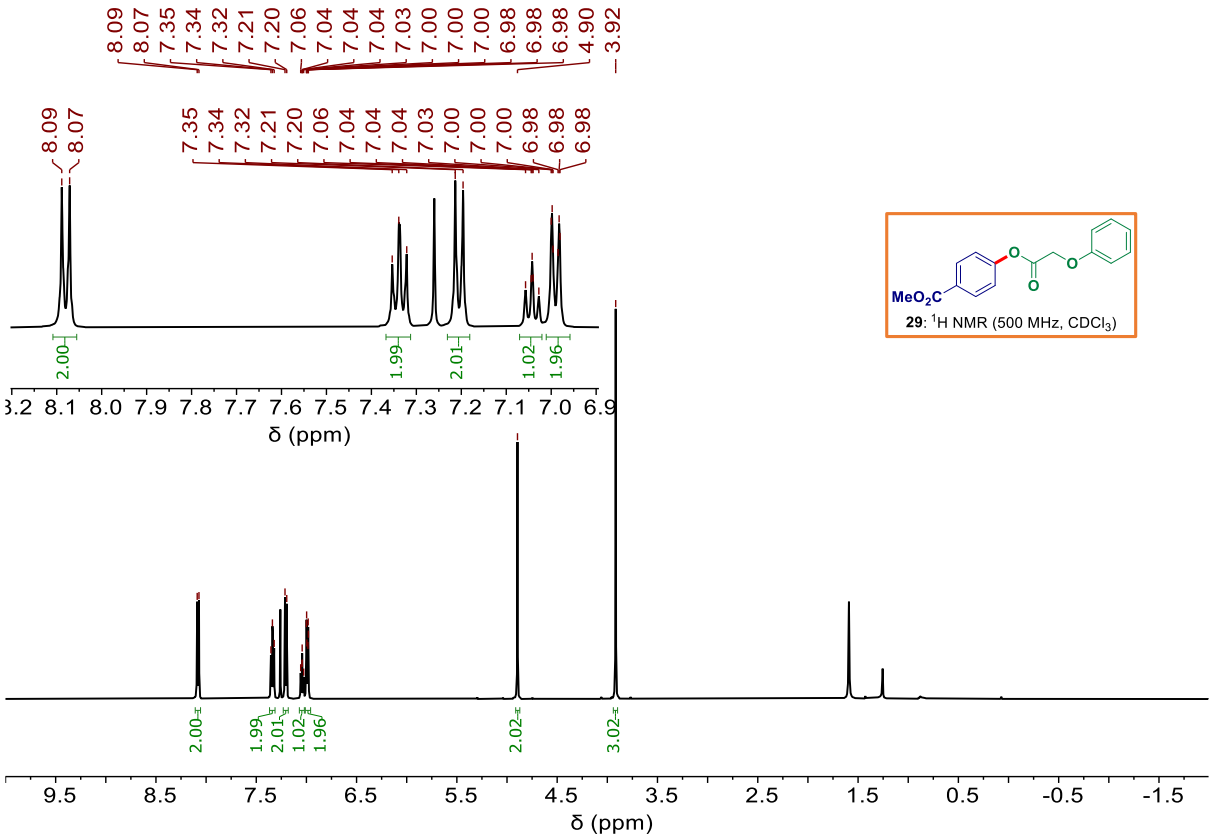

171.89 166.49 154.56 139.30 131.28 127.73 121.75 114.33 52.34 34.54 33.92 29.85 29.41 29.32 29.19 29.02 24.97
δ (ppm)
MeO2C
26: 13C NMR (126 MHz, CDCl3)

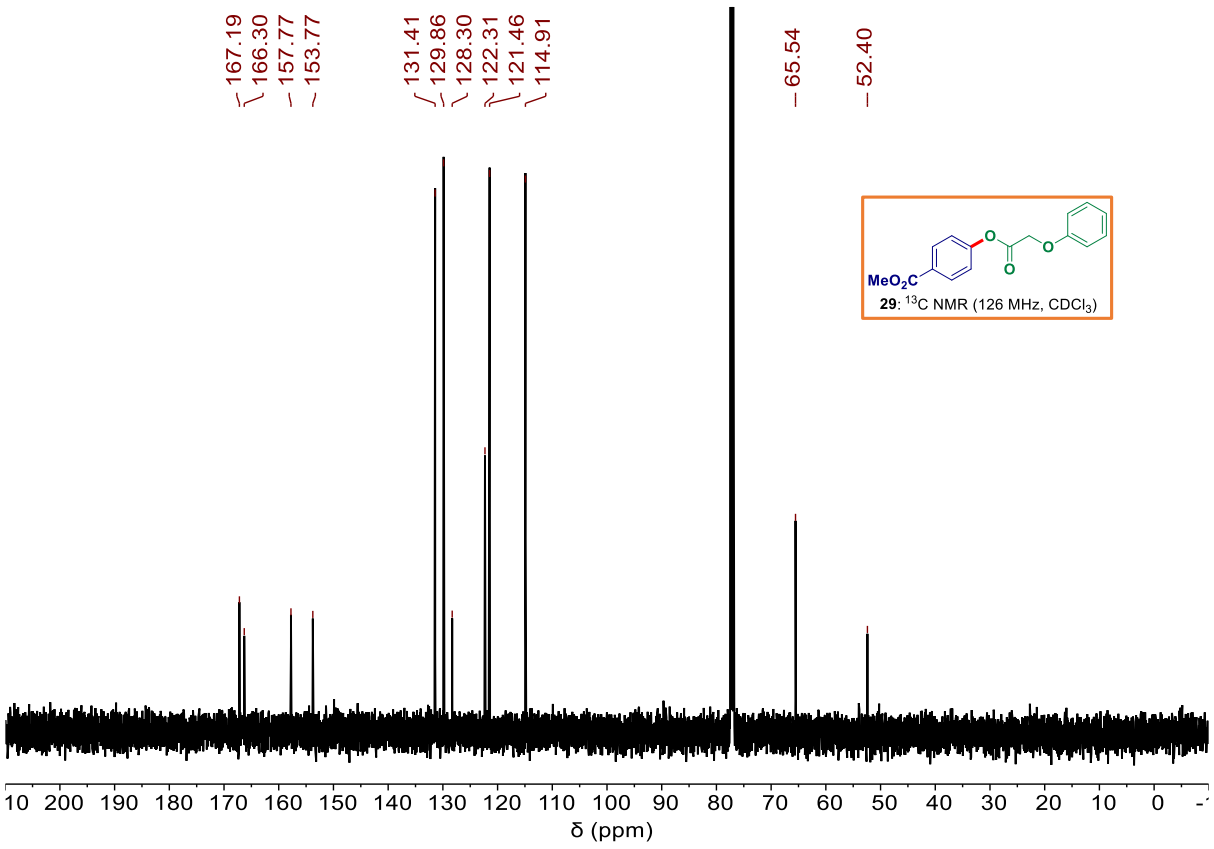

8.07
8.06
7.36
7.34
7.33
7.29
7.27
7.27
7.11
7.11
7.10
7.09
3.92
3.92
3.11
3.09
3.08
2.94
2.92
2.91
2.00
2.11
3.07
2.02
δ (ppm)
MeO2C
O
O
27: 1H NMR (500 MHz, CDCl3)
2.00
2.11
3.07
2.02
3.01
2.11
2.00
δ (ppm)

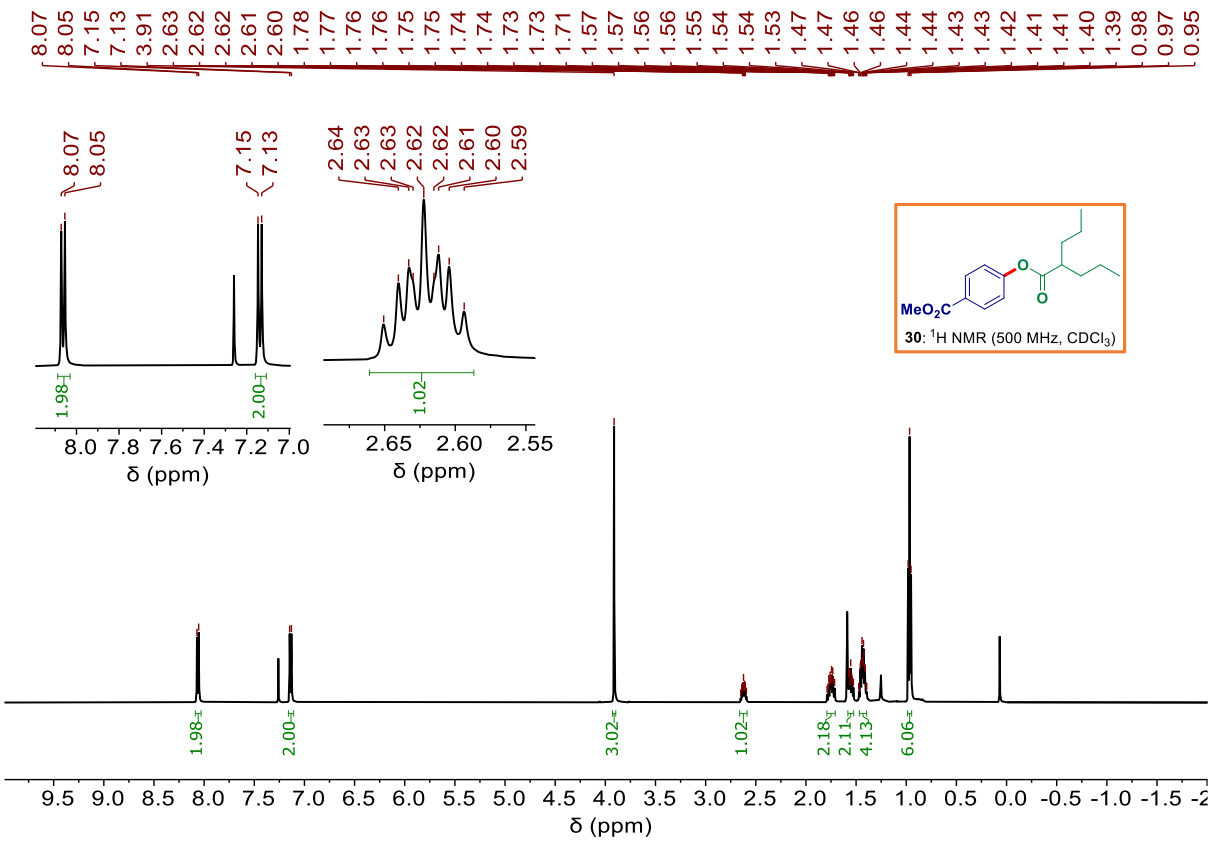

171.00
166.46
154.41
140.04
131.29
128.79
128.53
127.84
126.70
121.71
52.35
36.14
31.01
131.29
128.79
128.53
127.84
126.70
121.71
δ (ppm)
MeO2C
O
O
27: 13C NMR (126 MHz, CDCl3)
δ (ppm)

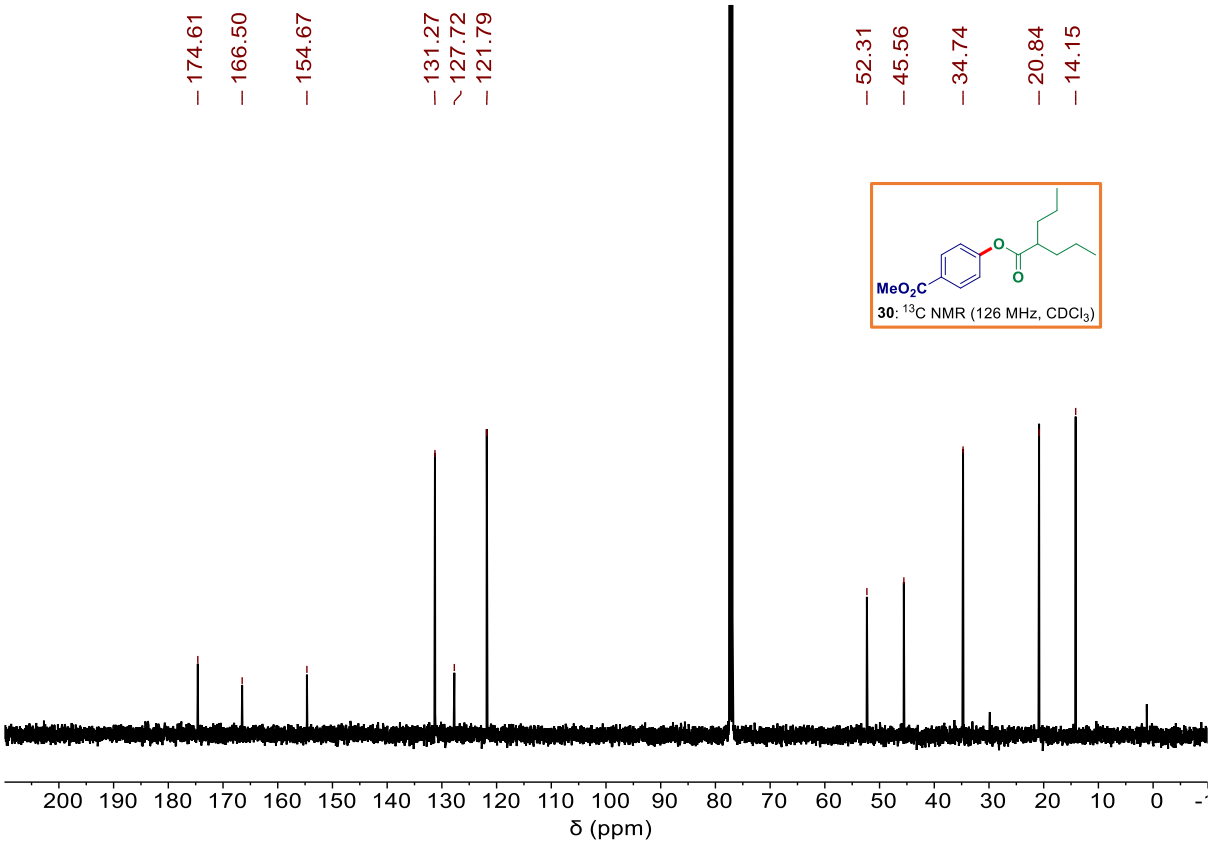

8.08
8.06
7.17
7.15
4.05
4.04
4.03
4.02
4.01
3.92
3.53
3.51
3.49
3.48
2.84
2.83
2.82
2.81
2.80
2.02
2.01
1.99
1.98
1.97
1.96
1.94
1.92
1.91
2.00
2.07
3.03
1.03
4.22
δ (ppm)
MeO2C
28: 1H NMR (500 MHz, CDCl3)

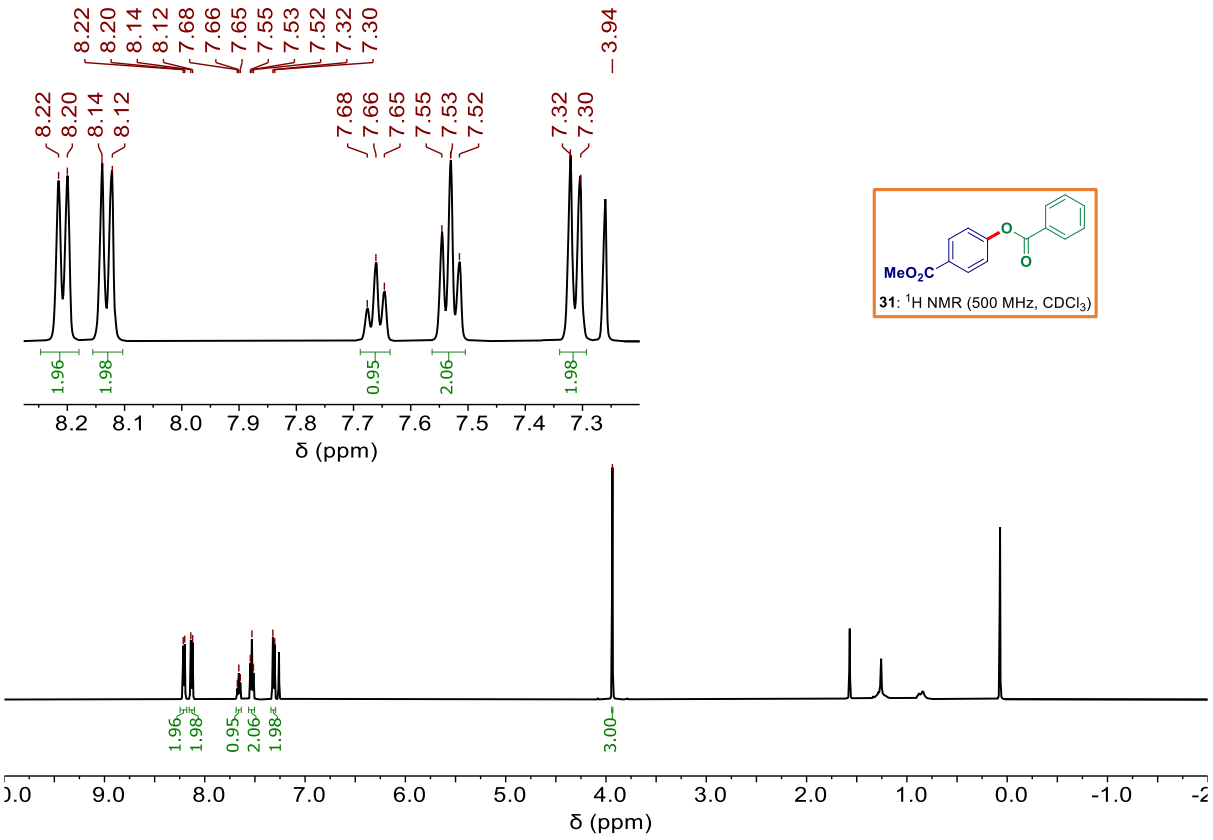

172.57
166.43
154.46
131.33
127.92
121.62
67.10
52.36
40.41
28.68
δ (ppm)
MeO2C
28: 13C NMR (126 MHz, CDCl3)

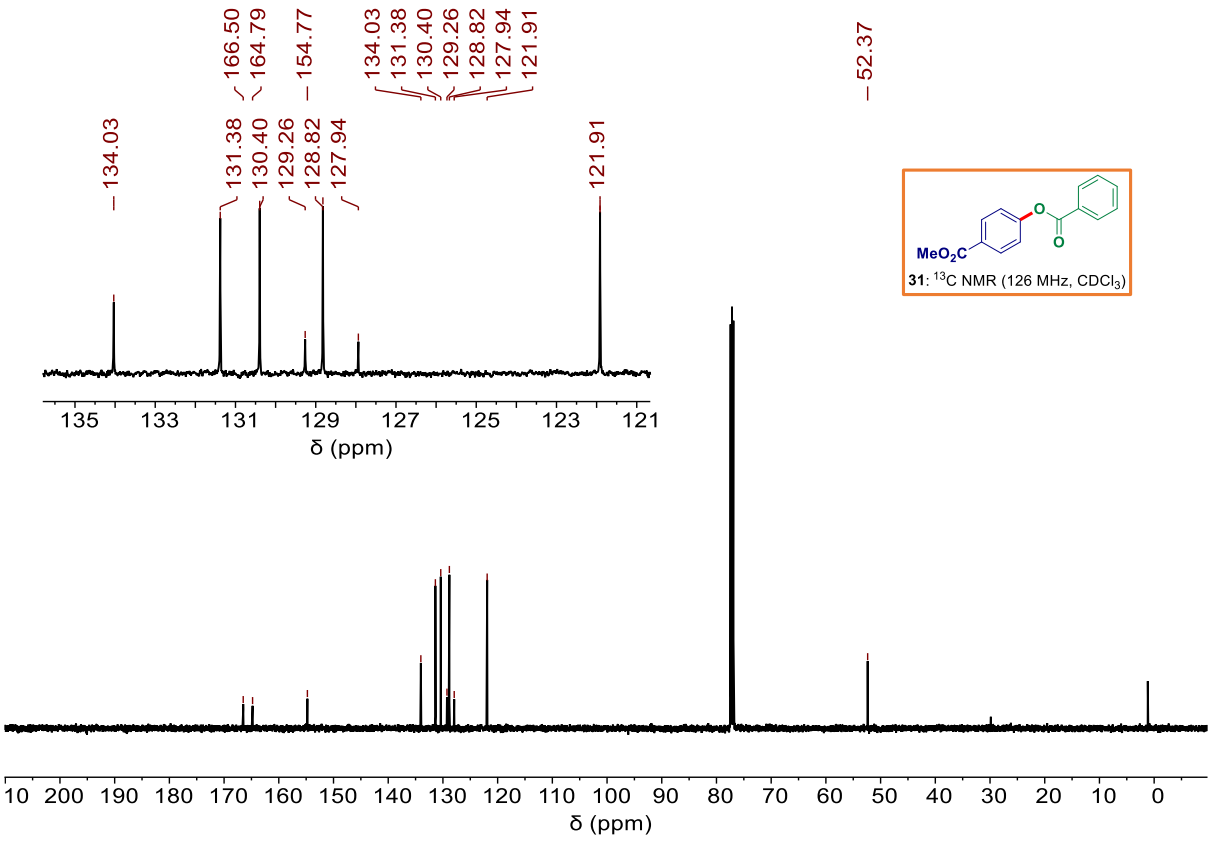

8.09
8.07
7.35
7.34
7.32
7.21
7.20
7.06
7.04
7.04
7.04
7.03
7.00
7.00
7.00
6.98
6.98
6.98
4.90
3.92
2.00
1.99
2.01
1.02
1.96
δ (ppm)
2.00
1.99
2.01
1.02
1.96
2.02
3.02
δ (ppm)
MeO2C
29: 1H NMR (500 MHz, CDCl3)

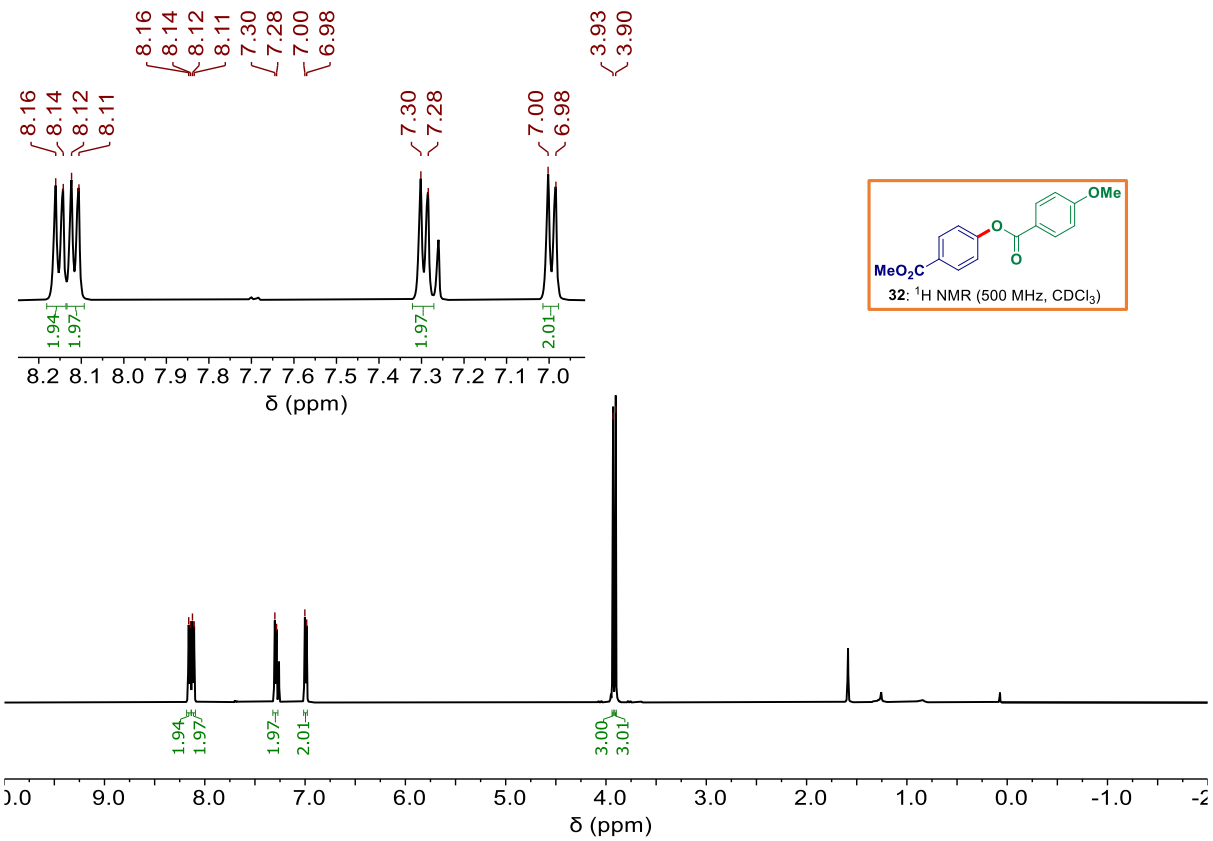

167.19
166.30
157.77
153.77
131.41
129.86
128.30
122.31
121.46
114.91
65.54
52.40
δ (ppm)
MeO2C
29: 13C NMR (126 MHz, CDCl3)

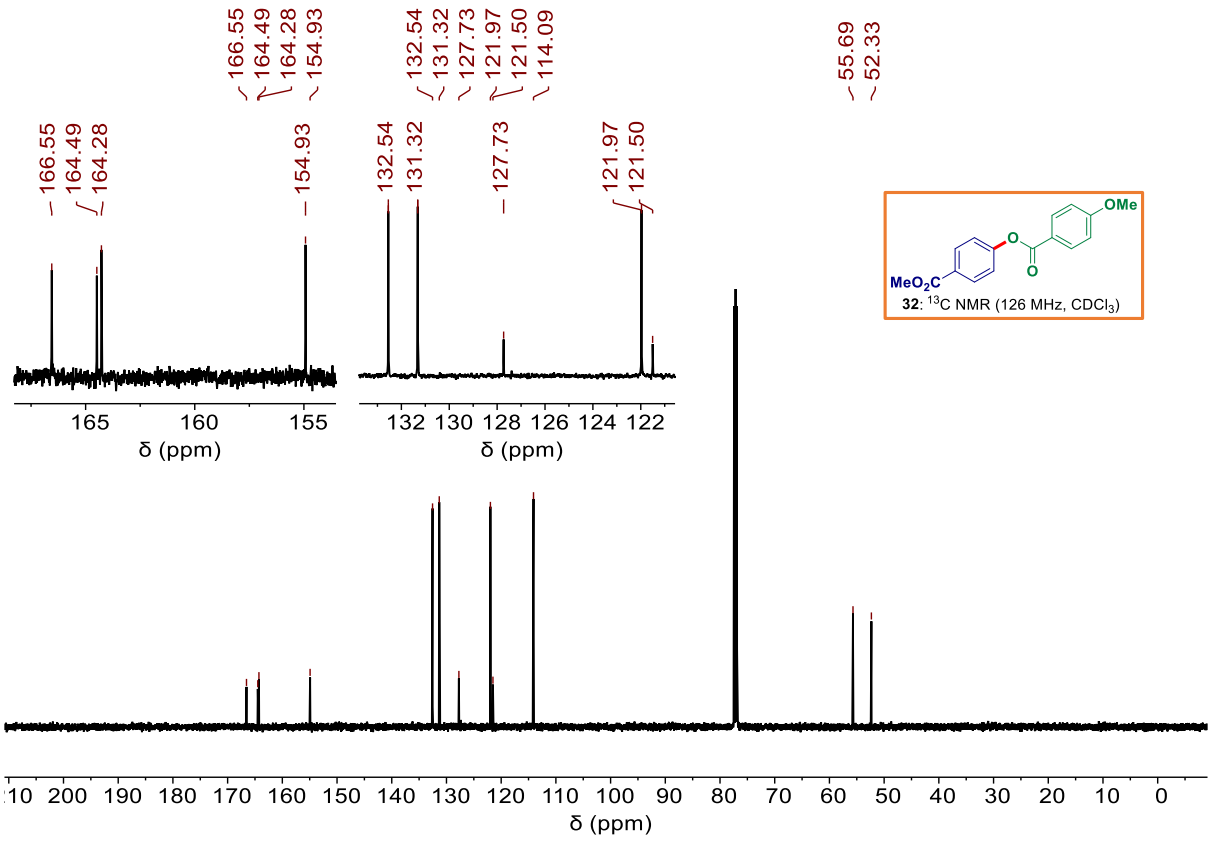

8.07 8.05 7.15 7.13 3.91 2.63 2.62 2.62 2.61 2.60 1.78 1.77 1.76 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.71 1.57 1.57 1.56 1.56 1.55 1.54 1.54 1.53 1.47 1.47 1.46 1.46 1.44 1.44 1.43 1.43 1.42 1.41 1.41 1.40 1.39 0.98 0.97 0.95
8.07 8.05 7.15 7.13
1.98 2.00
8.0 7.8 7.6 7.4 7.2 7.0
δ (ppm)
2.64 2.63 2.63 2.62 2.62 2.61 2.60 2.59
1.02
2.65 2.60 2.55
δ (ppm)
MeO2C
30: 1H NMR (500 MHz, CDCl3)
1.98 2.00 3.02 1.02 2.18 2.11 4.13 6.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
δ (ppm)

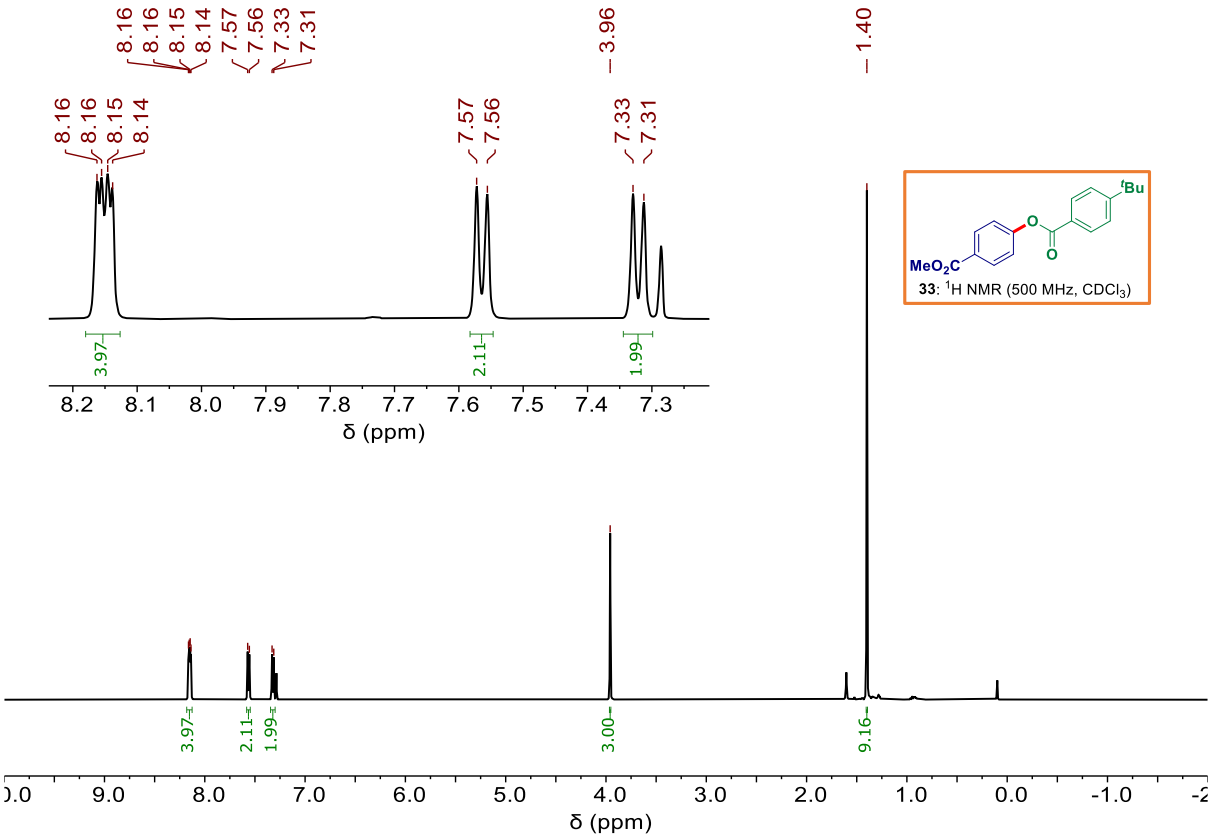

174.61 166.50 154.67 131.27 127.72 121.79 52.31 45.56 34.74 20.84 14.15
MeO2C
30: 13C NMR (126 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

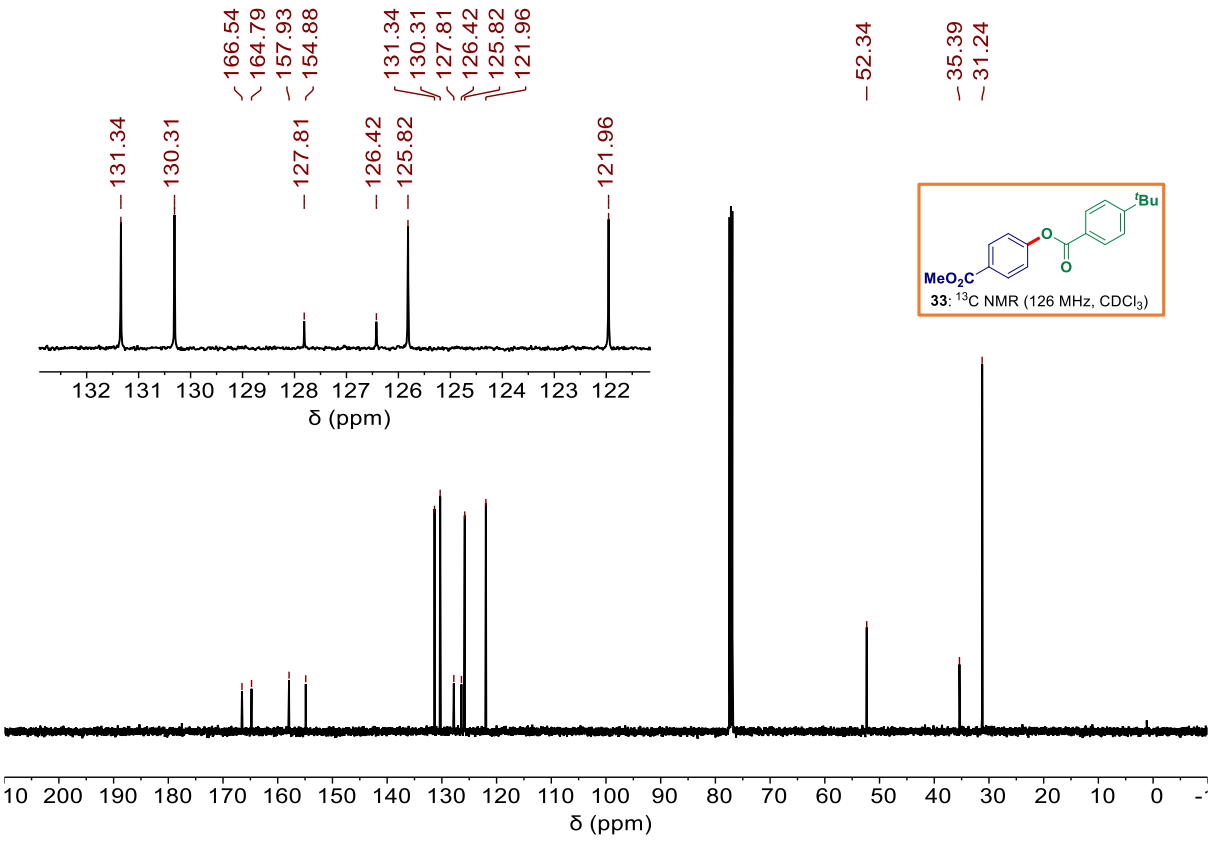

8.22
8.20
8.14
8.12
7.68
7.66
7.65
7.55
7.53
7.52
7.32
7.30
3.94
1.96
1.98
0.95
2.06
1.98
δ (ppm)
MeO2C
31: 1H NMR (500 MHz, CDCl3)
3.00
δ (ppm)

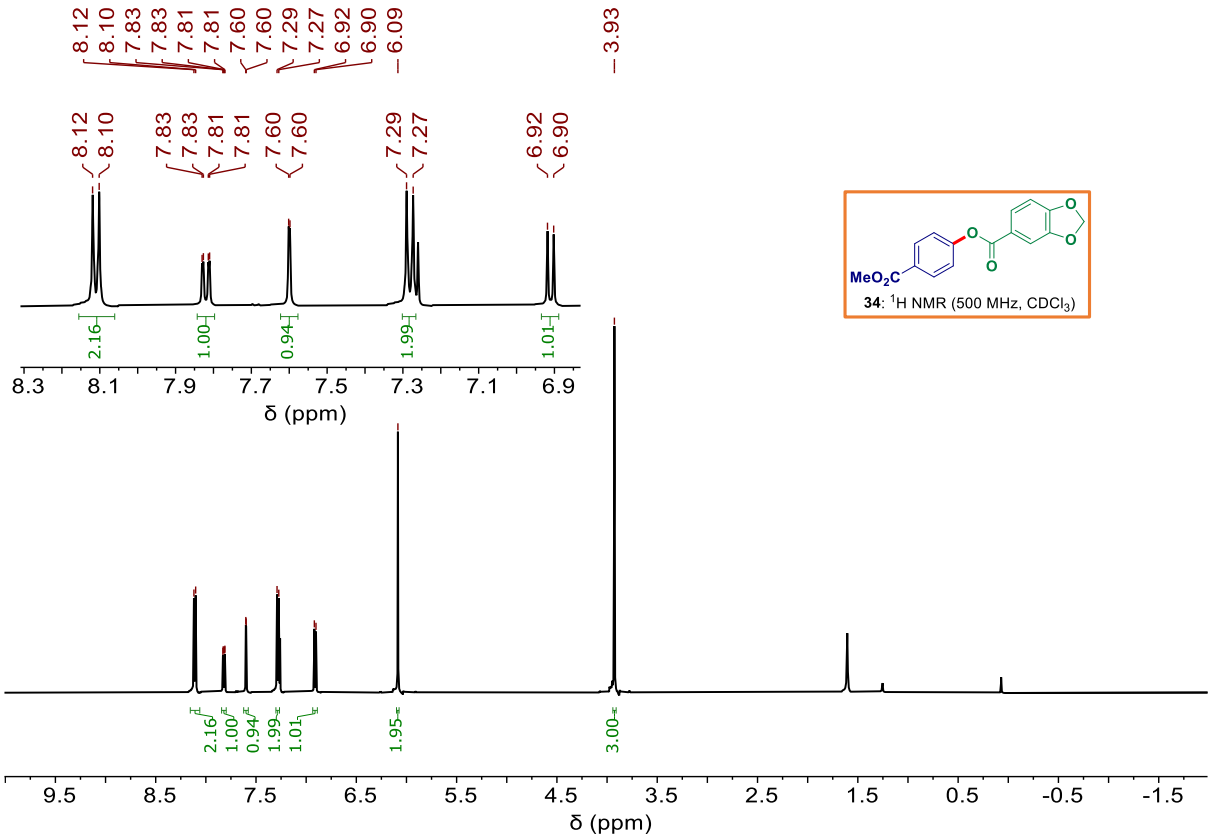

166.50
164.79
154.77
134.03
131.38
130.40
129.26
128.82
127.94
121.91
52.37
δ (ppm)
MeO2C
31: 13C NMR (126 MHz, CDCl3)
δ (ppm)

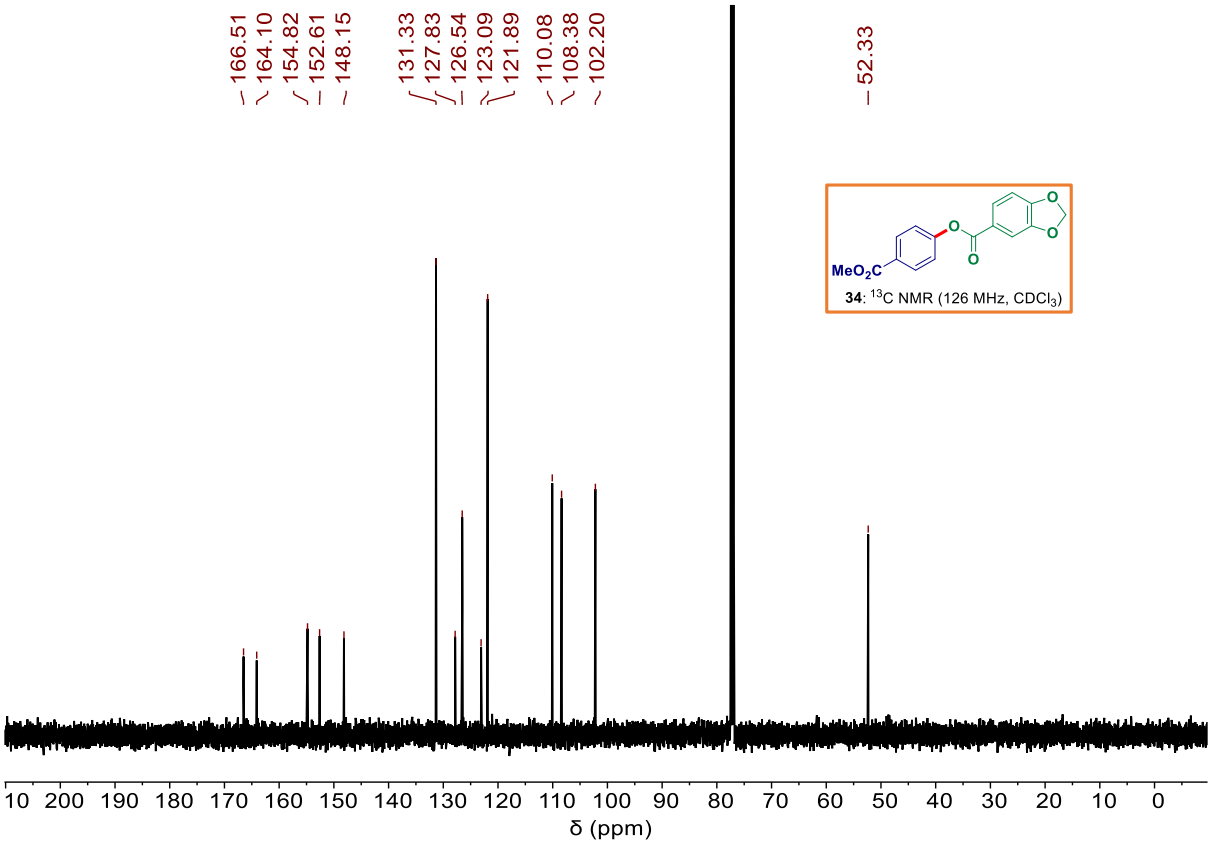

8.16
8.14
8.12
8.11
7.30
7.28
7.00
6.98
3.93
3.90
1.94
1.97
1.97
2.01
3.00
3.01
δ (ppm)
OMe
MeO2C
O
O
32: 1H NMR (500 MHz, CDCl3)

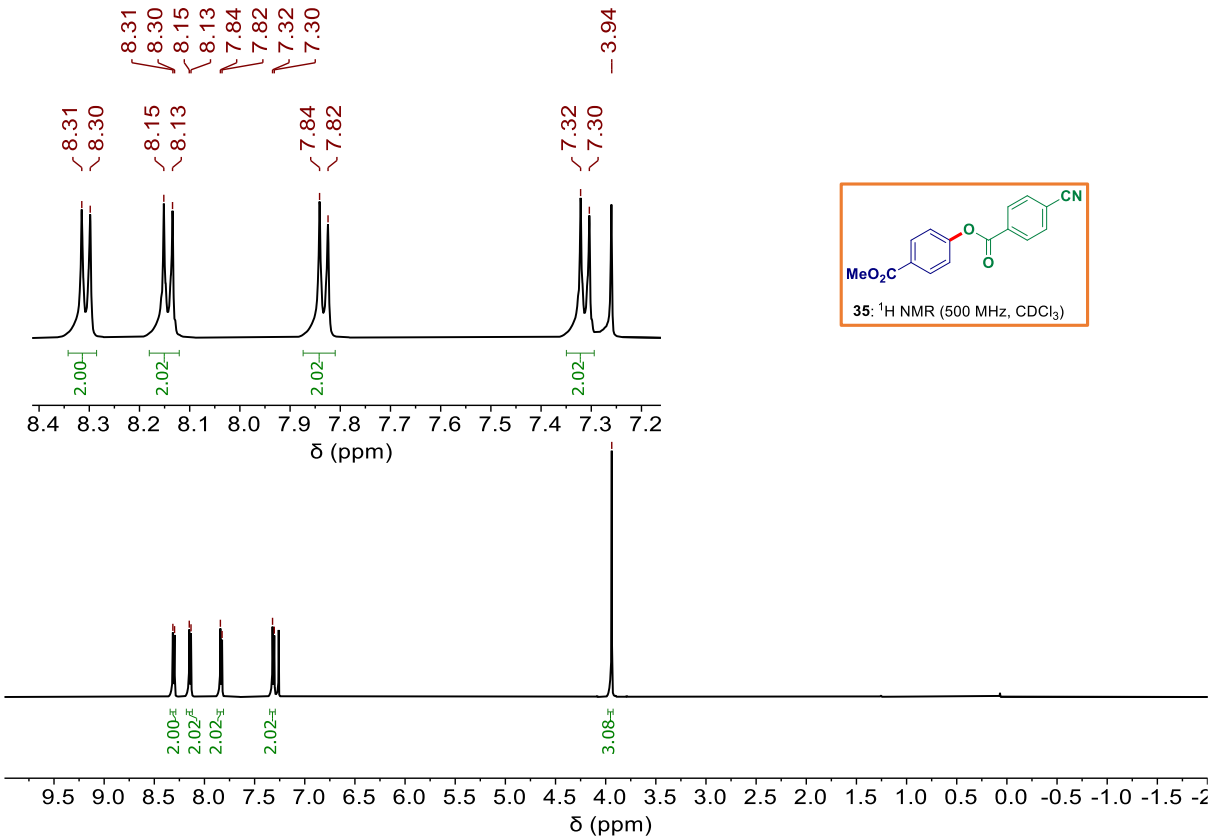

166.55
164.49
164.28
154.93
132.54
131.32
127.73
121.97
121.50
114.09
55.69
52.33
δ (ppm)
OMe
MeO2C
O
O
32: 13C NMR (126 MHz, CDCl3)

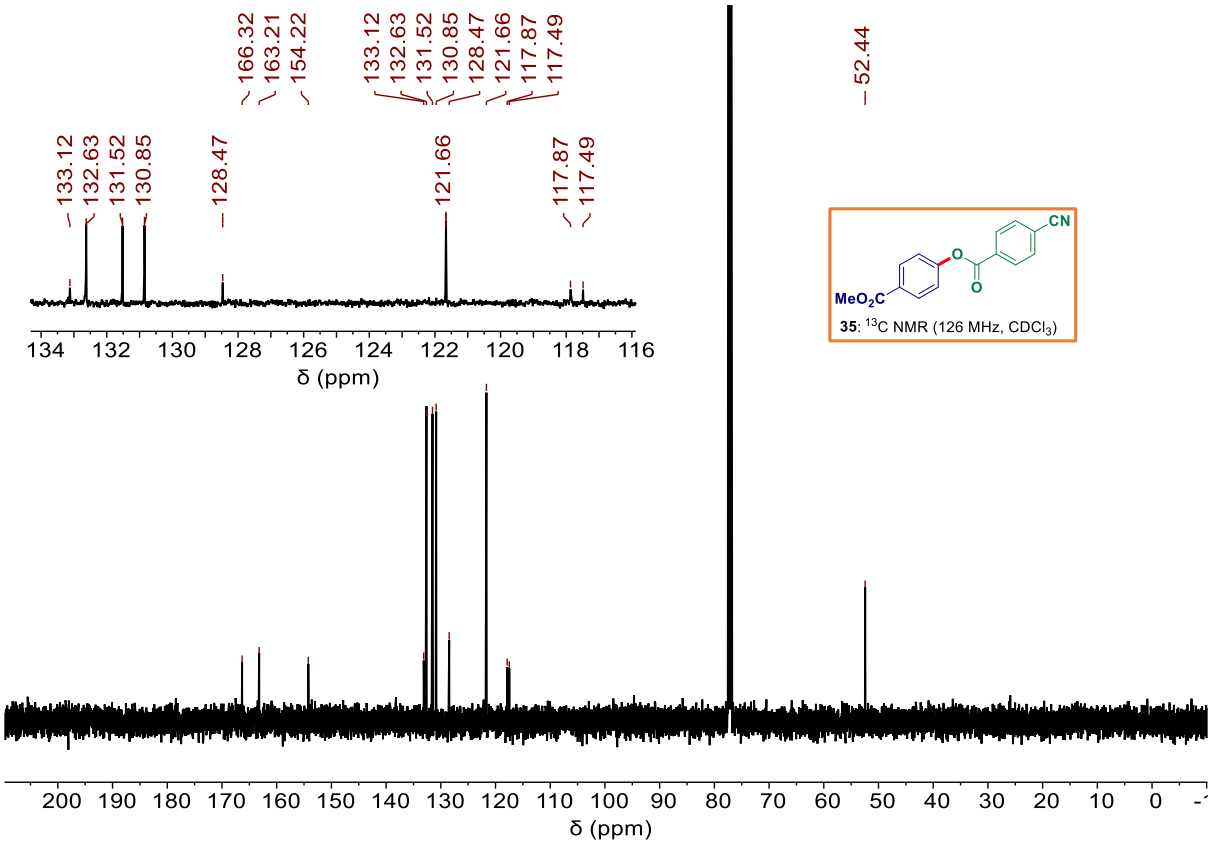

8.16
8.16
8.15
8.14
7.57
7.56
7.33
7.31
3.96
1.40
3.97
2.11
1.99
3.00
9.16
δ (ppm)
33: 1H NMR (500 MHz, CDCl3)

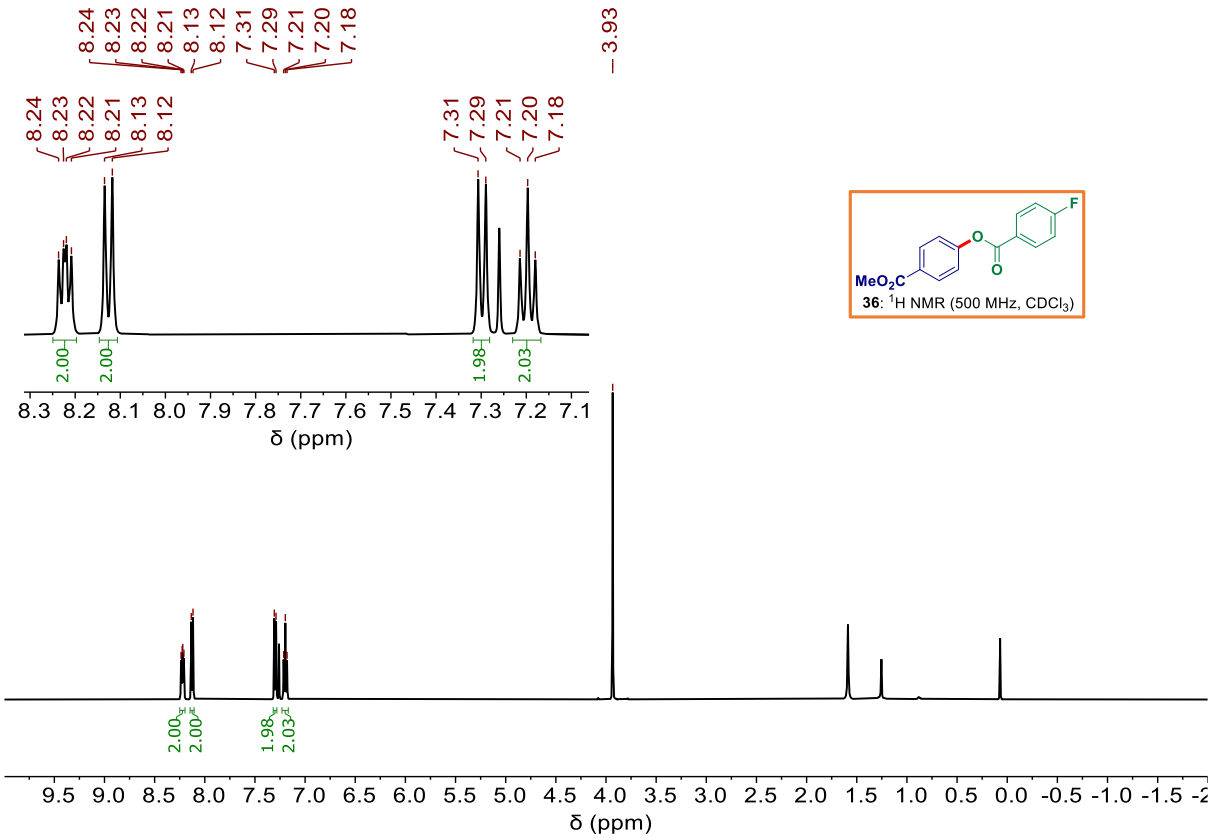

166.54
164.79
157.93
154.88
131.34
130.31
127.81
126.42
125.82
121.96
52.34
35.39
31.24
δ (ppm)
33: 13C NMR (126 MHz, CDCl3)

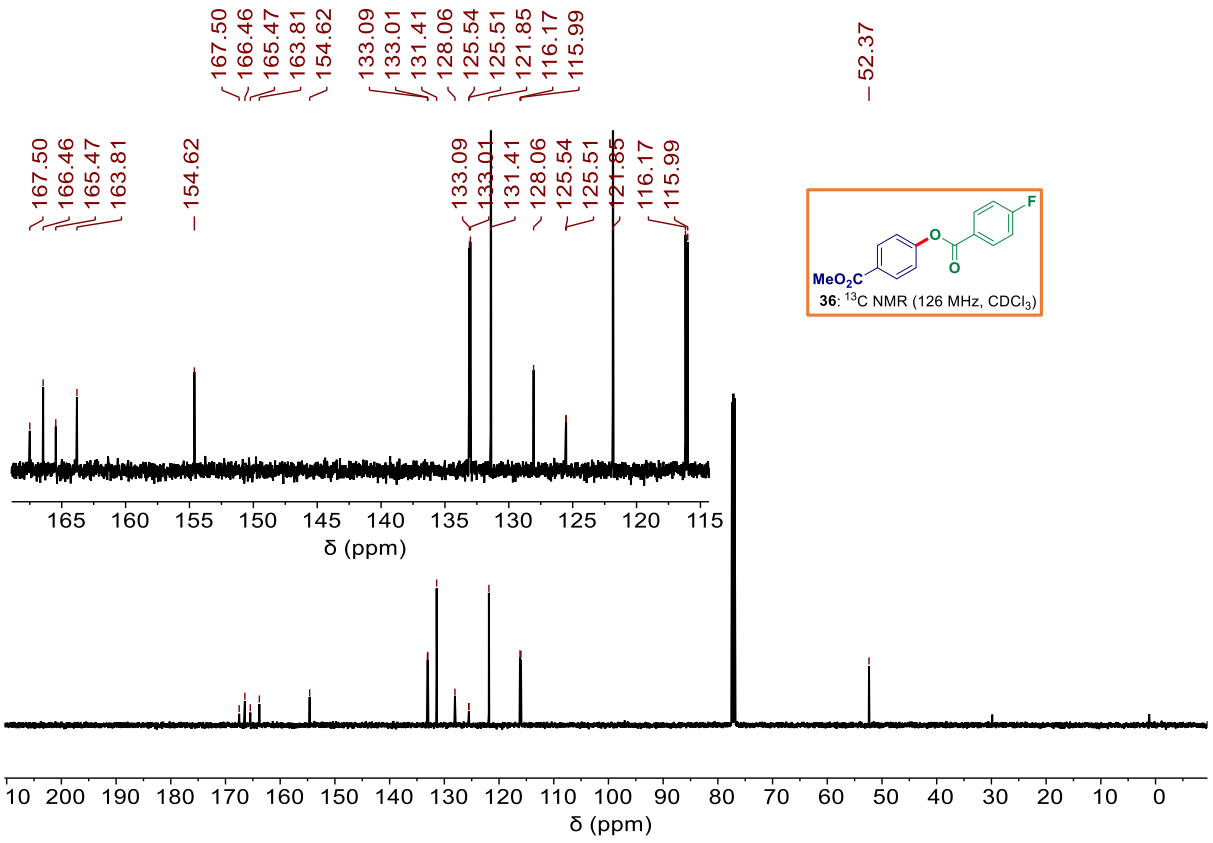

8.12
8.10
7.83
7.83
7.81
7.81
7.60
7.60
7.29
7.27
6.92
6.90
6.09
3.93
2.16
1.00
0.94
1.99
1.01
1.95
3.00
δ (ppm)
MeO2C
34: 1H NMR (500 MHz, CDCl3)

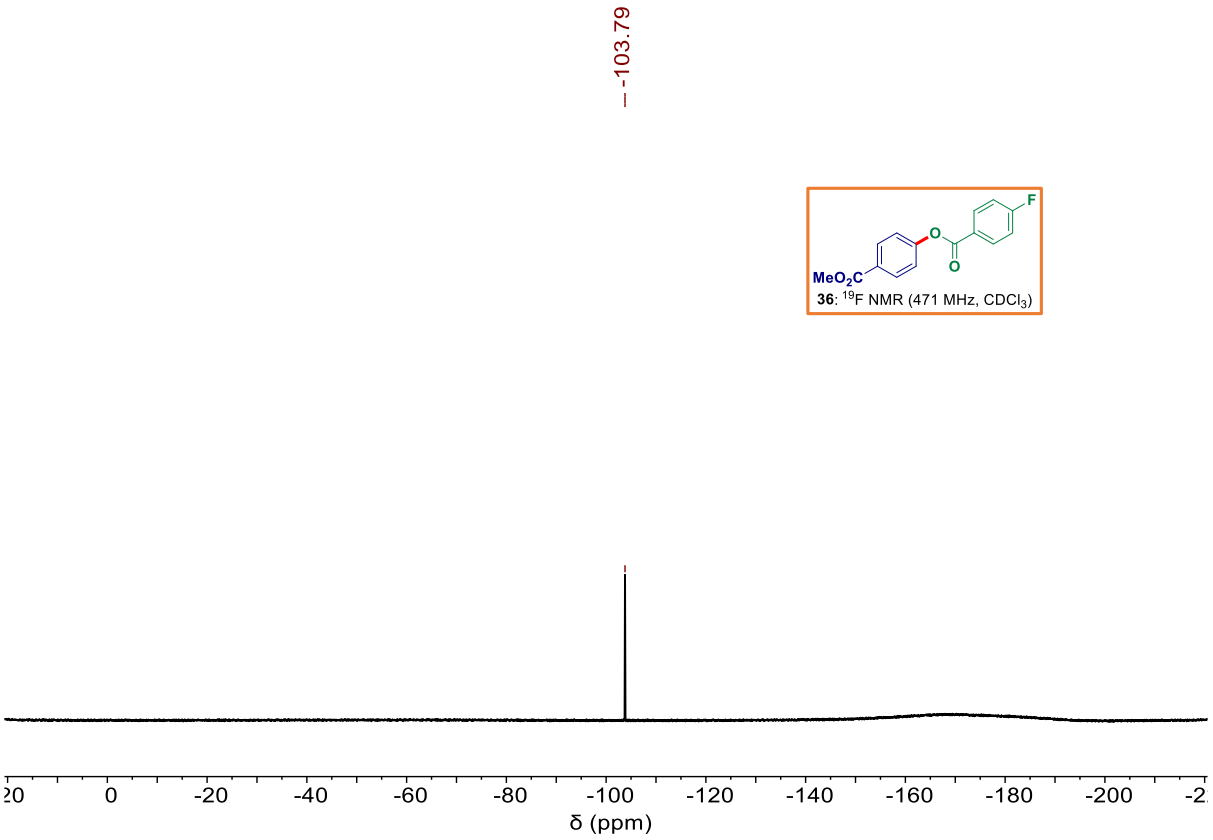

166.51
164.10
154.82
152.61
148.15
131.33
127.83
126.54
123.09
121.89
110.08
108.38
102.20
52.33
δ (ppm)
MeO2C
34: 13C NMR (126 MHz, CDCl3)

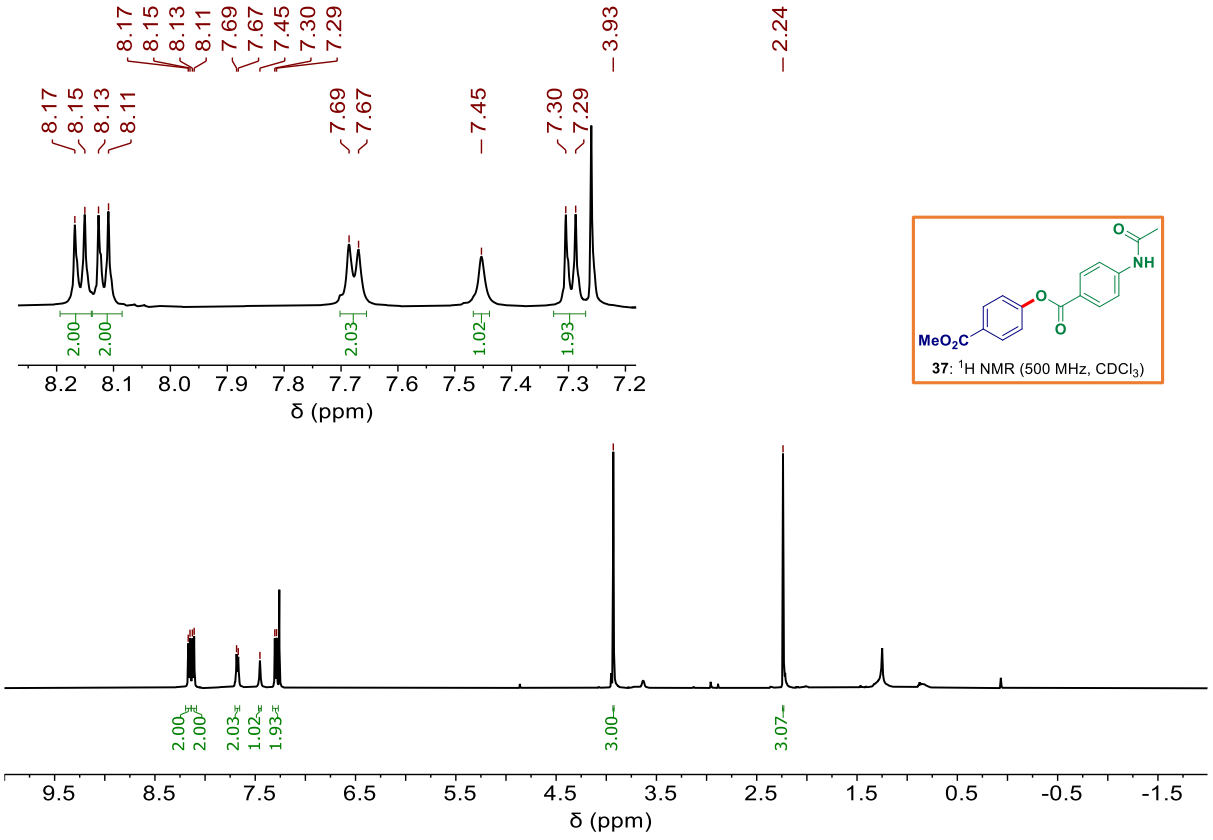

8.31
8.30
8.15
8.13
7.84
7.82
7.32
7.30
3.94
2.00
2.02
2.02
2.02
δ (ppm)
CN
O
O
MeO2C
35: 1H NMR (500 MHz, CDCl3)
2.00
2.02
2.02
2.02
3.08
δ (ppm)

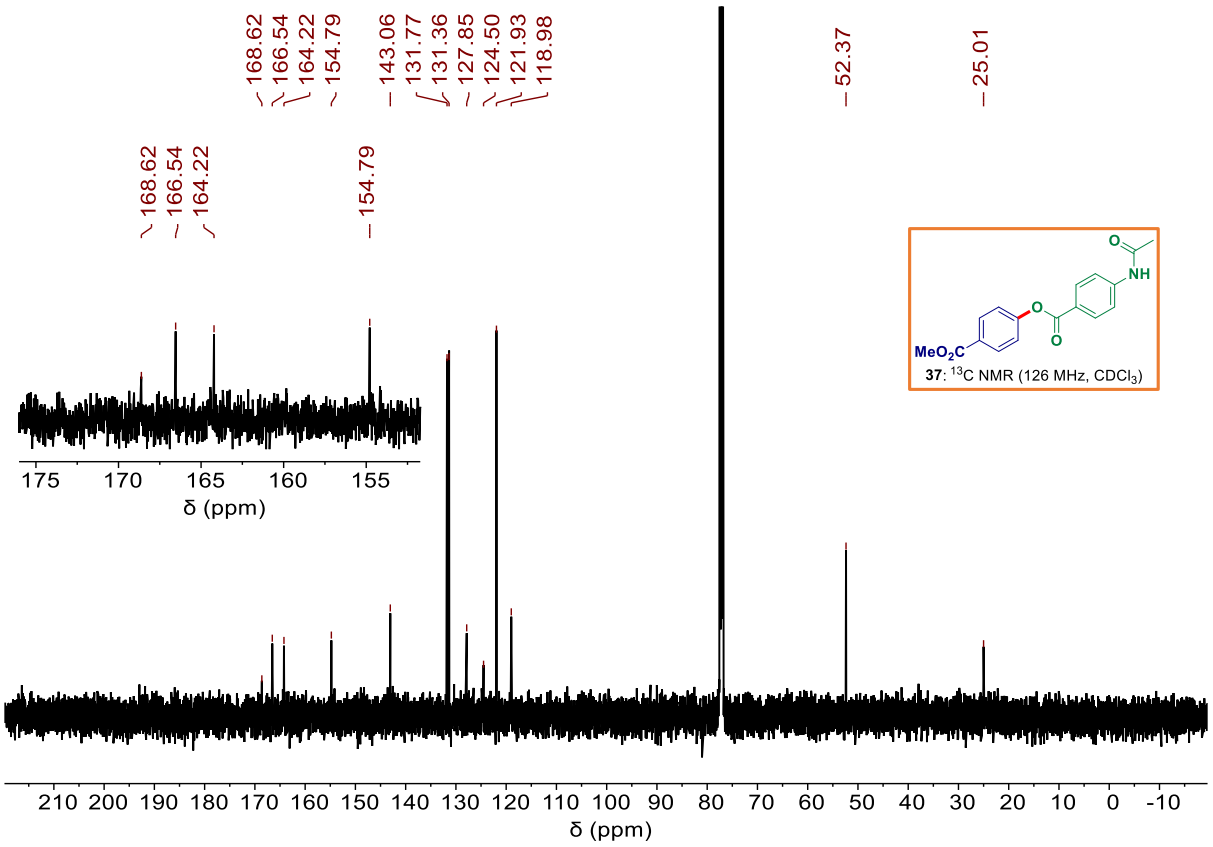

166.32
163.21
154.22
133.12
132.63
131.52
130.85
128.47
121.66
117.87
117.49
52.44
δ (ppm)
CN
O
O
MeO2C
35: 13C NMR (126 MHz, CDCl3)
δ (ppm)

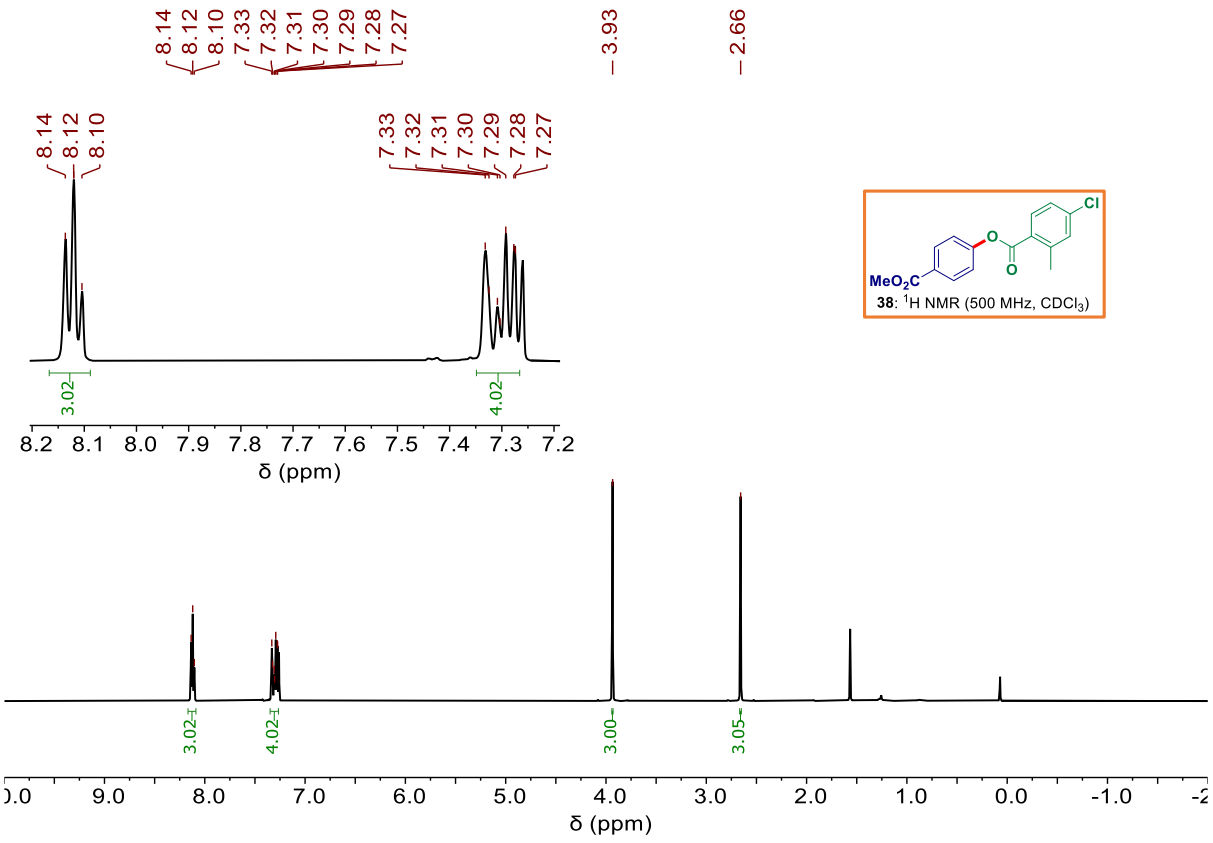

8.24
8.23
8.22
8.21
8.13
8.12
7.31
7.29
7.21
7.20
7.18
3.93
2.00
2.00
1.98
2.03
δ (ppm)
MeO2C
F
O
O
36: 1H NMR (500 MHz, CDCl3)

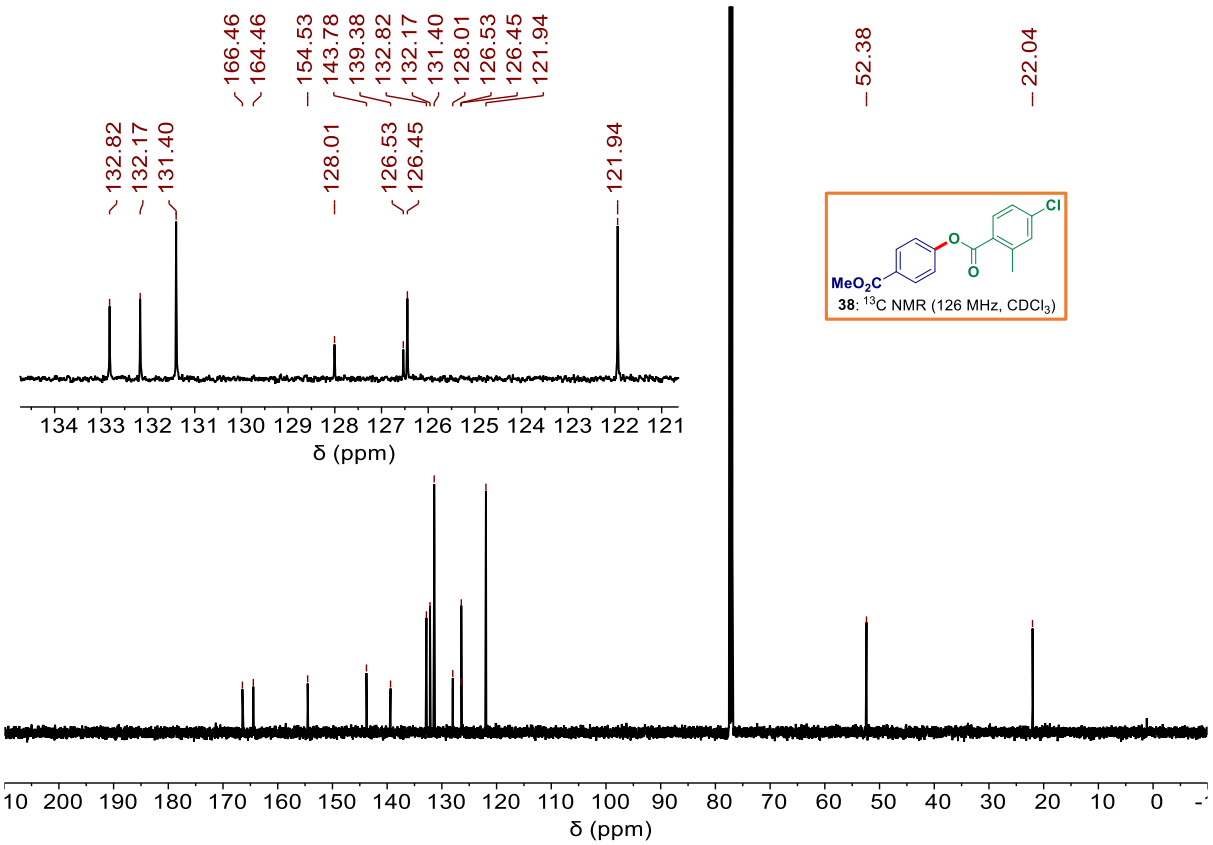

167.50
166.46
165.47
163.81
154.62
133.09
133.01
131.41
128.06
125.54
125.51
121.85
116.17
115.99
52.37
δ (ppm)
MeO2C
F
O
O
36: 13C NMR (126 MHz, CDCl3)

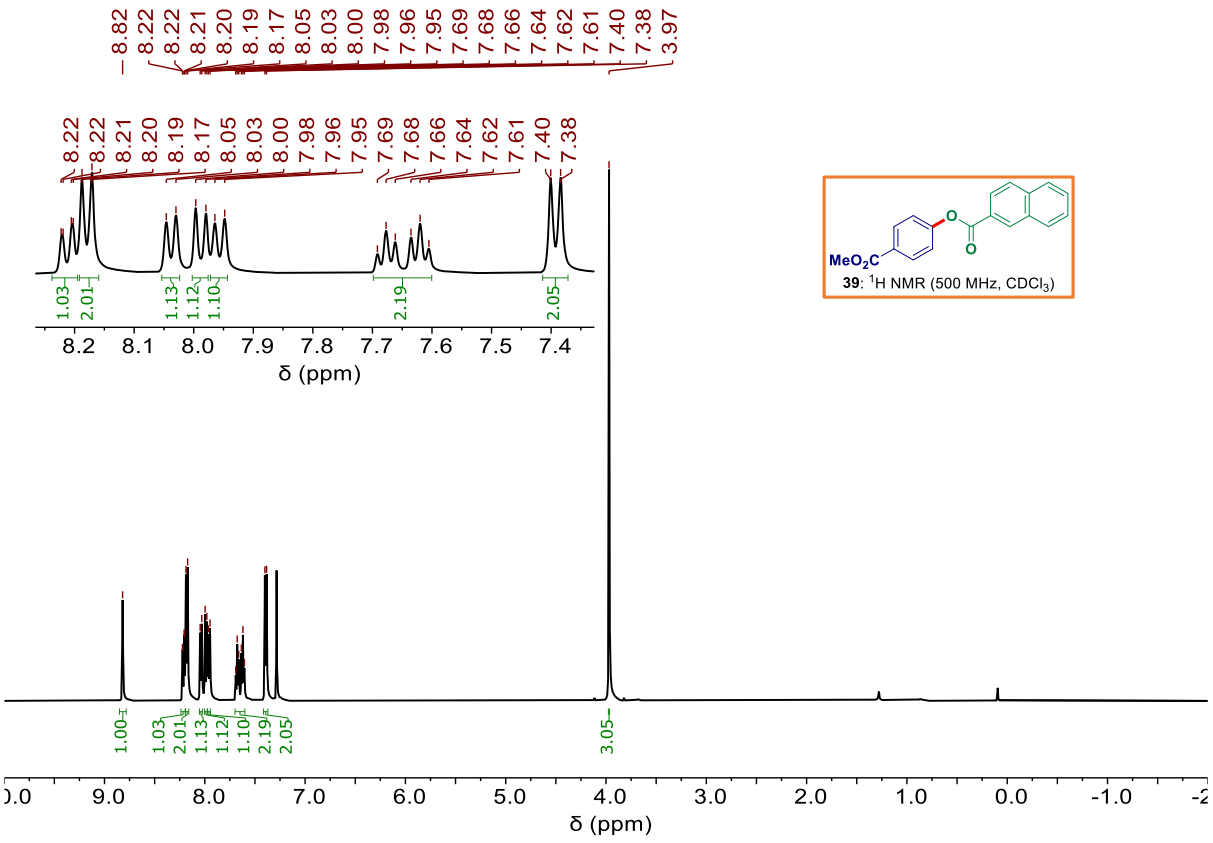

-103.79
MeO2C
F
O
O
36: 19F NMR (471 MHz, CDCl3)
δ (ppm)

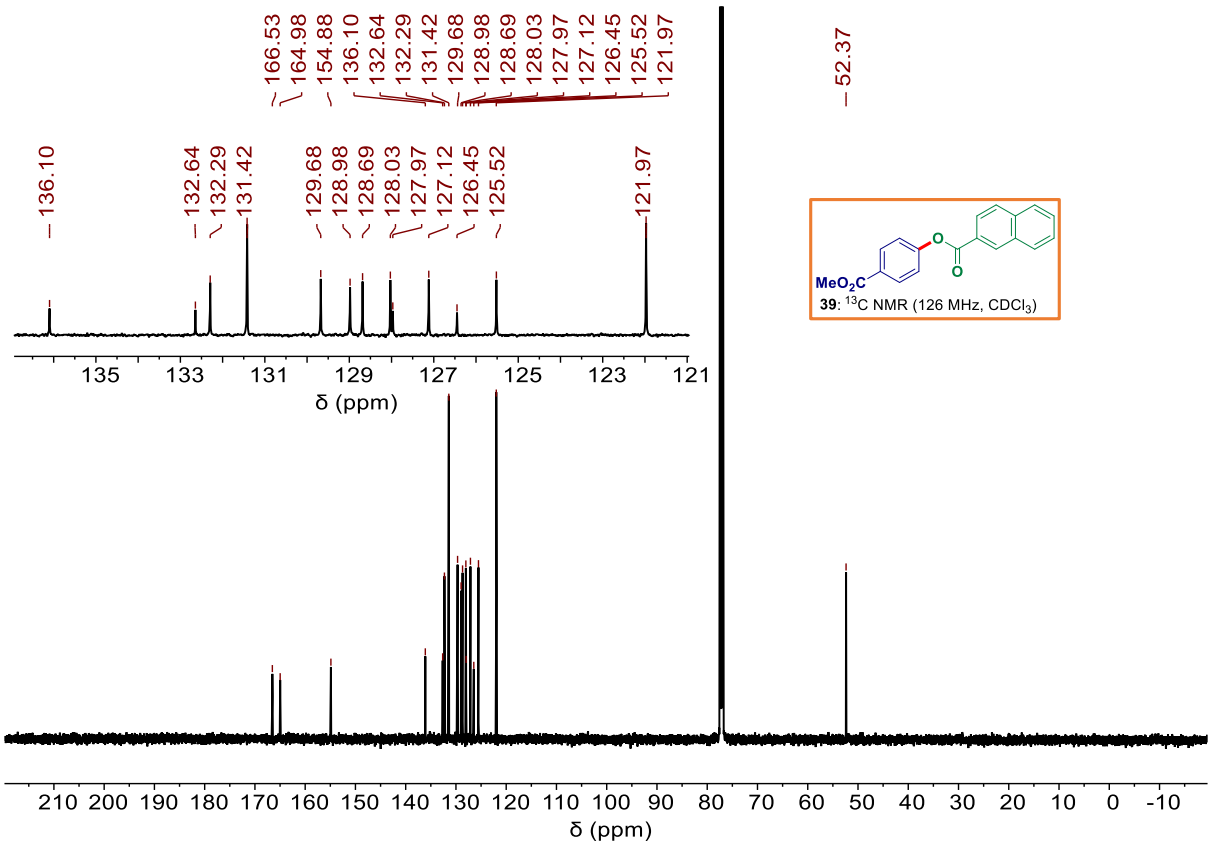

8.17
8.15
8.13
8.11
7.69
7.67
7.45
7.30
7.29
3.93
2.24
2.00
2.00
2.03
1.02
1.93
3.00
3.07
MeO2C
NH
O
O
37: 1H NMR (500 MHz, CDCl3)
δ (ppm)

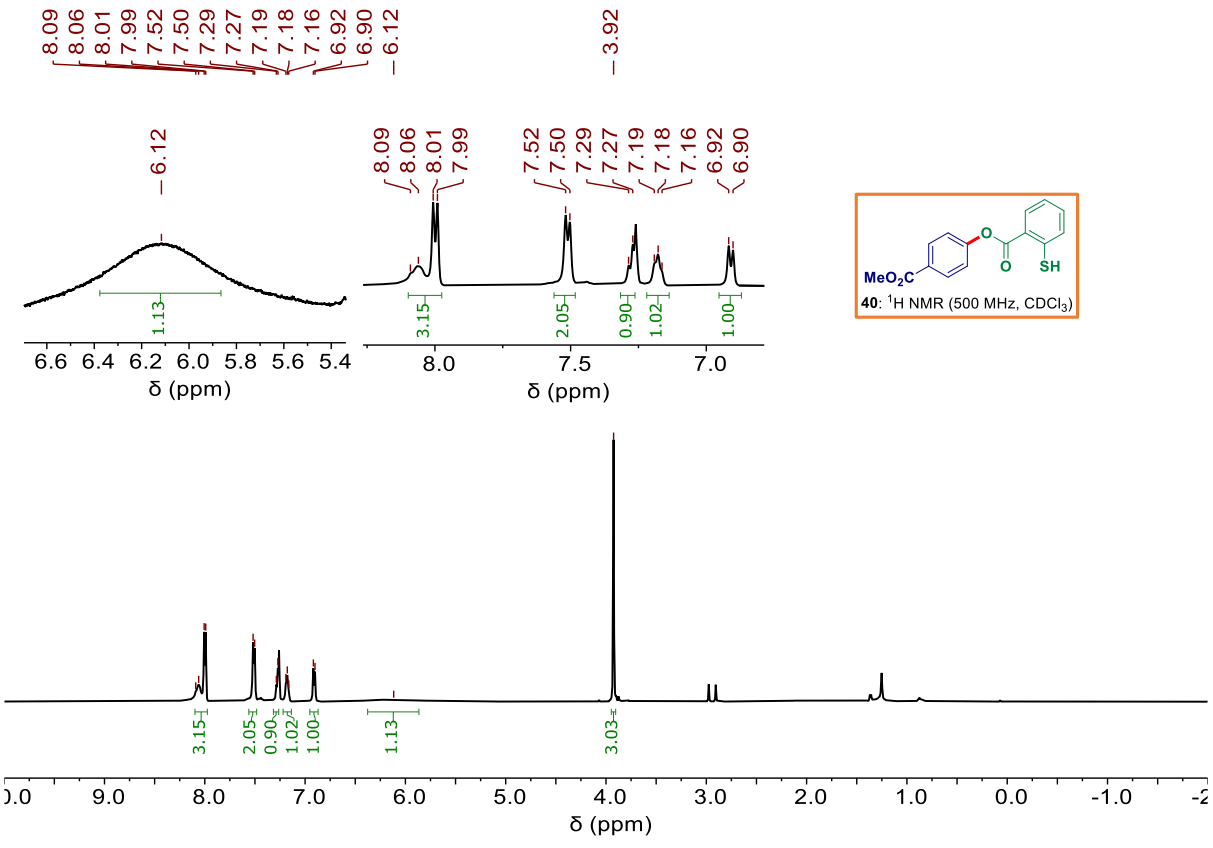

168.62
166.54
164.22
154.79
143.06
131.77
131.36
127.85
124.50
121.93
118.98
52.37
25.01
NH
O
MeO2C
37: 13C NMR (126 MHz, CDCl3)
δ (ppm)

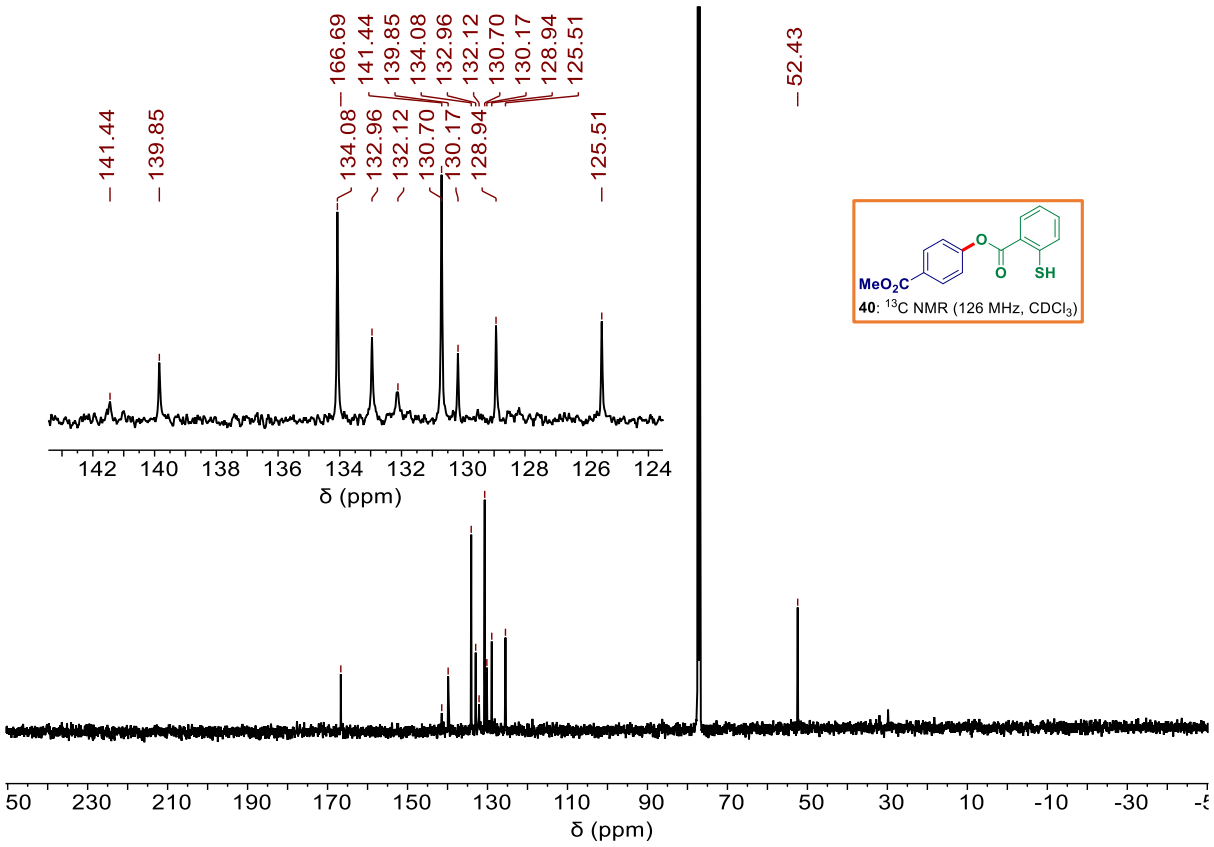

8.14
8.12
8.10
7.33
7.32
7.31
7.30
7.29
7.28
7.27
3.93
2.66
Cl
MeO2C
38: 1H NMR (500 MHz, CDCl3)
3.02
4.02
3.00
3.05
δ (ppm)

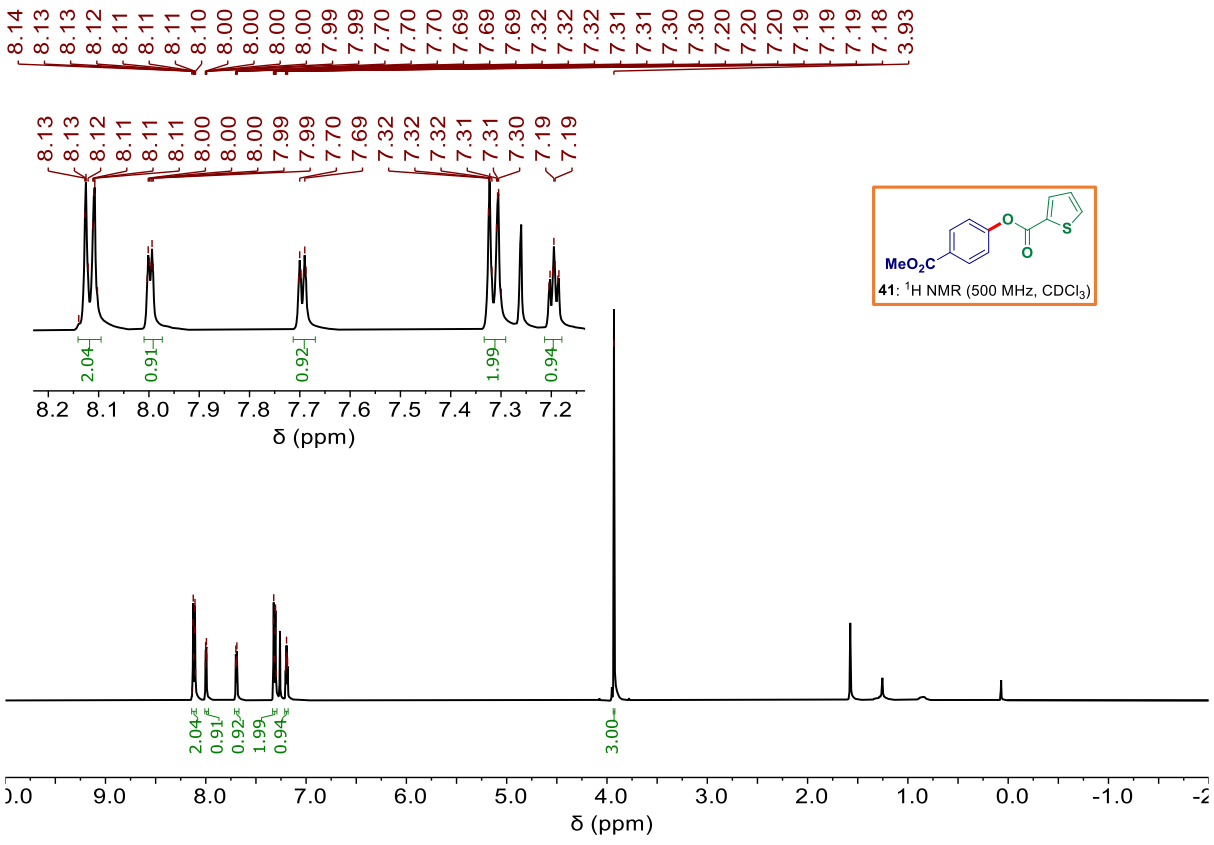

166.46
164.46
154.53
143.78
139.38
132.82
132.17
131.40
128.01
126.53
126.45
121.94
52.38
22.04
132.82
132.17
131.40
128.01
126.53
126.45
121.94
134 133 132 131 130 129 128 127 126 125 124 123 122 121
δ (ppm)
Cl
O
O
MeO2C
38: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

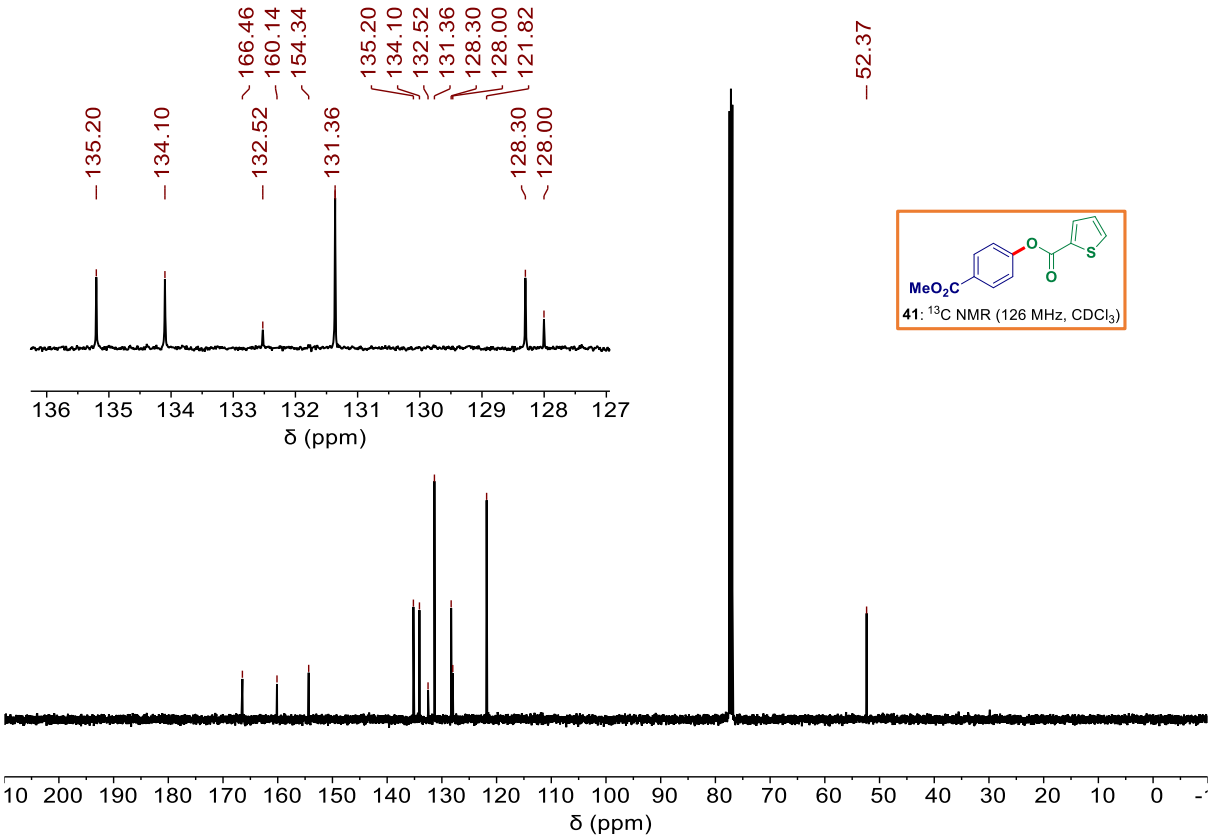

8.82
8.22
8.22
8.21
8.20
8.19
8.17
8.05
8.03
8.00
7.98
7.96
7.95
7.69
7.68
7.66
7.64
7.62
7.61
7.40
7.38
3.97
1.03
2.01
1.13
1.12
1.10
2.19
2.05
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
δ (ppm)
O
O
MeO2C
39: 1H NMR (500 MHz, CDCl3)
1.00
3.05
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

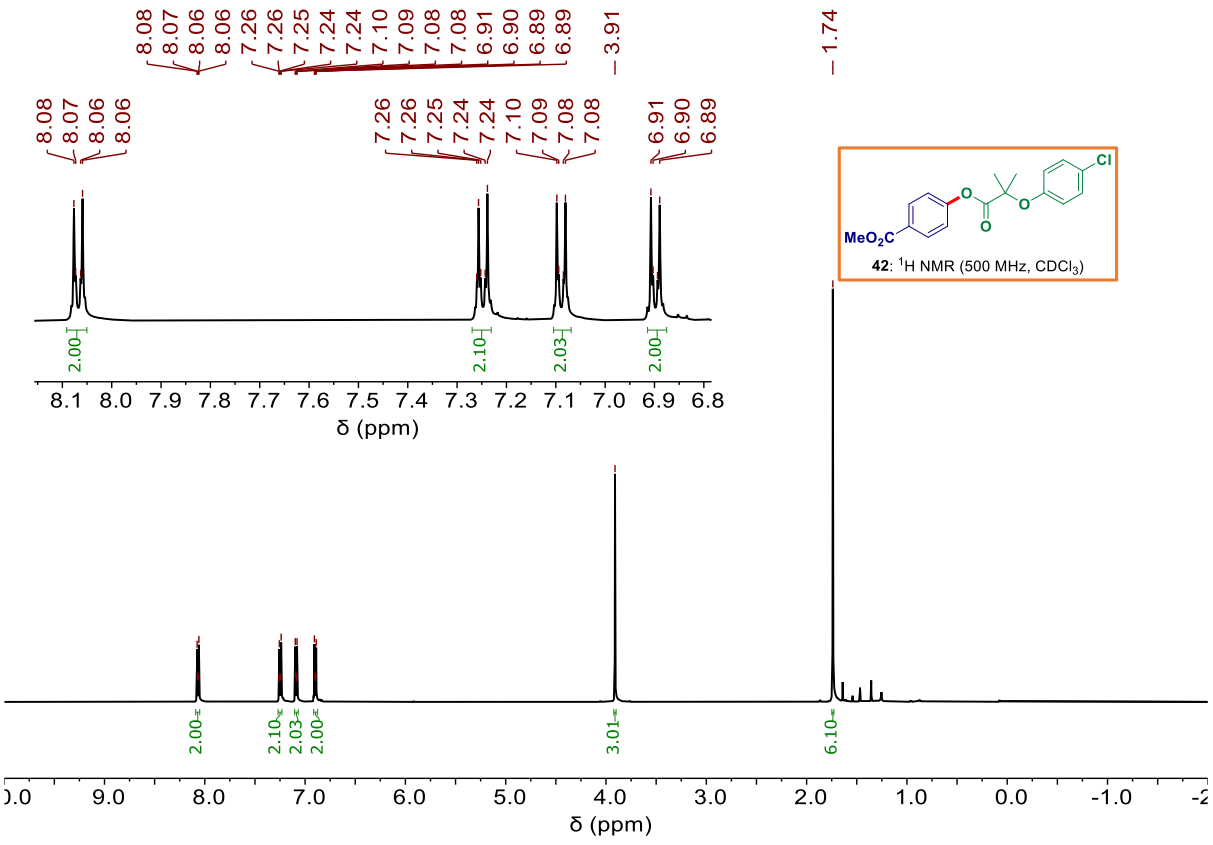

166.53
164.98
154.88
136.10
132.64
132.29
131.42
129.68
128.98
128.69
128.03
127.97
127.12
126.45
125.52
121.97
52.37
δ (ppm)
MeO2C
O
O
39: 13C NMR (126 MHz, CDCl3)

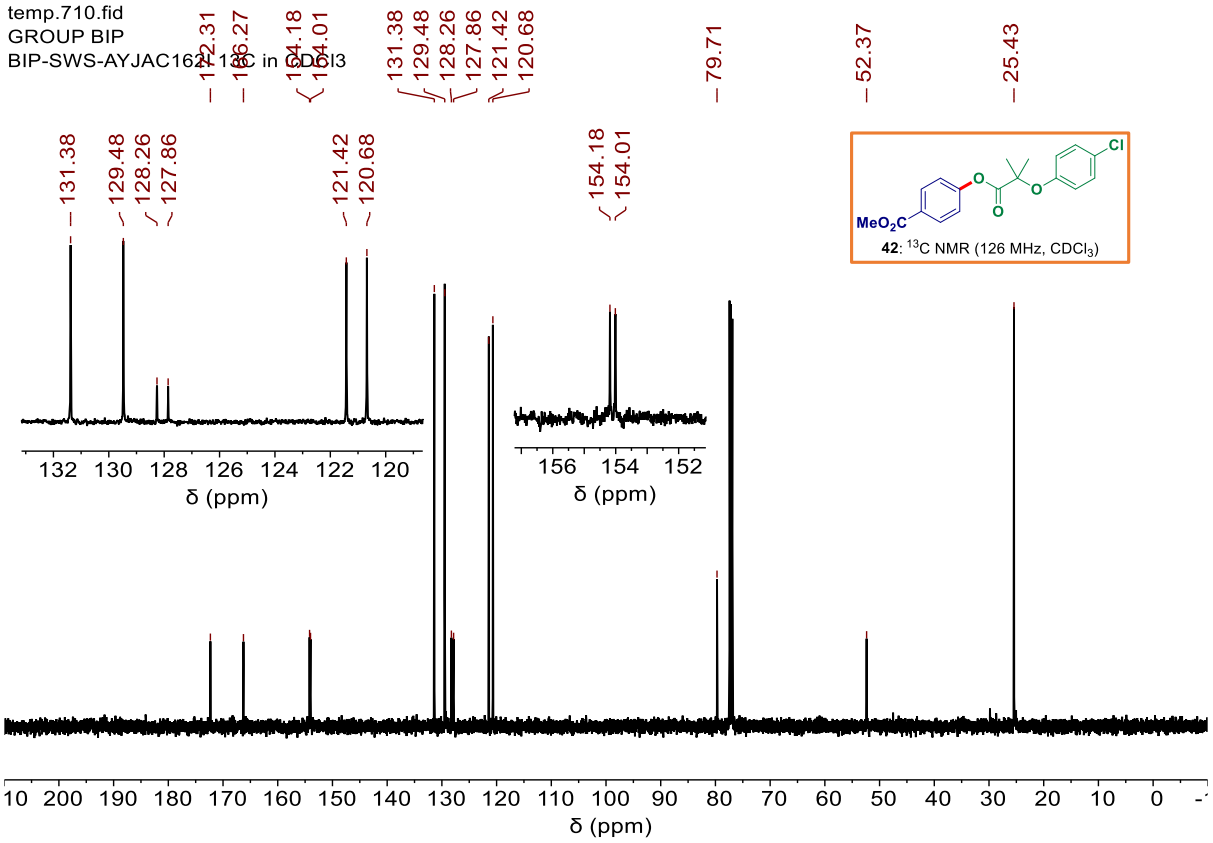

8.09
8.06
8.01
7.99
7.52
7.50
7.29
7.27
7.19
7.18
7.16
6.92
6.90
6.12
3.92
δ (ppm)
MeO2C
O
O
SH
40: 1H NMR (500 MHz, CDCl3)

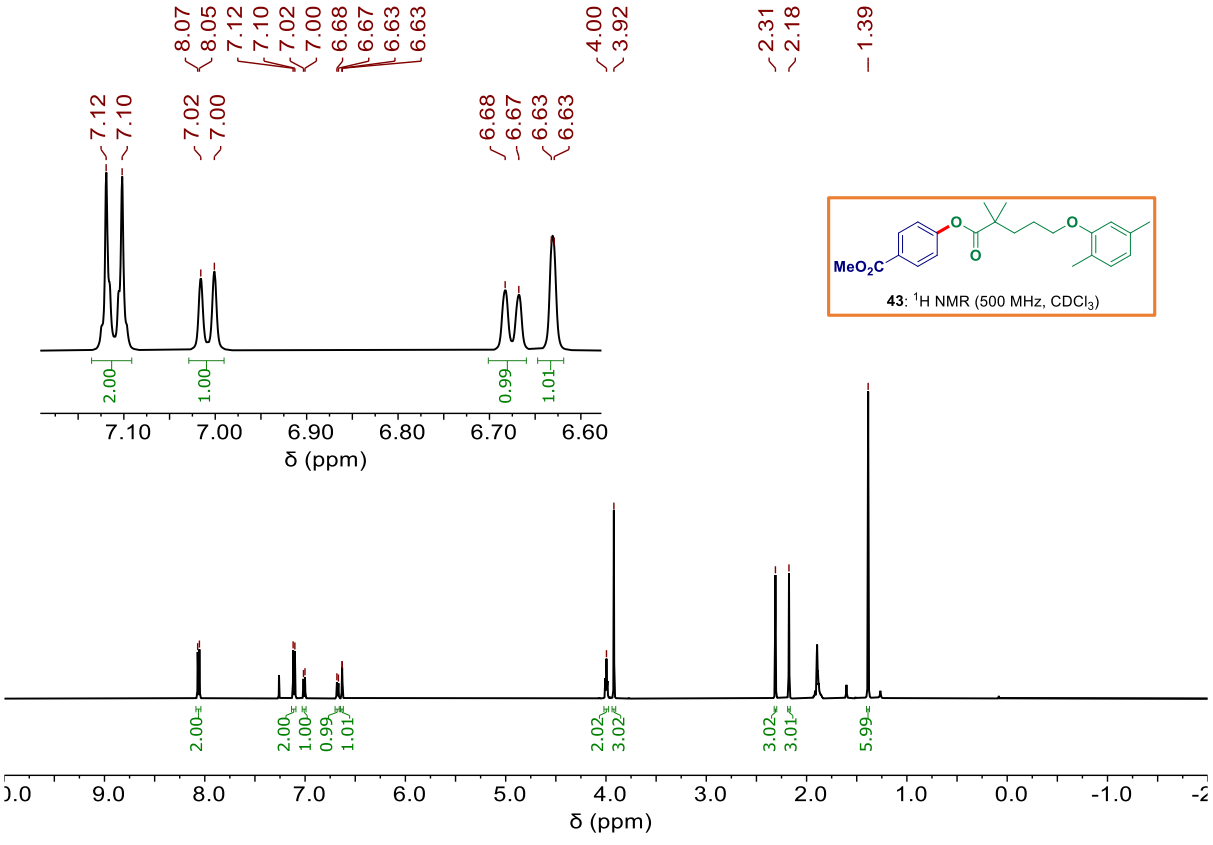

166.69
141.44
139.85
134.08
132.96
132.12
130.70
130.17
128.94
125.51
52.43
δ (ppm)
MeO2C
O
O
SH
40: 13C NMR (126 MHz, CDCl3)

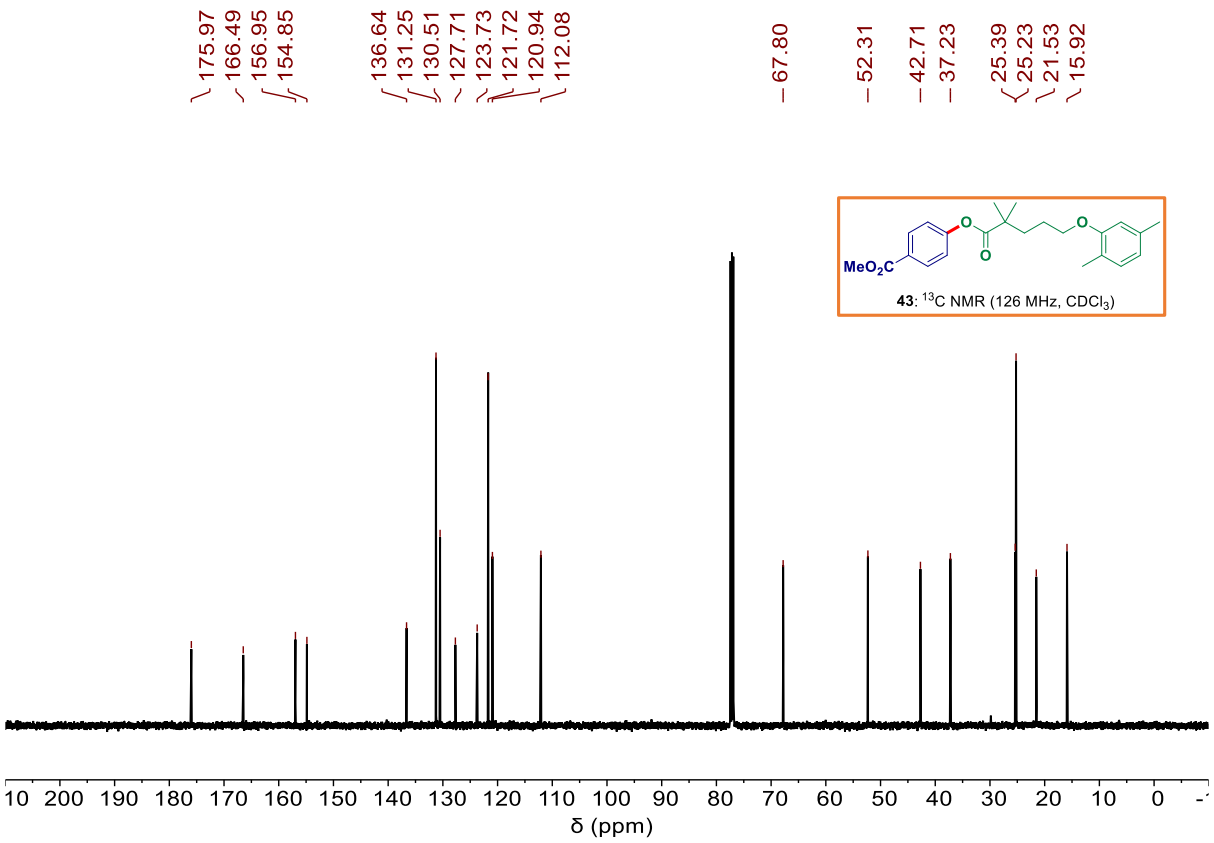

8.14
8.13
8.13
8.12
8.11
8.11
8.11
8.10
8.00
8.00
8.00
8.00
7.99
7.99
7.70
7.70
7.70
7.69
7.69
7.69
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.20
7.20
7.20
7.19
7.19
7.19
7.18
3.93
2.04
0.91
0.92
1.99
0.94
3.00
δ (ppm)
MeO2C
O
O
S
41: 1H NMR (500 MHz, CDCl3)

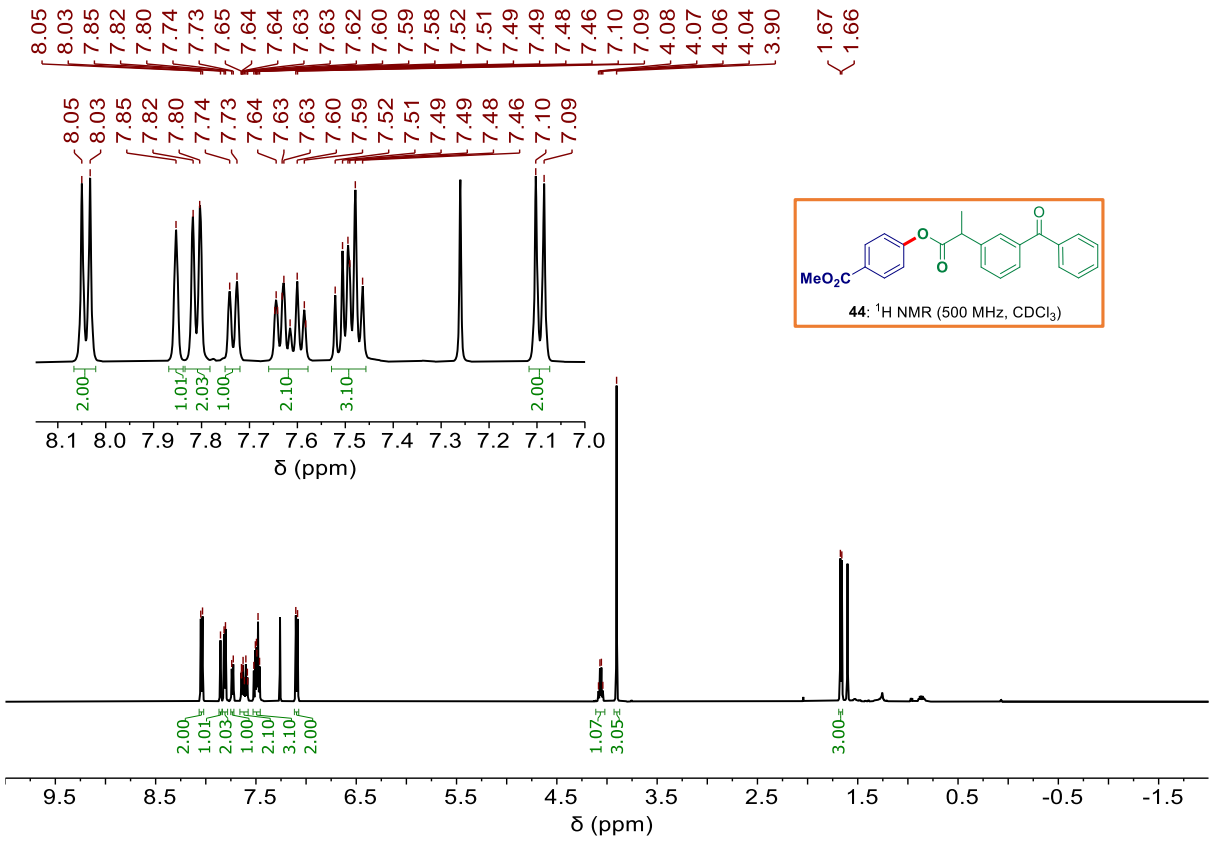

166.46
160.14
154.34
135.20
134.10
132.52
131.36
128.30
128.00
121.82
52.37
δ (ppm)
MeO2C
41: 13C NMR (126 MHz, CDCl3)

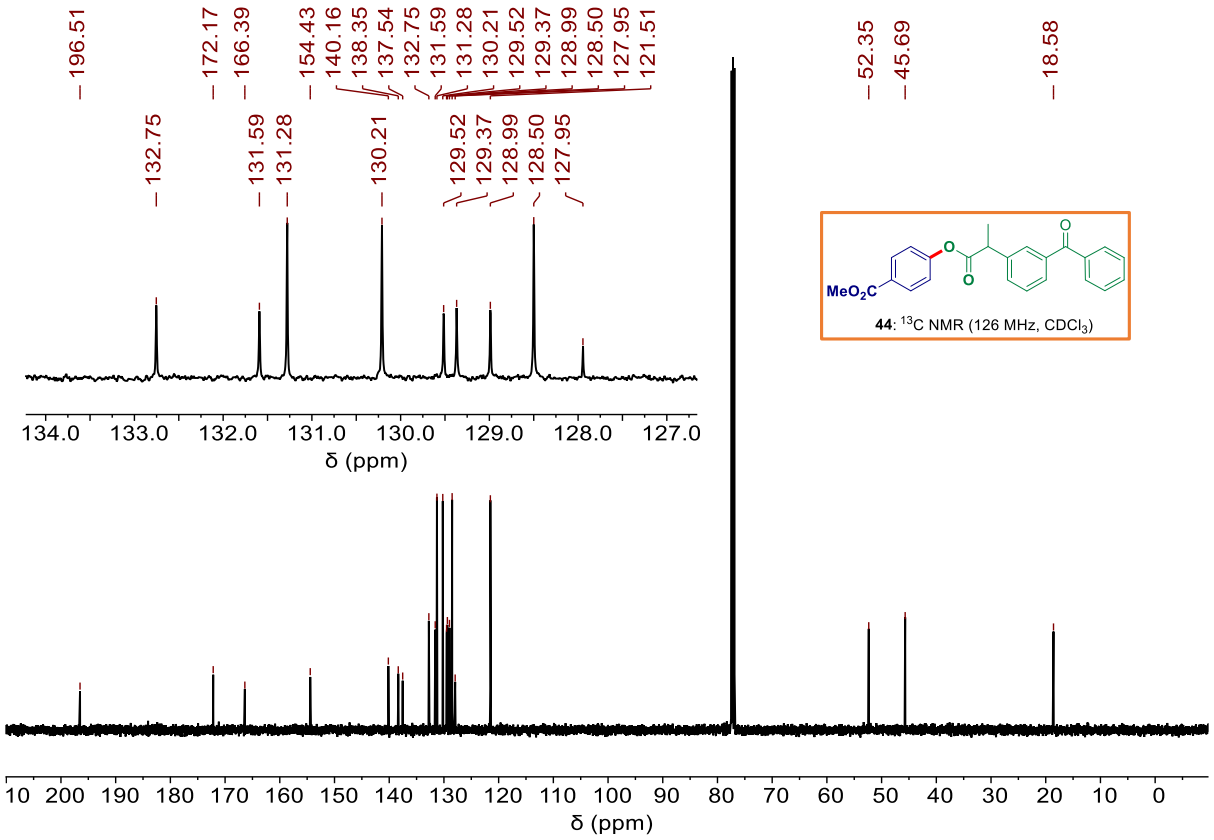

8.08
8.07
8.06
7.26
7.25
7.24
7.10
7.09
7.08
6.91
6.90
6.89
3.91
1.74
δ (ppm)
MeO2C
Cl
42: 1H NMR (500 MHz, CDCl3)

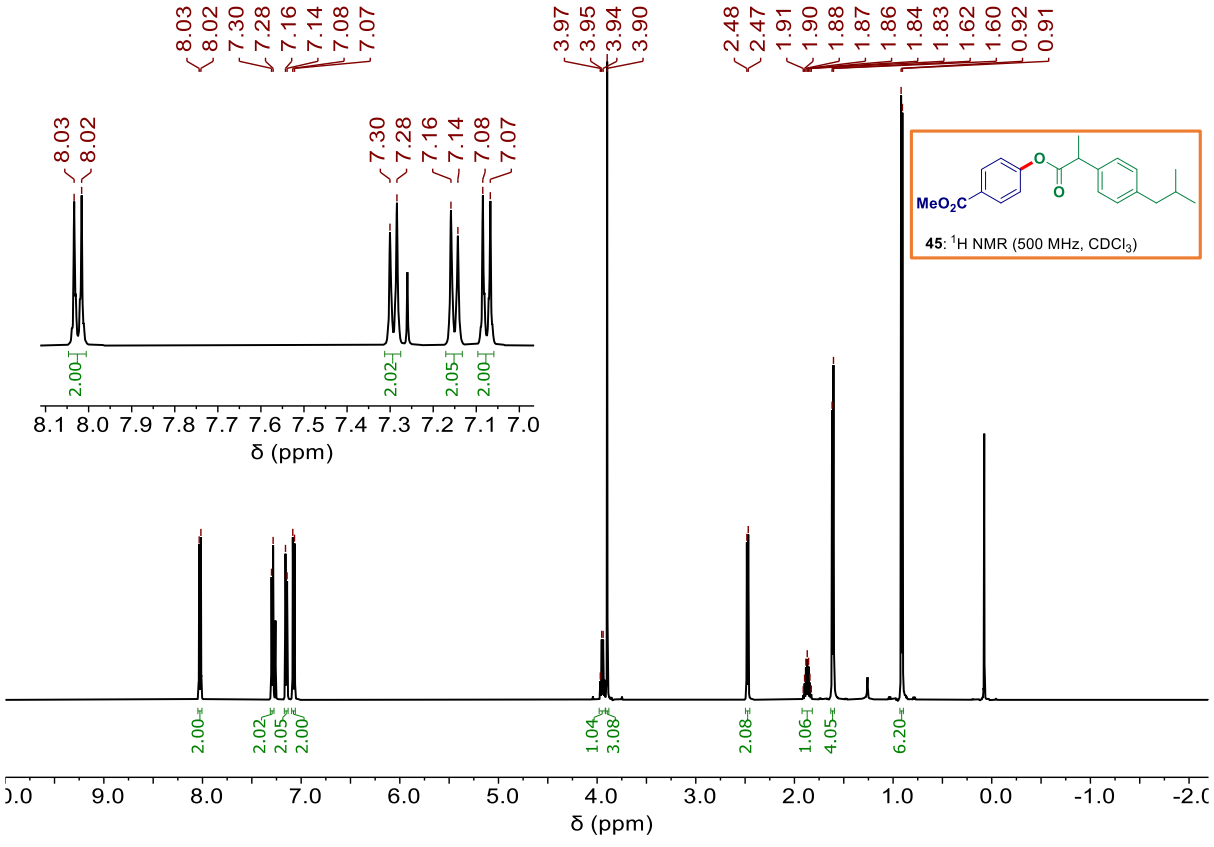

temp.710.fid
GROUP BIP
BIP-SWS-AYJAC162-13C in CDCl3
172.31
166.27
154.18
154.01
131.38
129.48
128.26
127.86
121.42
120.68
79.71
52.37
25.43
MeO2C
Cl
42: 13C NMR (126 MHz, CDCl3)
δ (ppm)

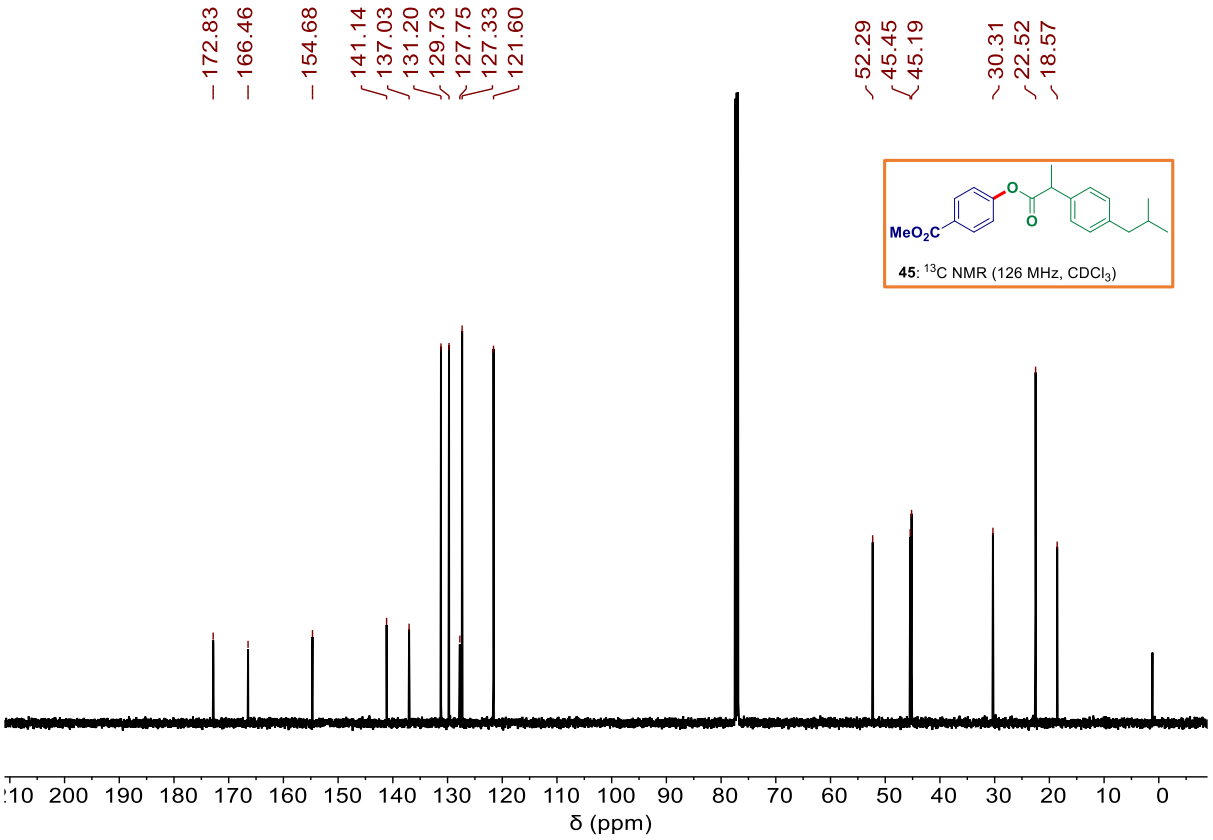

8.07
8.05
7.12
7.10
7.02
7.00
6.68
6.67
6.63
6.63
4.00
3.92
2.31
2.18
1.39
MeO2C
43: 1H NMR (500 MHz, CDCl3)
δ (ppm)

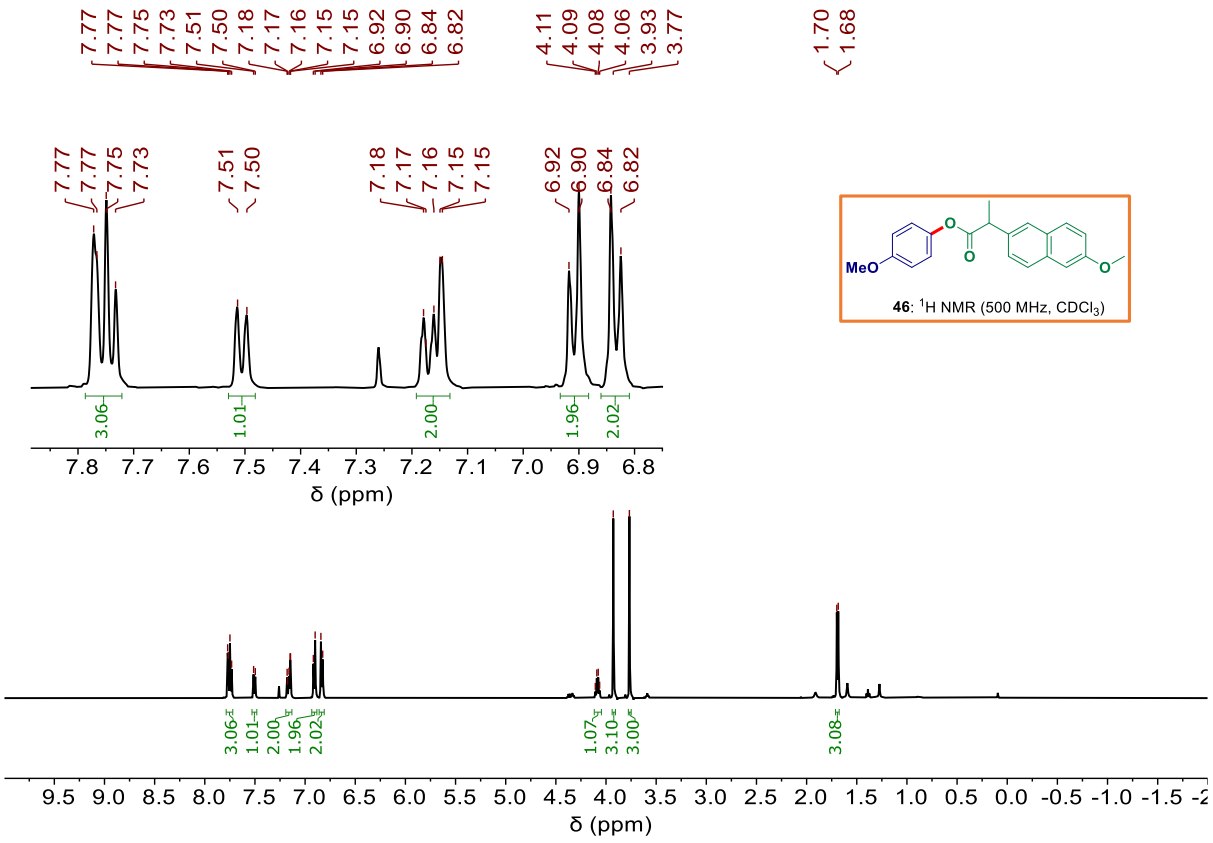

175.97
166.49
156.95
154.85
136.64
131.25
130.51
127.71
123.73
121.72
120.94
112.08
67.80
52.31
42.71
37.23
25.39
25.23
21.53
15.92
MeO2C
O
O
O
43: 13C NMR (126 MHz, CDCl3)
δ (ppm)

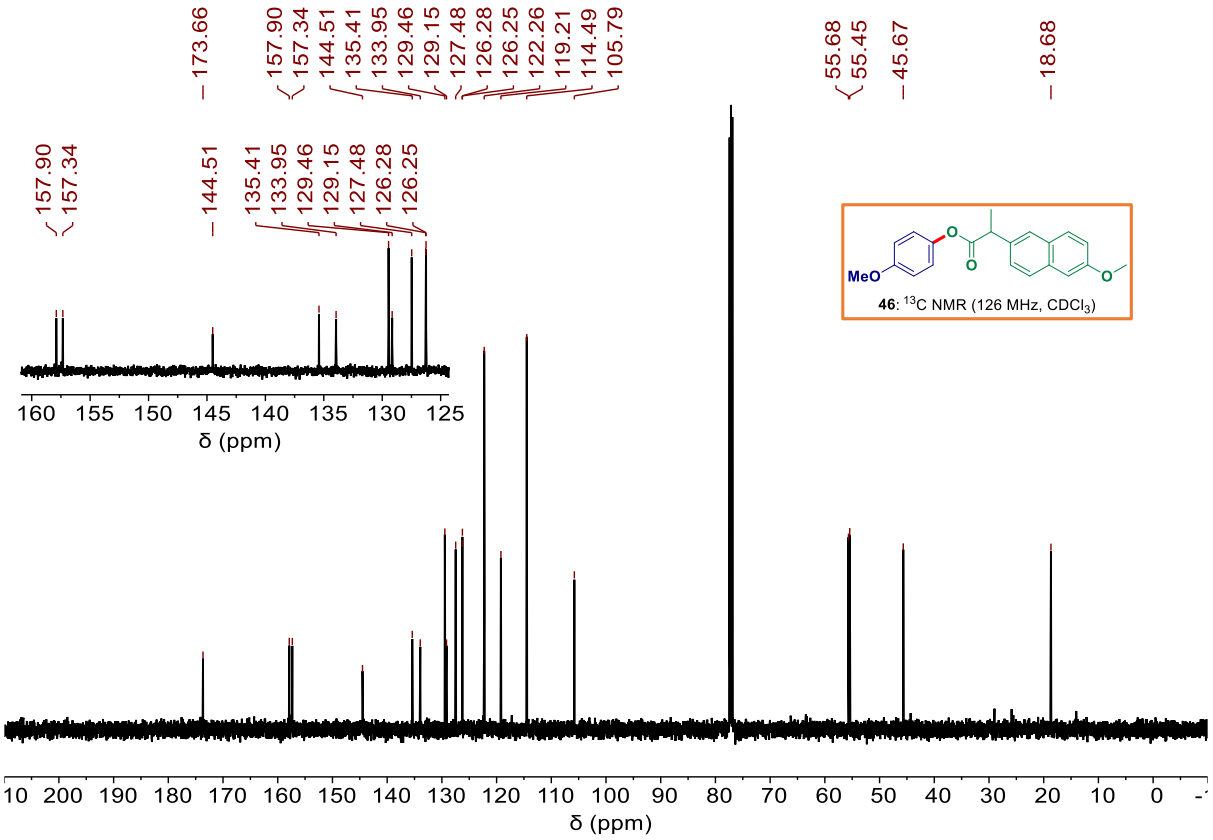

8.05
8.03
7.85
7.82
7.80
7.74
7.73
7.65
7.64
7.64
7.63
7.63
7.62
7.60
7.59
7.58
7.52
7.51
7.49
7.49
7.48
7.46
7.10
7.09
4.08
4.07
4.06
4.04
3.90
1.67
1.66
MeO2C
O
O
O
44: 1H NMR (500 MHz, CDCl3)
δ (ppm)

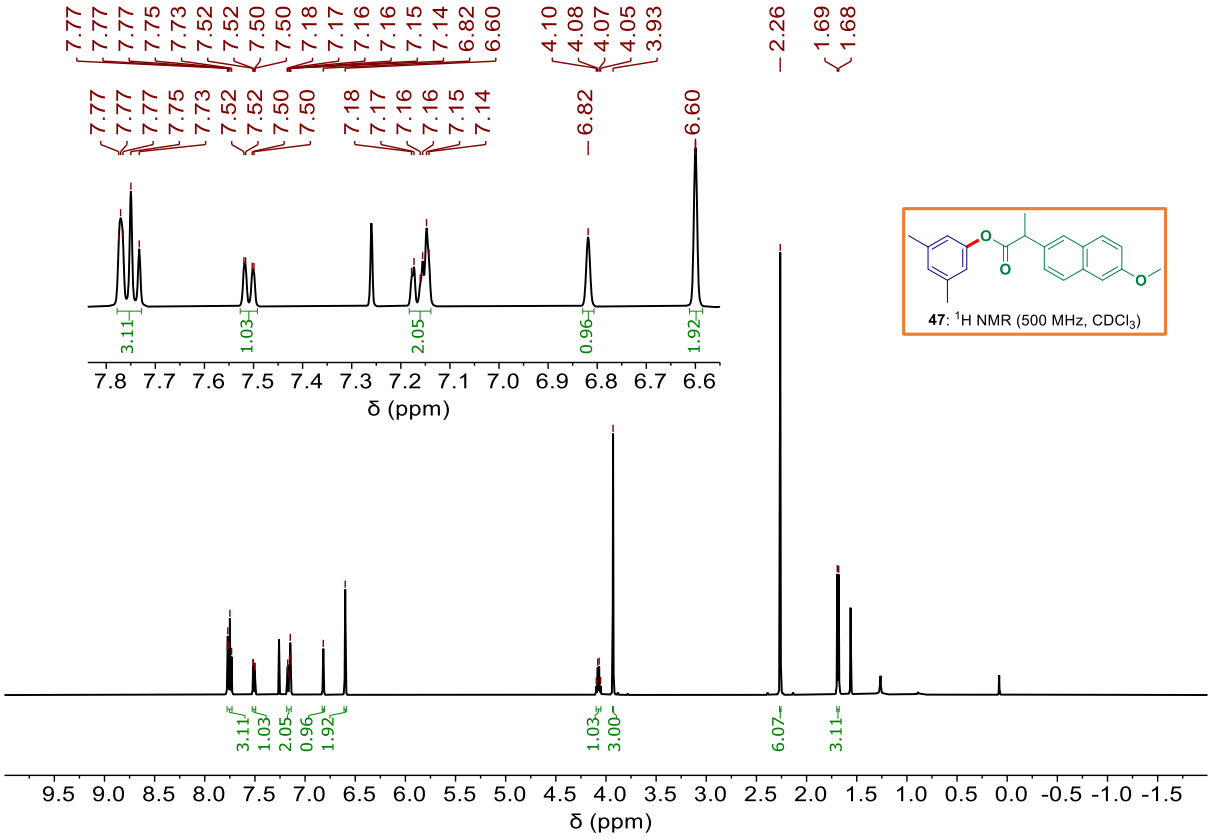

196.51
172.17
166.39
154.43
140.16
138.35
137.54
132.75
131.59
131.28
130.21
129.52
129.37
128.99
128.50
127.95
121.51
52.35
45.69
18.58
δ (ppm)
MeO2C
44: 13C NMR (126 MHz, CDCl3)

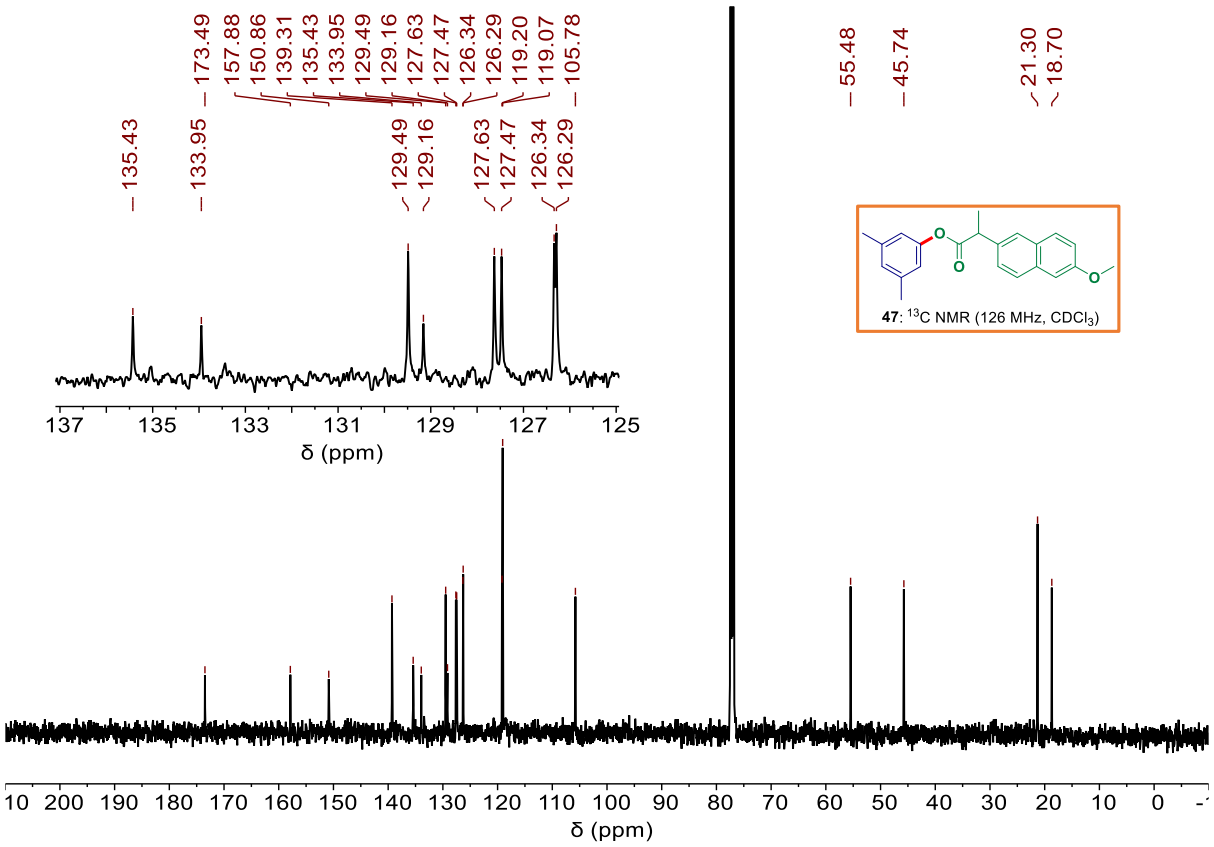

8.03
8.02
7.30
7.28
7.16
7.14
7.08
7.07
3.97
3.95
3.94
3.90
2.48
2.47
1.91
1.90
1.88
1.87
1.86
1.84
1.83
1.62
1.60
0.92
0.91
δ (ppm)
MeO2C
45: 1H NMR (500 MHz, CDCl3)

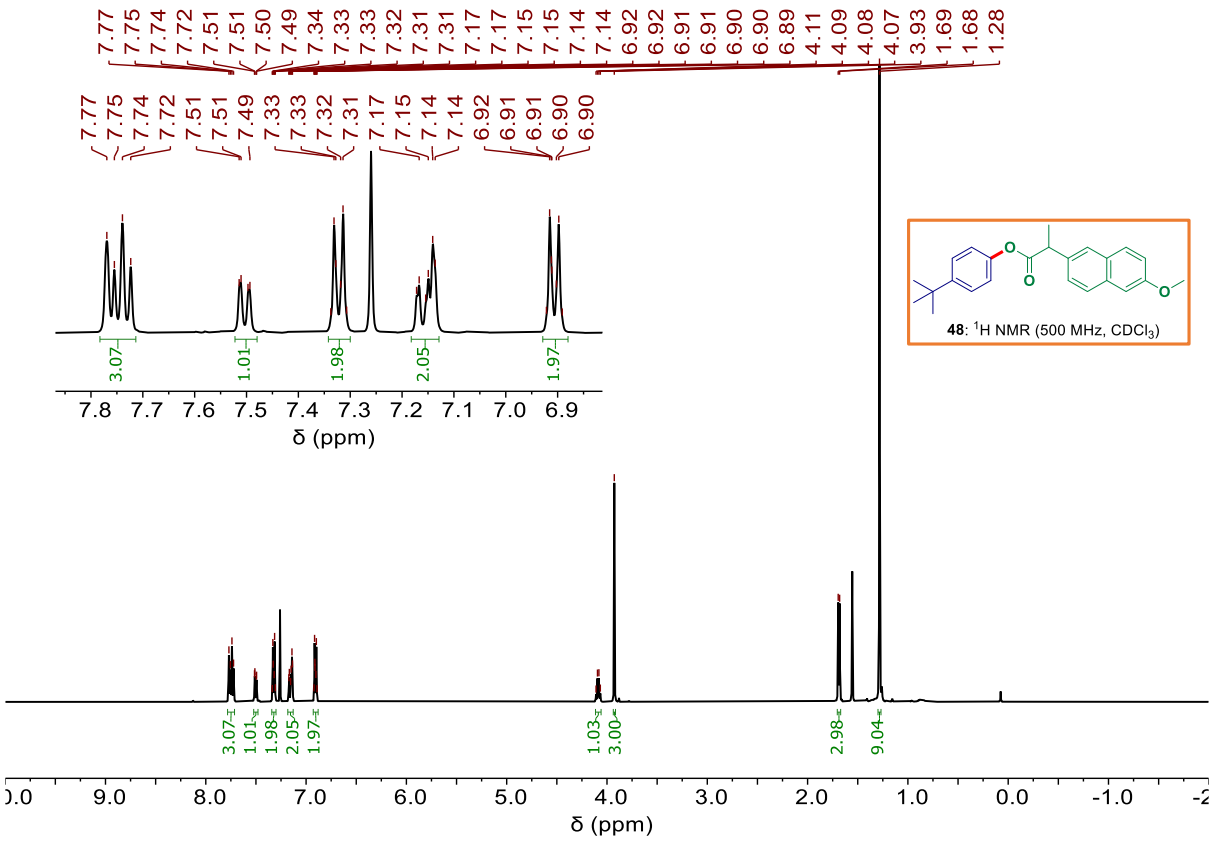

172.83
166.46
154.68
141.14
137.03
131.20
129.73
127.75
127.33
121.60
52.29
45.45
45.19
30.31
22.52
18.57
MeO2C
45: 13C NMR (126 MHz, CDCl3)
δ (ppm)

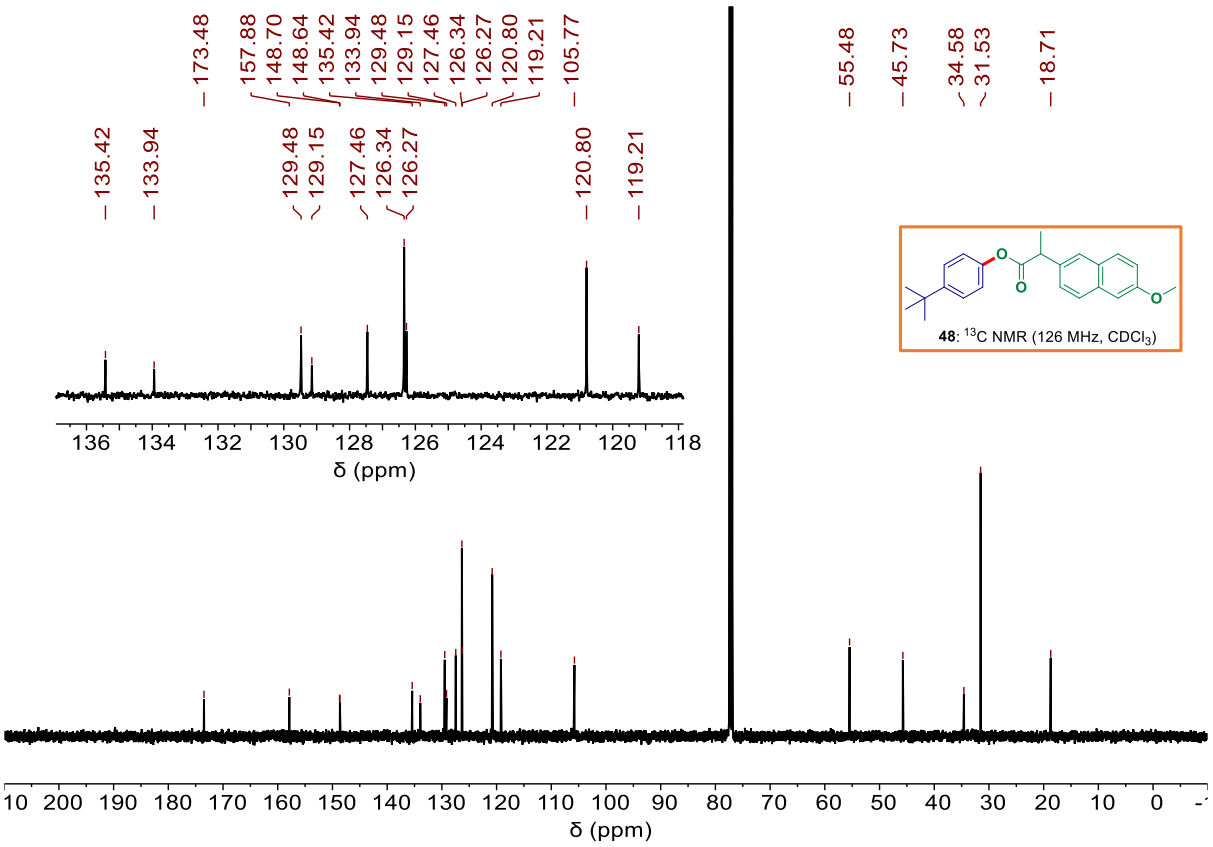

7.77
7.77
7.75
7.73
7.51
7.50
7.18
7.17
7.16
7.15
7.15
6.92
6.90
6.84
6.82
4.11
4.09
4.08
4.06
3.93
3.77
1.70
1.68
MeO
46: 1H NMR (500 MHz, CDCl3)
3.06
1.01
2.00
1.96
2.02
1.07
3.10
3.00
3.08
δ (ppm)

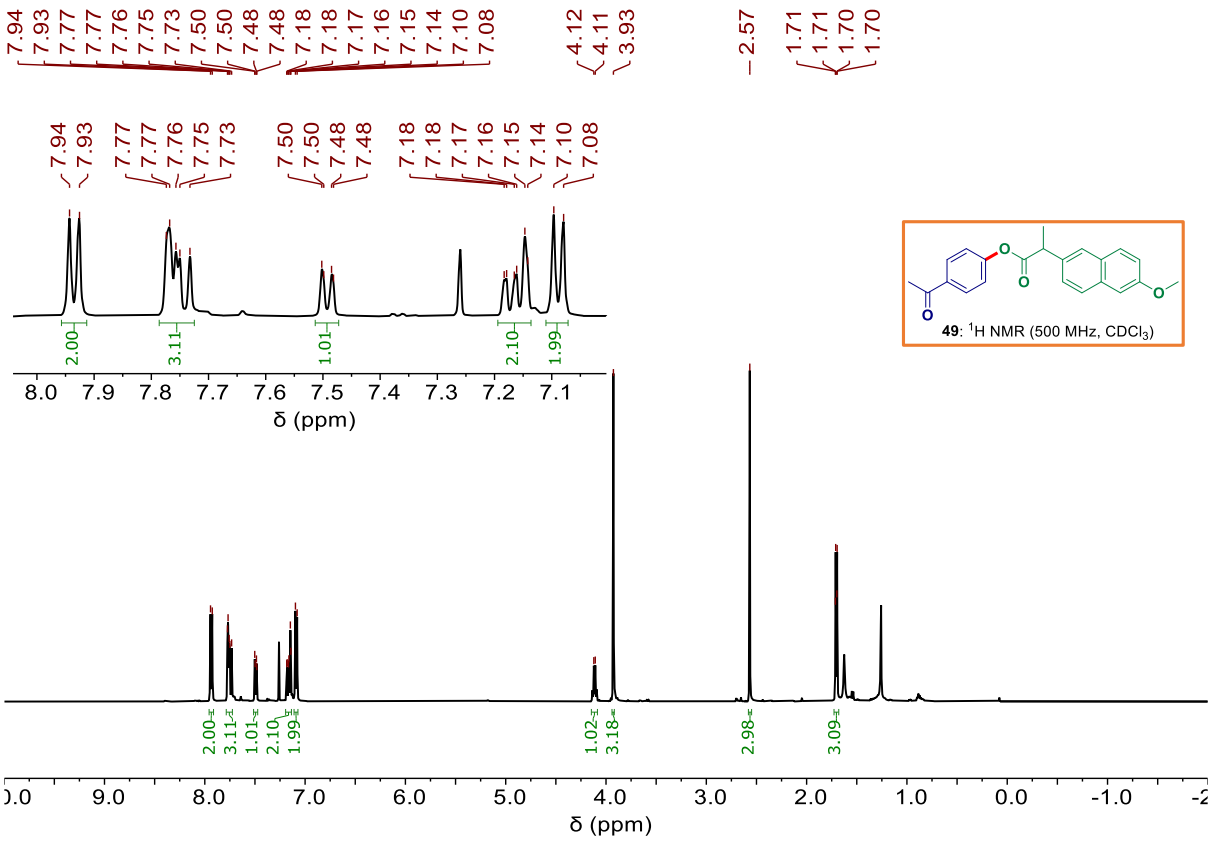

173.66
157.90
157.34
144.51
135.41
133.95
129.46
129.15
127.48
126.28
126.25
122.26
119.21
114.49
105.79
55.68
55.45
45.67
18.68
MeO
46: 13C NMR (126 MHz, CDCl3)
δ (ppm)

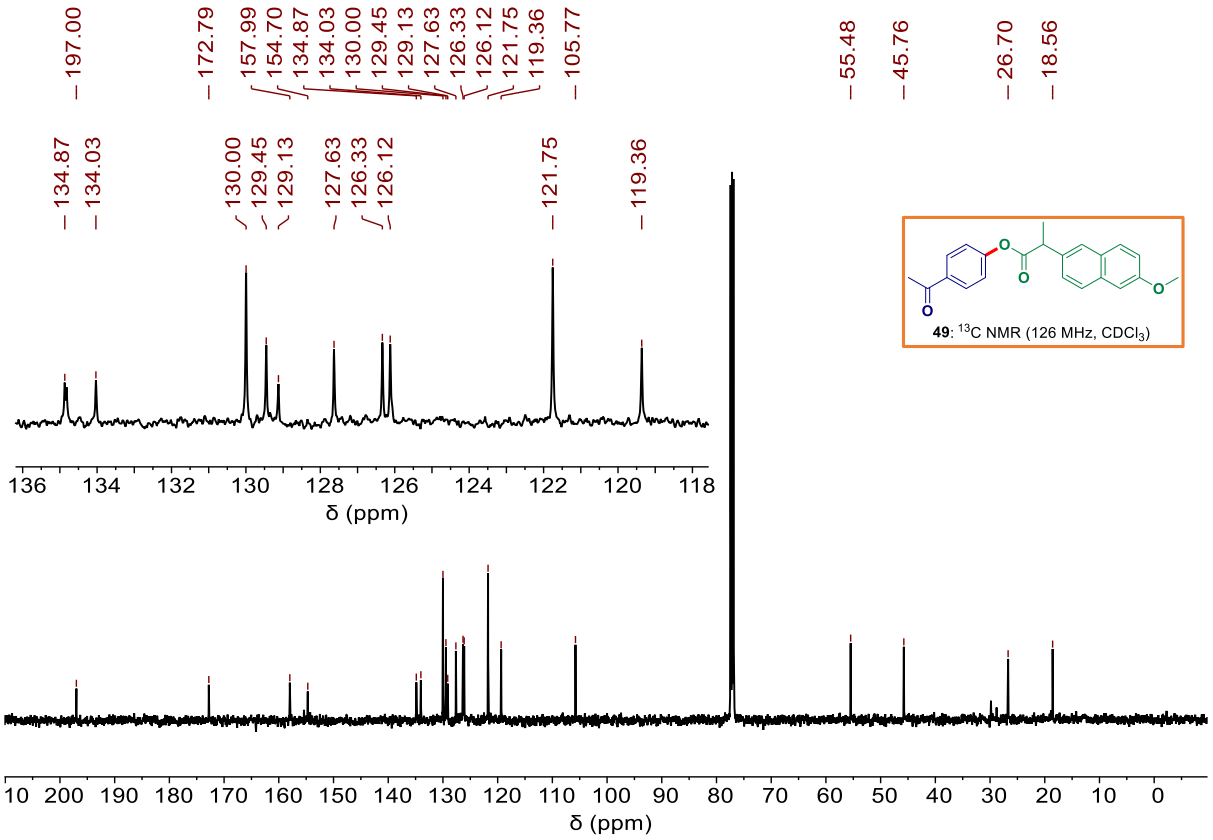

7.77
7.77
7.77
7.75
7.73
7.52
7.52
7.50
7.50
7.18
7.17
7.16
7.16
7.15
7.14
6.82
6.60
4.10
4.08
4.07
4.05
3.93
2.26
1.69
1.68
3.11
1.03
2.05
0.96
1.92
1.03
3.00
6.07
3.11
47: 1H NMR (500 MHz, CDCl3)
δ (ppm)

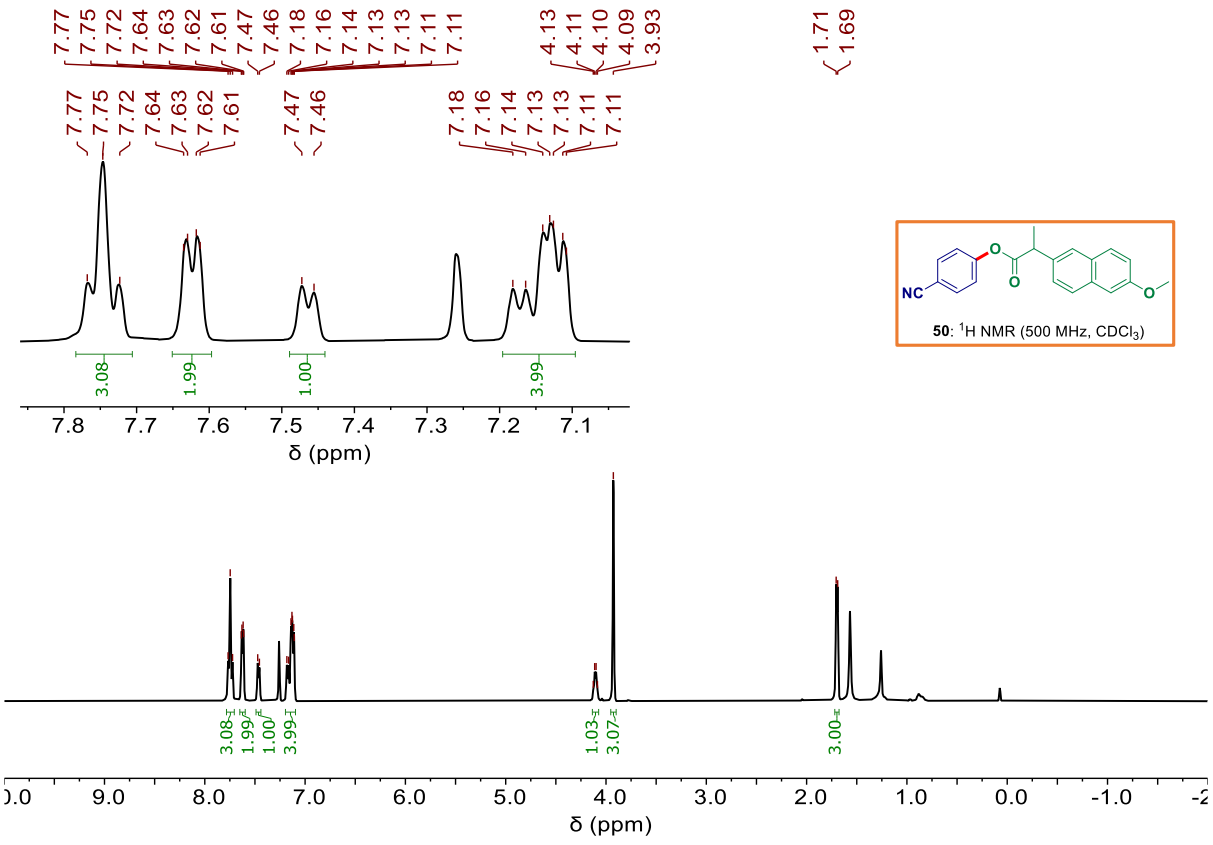

173.49
157.88
150.86
139.31
135.43
133.95
129.49
129.16
127.63
127.47
126.34
126.29
119.20
119.07
105.78
55.48
45.74
21.30
18.70
135.43
133.95
129.49
129.16
127.63
127.47
126.34
126.29
δ (ppm)
47: 13C NMR (126 MHz, CDCl3)
δ (ppm)

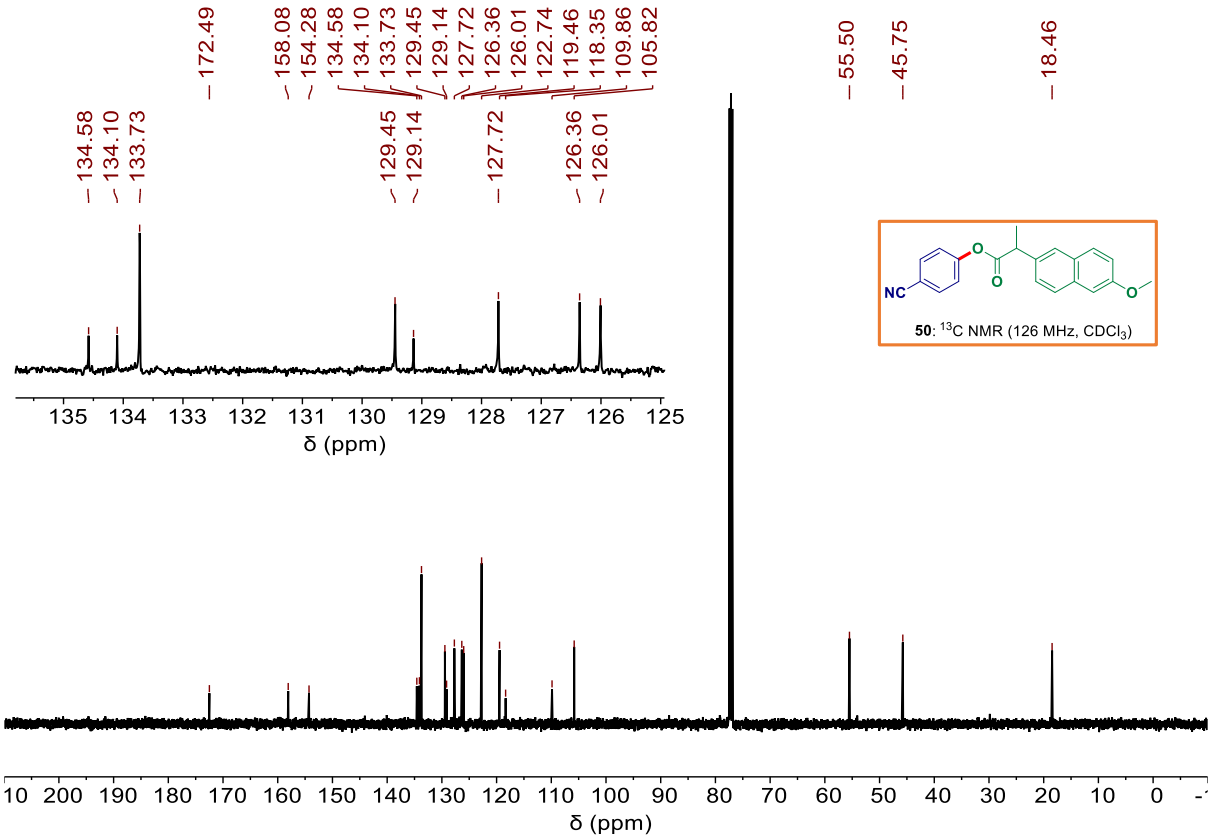

7.77
7.75
7.74
7.72
7.51
7.51
7.50
7.49
7.34
7.33
7.33
7.32
7.31
7.31
7.17
7.17
7.15
7.15
7.14
6.92
6.92
6.91
6.91
6.90
6.90
6.89
4.11
4.09
4.08
4.07
3.93
1.69
1.68
1.28
3.07
1.01
1.98
2.05
1.97
δ (ppm)
48: 1H NMR (500 MHz, CDCl3)
δ (ppm)

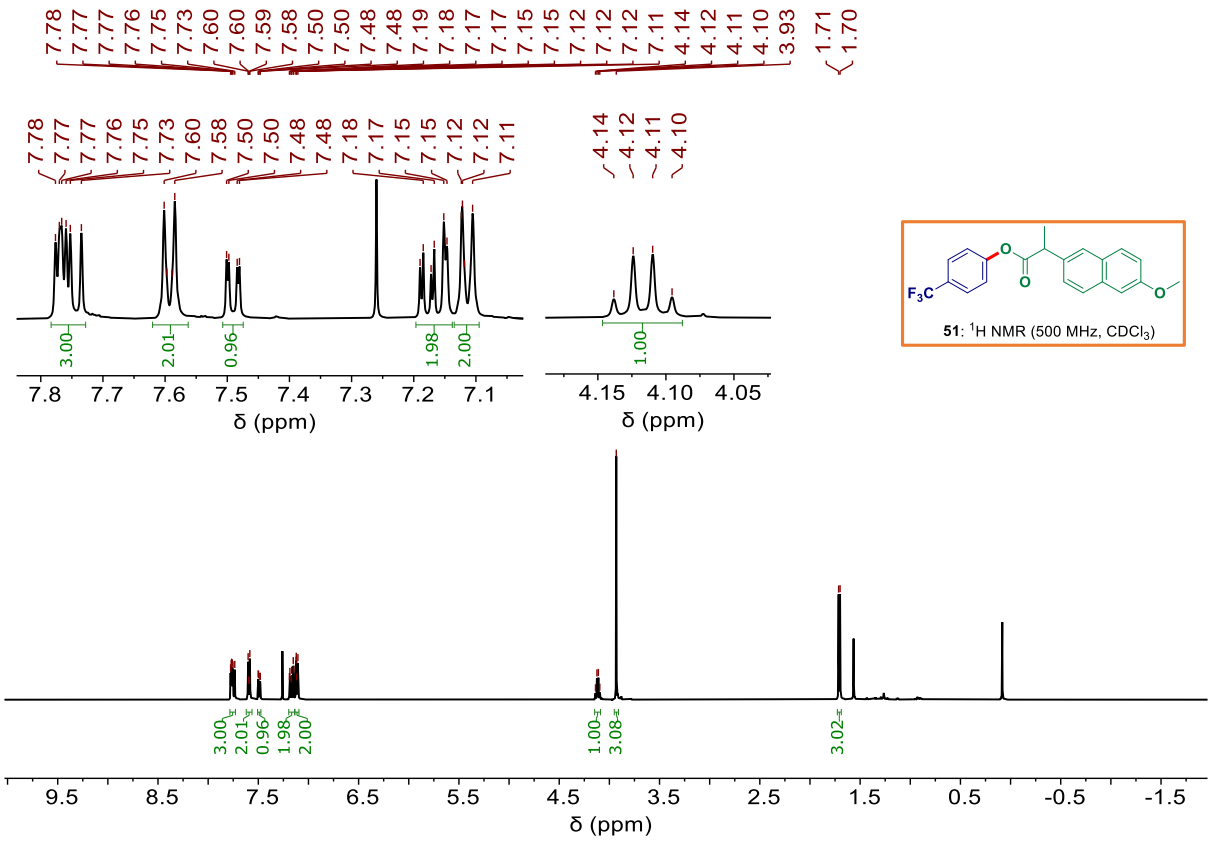

173.48
157.88
148.70
148.64
135.42
133.94
129.48
129.15
127.46
126.34
126.27
120.80
119.21
105.77
55.48
45.73
34.58
31.53
18.71
δ (ppm)
48: 13C NMR (126 MHz, CDCl3)

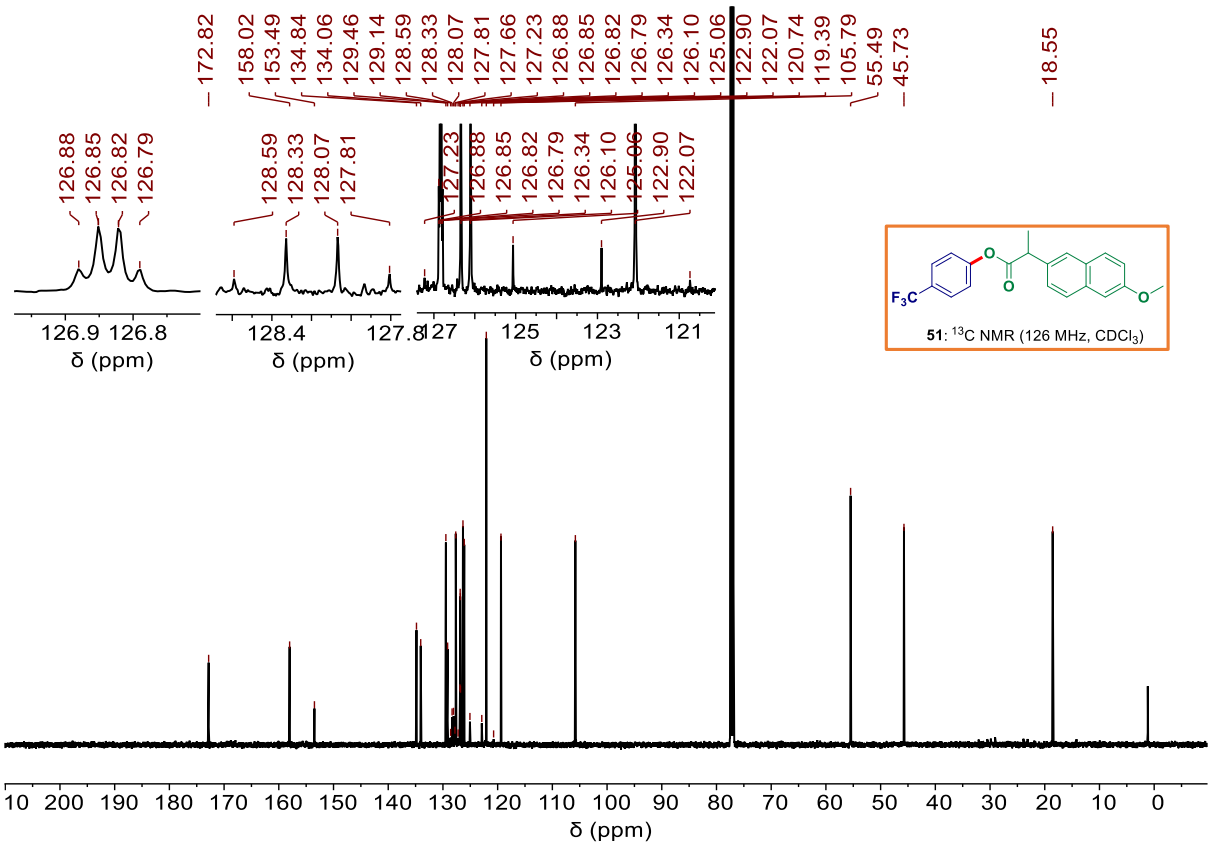

7.94
7.93
7.77
7.77
7.76
7.75
7.73
7.50
7.50
7.48
7.48
7.18
7.18
7.17
7.16
7.15
7.14
7.10
7.08
4.12
4.11
3.93
2.57
1.71
1.71
1.70
1.70
2.00
3.11
1.01
2.10
1.99
1.02
3.18
2.98
3.09
δ (ppm)
49: 1H NMR (500 MHz, CDCl3)

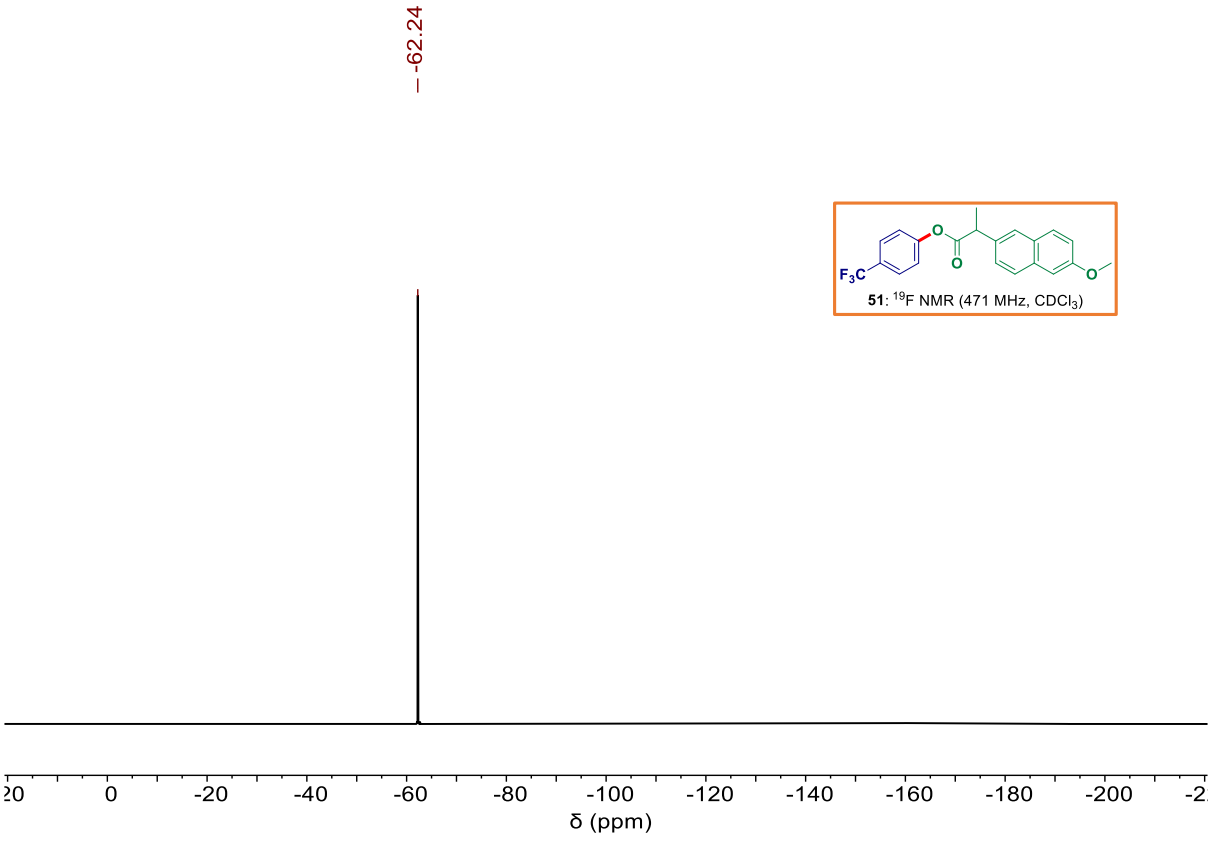

197.00
172.79
157.99
154.70
134.87
134.03
130.00
129.45
129.13
127.63
126.33
126.12
121.75
119.36
105.77
55.48
45.76
26.70
18.56
δ (ppm)
49: 13C NMR (126 MHz, CDCl3)

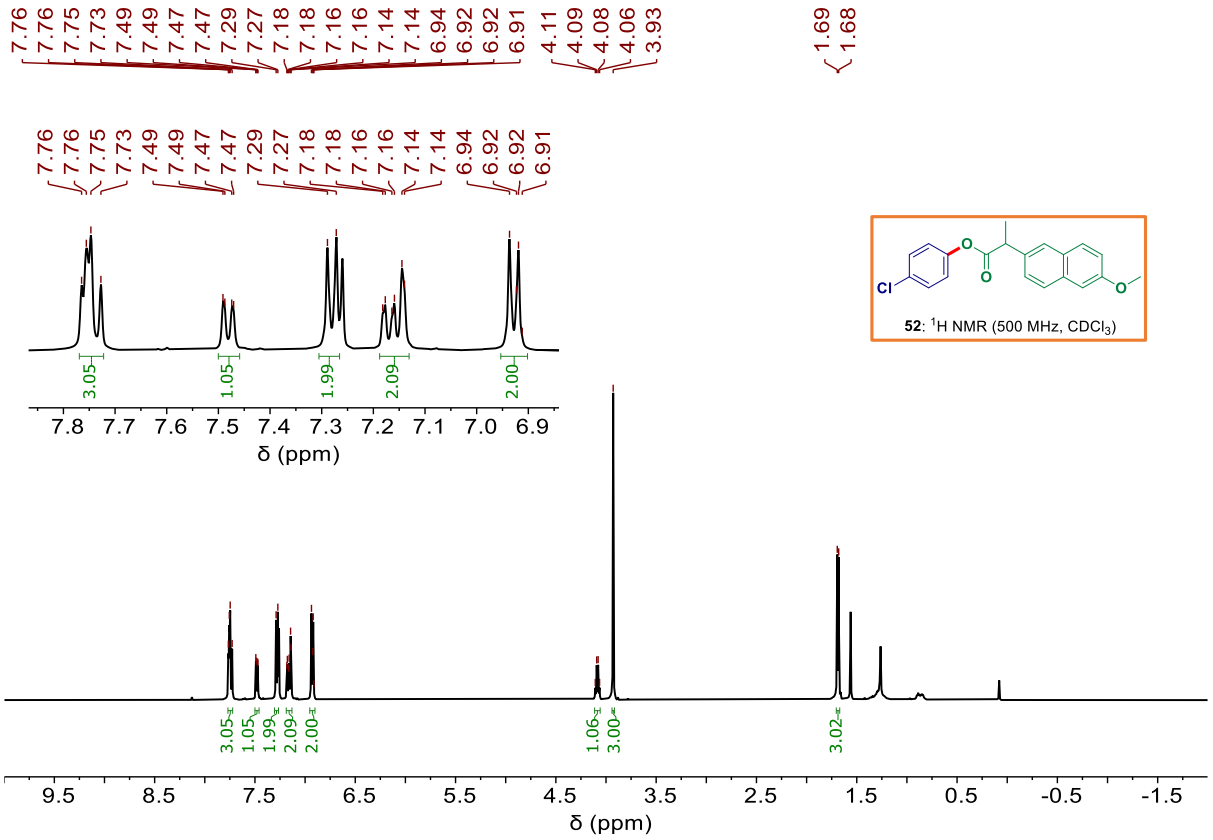

7.77
7.75
7.72
7.64
7.63
7.62
7.61
7.47
7.46
7.18
7.16
7.14
7.13
7.13
7.11
7.11
4.13
4.11
4.10
4.09
3.93
1.71
1.69
3.08
1.99
1.00
3.99
3.08
1.99
1.00
3.99
1.03
3.07
3.00
δ (ppm)
50: 1H NMR (500 MHz, CDCl3)

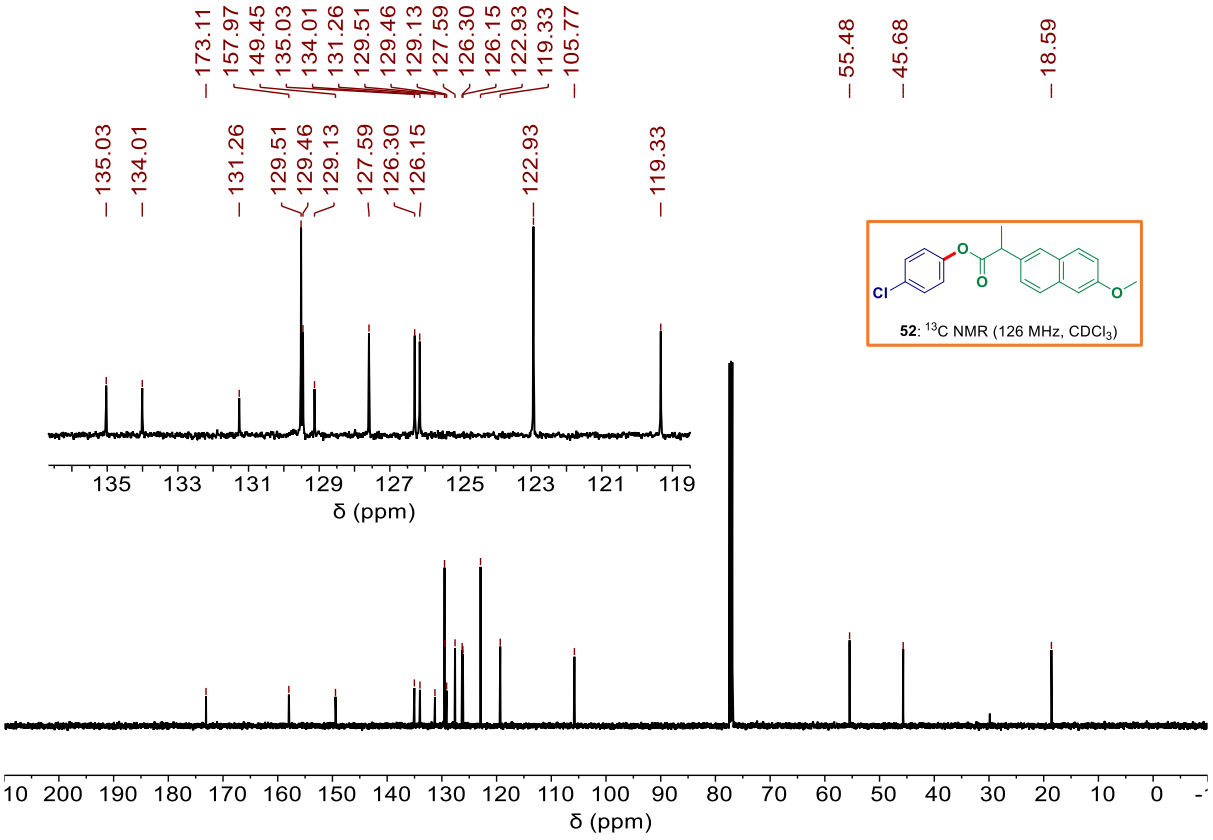

172.49
158.08
154.28
134.58
134.10
133.73
129.45
129.14
127.72
126.36
126.01
122.74
119.46
118.35
109.86
105.82
55.50
45.75
18.46
δ (ppm)
NC
O
O
O
50: 13C NMR (126 MHz, CDCl3)

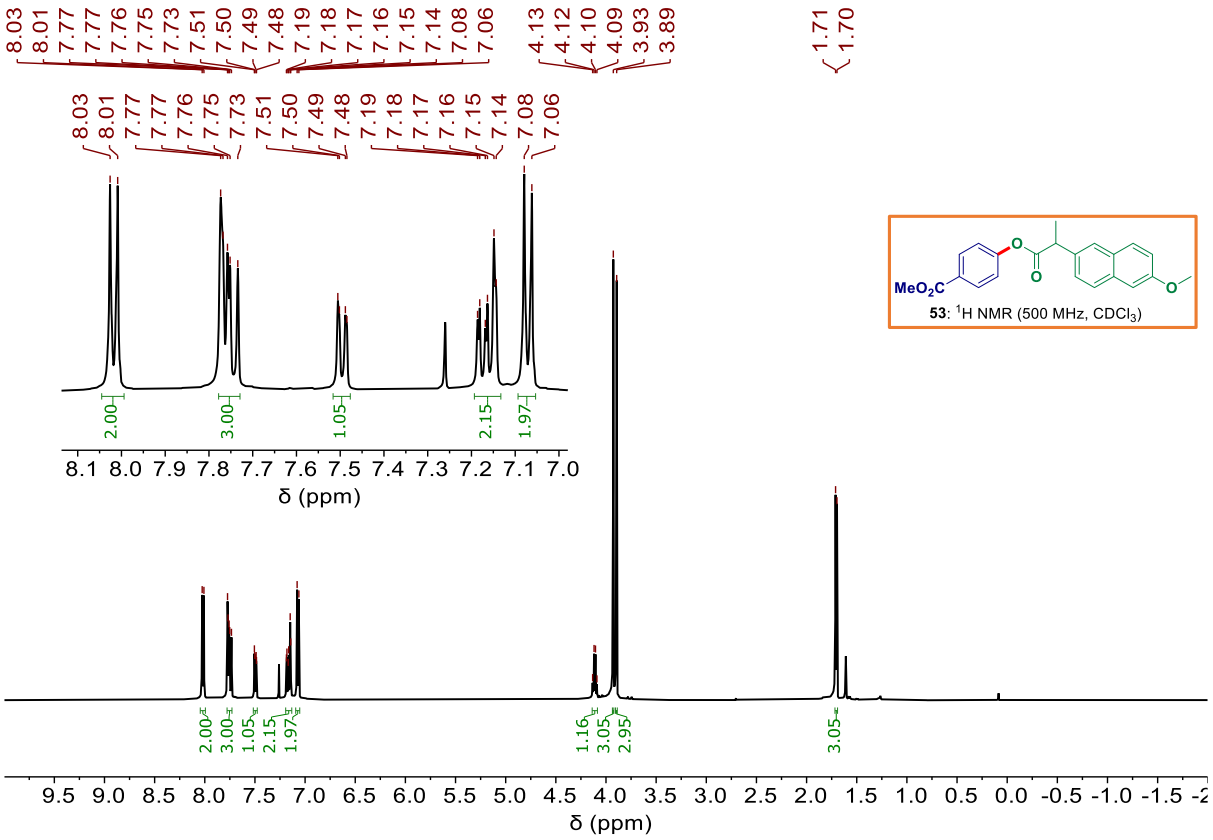

7.78
7.77
7.77
7.76
7.75
7.73
7.60
7.59
7.58
7.50
7.50
7.48
7.48
7.19
7.18
7.17
7.17
7.15
7.15
7.12
7.12
7.11
4.14
4.12
4.11
4.10
3.93
1.71
1.70
3.00
2.01
0.96
1.98
2.00
1.00
3.08
3.02
δ (ppm)
F3C
O
O
O
51: 1H NMR (500 MHz, CDCl3)

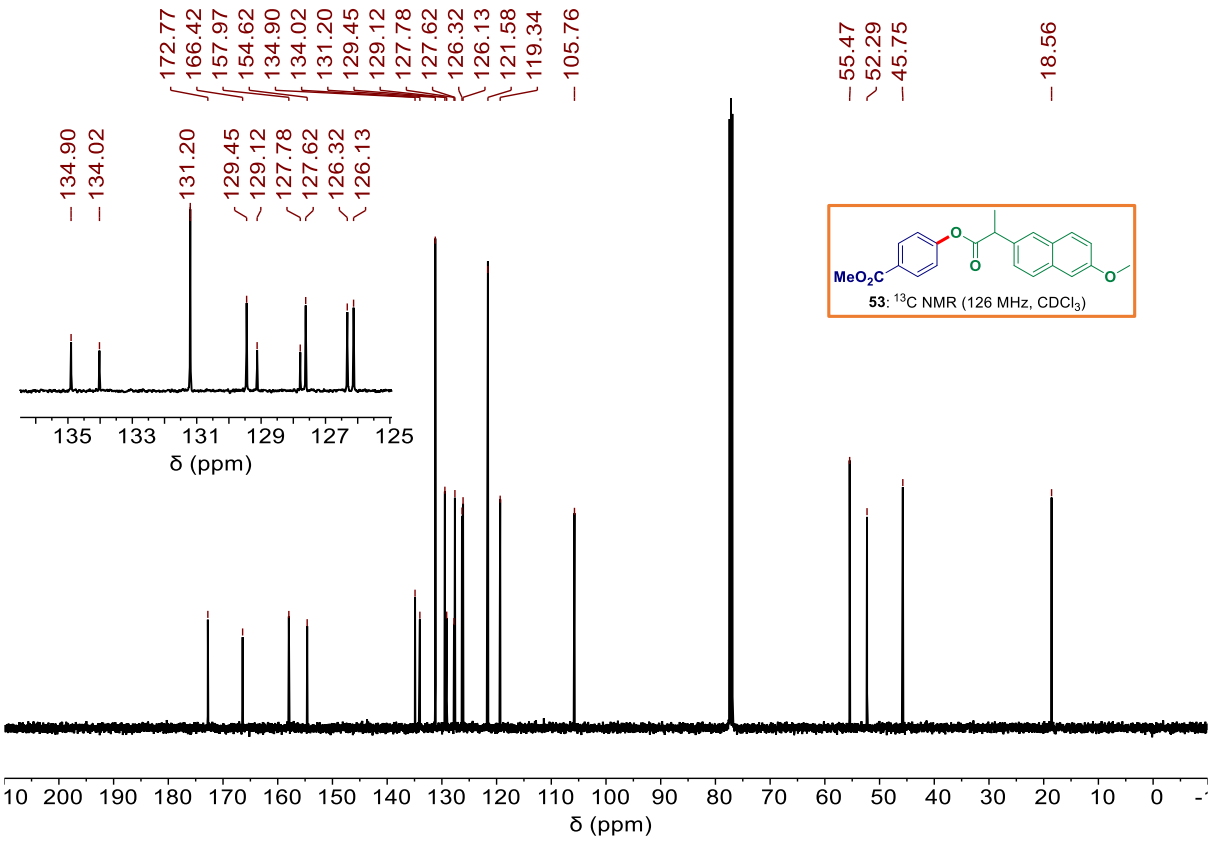

172.82
158.02
153.49
134.84
134.06
129.46
129.14
128.59
128.33
128.07
127.81
127.66
127.23
126.88
126.85
126.82
126.79
126.34
126.10
125.06
122.90
122.07
120.74
119.39
105.79
55.49
45.73
18.55
126.88
126.85
126.82
126.79
128.59
128.33
128.07
127.81
127.23
126.88
126.85
126.82
126.79
126.34
126.10
125.06
122.90
122.07
126.9 126.8
δ (ppm)
128.4
127.8
δ (ppm)
127
125
123
121
δ (ppm)
51: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


-62.24
51: 19F NMR (471 MHz, CDCl3)
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -2
δ (ppm)

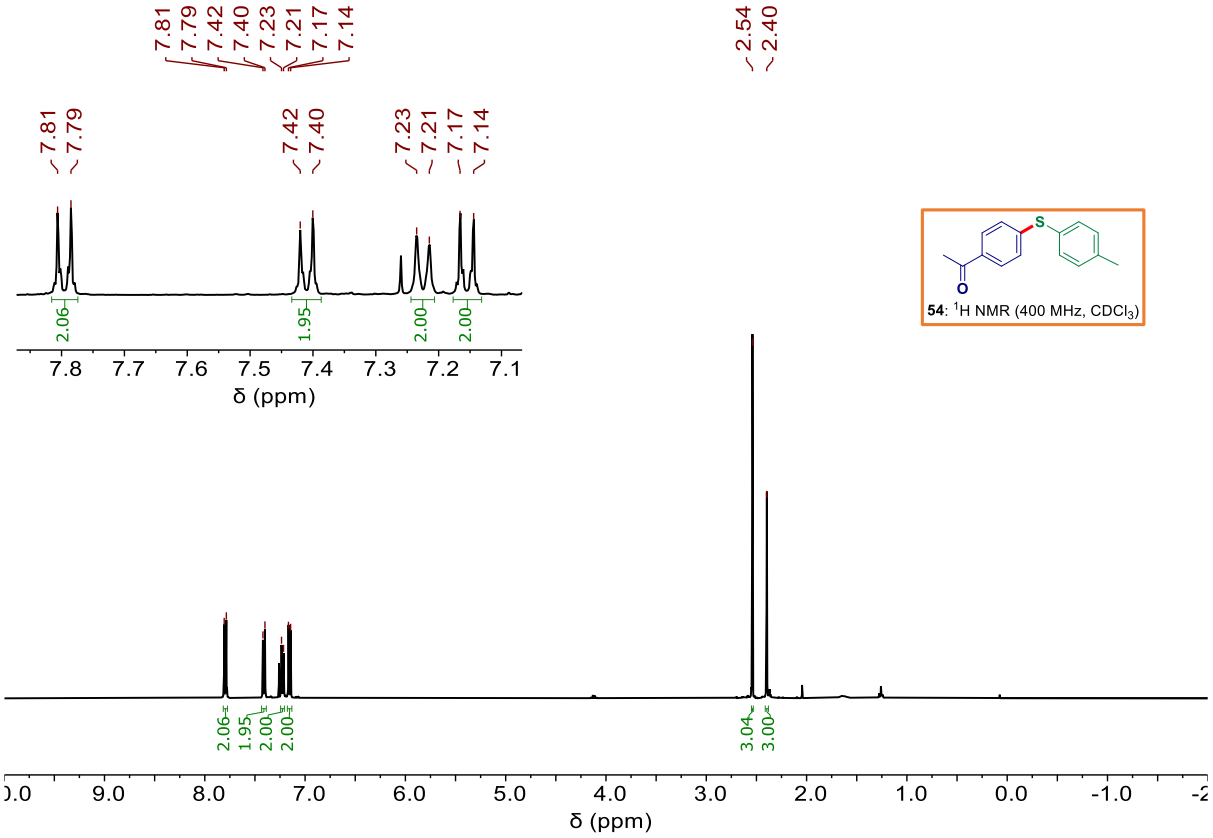

7.76 7.76 7.75 7.73 7.49 7.49 7.47 7.47 7.29 7.27 7.18 7.18 7.16 7.16 7.14 7.14 6.94 6.92 6.92 6.91 4.11 4.09 4.08 4.06 3.93 1.69 1.68
3.05 1.05 1.99 2.09 2.00
δ (ppm)
Cl O O O
52: 1H NMR (500 MHz, CDCl3)
3.05 1.05 1.99 2.09 2.00 1.06 3.00 3.02
δ (ppm)

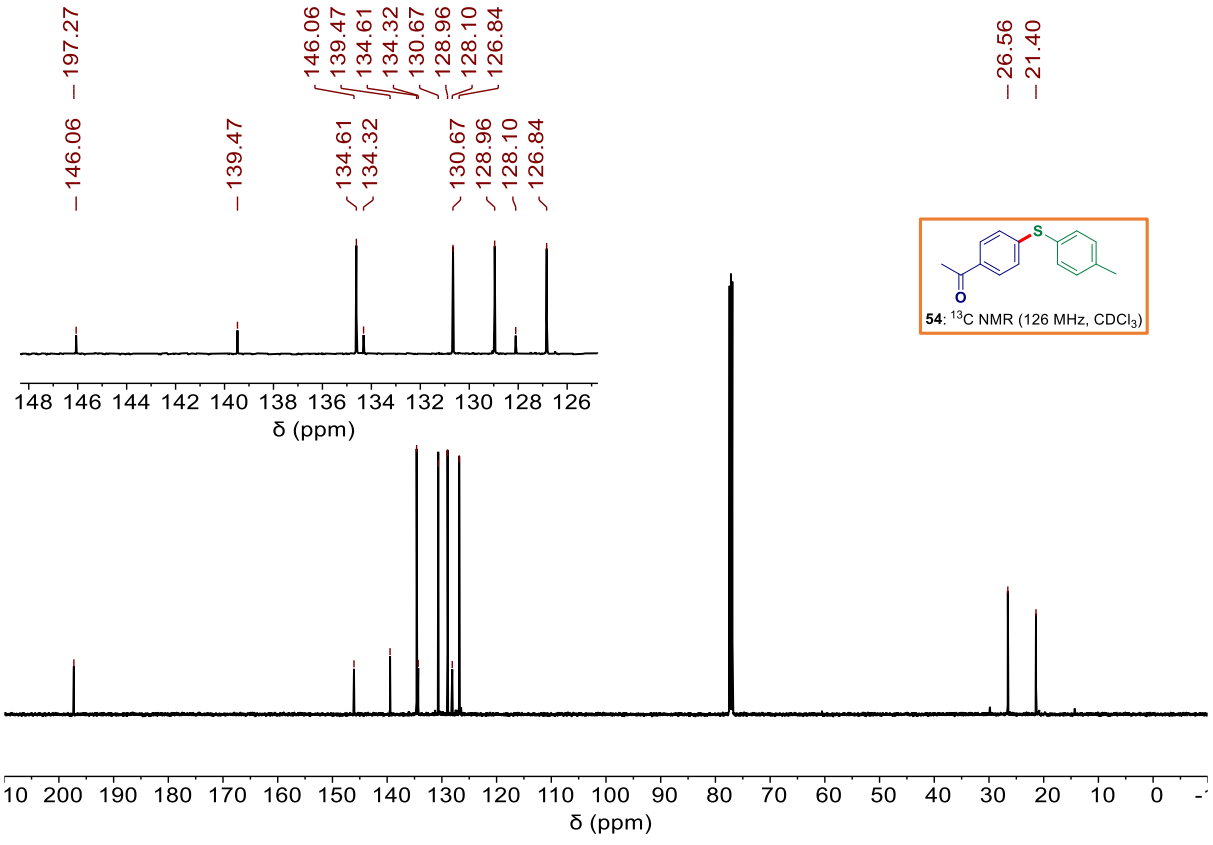

173.11 157.97 149.45 135.03 134.01 131.26 129.51 129.46 129.13 127.59 126.30 126.15 122.93 119.33 105.77 55.48 45.68 18.59
δ (ppm)
Cl O O O
52: 13C NMR (126 MHz, CDCl3)
δ (ppm)

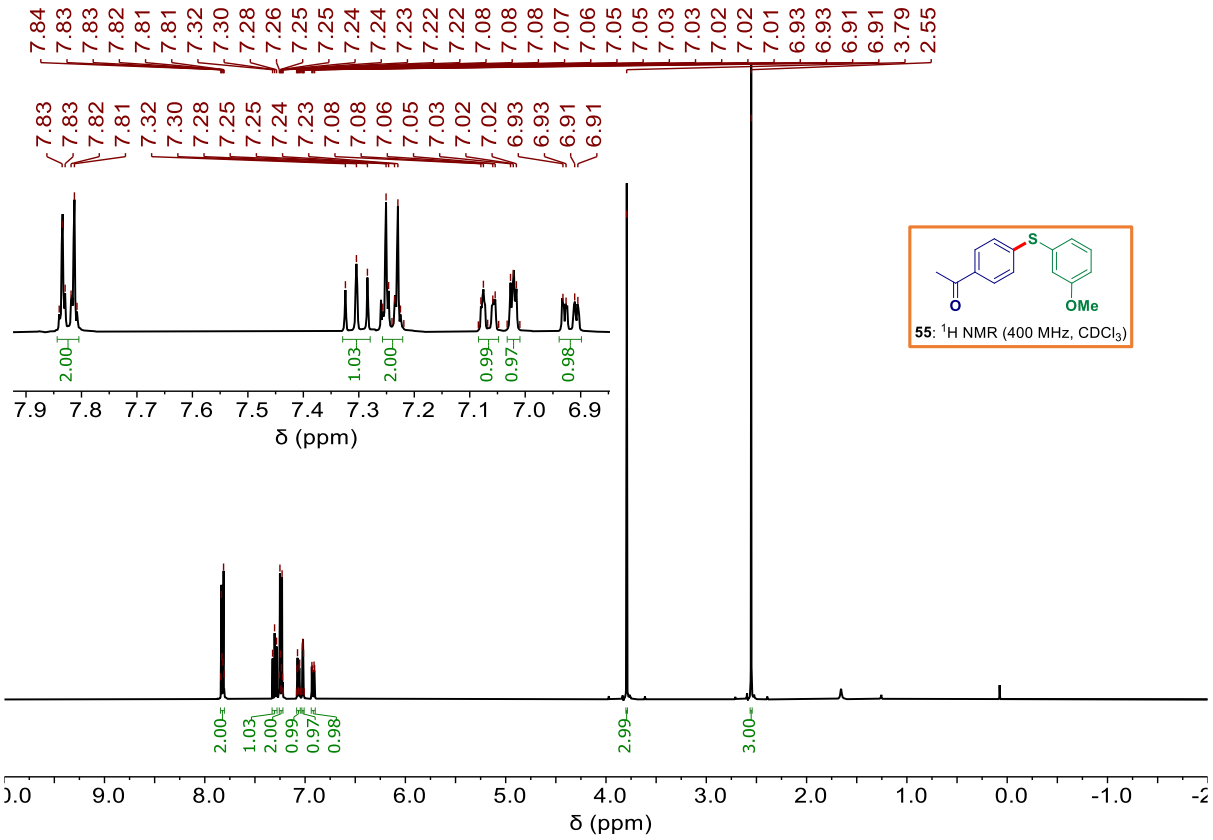

8.03 8.01 7.77 7.77 7.76 7.75 7.73 7.51 7.50 7.49 7.48 7.19 7.18 7.17 7.16 7.15 7.14 7.08 7.06
4.13 4.12 4.10 4.09 3.93 3.89
1.71 1.70
2.00 3.00 1.05 2.15 1.97
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
δ (ppm)
MeO2C
53: 1H NMR (500 MHz, CDCl3)
2.00 3.00 1.05 2.15 1.97 1.16 3.05 2.95 3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
δ (ppm)

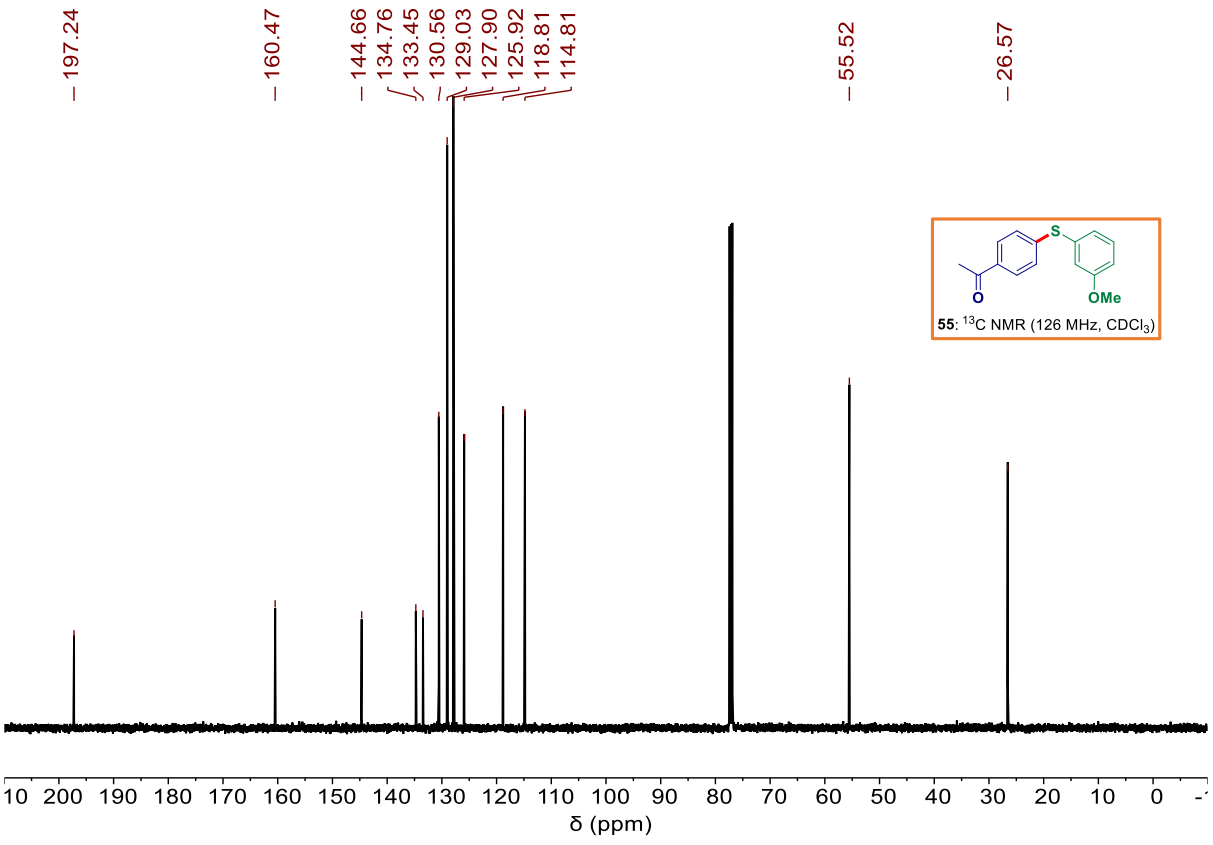

172.77 166.42 157.97 154.62 134.90 134.02 131.20 129.45 129.12 127.78 127.62 126.32 126.13 121.58 119.34 105.76
55.47 52.29 45.75
18.56
134.90 134.02 131.20 129.45 129.12 127.78 127.62 126.32 126.13
135 133 131 129 127 125
δ (ppm)
MeO2C
53: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

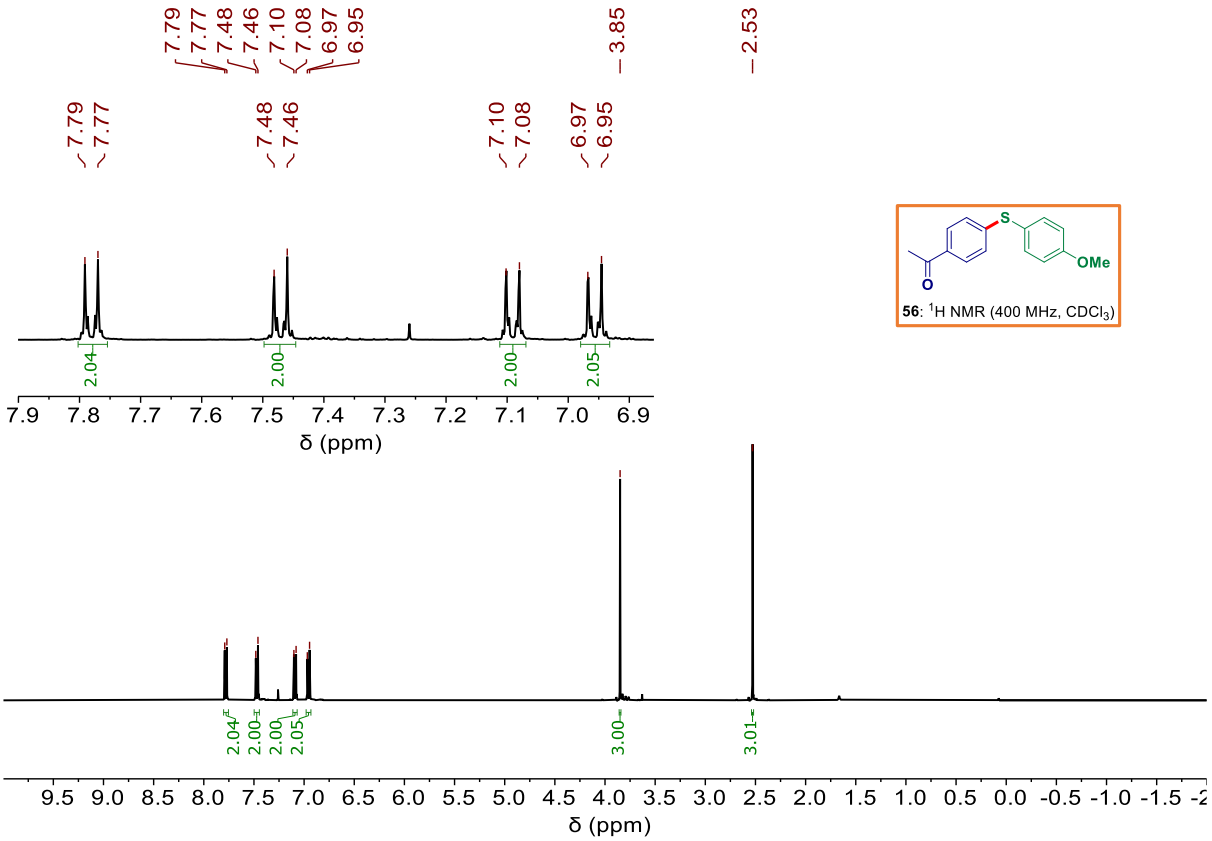
NMR Copies for Thioether Substrate Scopes

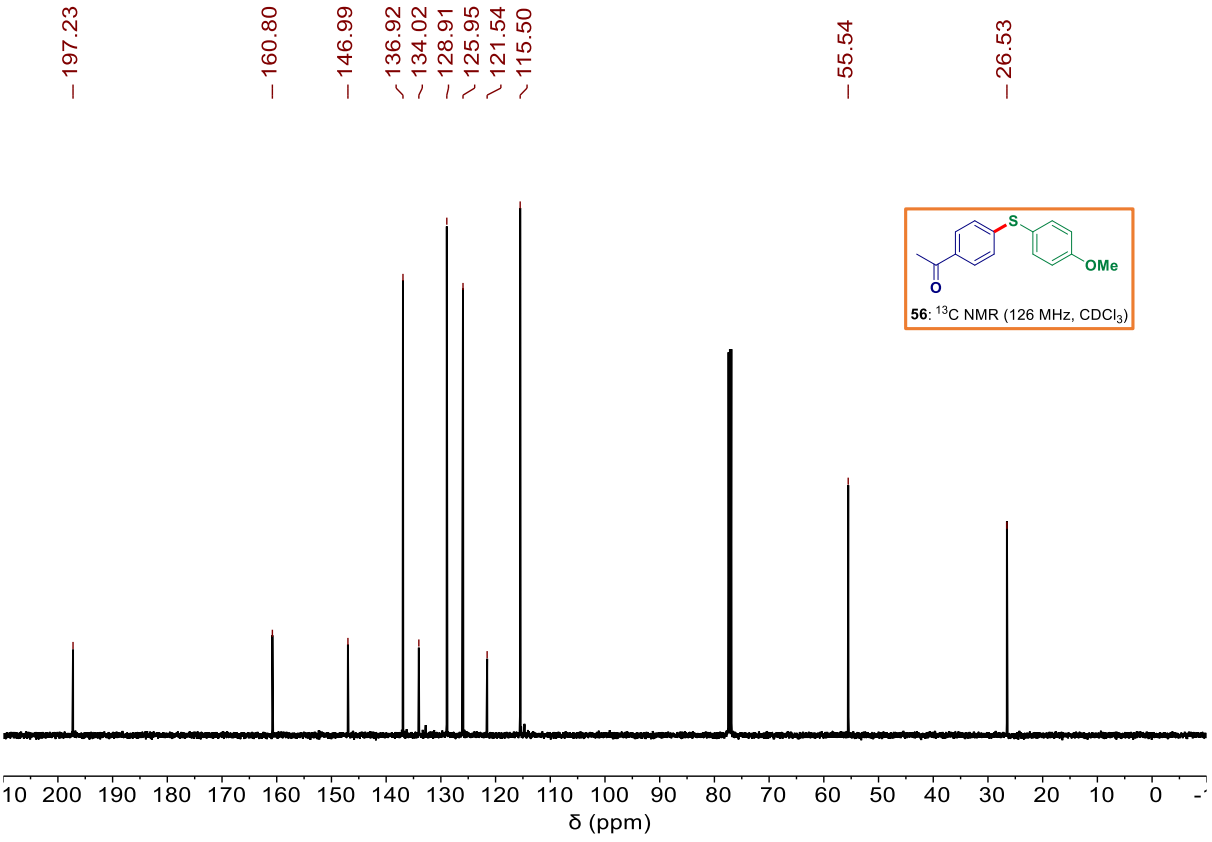


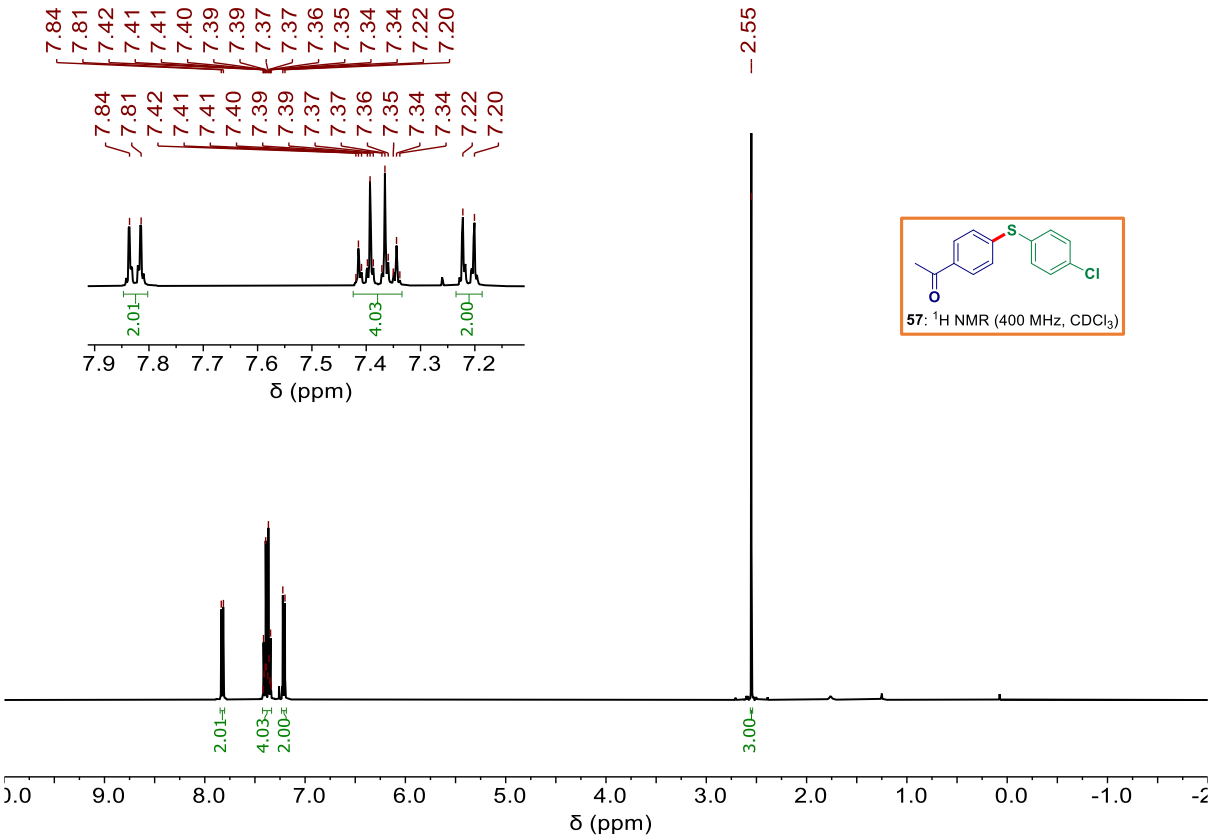


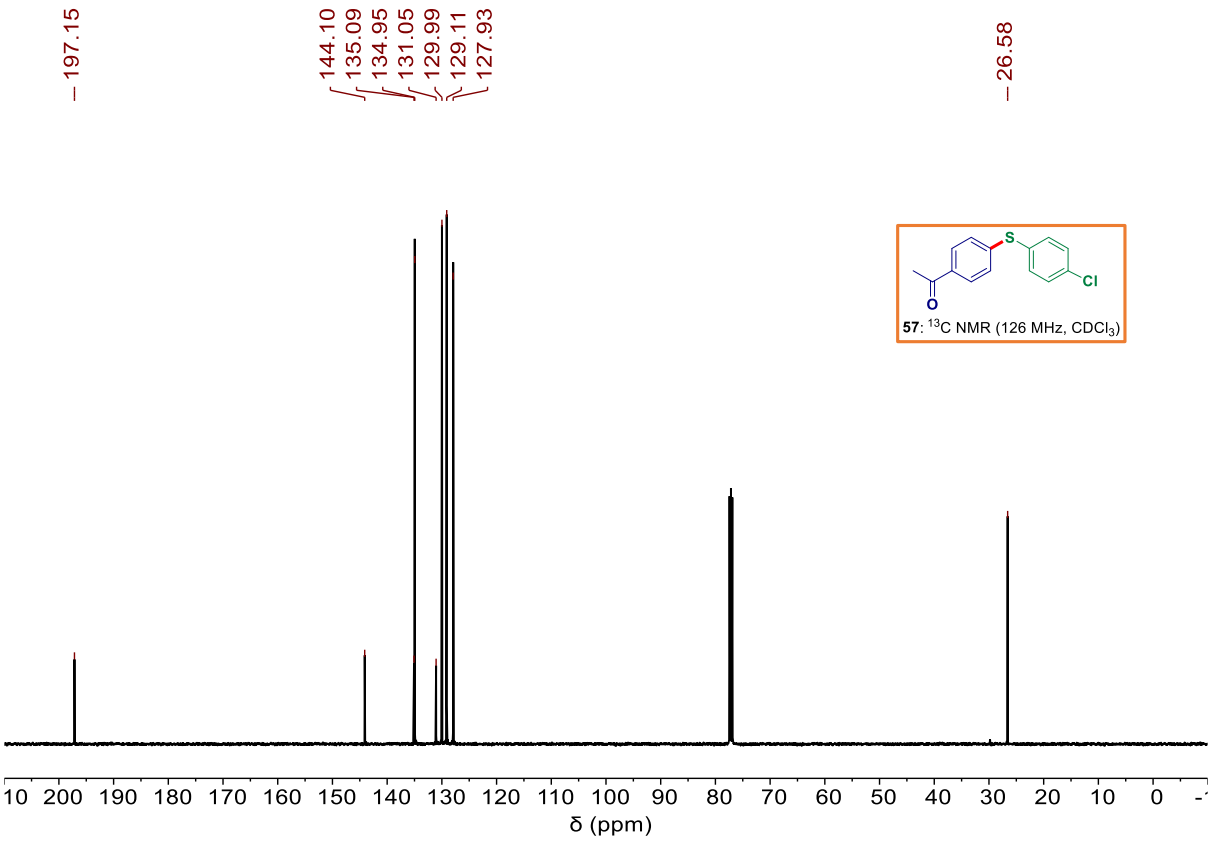

7.84 7.83 7.83 7.82 7.81 7.81 7.32 7.30 7.28 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.08 7.08 7.08 7.07 7.06 7.05 7.05 7.03 7.03 7.02 7.02 7.01 6.93 6.93 6.91 6.91 3.79 2.55
2.00 1.03 2.00 0.99 0.97 0.98 2.99 3.00
δ (ppm)
55: ^{1}H NMR (400 MHz, $CDCl_3$)

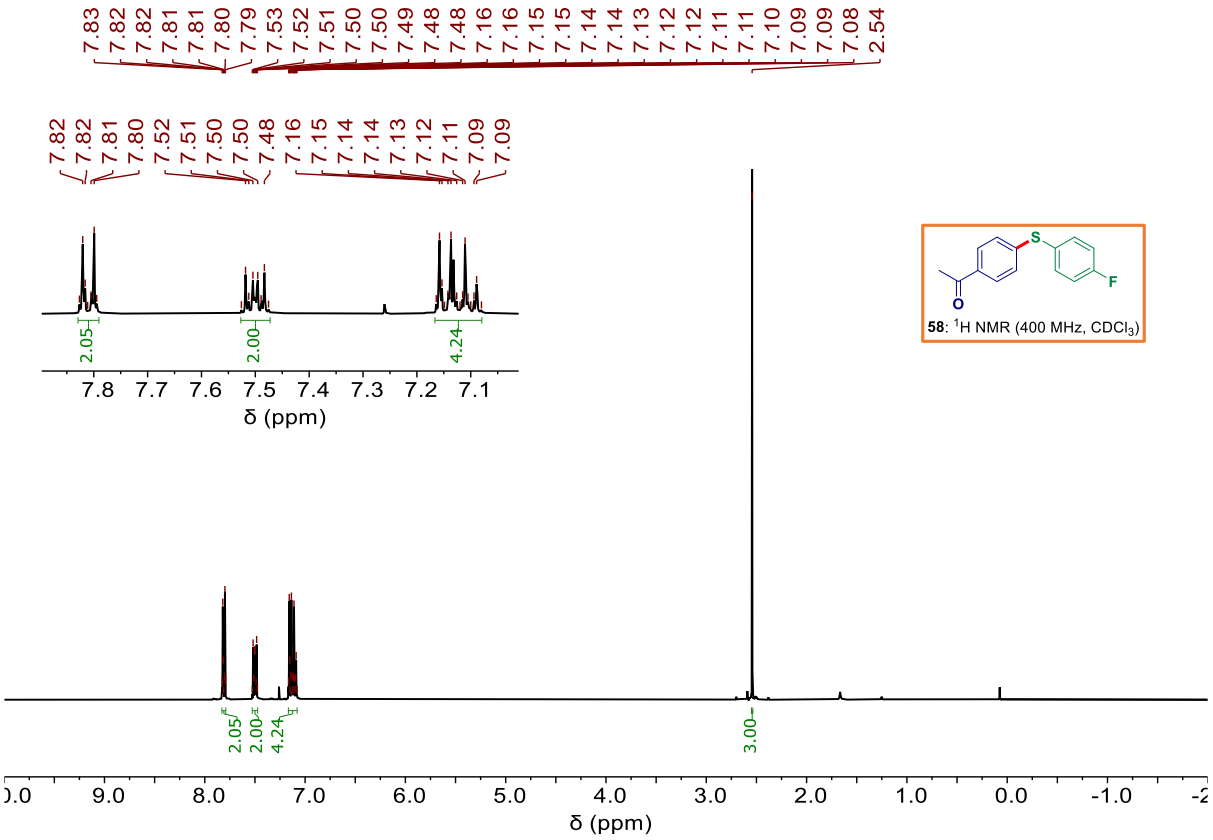

197.24 160.47 144.66 134.76 133.45 130.56 129.03 127.90 125.92 118.81 114.81 55.52 26.57
δ (ppm)
55: ^{13}C NMR (126 MHz, $CDCl_3$)

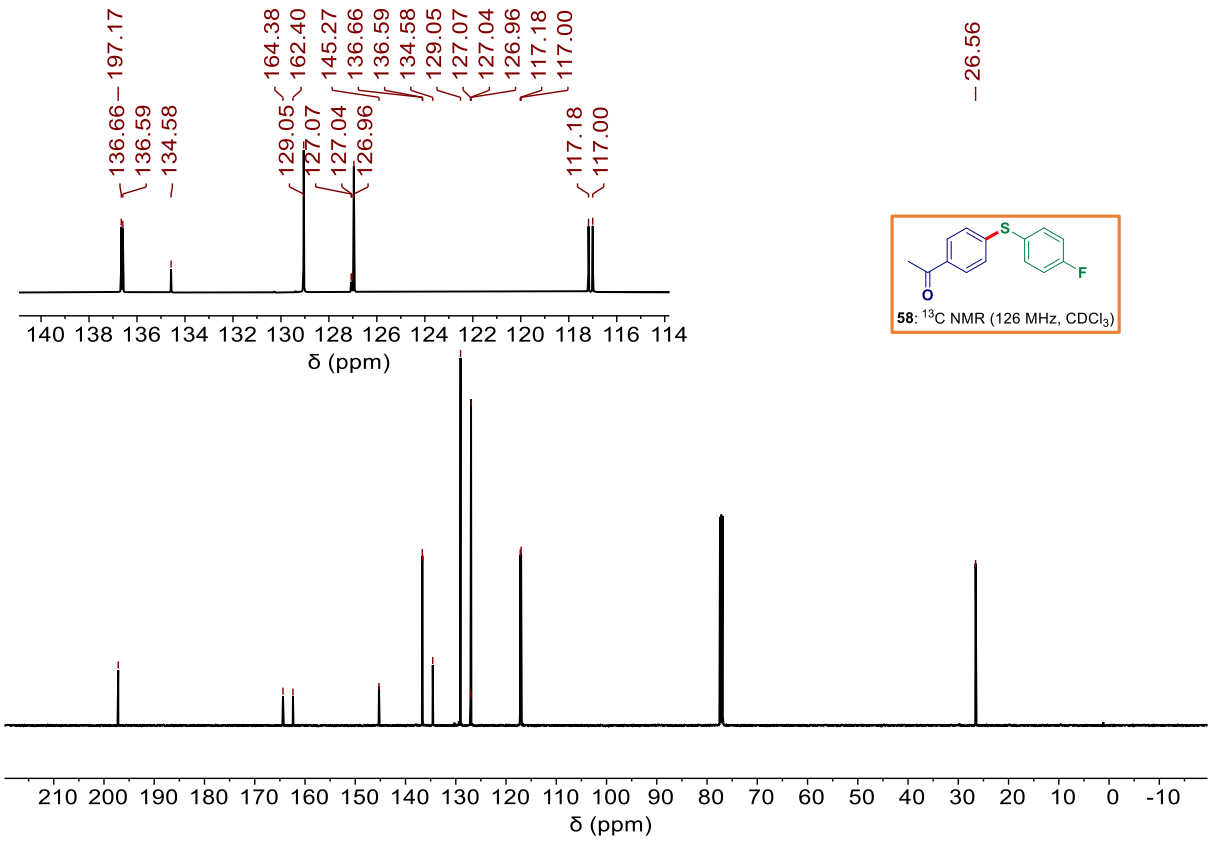

7.79
7.77
7.48
7.46
7.10
7.08
6.97
6.95
3.85
2.53
2.04
2.00
2.00
2.05
3.00
3.01
δ (ppm)
OMe
O
56: 1H NMR (400 MHz, CDCl3)

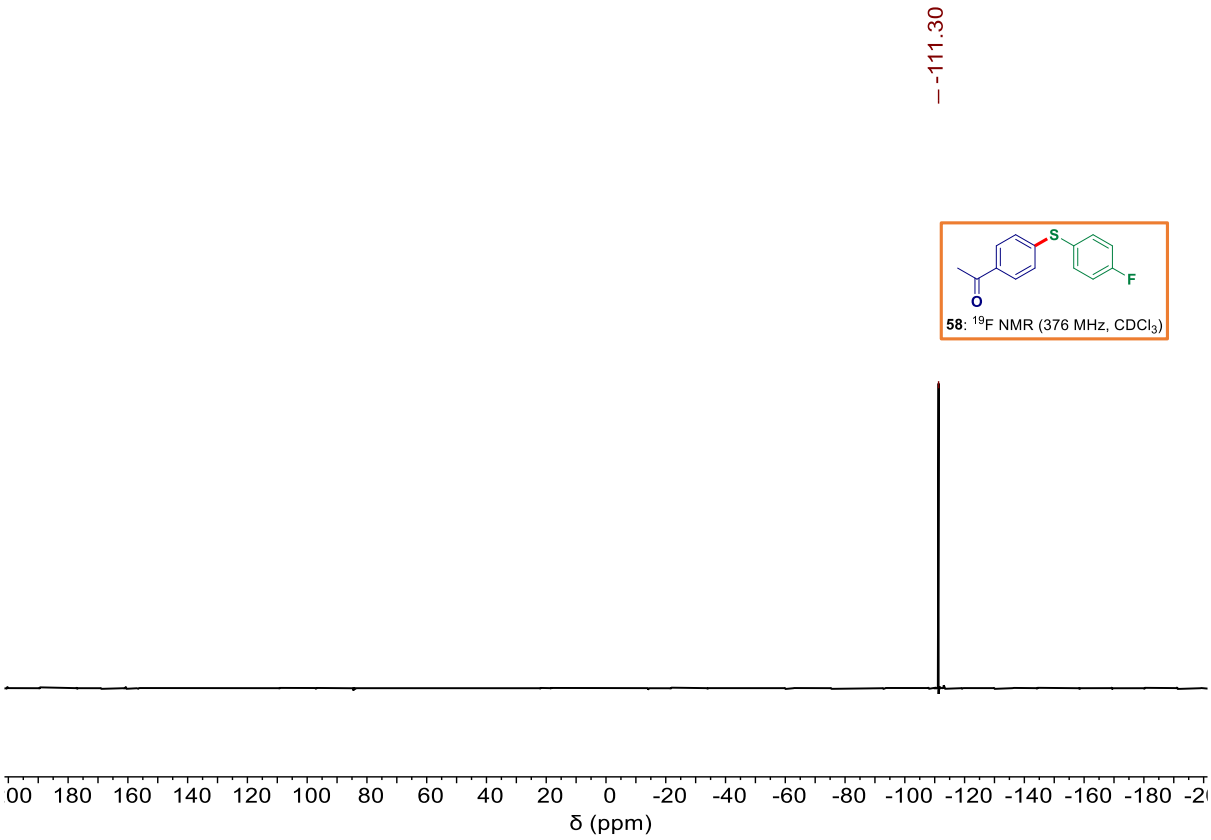

197.23
160.80
146.99
136.92
134.02
128.91
125.95
121.54
115.50
55.54
26.53
δ (ppm)
OMe
O
56: 13C NMR (126 MHz, CDCl3)

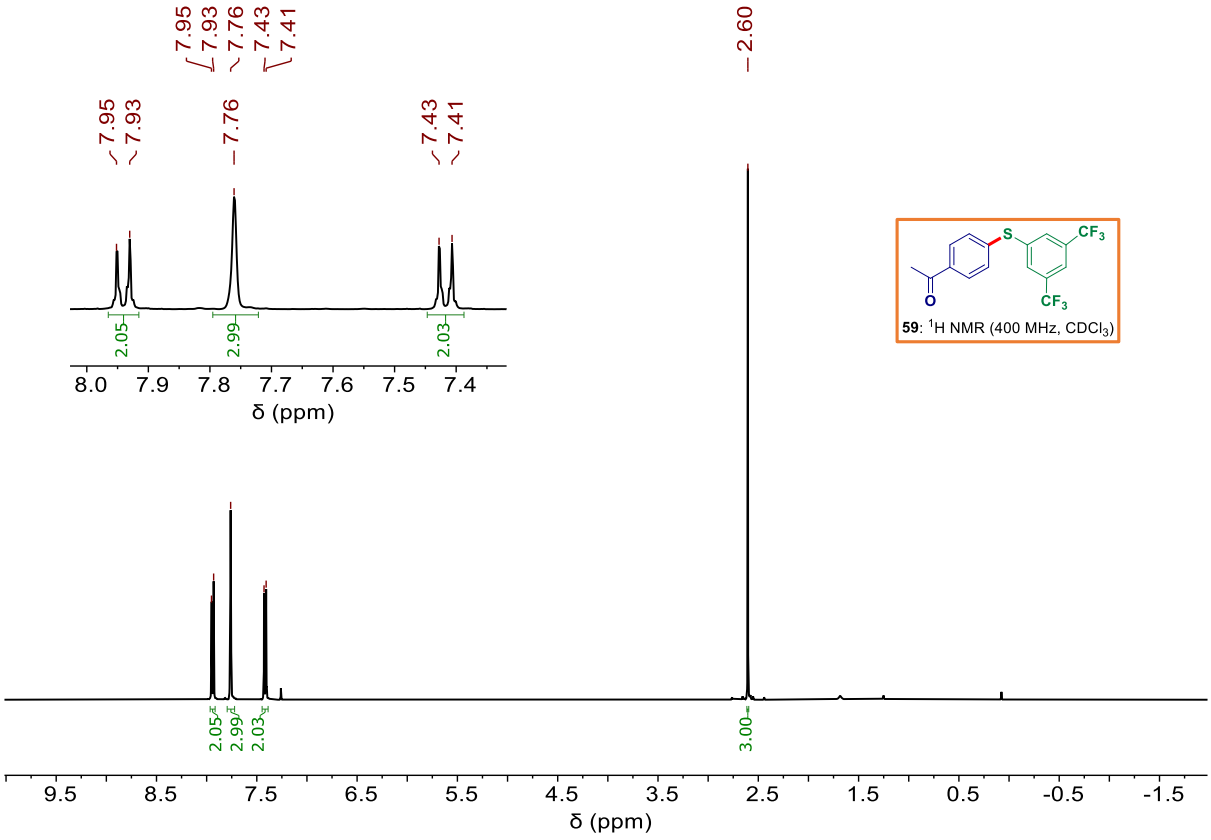

7.84
7.81
7.42
7.41
7.41
7.40
7.39
7.39
7.37
7.37
7.36
7.35
7.34
7.34
7.22
7.20
2.55
2.01
4.03
2.00
3.00
δ (ppm)
57: 1H NMR (400 MHz, CDCl3)

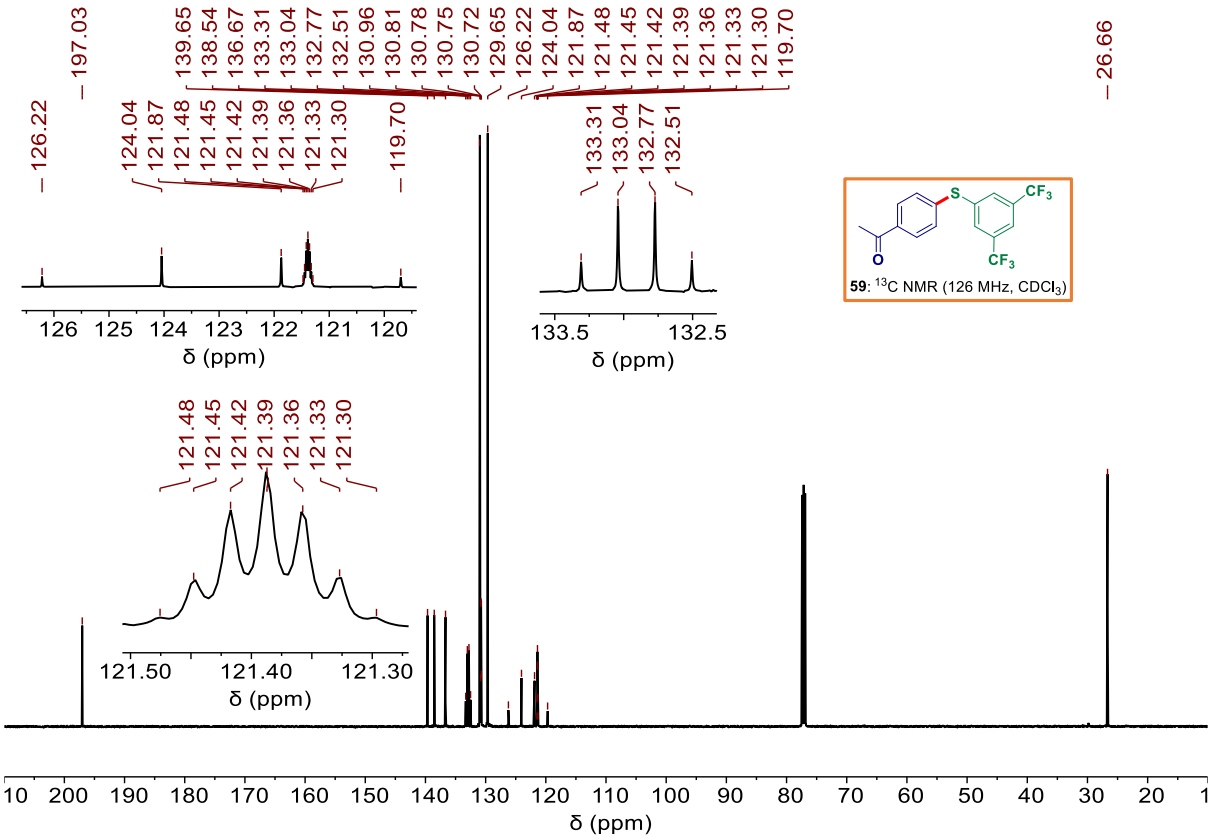

197.15
144.10
135.09
134.95
131.05
129.99
129.11
127.93
26.58
δ (ppm)
57: 13C NMR (126 MHz, CDCl3)

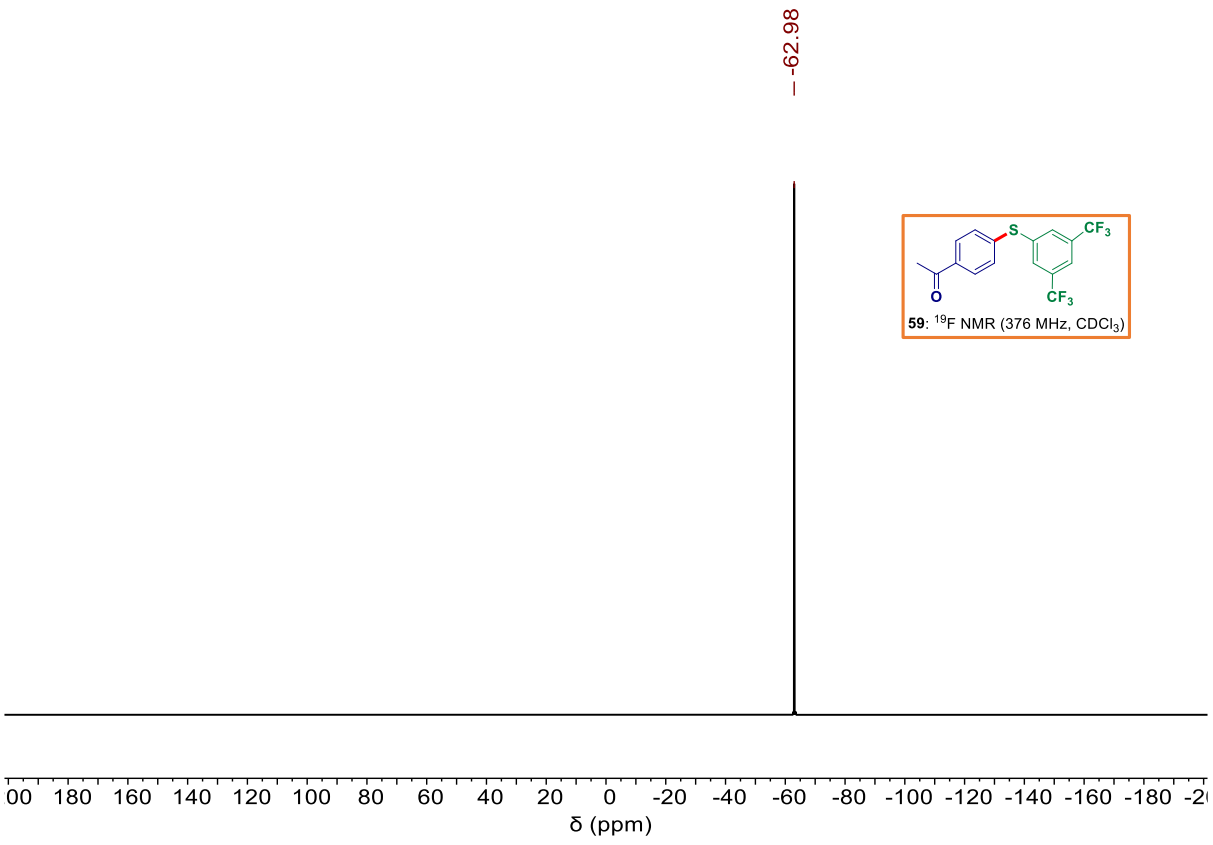

7.83 7.82 7.82 7.81 7.81 7.80 7.79 7.53 7.52 7.51 7.50 7.50 7.49 7.48 7.48 7.16 7.16 7.15 7.15 7.14 7.14 7.13 7.12 7.12 7.11 7.11 7.10 7.09 7.09 7.08 2.54
7.82 7.82 7.81 7.80 7.52 7.51 7.50 7.50 7.48 7.16 7.15 7.14 7.14 7.13 7.12 7.11 7.09 7.09
2.05 2.00 4.24
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
δ (ppm)
S F O
58: 1H NMR (400 MHz, CDCl3)
2.05 2.00 4.24 3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

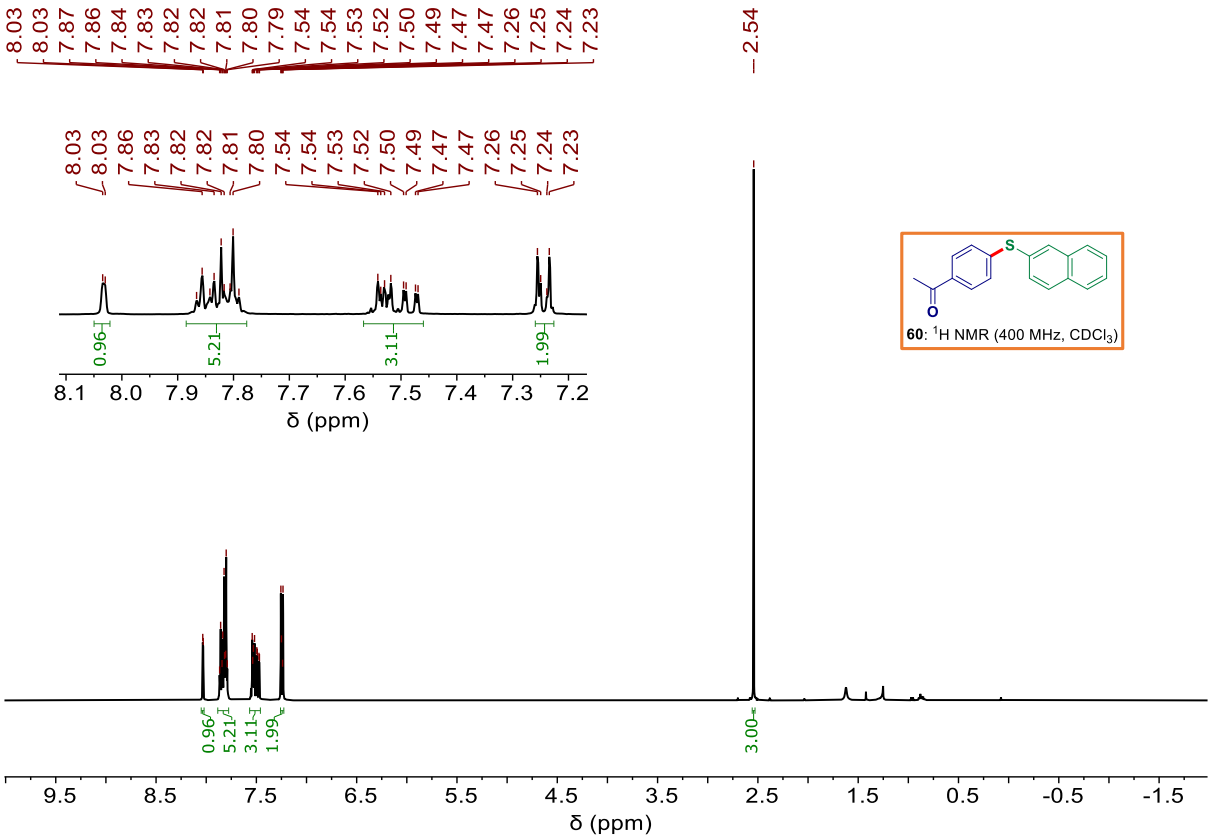

136.66 197.17
136.59
134.58
164.38
162.40
145.27
136.66
136.59
134.58
129.05
127.07
127.04
126.96
117.18
117.00
129.05 127.07 127.04 126.96 117.18 117.00
26.56
S F O
58: 13C NMR (126 MHz, CDCl3)
140 138 136 134 132 130 128 126 124 122 120 118 116 114
δ (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

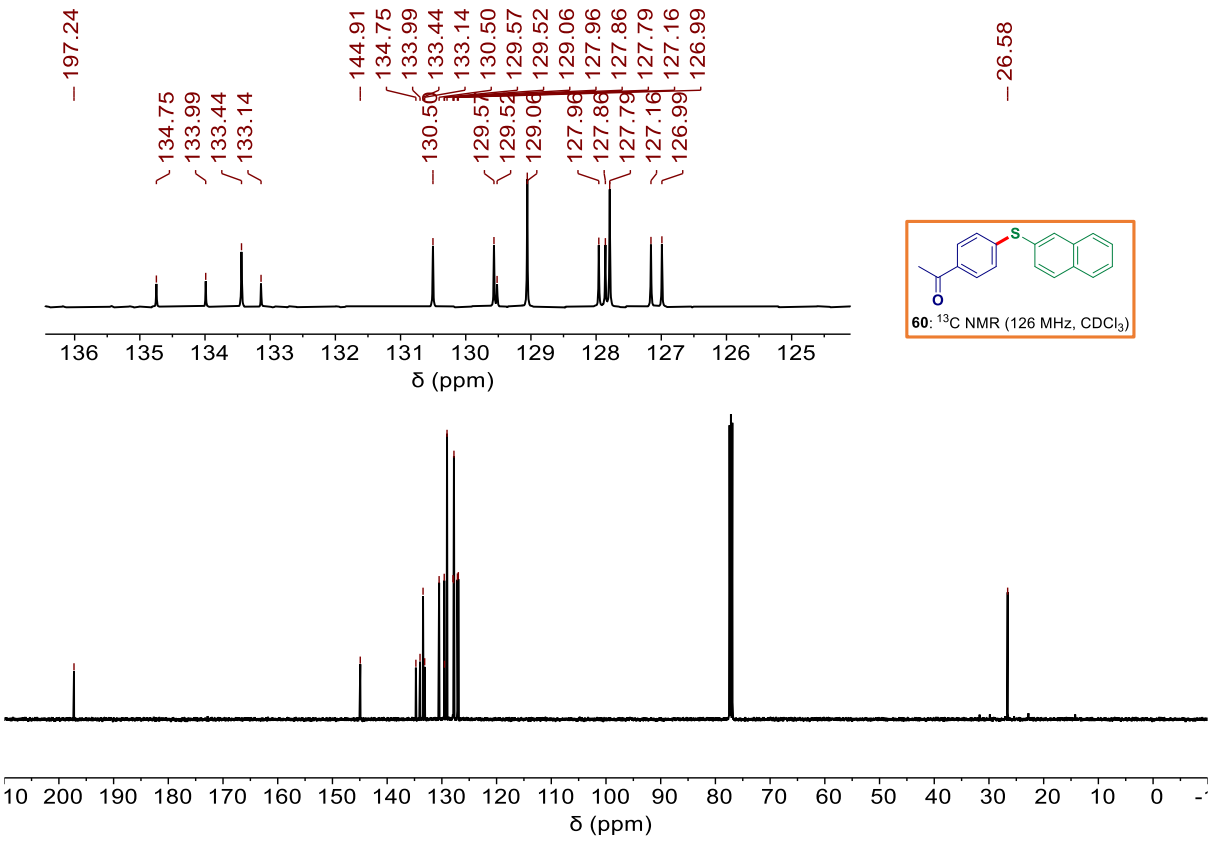

-111.30
58: ^{19}F NMR (376 MHz, $CDCl_3$)
δ (ppm)

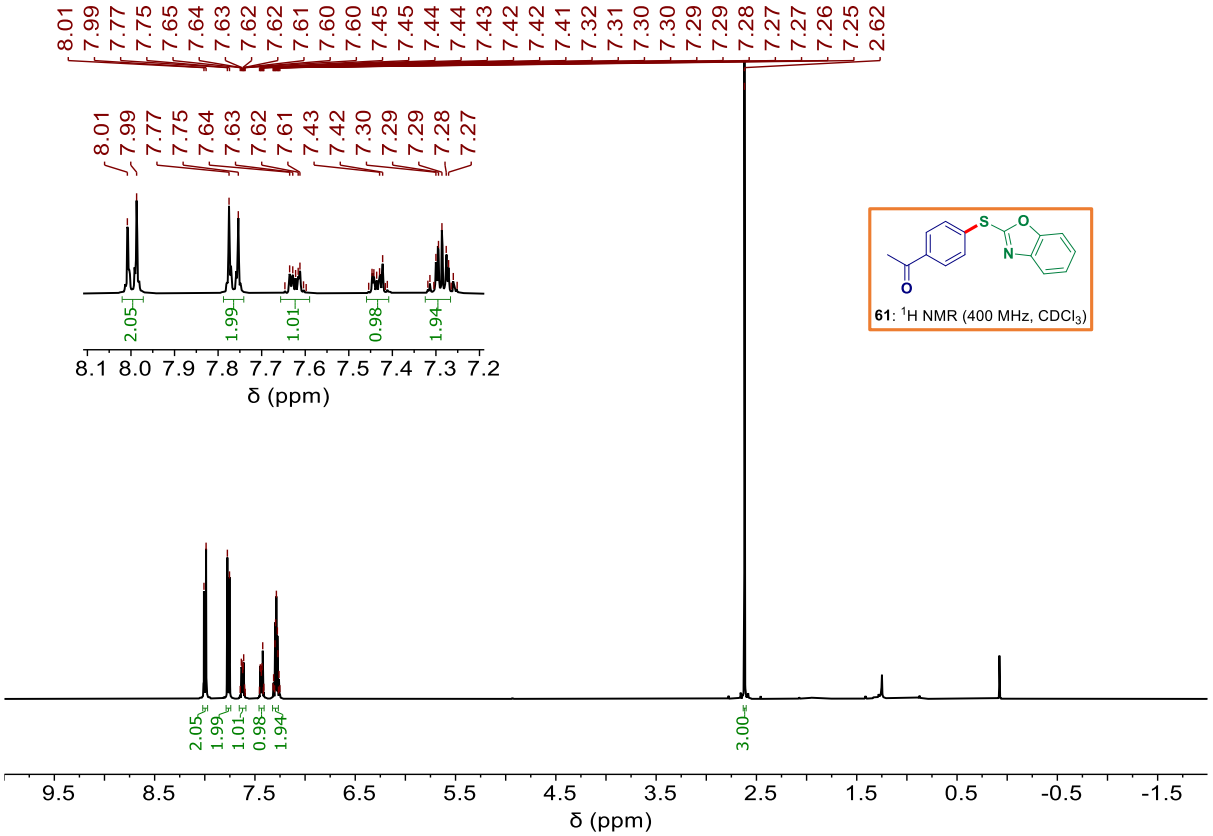

7.95
7.93
7.76
7.43
7.41
2.60
2.05
2.99
2.03
3.00
59: ^{1}H NMR (400 MHz, $CDCl_3$)
δ (ppm)

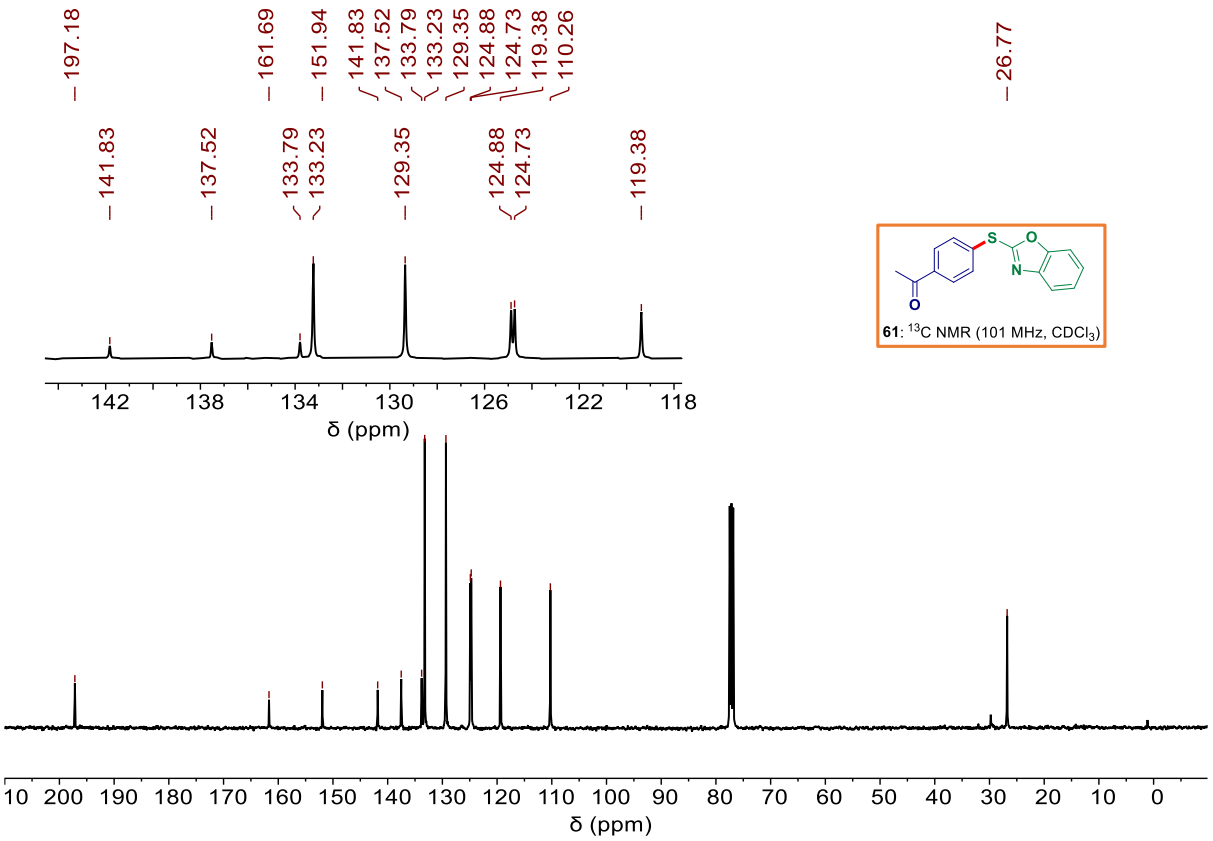

197.03
139.65
138.54
136.67
133.31
133.04
132.77
132.51
130.96
130.81
130.78
130.75
130.72
129.65
126.22
124.04
121.87
121.48
121.45
121.42
121.39
121.36
121.33
121.30
119.70
26.66
δ (ppm)
59: 13C NMR (126 MHz, CDCl3)

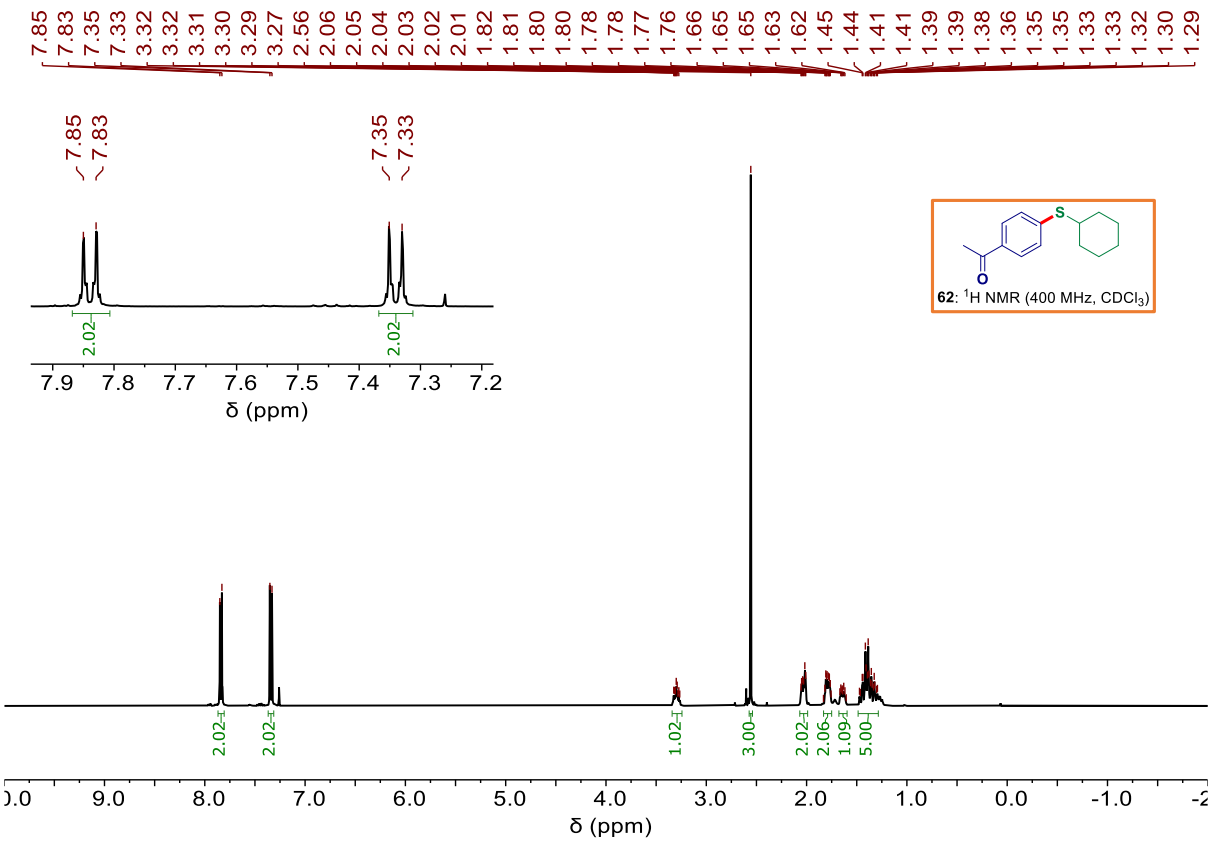

-62.98
δ (ppm)
59: 19F NMR (376 MHz, CDCl3)

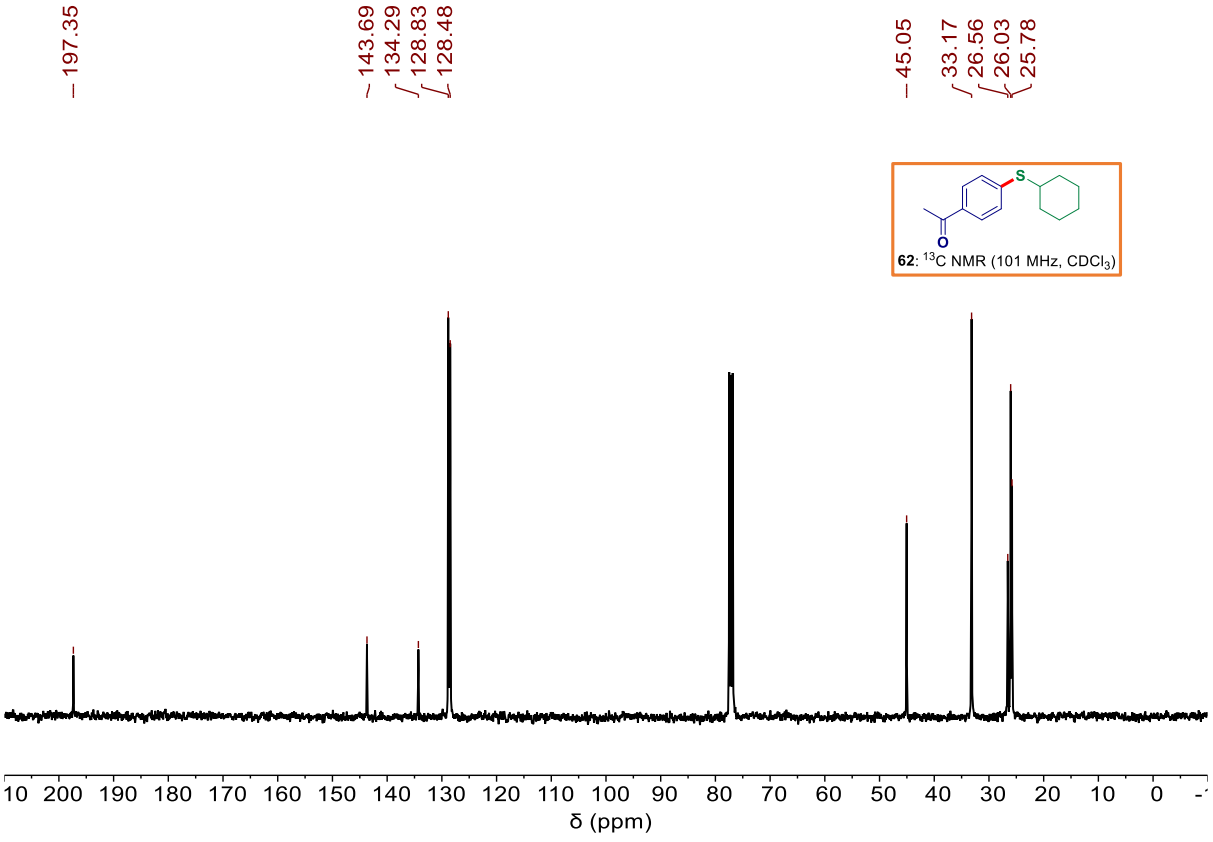

8.03 8.03 7.87 7.86 7.84 7.83 7.82 7.82 7.81 7.80 7.79 7.54 7.54 7.53 7.52 7.50 7.49 7.47 7.47 7.26 7.25 7.24 7.23
2.54
0.96 5.21 3.11 1.99
3.00
δ (ppm)
60: 1H NMR (400 MHz, CDCl3)

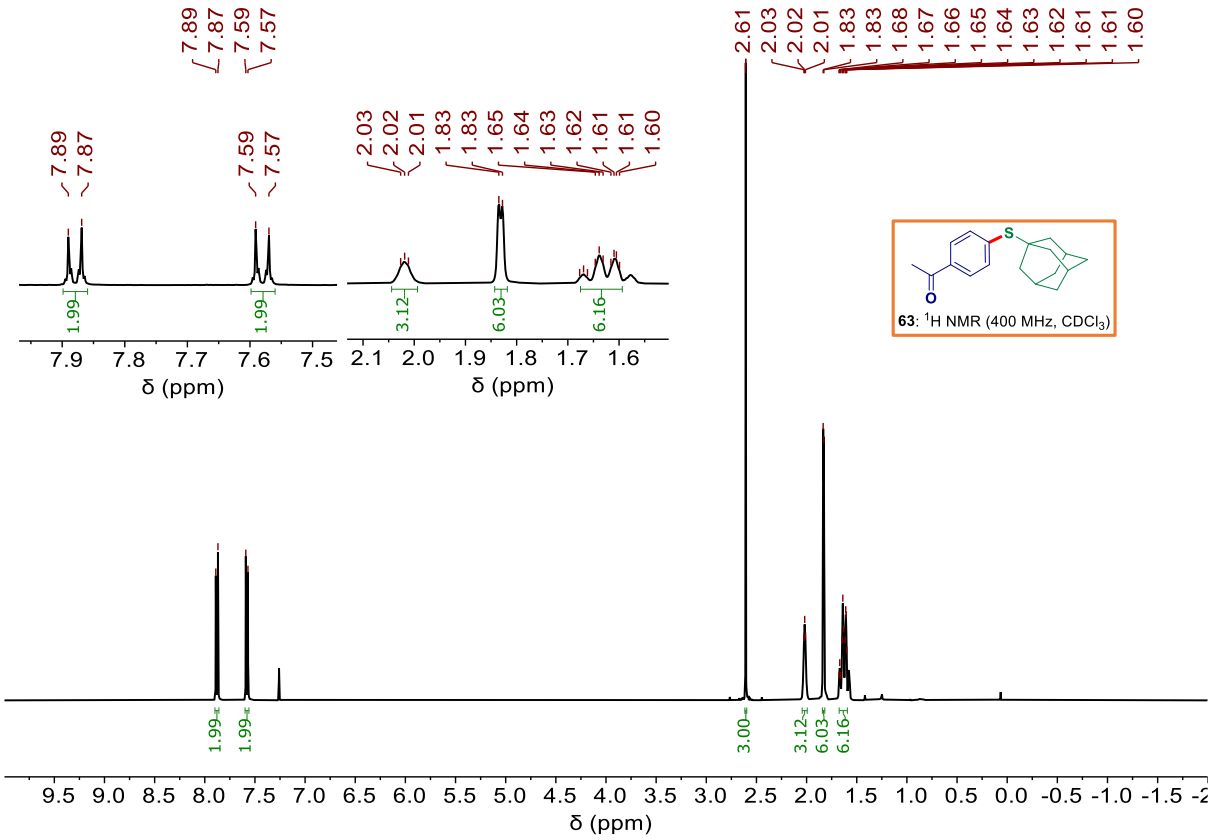

197.24
144.91 134.75 133.99 133.44 133.14 130.50 129.57 129.52 129.06 127.96 127.86 127.79 127.16 126.99
26.58
δ (ppm)
60: 13C NMR (126 MHz, CDCl3)

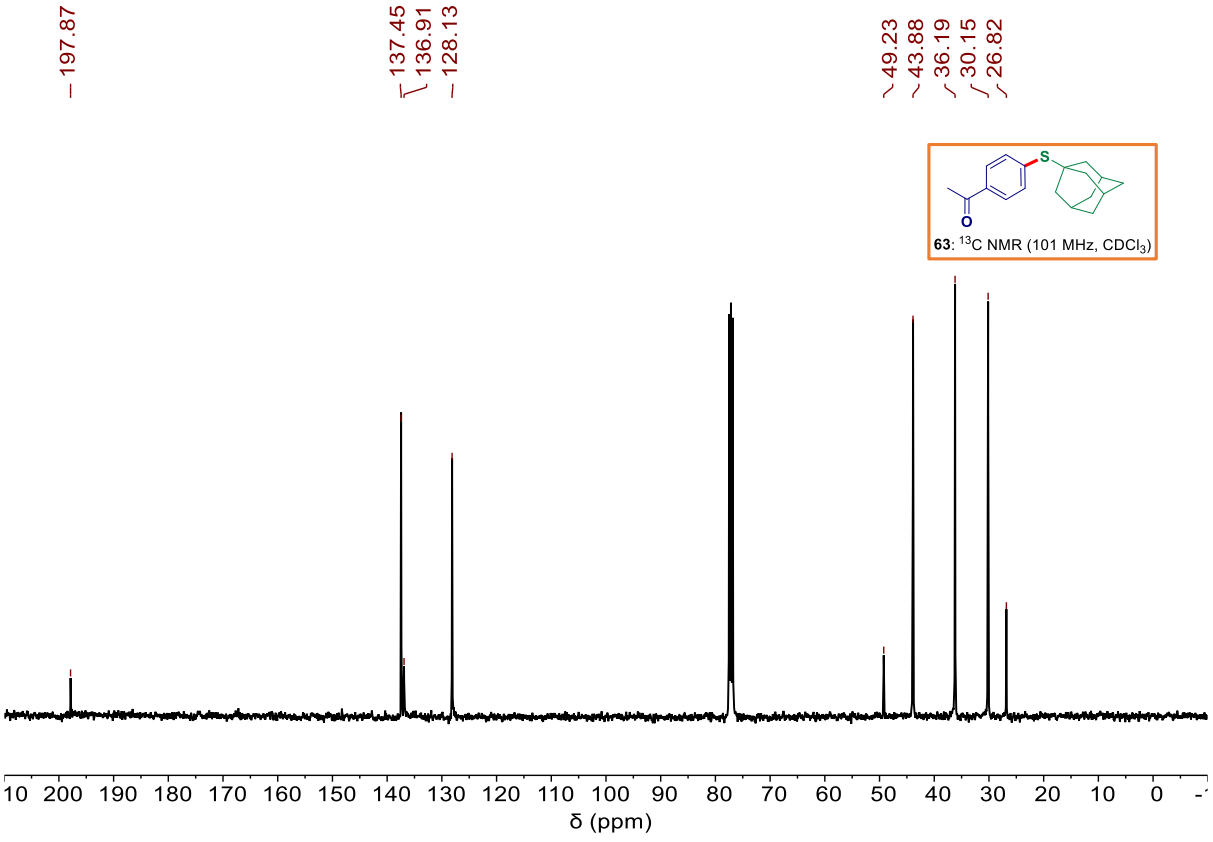

8.01 7.99 7.77 7.75 7.65 7.64 7.63 7.62 7.62 7.61 7.60 7.60 7.45 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.25 2.62
2.05 1.99 1.01 0.98 1.94 3.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)
61: ^{1}H NMR (400 MHz, $CDCl_3$)

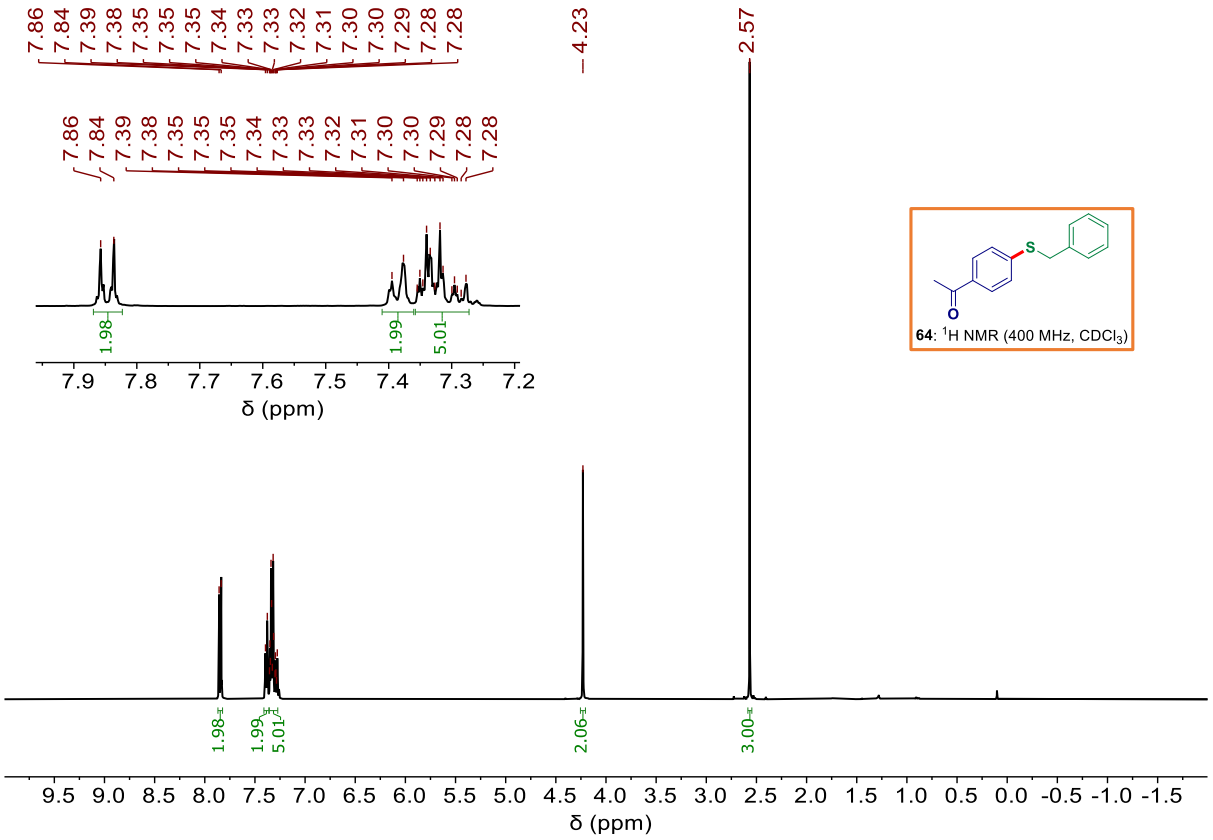

197.18 161.69 151.94 141.83 137.52 133.79 133.23 129.35 124.88 124.73 119.38 110.26 26.77
142 138 134 130 126 122 118
δ (ppm)
61: ^{13}C NMR (101 MHz, $CDCl_3$)

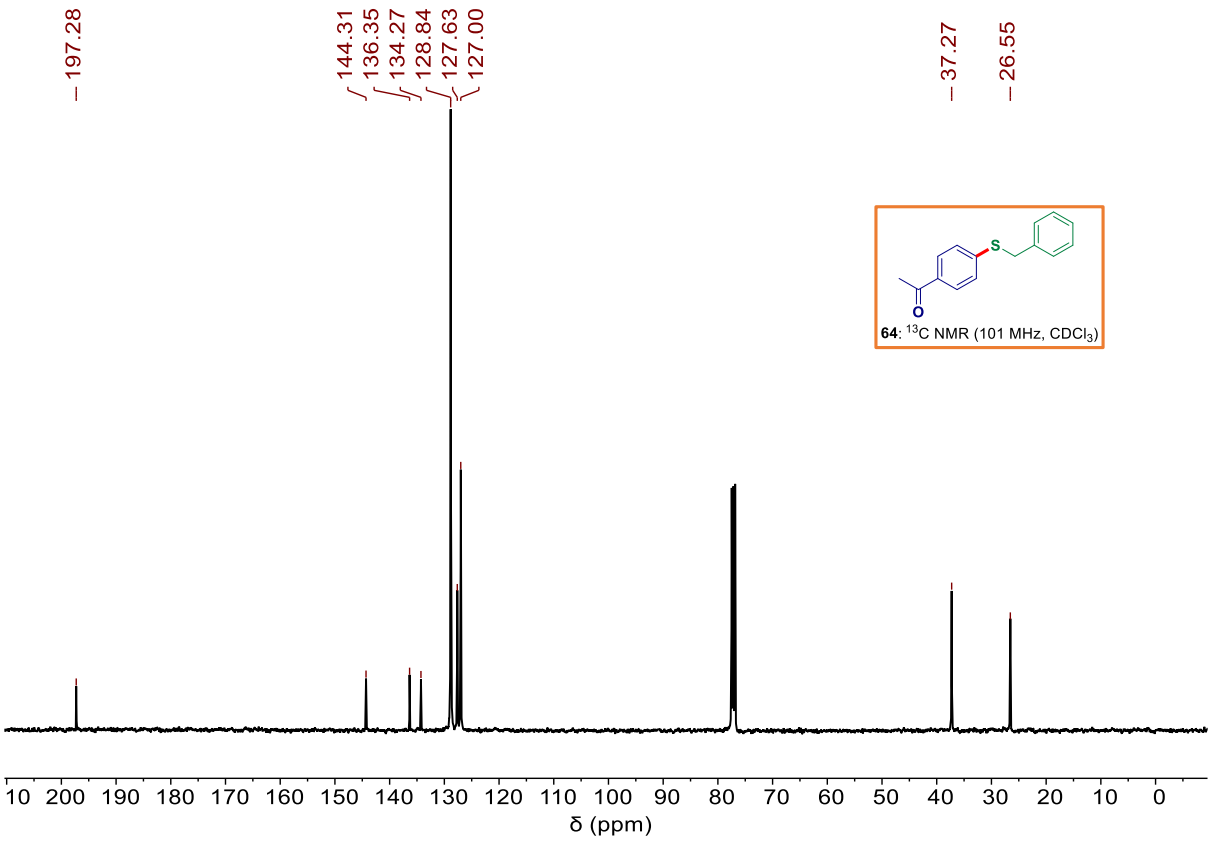

7.85 7.83 7.35 7.33 3.32 3.32 3.31 3.30 3.29 3.27 2.56 2.06 2.05 2.04 2.03 2.02 2.01 1.82 1.81 1.80 1.80 1.78 1.78 1.77 1.76 1.66 1.65 1.65 1.63 1.62 1.45 1.44 1.41 1.41 1.39 1.39 1.38 1.36 1.35 1.35 1.33 1.33 1.32 1.30 1.29
7.85 7.83 7.35 7.33
2.02 2.02
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
δ (ppm)
62: ^{1}H NMR (400 MHz, $CDCl_3$)
2.02 2.02 1.02 3.00 2.02 2.06 1.09 5.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

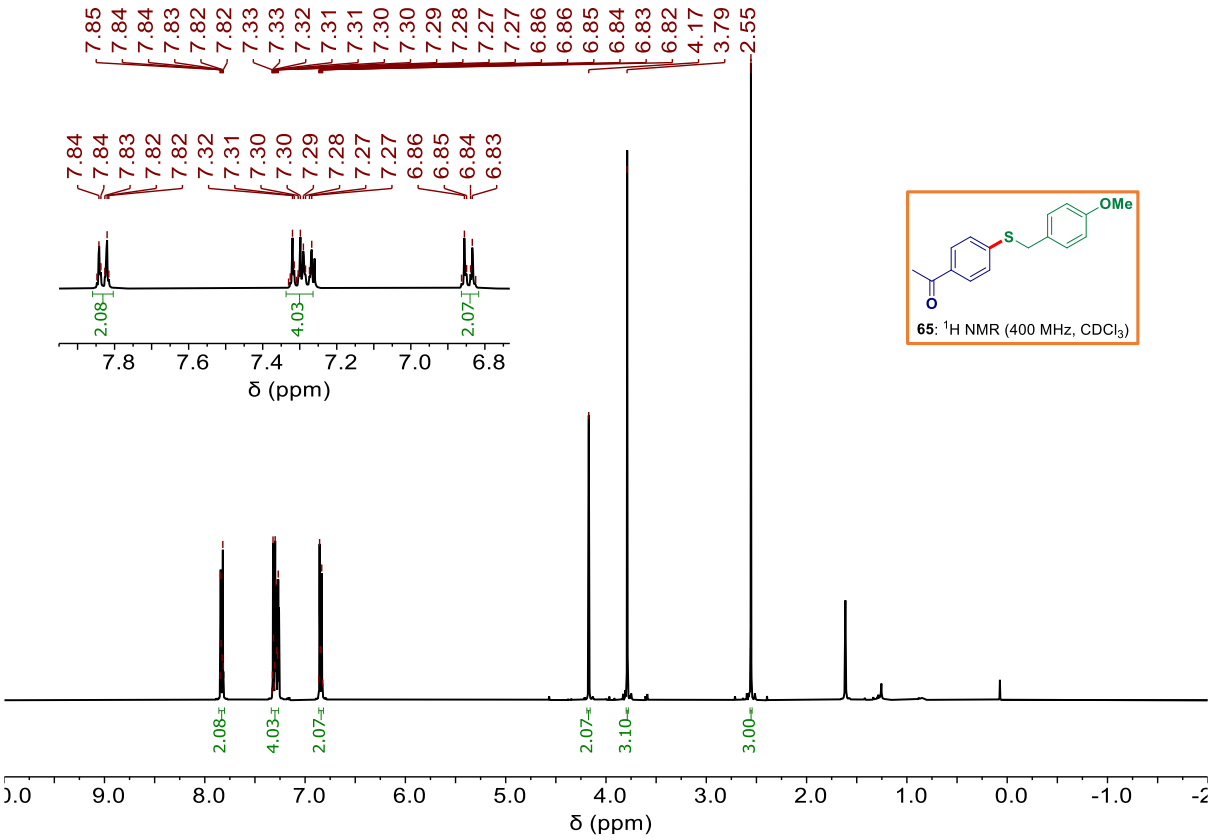

197.35
143.69 134.29 128.83 128.48
45.05 33.17 26.56 26.03 25.78
62: ^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

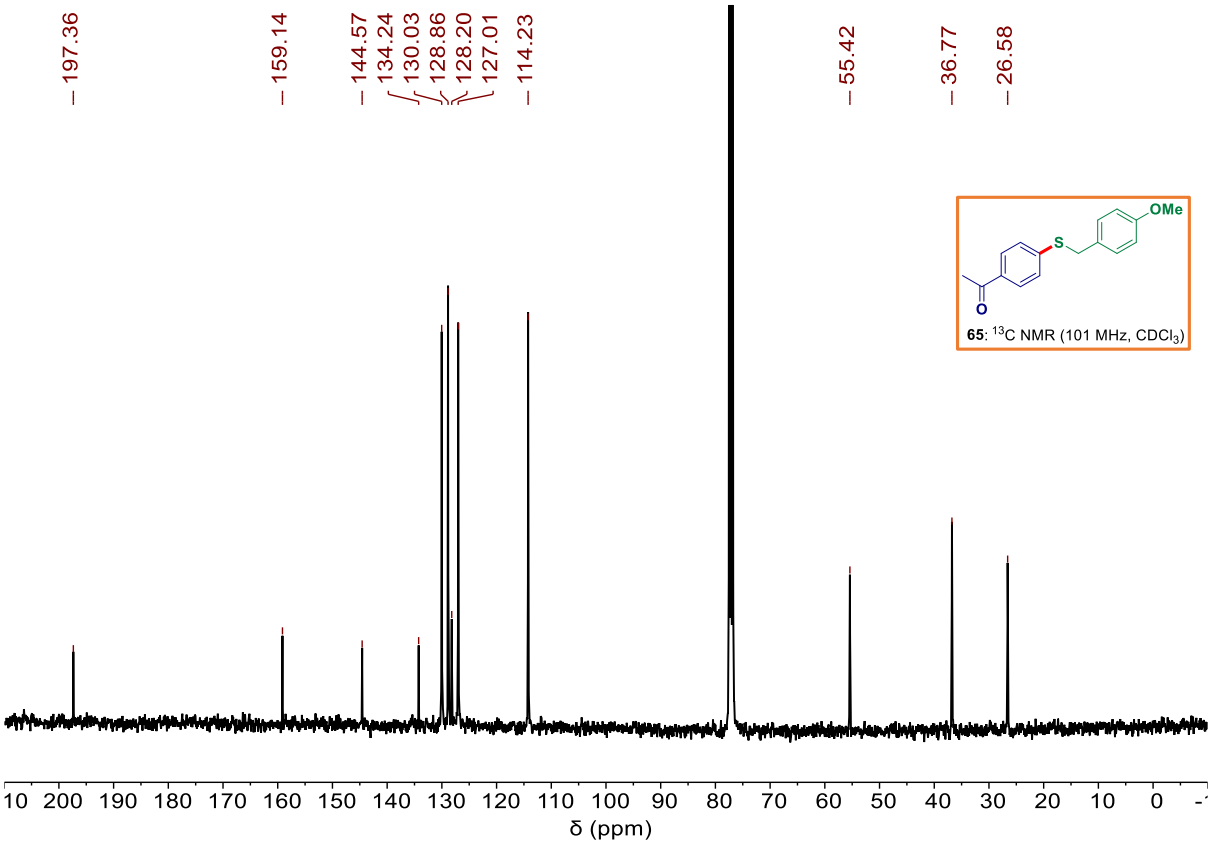

7.89
7.87
7.59
7.57
2.61
2.03
2.02
2.01
1.83
1.83
1.68
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.61
1.60
2.03
2.02
2.01
1.83
1.83
1.65
1.64
1.63
1.62
1.61
1.61
1.60
1.99
1.99
3.12
6.03
6.16
δ (ppm)
δ (ppm)
63: ^{1}H NMR (400 MHz, $CDCl_3$)
1.99
1.99
3.00
3.12
6.03
6.16
δ (ppm)

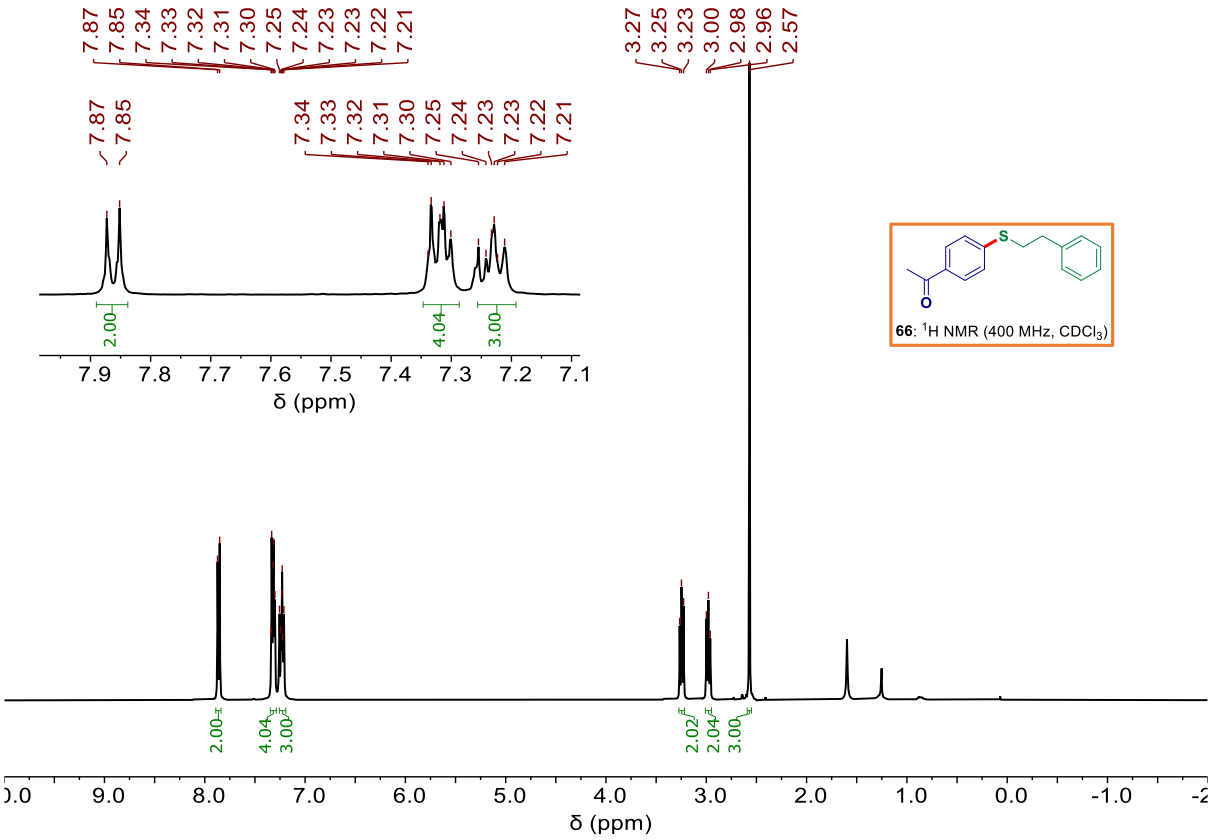

197.87
137.45
136.91
128.13
49.23
43.88
36.19
30.15
26.82
63: ^{13}C NMR (101 MHz, $CDCl_3$)
δ (ppm)

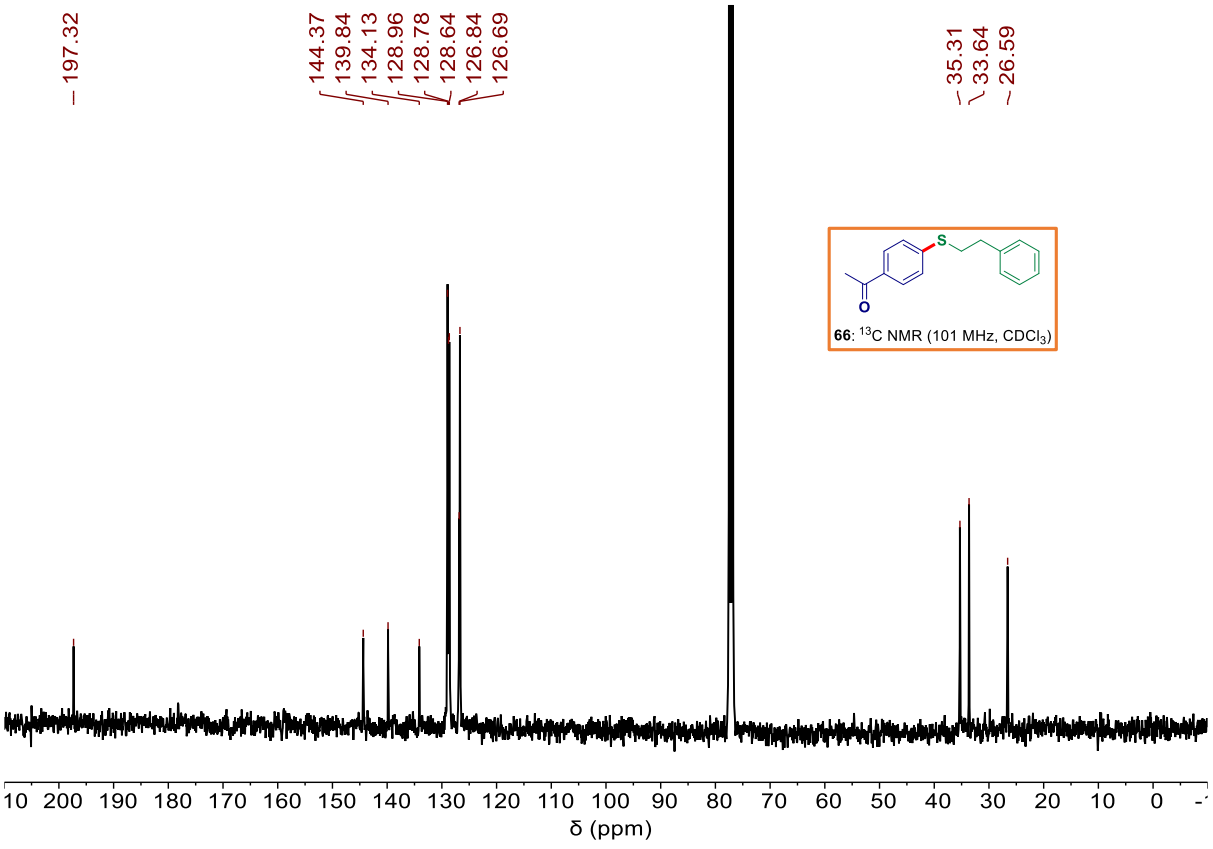

7.86 7.84 7.39 7.38 7.35 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.28 7.28
4.23
2.57
1.98
1.99
5.01
2.06
3.00
δ (ppm)
64: 1H NMR (400 MHz, CDCl3)

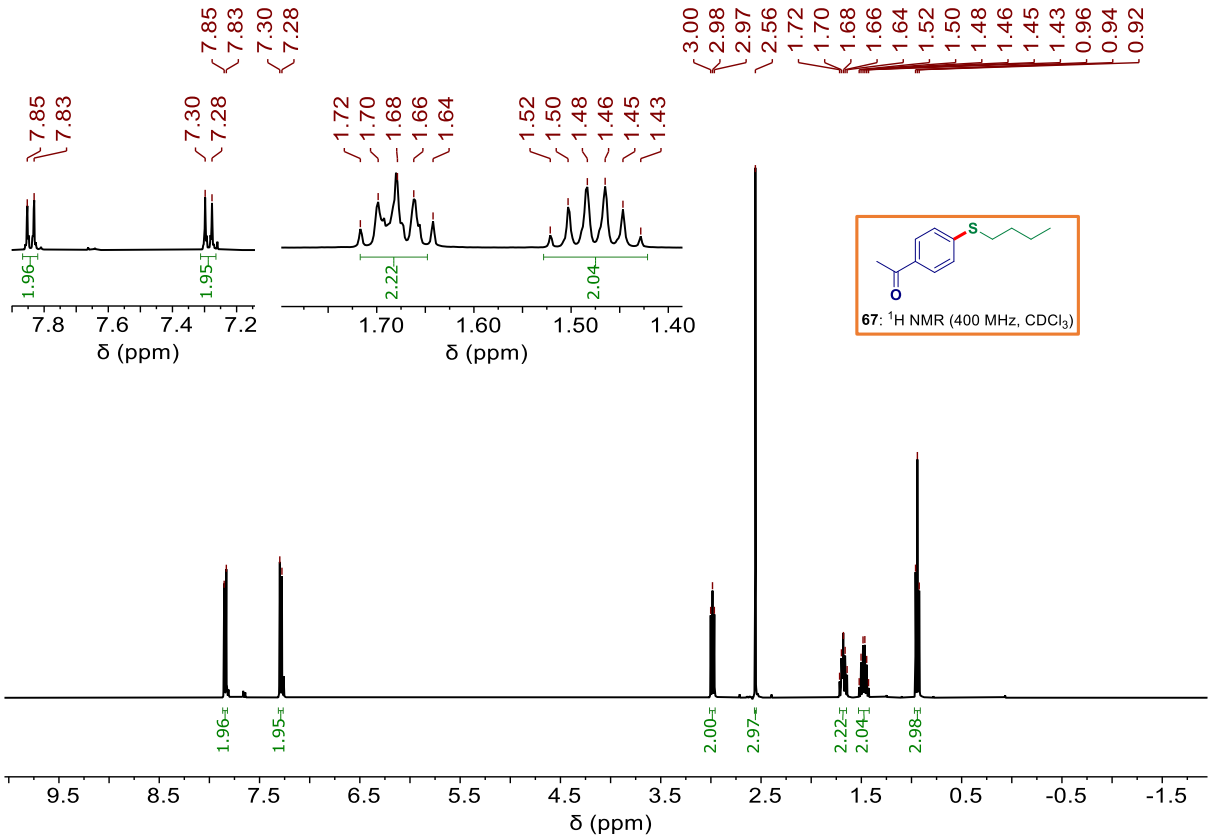

197.28
144.31
136.35
134.27
128.84
127.63
127.00
37.27
26.55
δ (ppm)
64: 13C NMR (101 MHz, CDCl3)

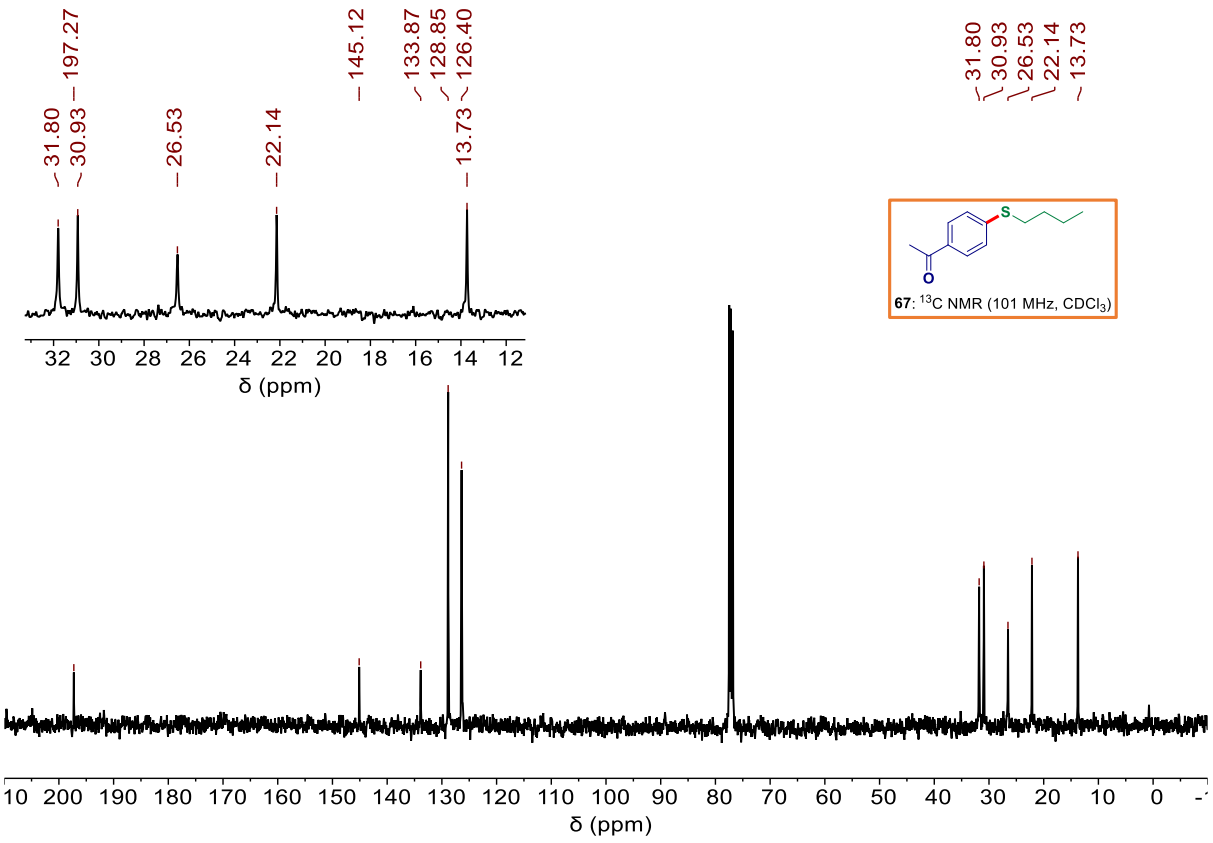

7.85 7.84 7.84 7.83 7.82 7.82 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.27 7.27 6.86 6.86 6.85 6.84 6.83 6.82 4.17 3.79 2.55
7.84 7.84 7.83 7.82 7.82 7.32 7.31 7.30 7.30 7.29 7.28 7.27 7.27 6.86 6.85 6.84 6.83
2.08 4.03 2.07
7.8 7.6 7.4 7.2 7.0 6.8
δ (ppm)
OMe
S
O
65: 1H NMR (400 MHz, CDCl3)
2.08 4.03 2.07 2.07 3.10 3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

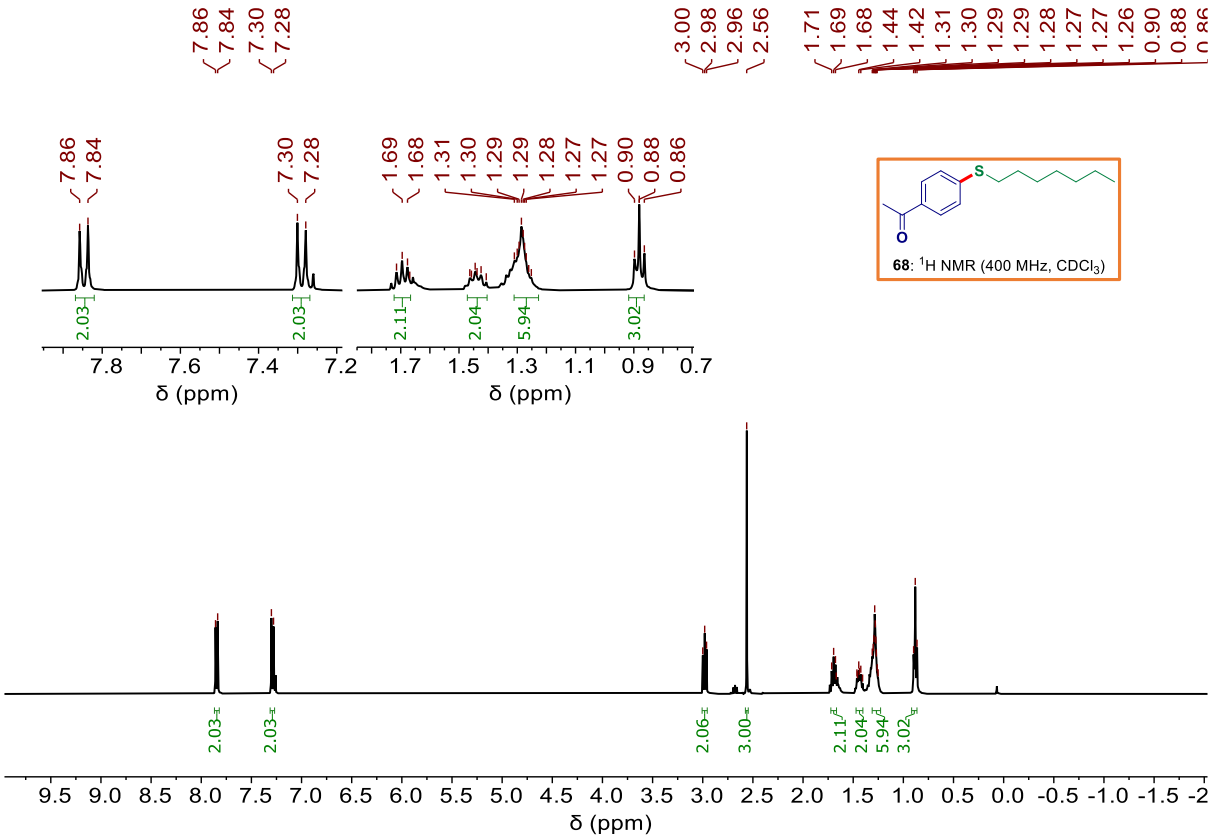

197.36
159.14
144.57
134.24
130.03
128.86
128.20
127.01
114.23
55.42
36.77
26.58
OMe
S
O
65: 13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

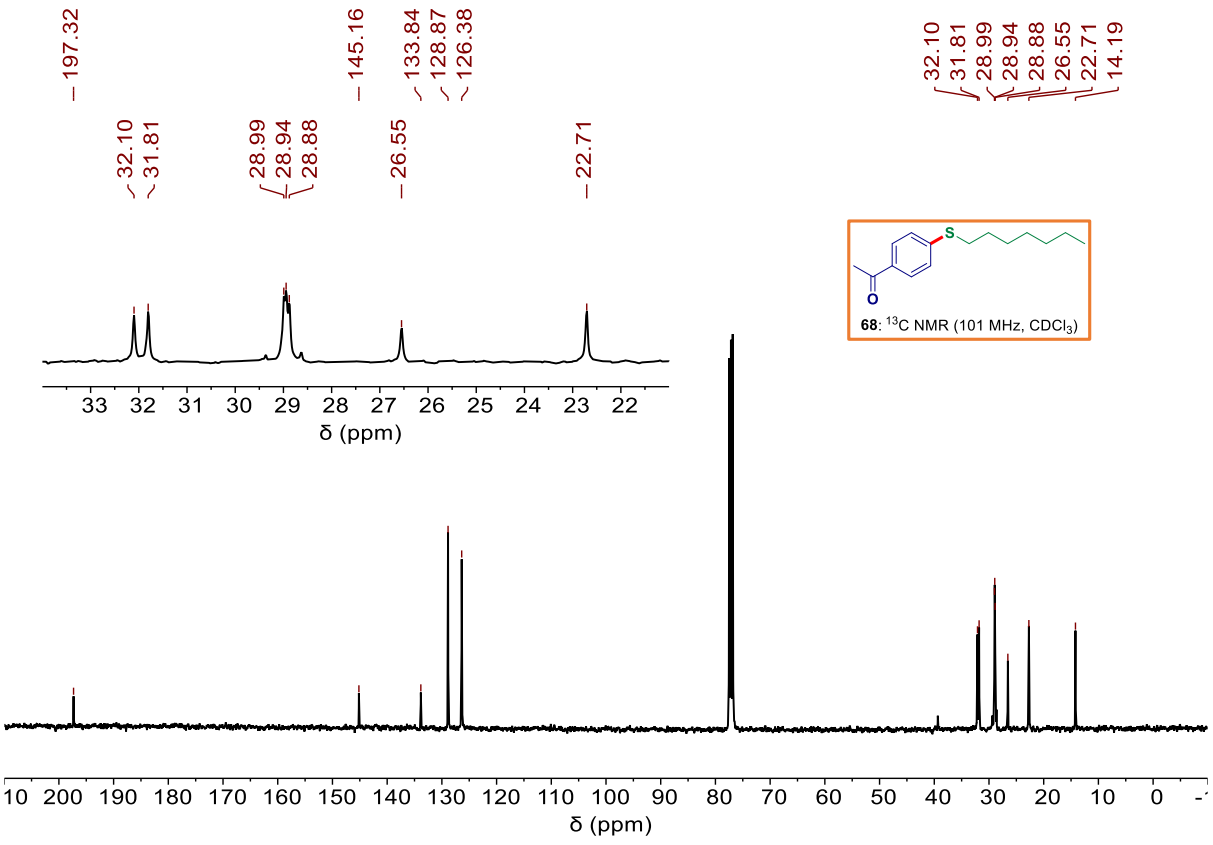

7.87
7.85
7.34
7.33
7.32
7.31
7.30
7.25
7.24
7.23
7.23
7.22
7.21
3.27
3.25
3.23
3.00
2.98
2.96
2.57
2.00
4.04
3.00
δ (ppm)
66: 1H NMR (400 MHz, CDCl3)
δ (ppm)

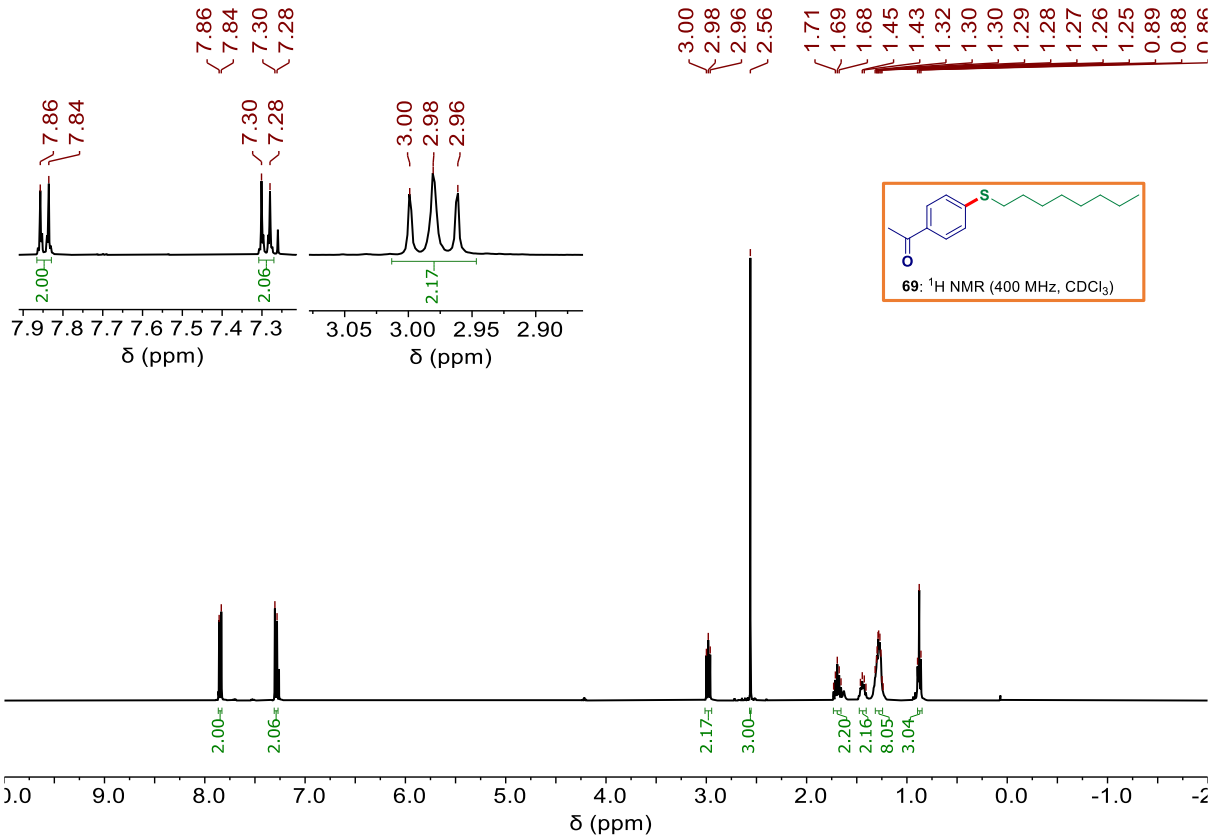

197.32
144.37
139.84
134.13
128.96
128.78
128.64
126.84
126.69
35.31
33.64
26.59
66: 13C NMR (101 MHz, CDCl3)
δ (ppm)

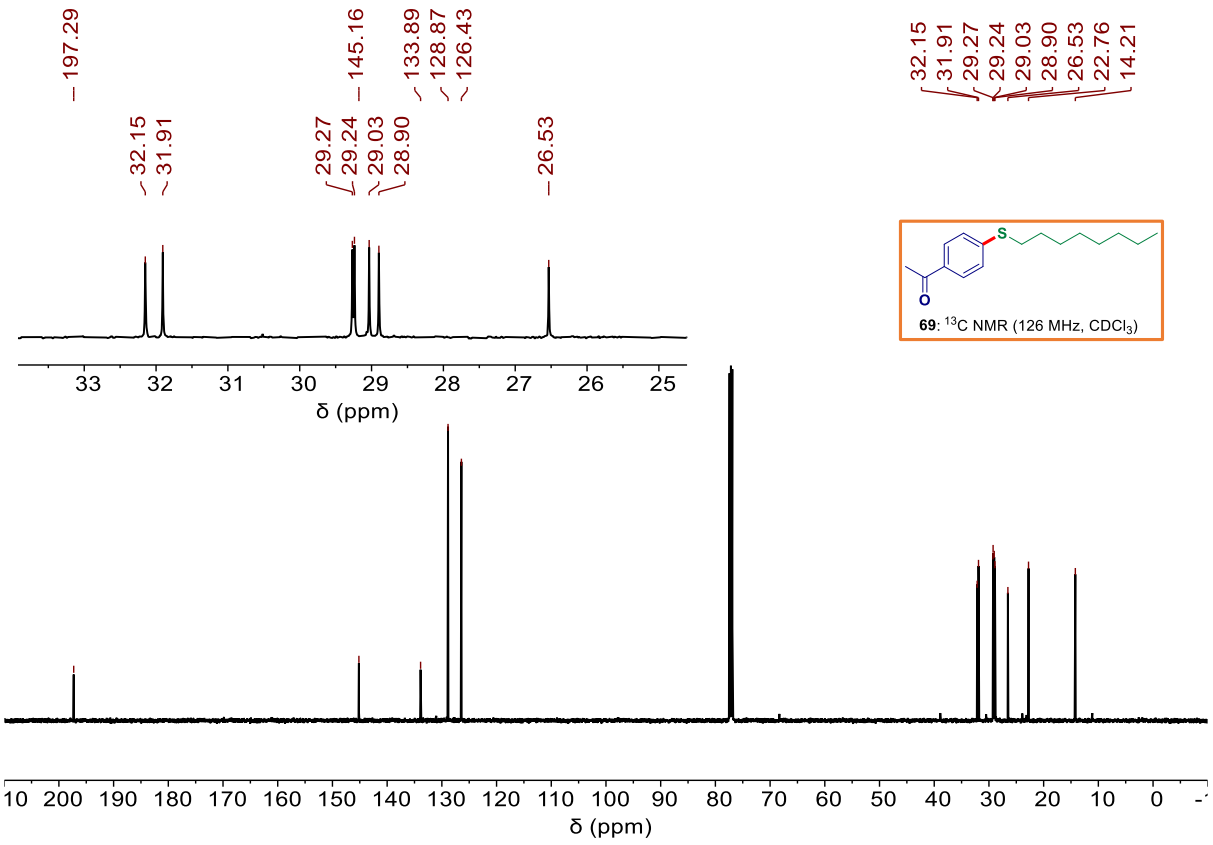

7.85
7.83
7.30
7.28
3.00
2.98
2.97
2.56
1.72
1.70
1.68
1.66
1.64
1.52
1.50
1.48
1.46
1.45
1.43
0.96
0.94
0.92
1.96
1.95
2.22
2.04
δ (ppm)
67: 1H NMR (400 MHz, CDCl3)
1.96
1.95
2.00
2.97
2.22
2.04
2.98
δ (ppm)

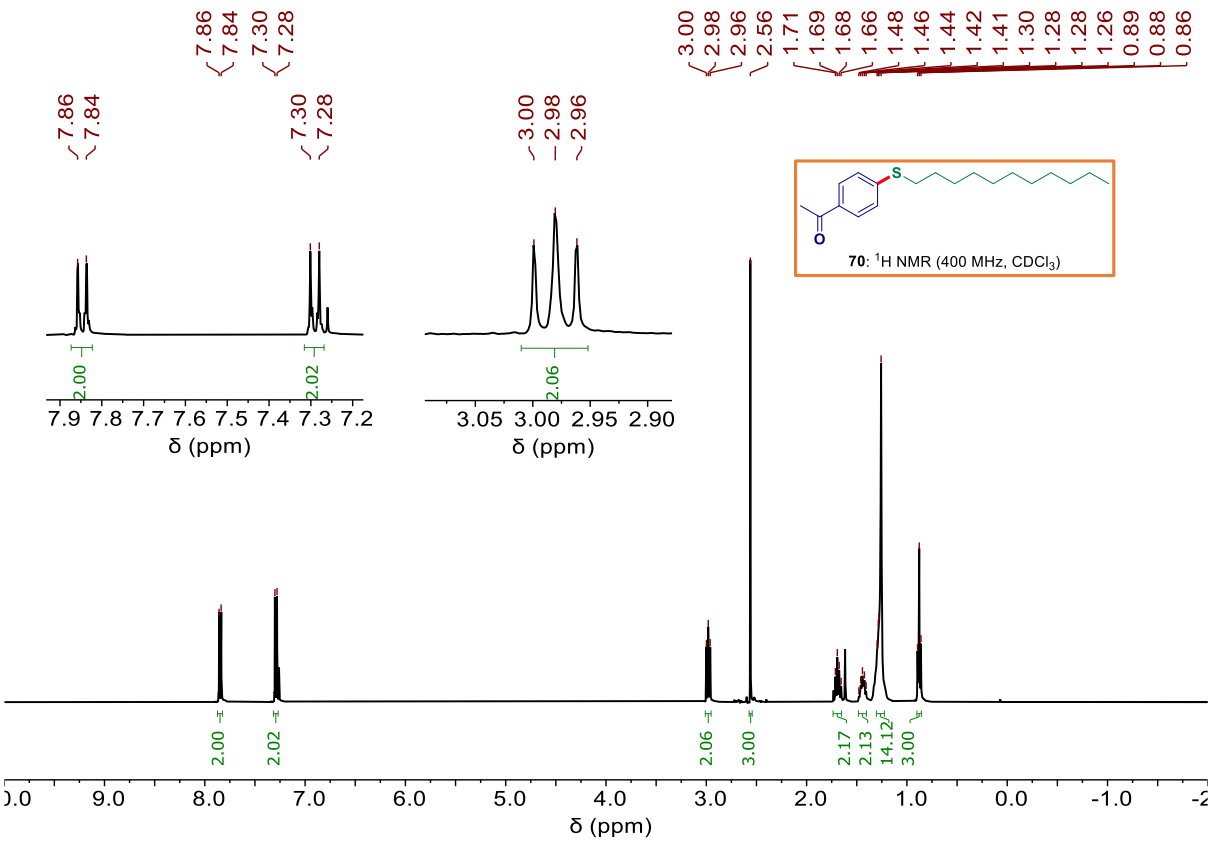

31.80
30.93
197.27
26.53
22.14
145.12
133.87
128.85
126.40
13.73
δ (ppm)
67: 13C NMR (101 MHz, CDCl3)
δ (ppm)

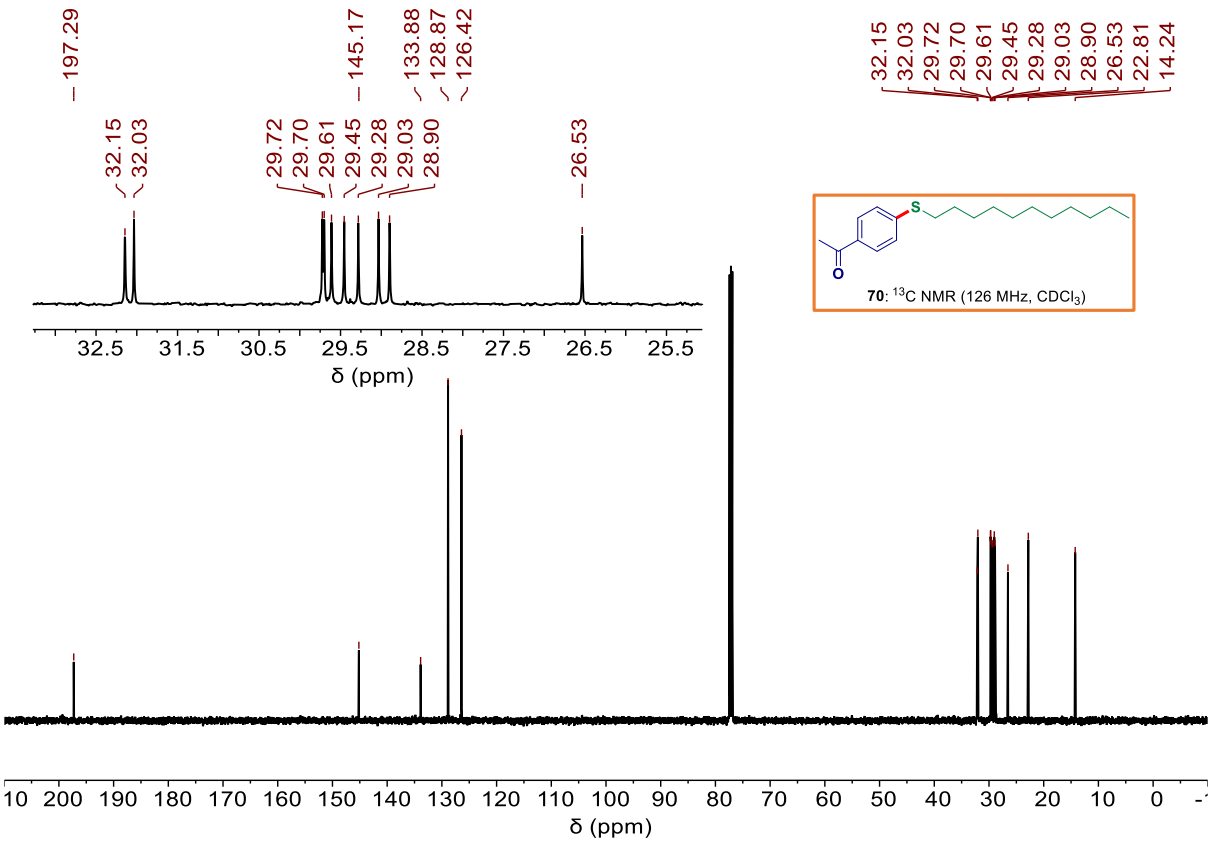

7.86
7.84
7.30
7.28
3.00
2.98
2.96
2.56
1.71
1.69
1.68
1.44
1.42
1.31
1.30
1.29
1.29
1.28
1.27
1.27
1.26
0.90
0.88
0.86
2.03
2.03
2.11
2.04
5.94
3.02
δ (ppm)
δ (ppm)
68: 1H NMR (400 MHz, CDCl3)
2.03
2.03
2.06
3.00
2.11
2.04
5.94
3.02
δ (ppm)

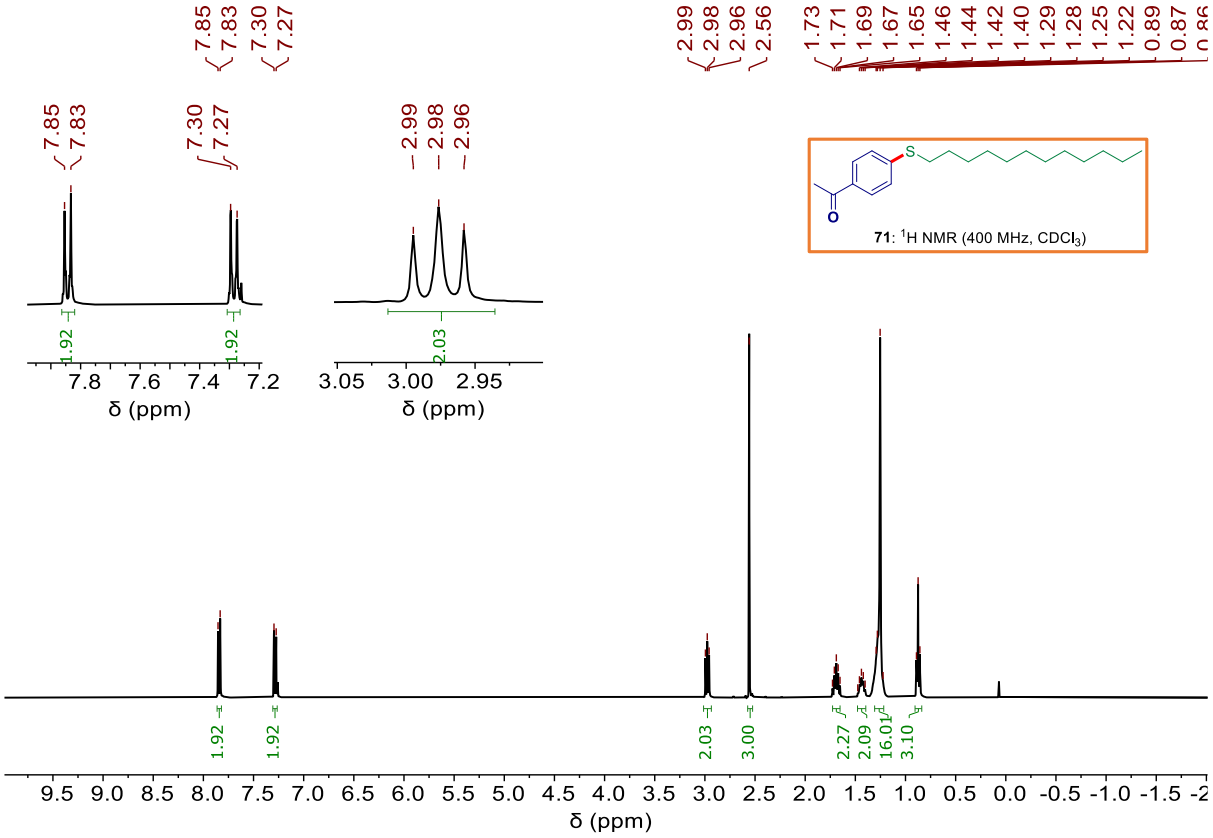

197.32
145.16
133.84
128.87
126.38
32.10
31.81
28.99
28.94
28.88
26.55
22.71
14.19
δ (ppm)
68: 13C NMR (101 MHz, CDCl3)
δ (ppm)

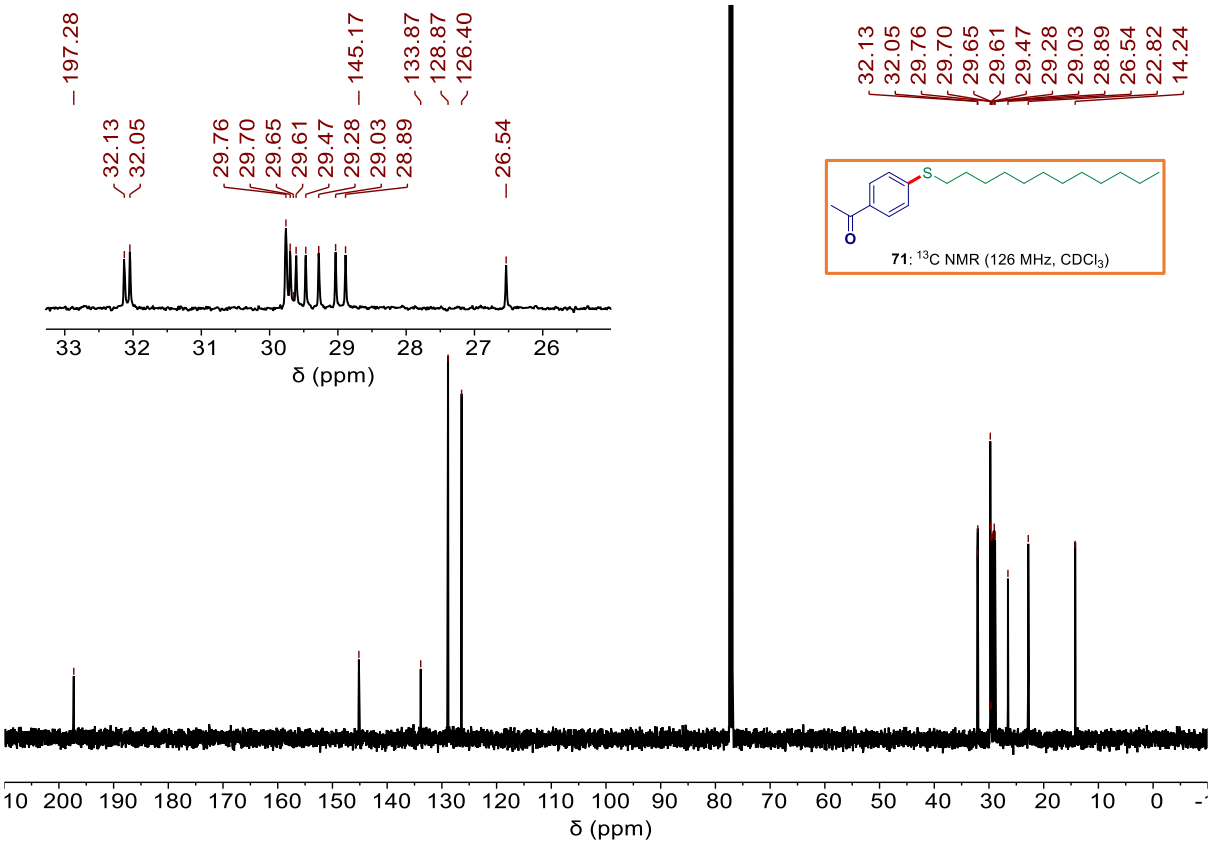

7.86
7.84
7.30
7.28
3.00
2.98
2.96
2.56
1.71
1.69
1.68
1.45
1.43
1.32
1.30
1.30
1.29
1.28
1.27
1.26
1.25
0.89
0.88
2.00
2.06
2.17
3.00
2.20
2.16
8.05
3.04
δ (ppm)
69: 1H NMR (400 MHz, CDCl3)

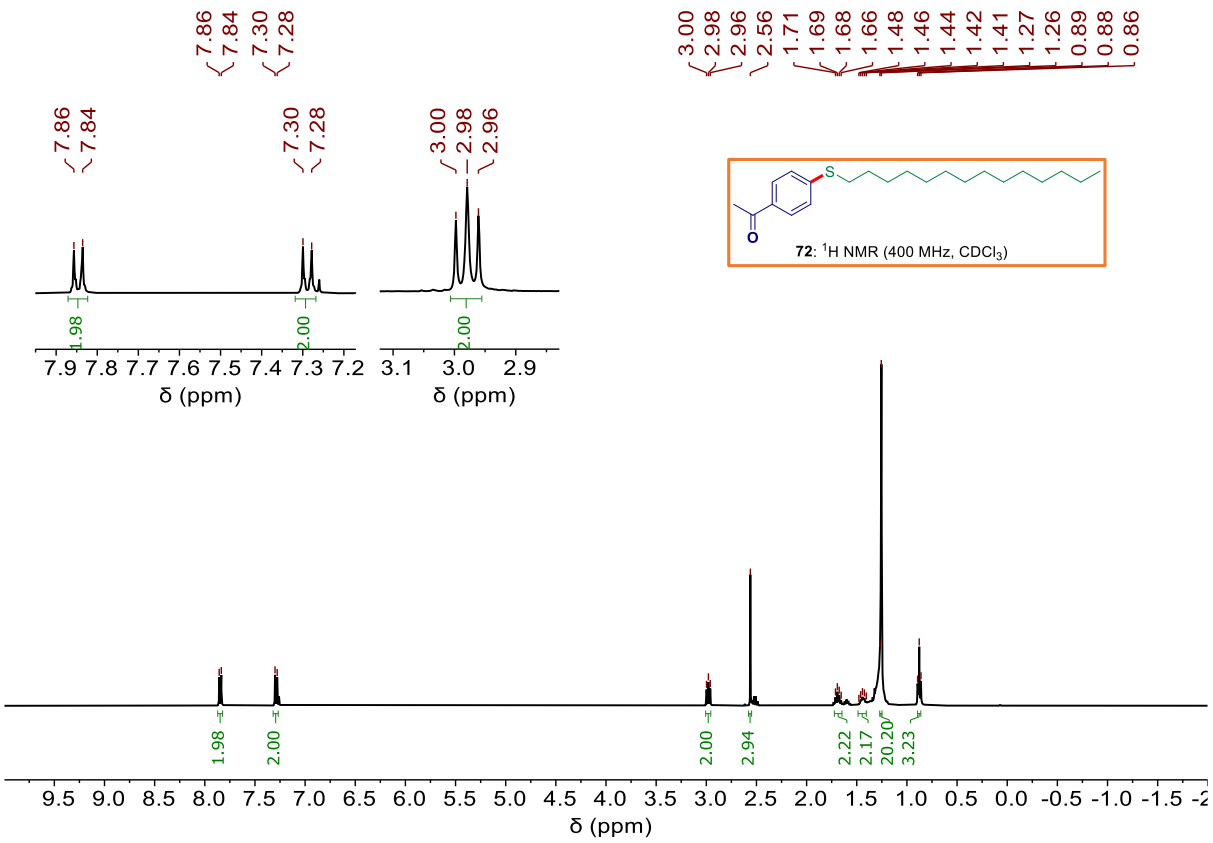

197.29
145.16
133.89
128.87
126.43
32.15
31.91
29.27
29.24
29.03
28.90
26.53
22.76
14.21
δ (ppm)
69: 13C NMR (126 MHz, CDCl3)

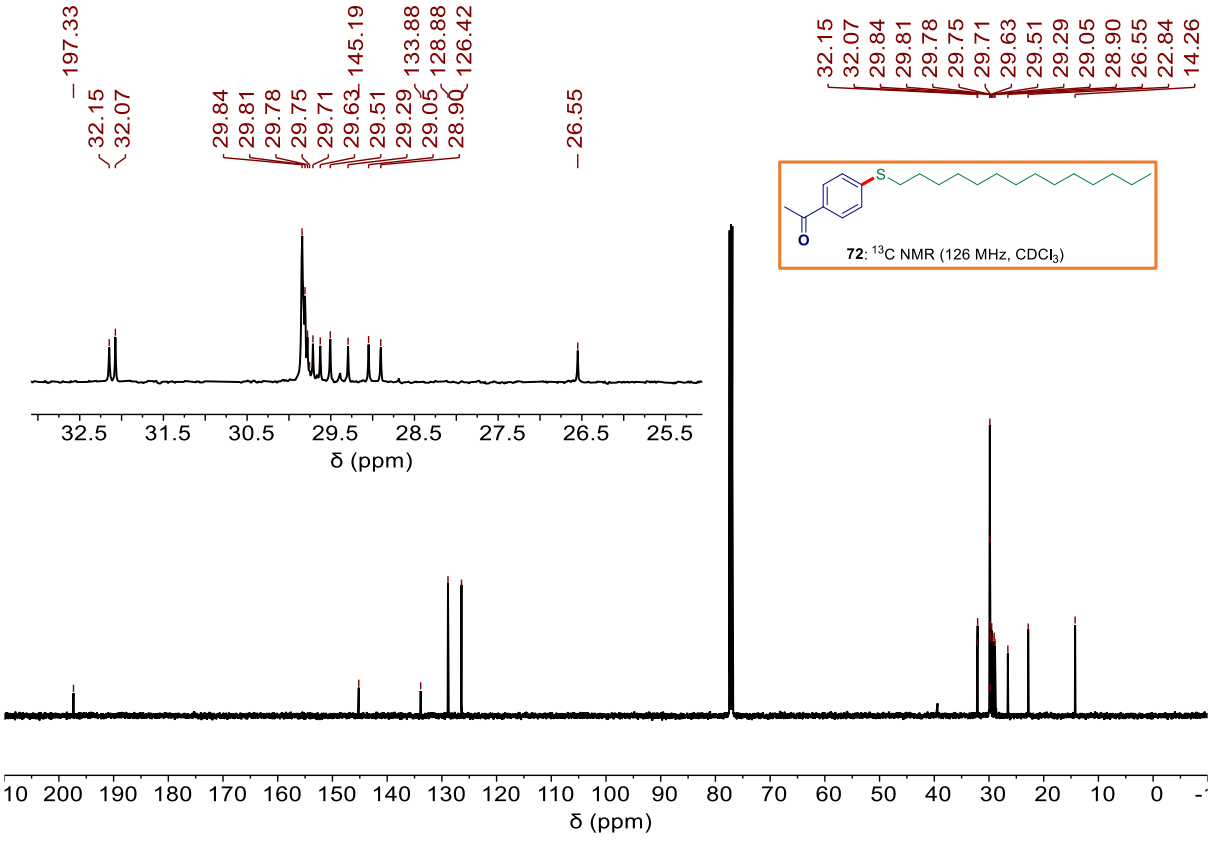

7.86
7.84
7.30
7.28
3.00
2.98
2.96
2.56
1.71
1.69
1.68
1.66
1.48
1.46
1.44
1.42
1.41
1.30
1.28
1.28
1.26
0.89
0.88
0.86
2.00
2.02
2.06
δ (ppm)
70: 1H NMR (400 MHz, CDCl3)

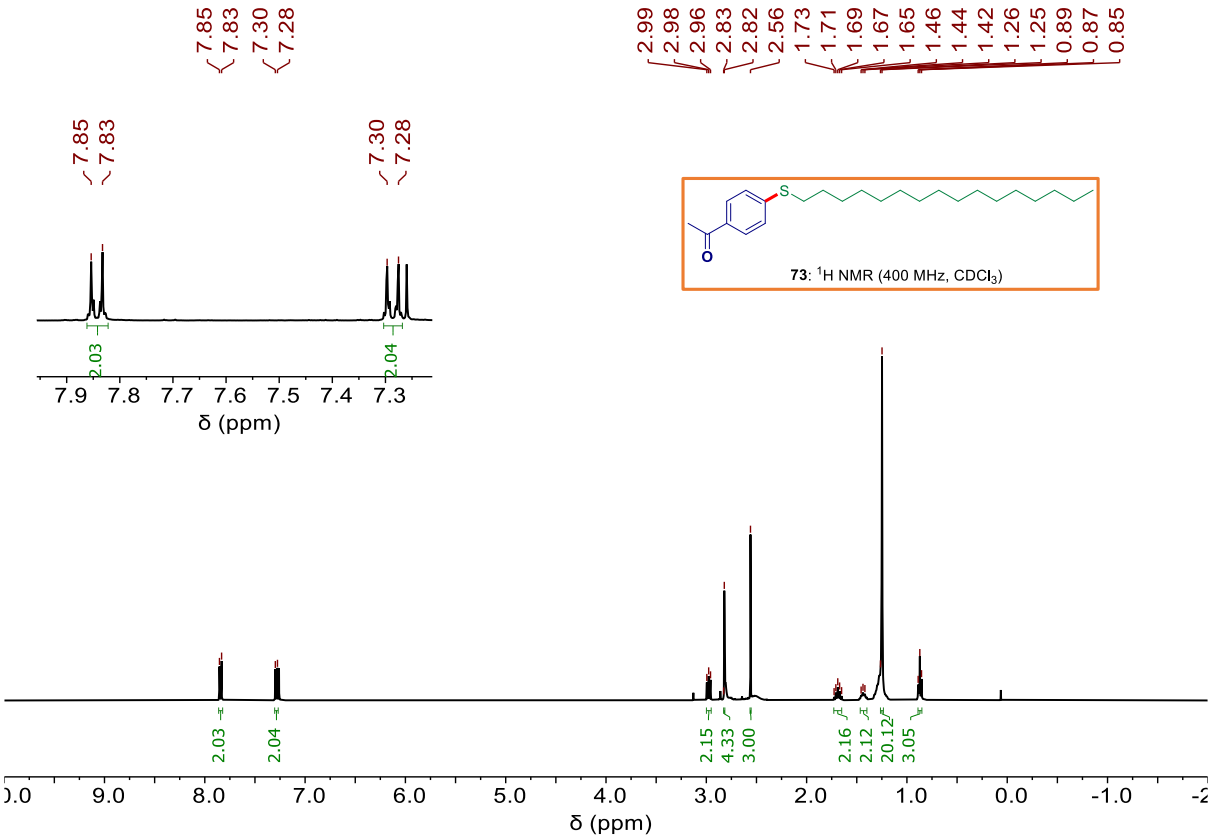

197.29
145.17
133.88
128.87
126.42
32.15
32.03
29.72
29.70
29.61
29.45
29.28
29.03
28.90
26.53
22.81
14.24
δ (ppm)
70: 13C NMR (126 MHz, CDCl3)

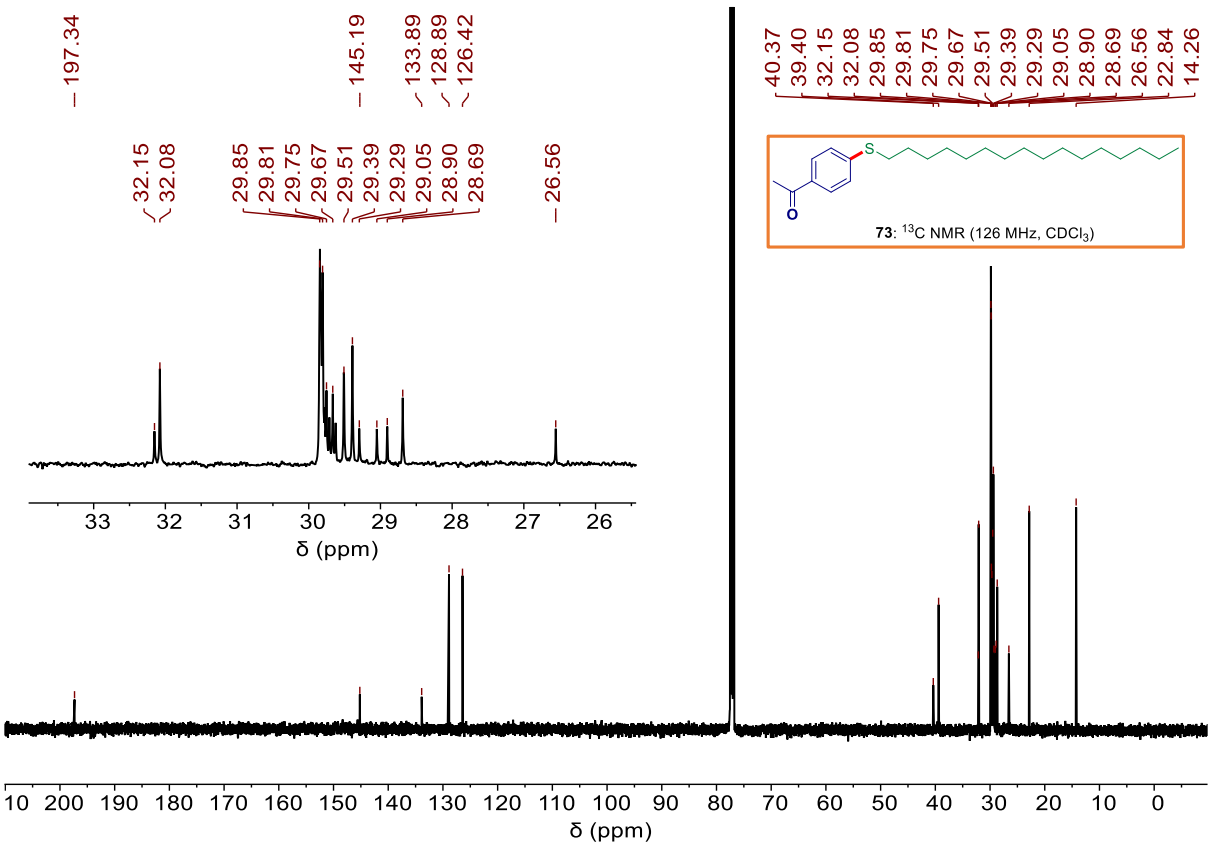

7.85
7.83
7.30
7.27
2.99
2.98
2.96
2.56
1.73
1.71
1.69
1.67
1.65
1.46
1.44
1.42
1.40
1.29
1.28
1.25
1.22
0.89
0.87
1.92
1.92
2.03
3.00
2.27
2.09
16.01
3.10
δ (ppm)
71: 1H NMR (400 MHz, CDCl3)

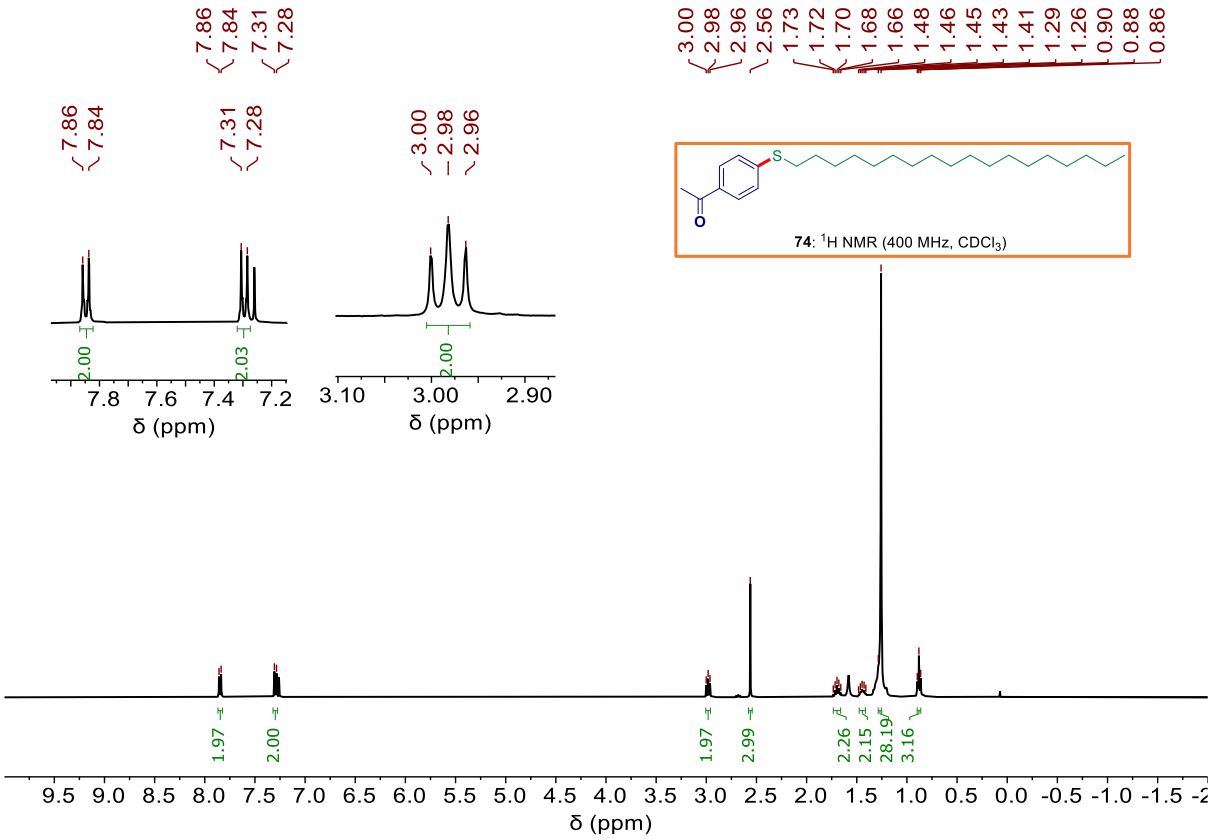

197.28
145.17
133.87
128.87
126.40
32.13
32.05
29.76
29.70
29.65
29.61
29.47
29.28
29.03
28.89
26.54
22.82
14.24
δ (ppm)
71: 13C NMR (126 MHz, CDCl3)

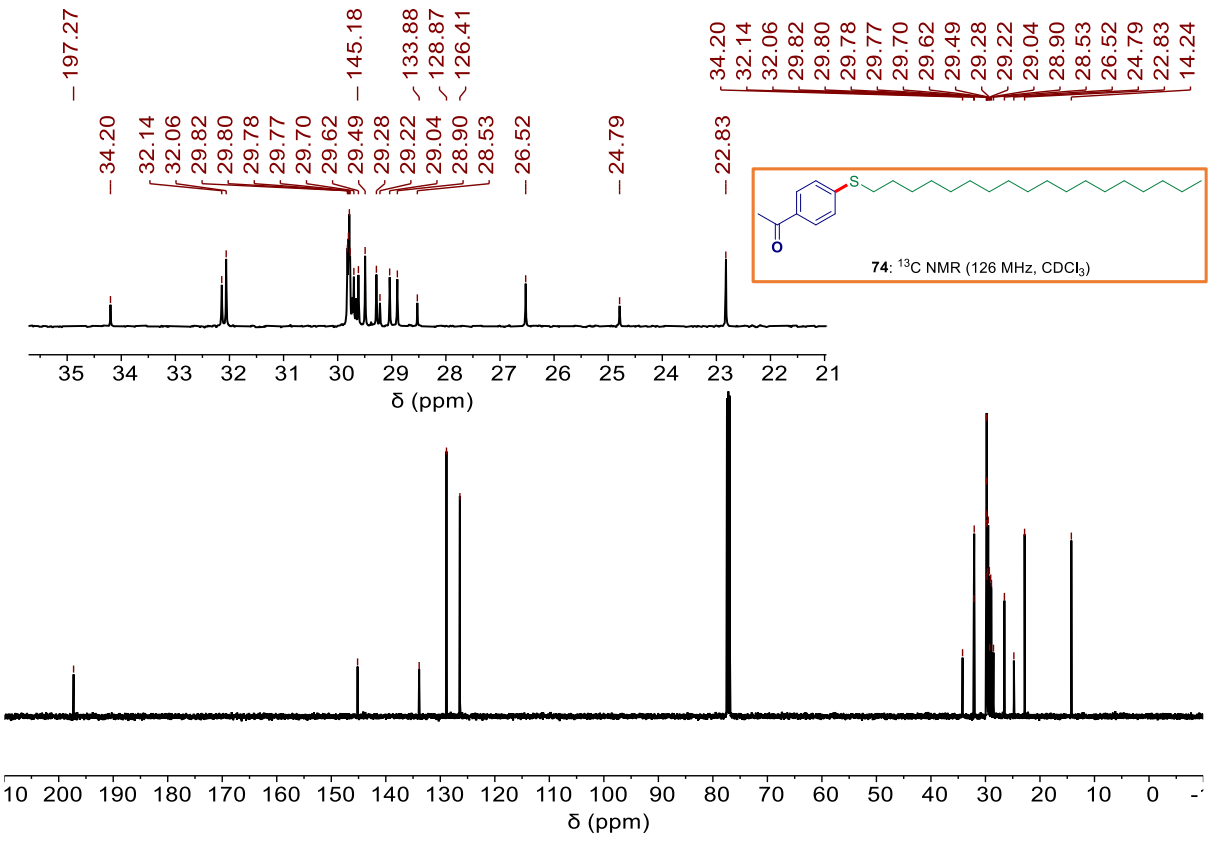

7.86
7.84
7.30
7.28
3.00
2.98
2.96
2.56
1.71
1.69
1.68
1.66
1.48
1.46
1.44
1.42
1.41
1.27
1.26
0.89
0.88
0.86
72: 1H NMR (400 MHz, CDCl3)
1.98
2.00
2.00
δ (ppm)
1.98
2.00
2.00
2.94
2.22
2.17
20.20
3.23
δ (ppm)

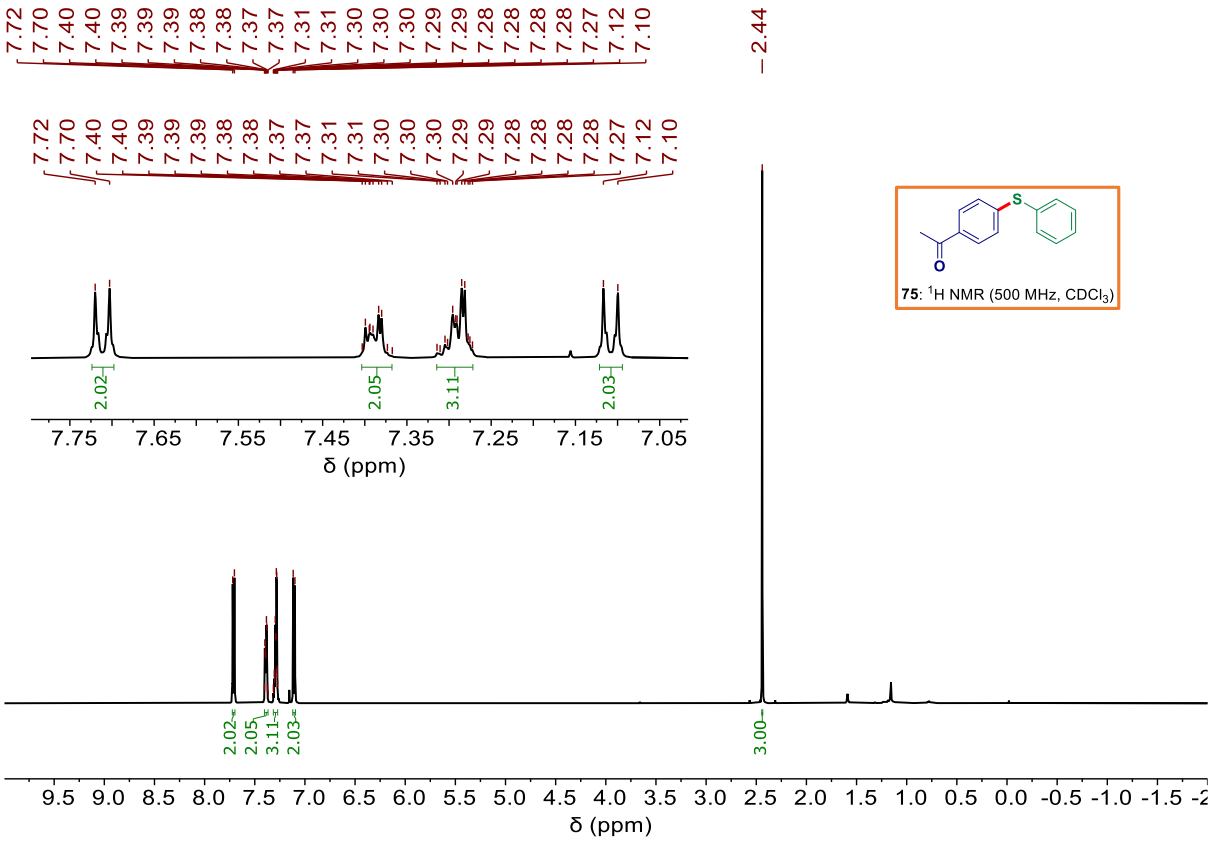

197.33
32.15
32.07
29.84
29.81
29.78
29.75
29.71
29.63
29.51
29.29
29.05
28.90
145.19
133.88
128.88
126.42
26.55
32.15
32.07
29.84
29.81
29.78
29.75
29.71
29.63
29.51
29.29
29.05
28.90
26.55
22.84
14.26
72: 13C NMR (126 MHz, CDCl3)
δ (ppm)
δ (ppm)

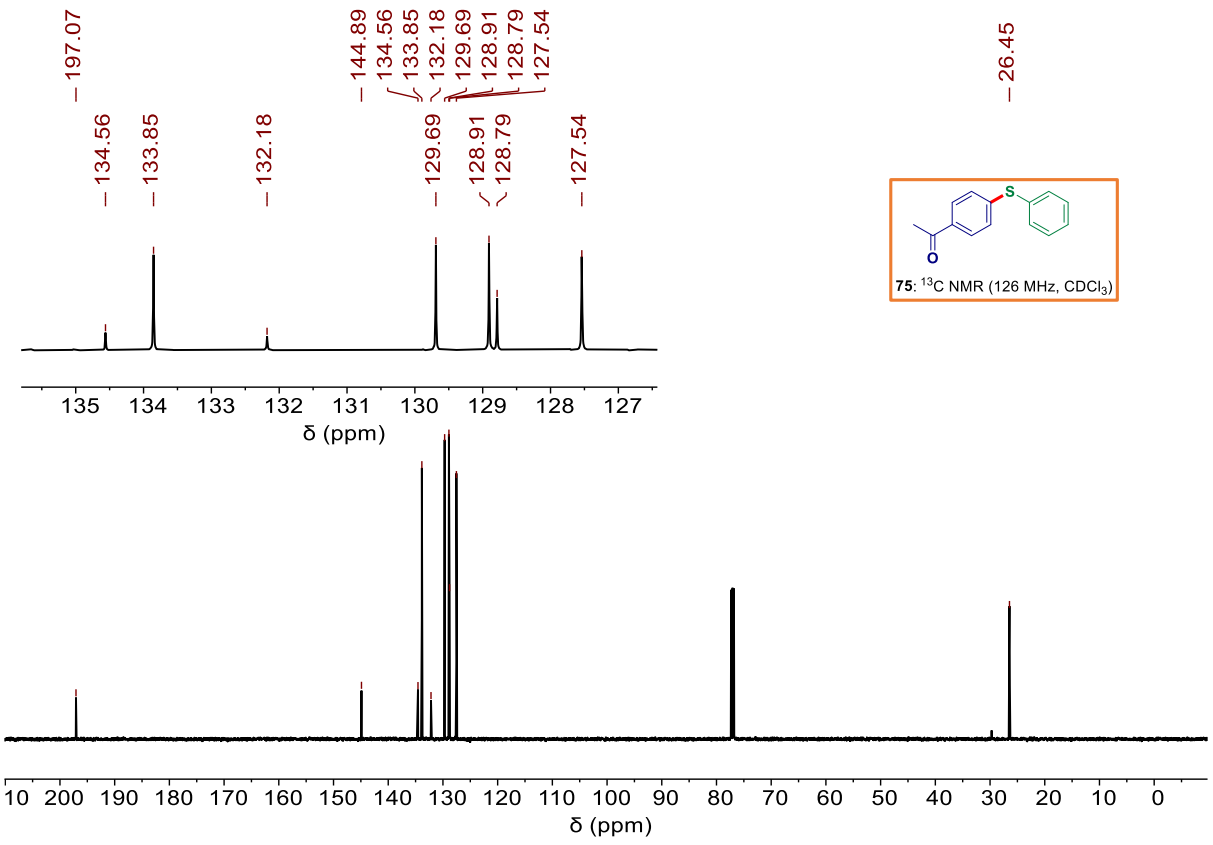

7.85
7.83
7.30
7.28
2.99
2.98
2.96
2.83
2.82
2.56
1.73
1.71
1.69
1.67
1.65
1.46
1.44
1.42
1.26
1.25
0.89
0.87
0.85
2.03
2.04
δ (ppm)
73: ^{1}H NMR (400 MHz, CDCl$_3$)
2.03
2.04
2.15
4.33
3.00
2.16
2.12
20.12
3.05
δ (ppm)

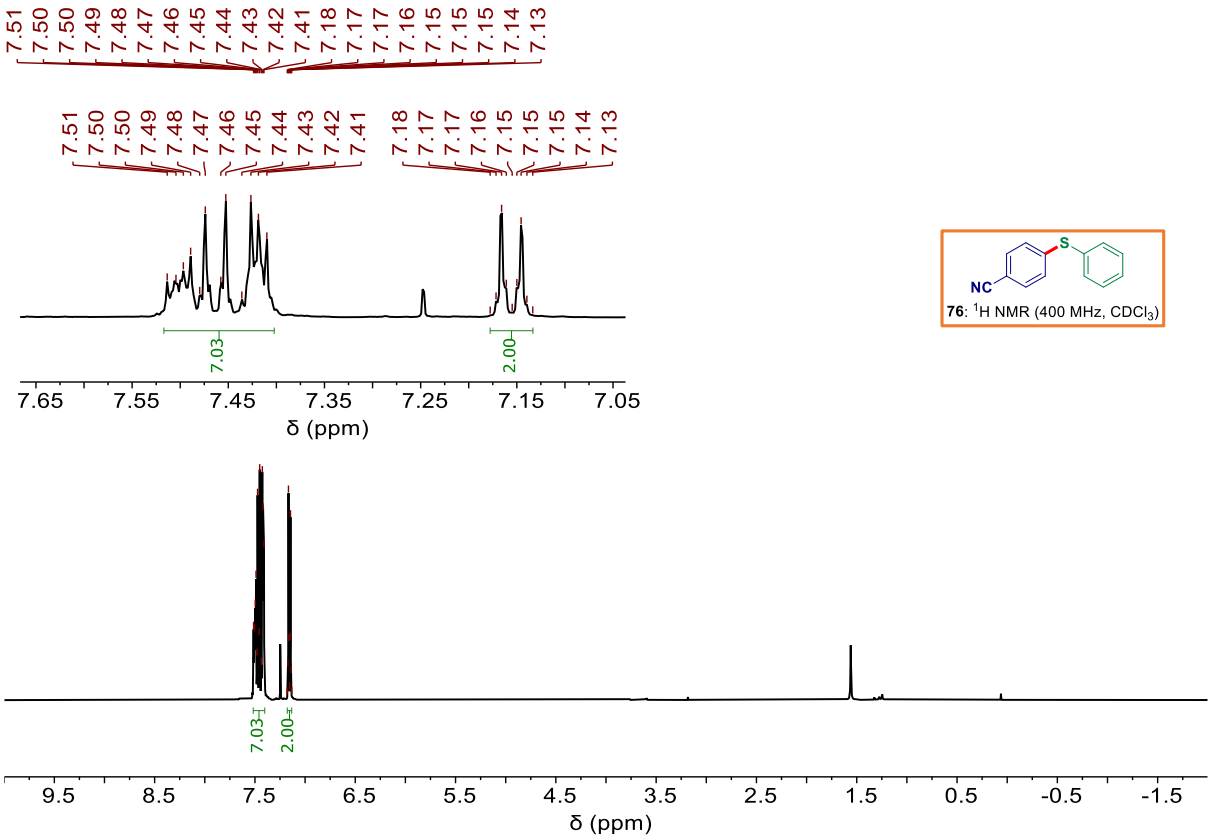

197.34
145.19
133.89
128.89
126.42
40.37
39.40
32.15
32.08
29.85
29.81
29.75
29.67
29.51
29.39
29.29
29.05
28.90
28.69
26.56
22.84
14.26
73: ^{13}C NMR (126 MHz, CDCl$_3$)
δ (ppm)
δ (ppm)

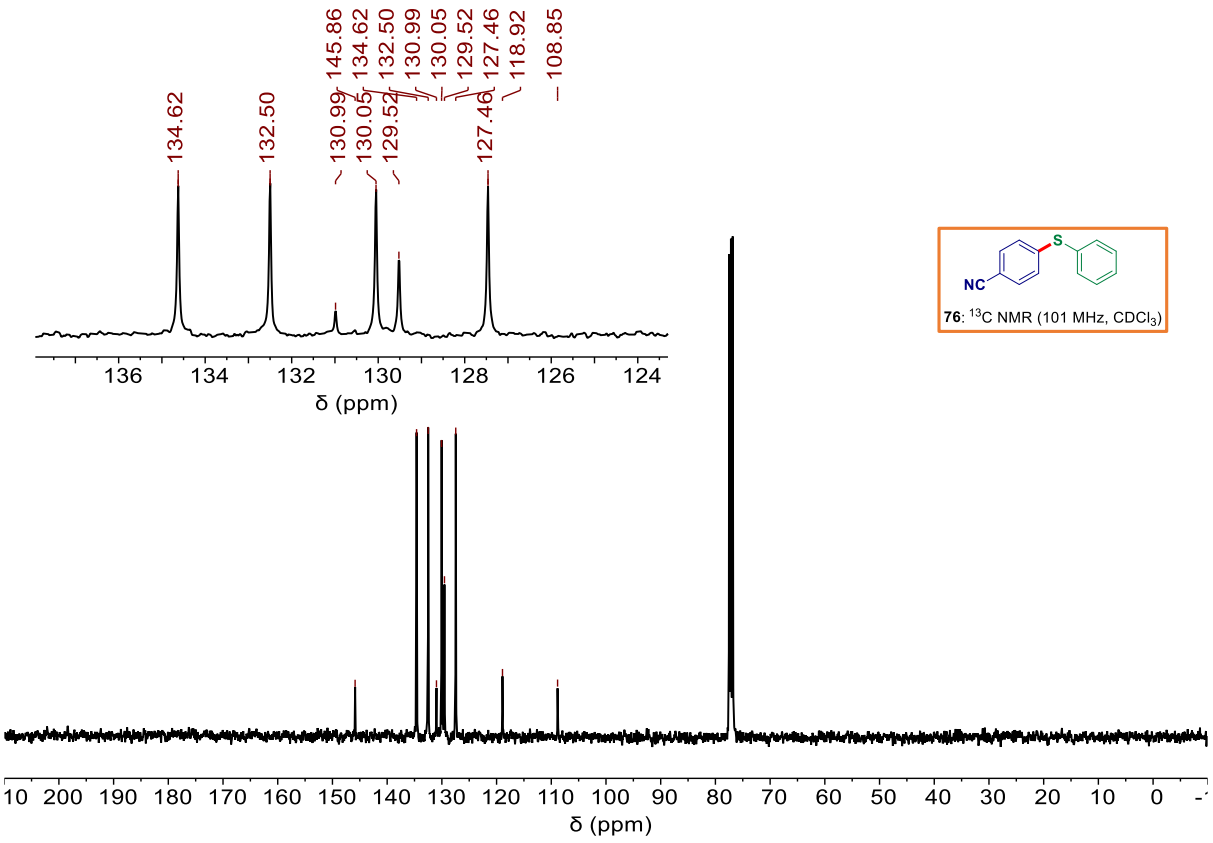

7.86
7.84
7.31
7.28
3.00
2.98
2.96
2.56
1.73
1.72
1.70
1.68
1.66
1.48
1.46
1.45
1.43
1.41
1.29
1.26
0.90
0.88
0.86
2.00
2.03
2.00
δ (ppm)
74: 1H NMR (400 MHz, CDCl3)
1.97
2.00
1.97
2.99
2.26
2.15
28.19
3.16
δ (ppm)

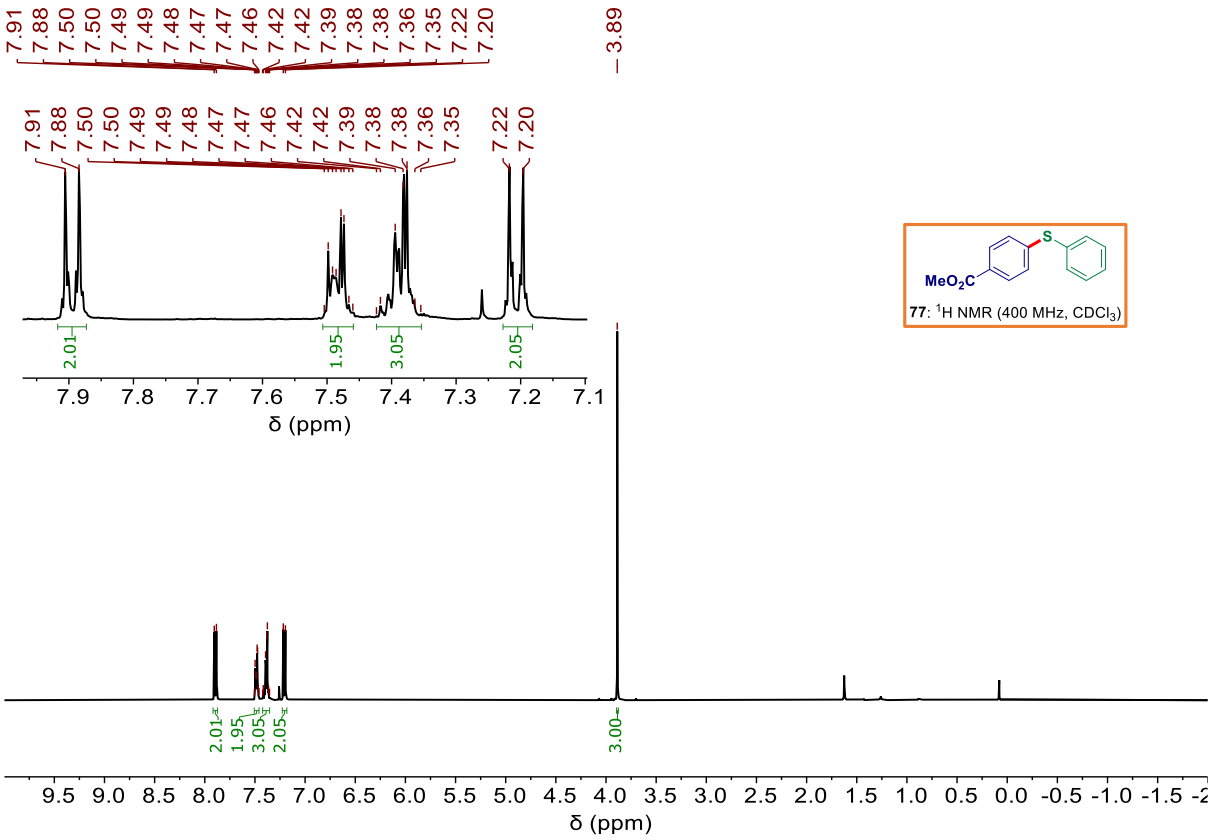

197.27
145.18
133.88
128.87
126.41
34.20
32.14
32.06
29.82
29.80
29.78
29.77
29.70
29.62
29.49
29.28
29.22
29.04
28.90
28.53
26.52
24.79
22.83
δ (ppm)
74: 13C NMR (126 MHz, CDCl3)
δ (ppm)

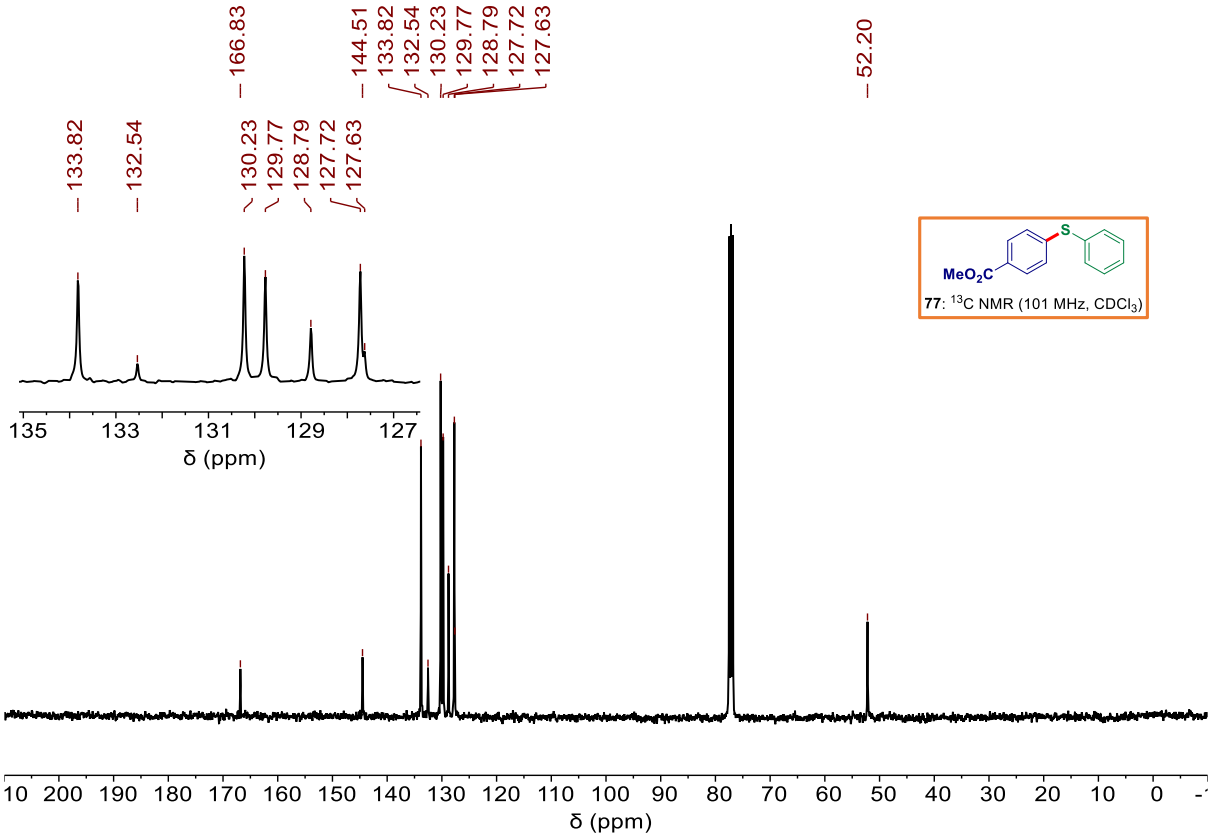

7.72 7.70 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.28 7.27 7.12 7.10
2.44
2.02
2.05
3.11
2.03
7.75 7.65 7.55 7.45 7.35 7.25 7.15 7.05
δ (ppm)
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
δ (ppm)
75: 1H NMR (500 MHz, CDCl3)

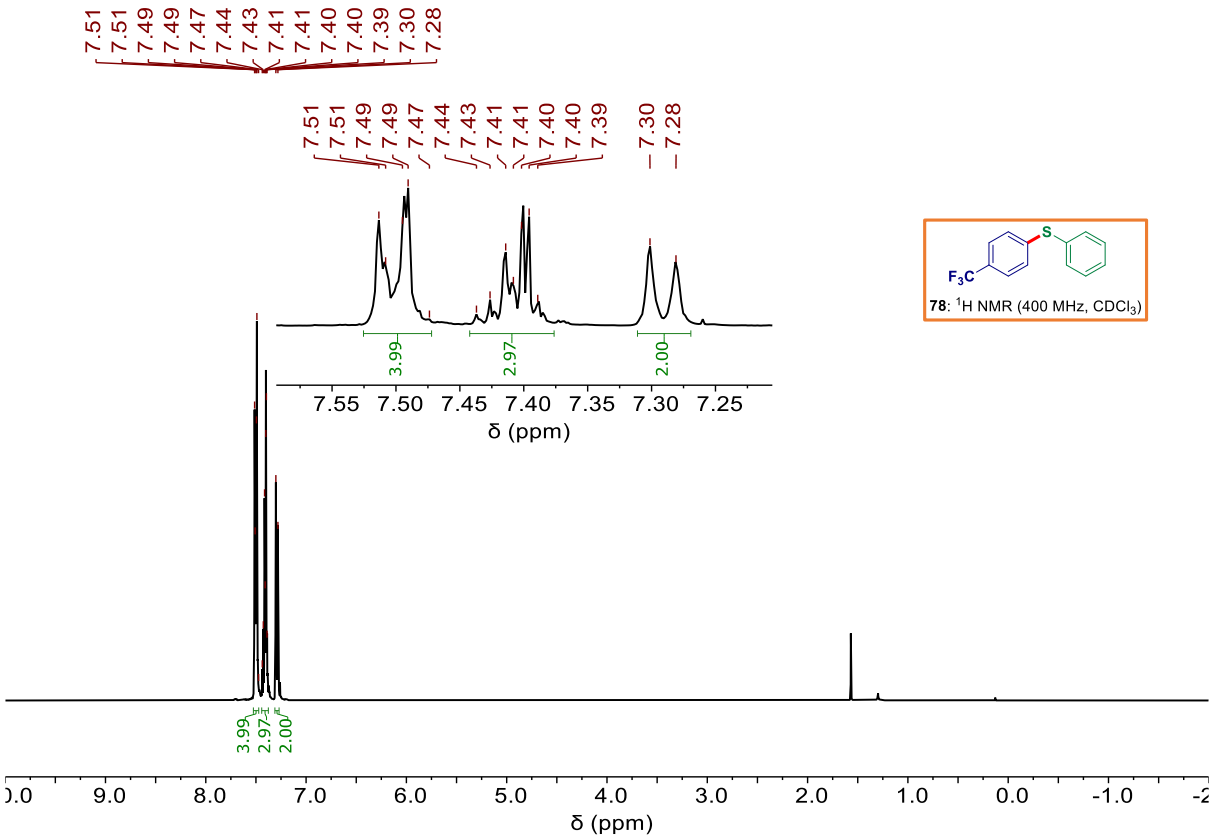

197.07
144.89
134.56
133.85
132.18
129.69
128.91
128.79
127.54
26.45
135 134 133 132 131 130 129 128 127
δ (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)
75: 13C NMR (126 MHz, CDCl3)

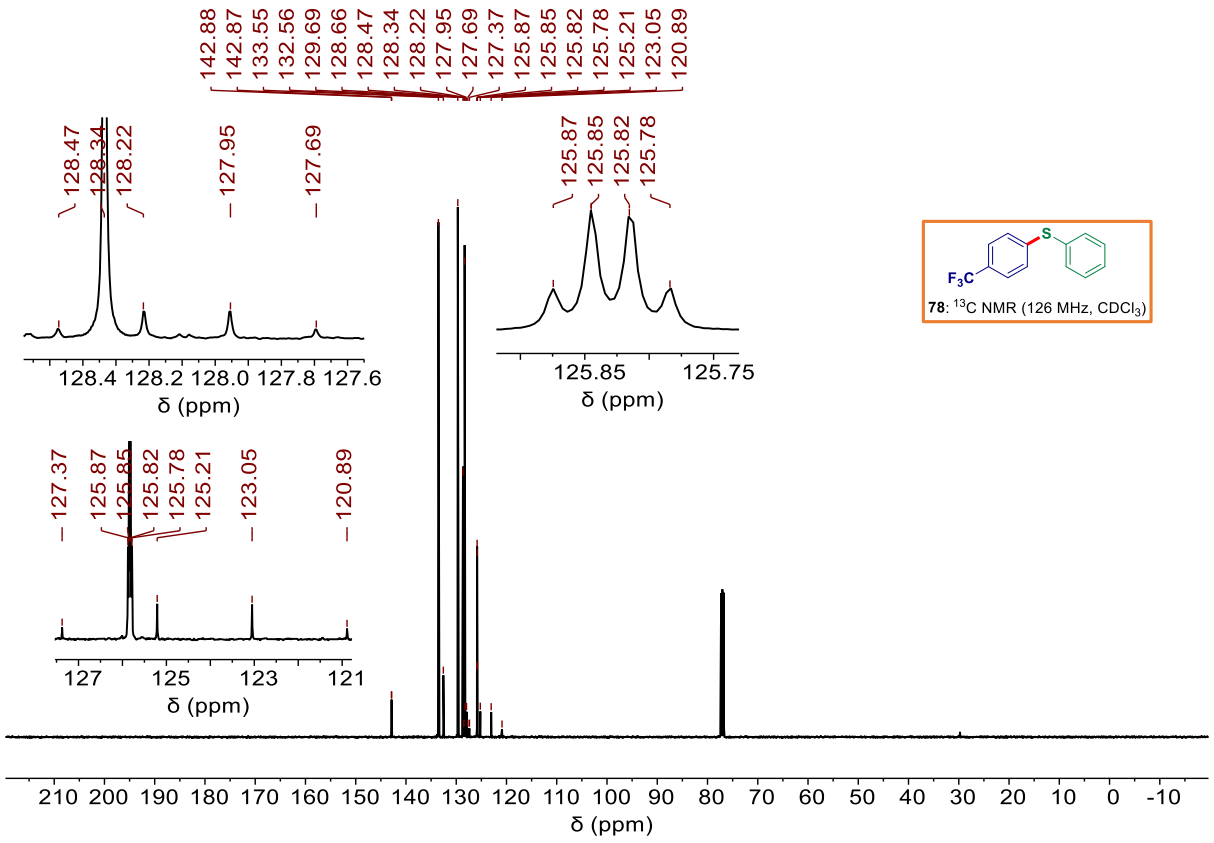

7.51 7.50 7.50 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.18 7.17 7.17 7.16 7.15 7.15 7.15 7.14 7.13
7.03
2.00
7.65 7.55 7.45 7.35 7.25 7.15 7.05
δ (ppm)
7.03
2.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)
NC
S
76: 1H NMR (400 MHz, CDCl3)

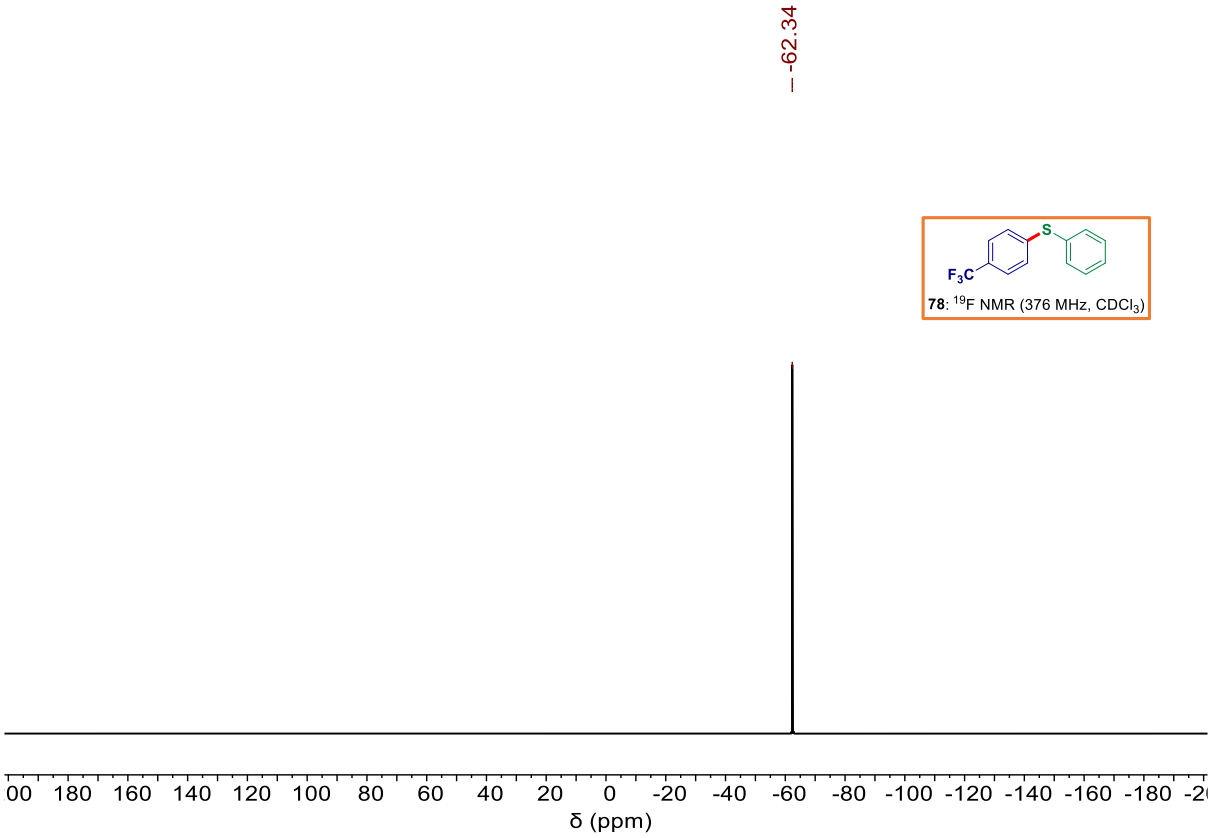

134.62 132.50 130.99 145.86 134.62 132.50 130.99 130.05 129.52 127.46 118.92 108.85
136 134 132 130 128 126 124
δ (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)
NC
S
76: 13C NMR (101 MHz, CDCl3)

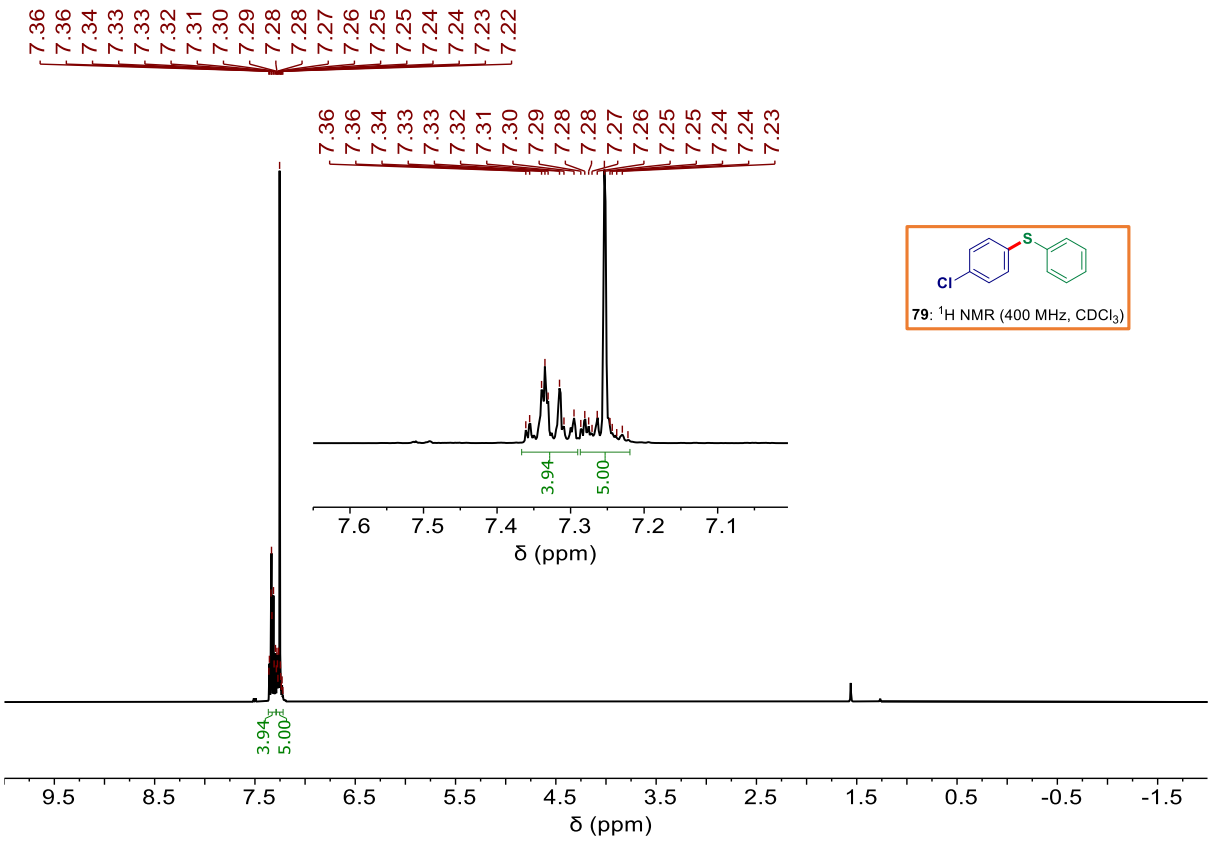

7.91
7.88
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.42
7.42
7.39
7.38
7.38
7.36
7.35
7.22
7.20
3.89
2.01
1.95
3.05
2.05
3.00
δ (ppm)
MeO2C
S
77: 1H NMR (400 MHz, CDCl3)

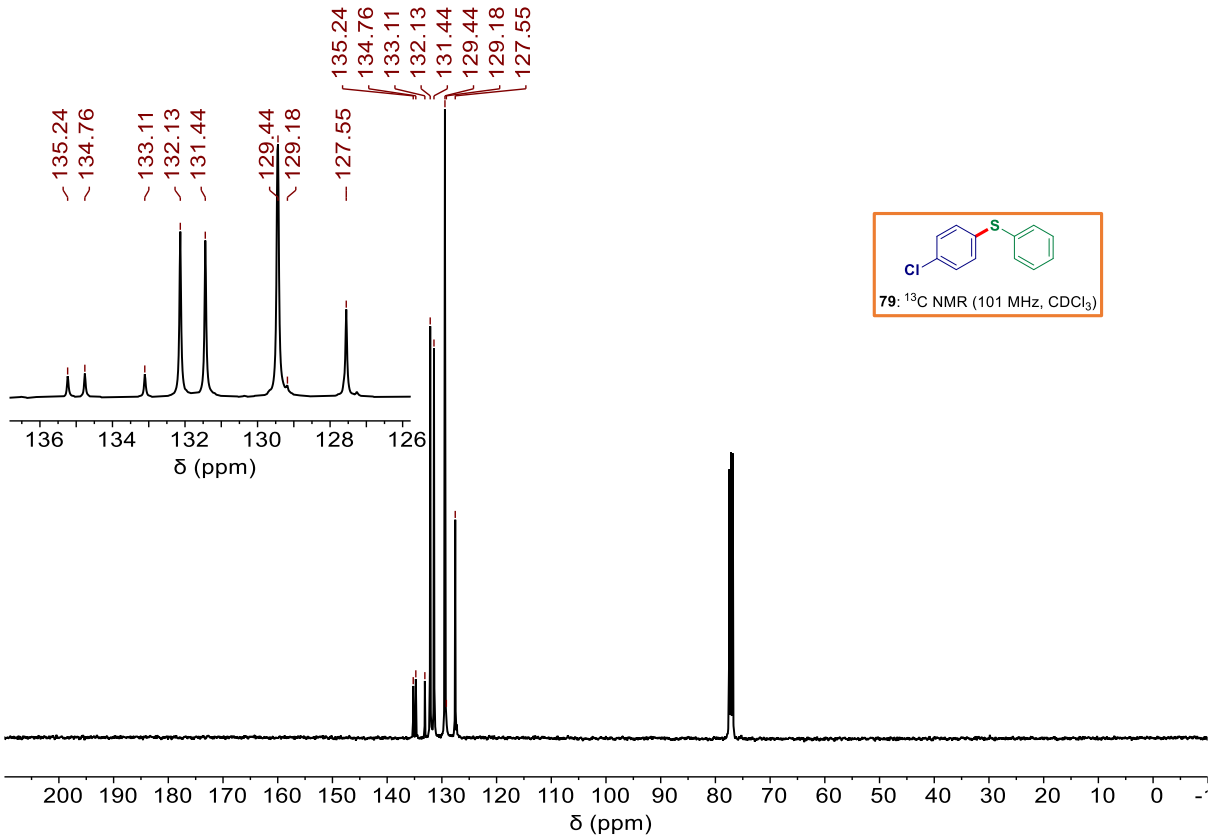

166.83
144.51
133.82
132.54
130.23
129.77
128.79
127.72
127.63
52.20
δ (ppm)
MeO2C
S
77: 13C NMR (101 MHz, CDCl3)

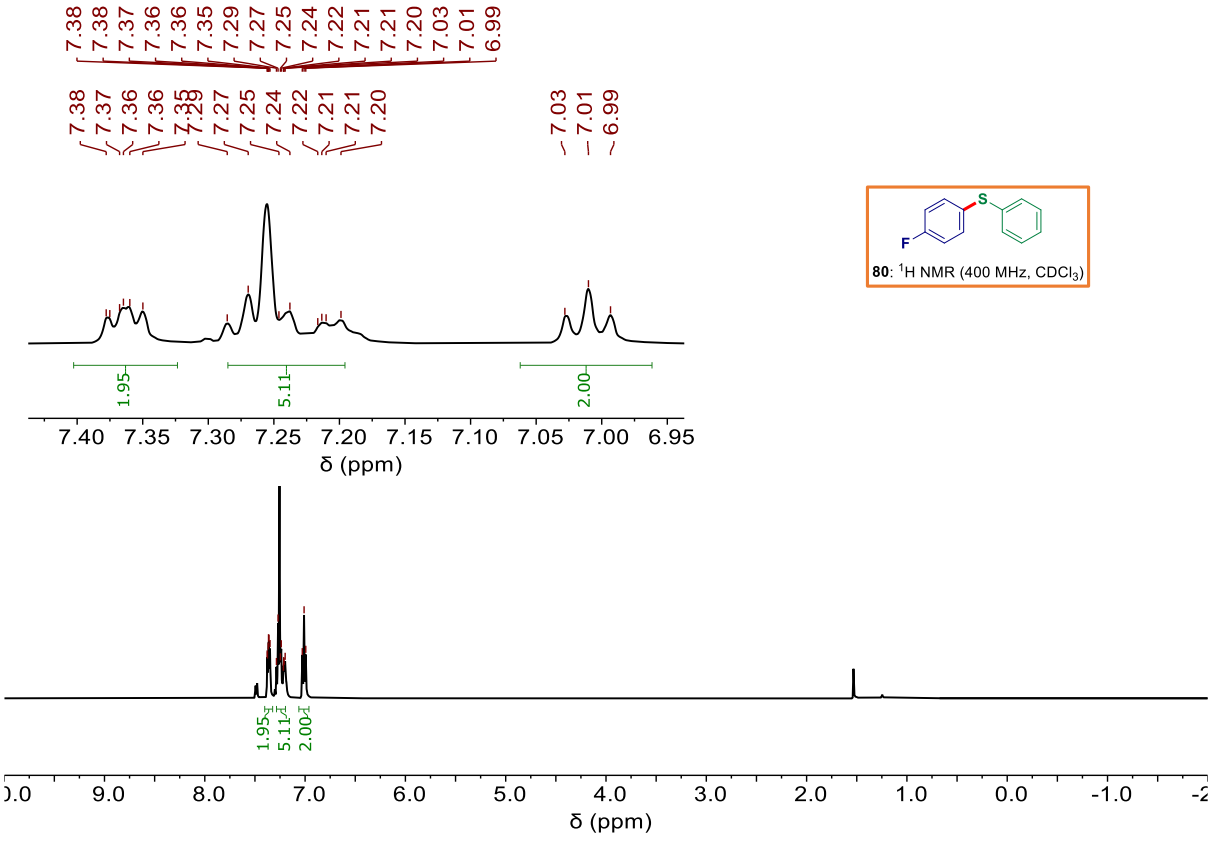

7.51
7.51
7.49
7.49
7.47
7.44
7.43
7.41
7.41
7.40
7.40
7.39
7.30
7.28
3.99
2.97
2.00
7.55 7.50 7.45 7.40 7.35 7.30 7.25
δ (ppm)
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)
78: 1H NMR (400 MHz, CDCl3)

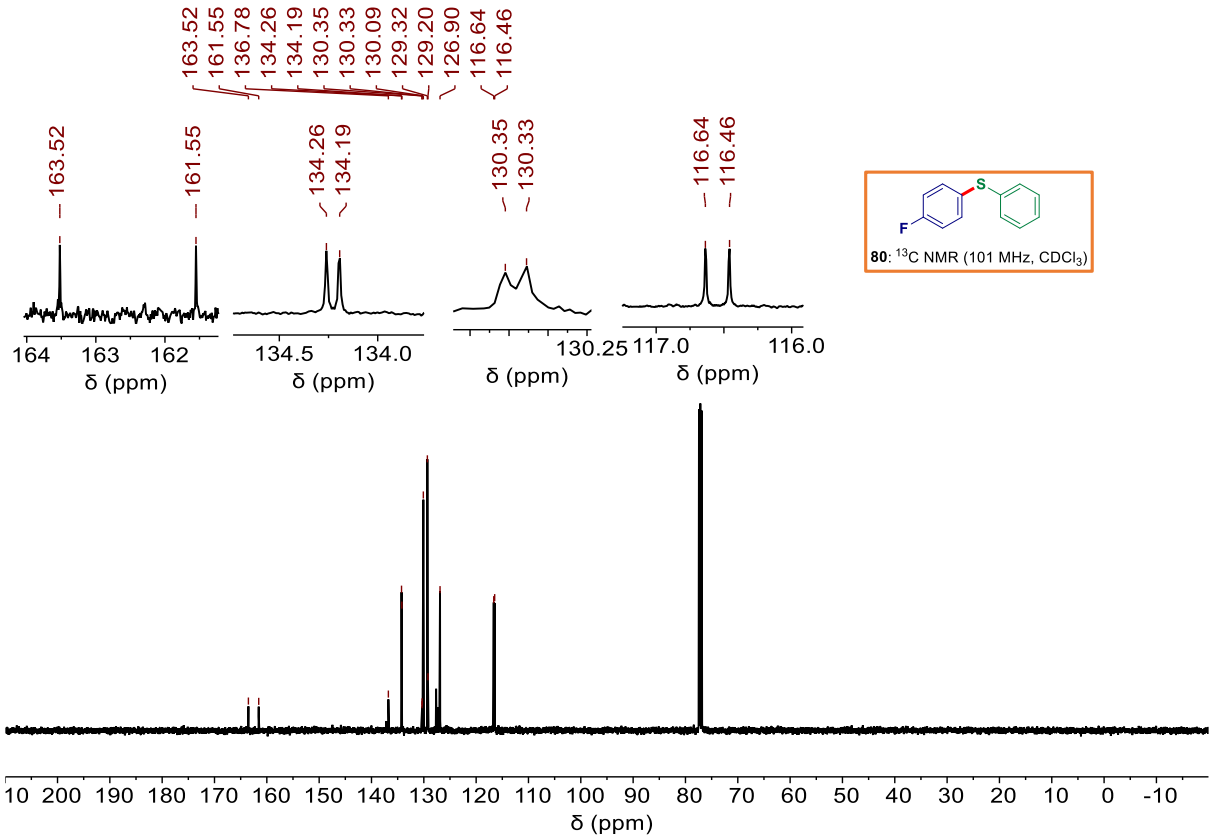

142.88
142.87
133.55
132.56
129.69
128.66
128.47
128.34
128.22
127.95
127.69
127.37
125.87
125.85
125.82
125.78
125.21
123.05
120.89
128.4 128.2 128.0 127.8 127.6
δ (ppm)
125.85 125.75
δ (ppm)
127 125 123 121
δ (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)
78: 13C NMR (126 MHz, CDCl3)

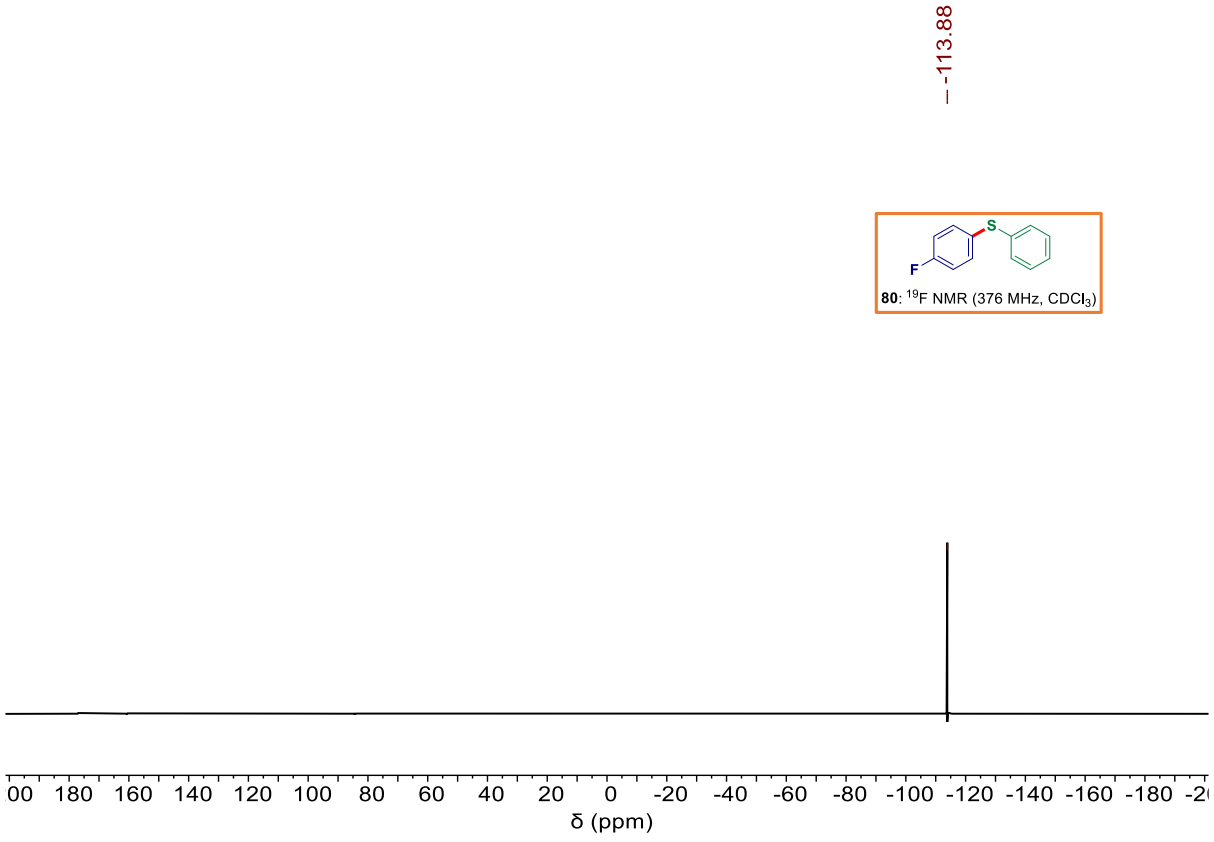

-62.34
78: 19F NMR (376 MHz, CDCl3)
00 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -2
δ (ppm)

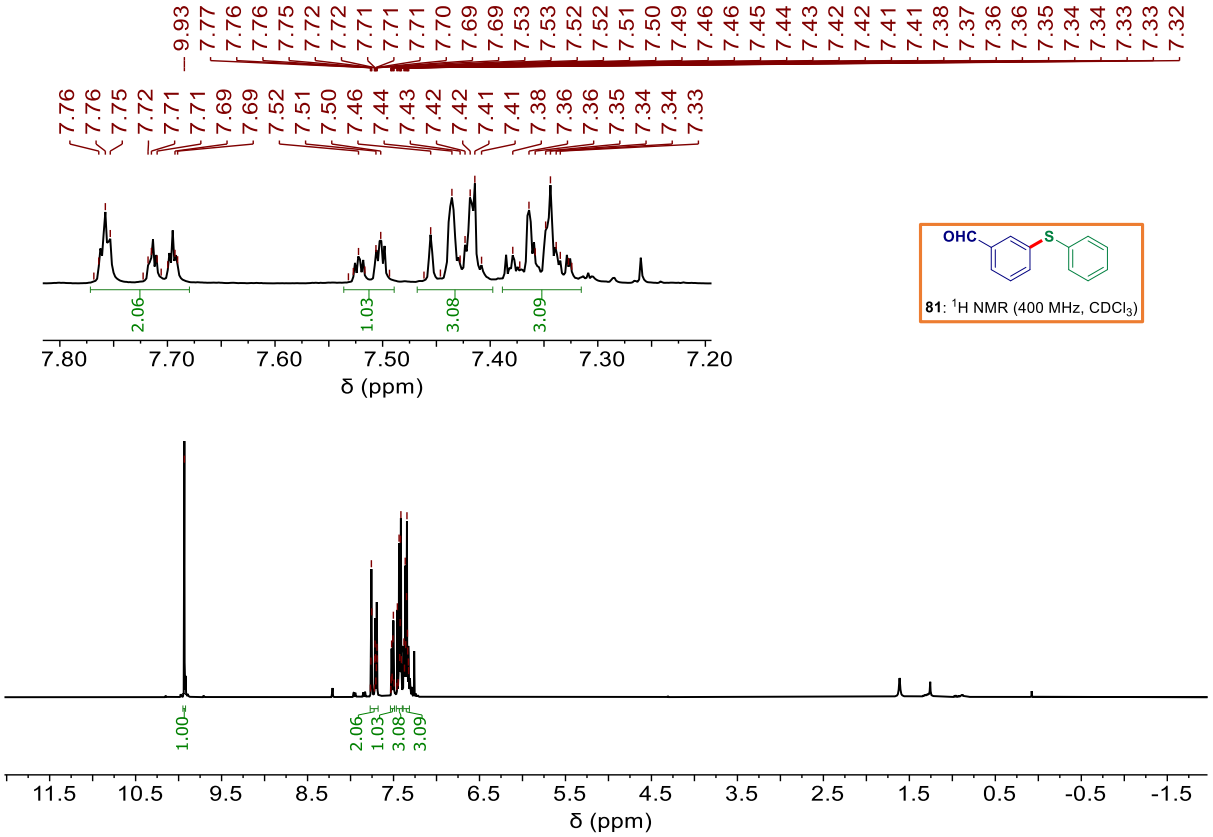

7.36 7.36 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.22
7.36 7.36 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.25 7.25 7.24 7.24 7.23
3.94
5.00
7.6 7.5 7.4 7.3 7.2 7.1
δ (ppm)
79: 1H NMR (400 MHz, CDCl3)
3.94
5.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)

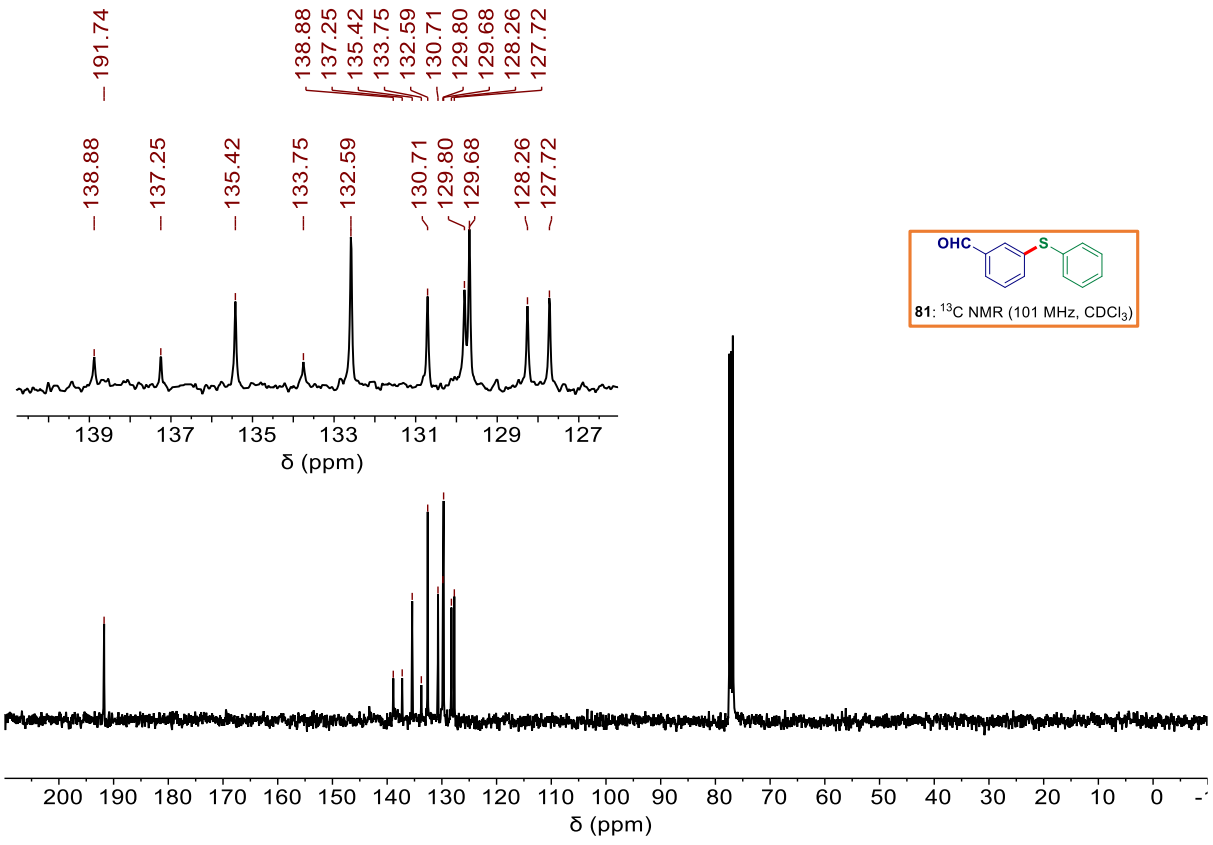

135.24
134.76
133.11
132.13
131.44
129.44
129.18
127.55
δ (ppm)
79: 13C NMR (101 MHz, CDCl3)

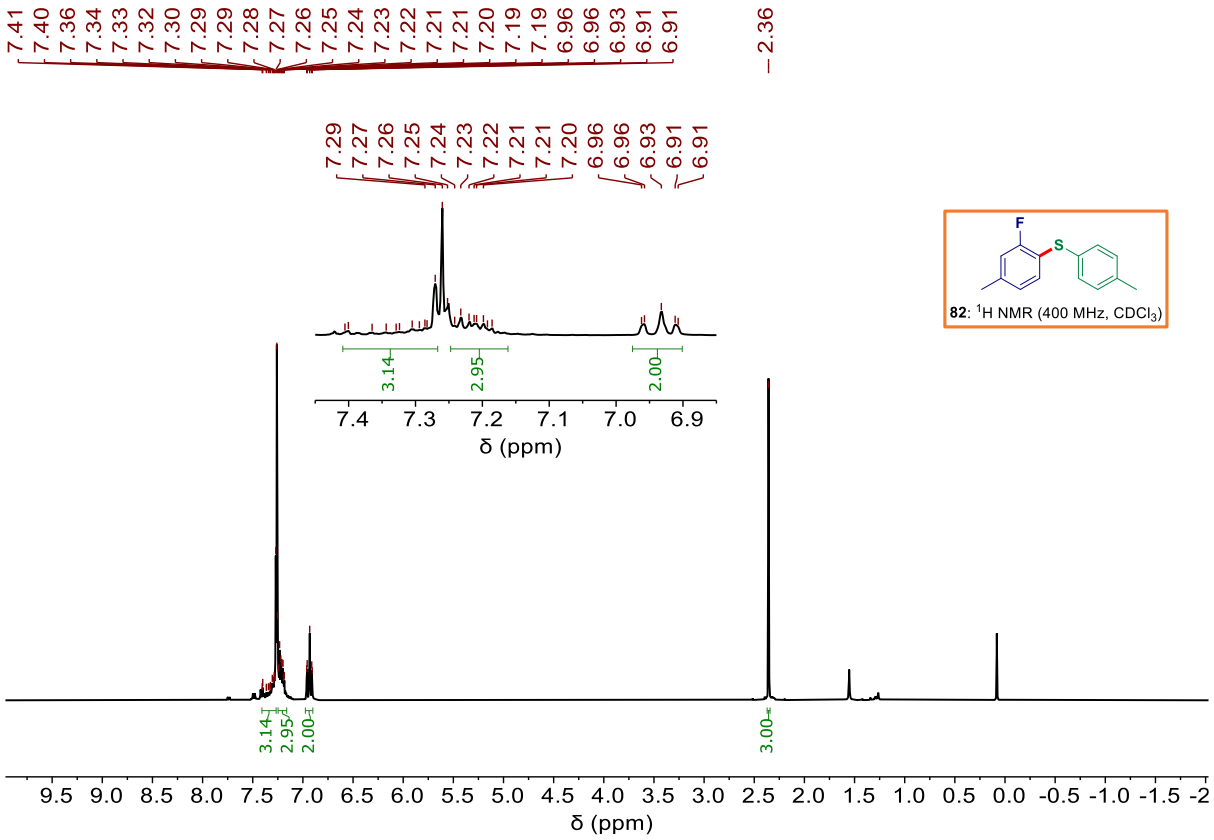

7.38
7.37
7.36
7.35
7.29
7.27
7.25
7.24
7.22
7.21
7.20
7.03
7.01
6.99
1.95
5.11
2.00
δ (ppm)
80: 1H NMR (400 MHz, CDCl3)

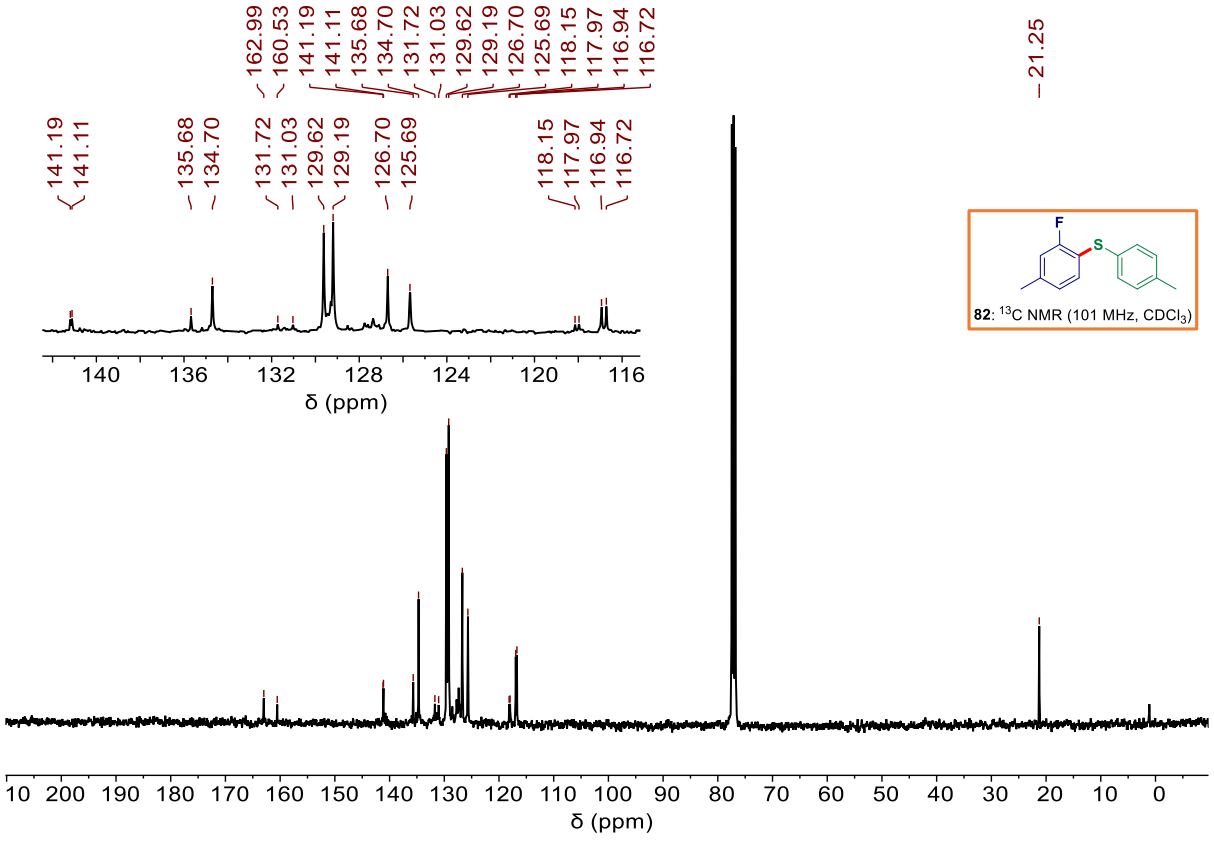

163.52
161.55
136.78
134.26
134.19
130.35
130.33
130.09
129.32
129.20
126.90
116.64
116.46
163.52
161.55
134.26
134.19
130.35
130.33
116.64
116.46
164 163 162
δ (ppm)
134.5 134.0
δ (ppm)
130.25
δ (ppm)
117.0 116.0
δ (ppm)
80: 13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

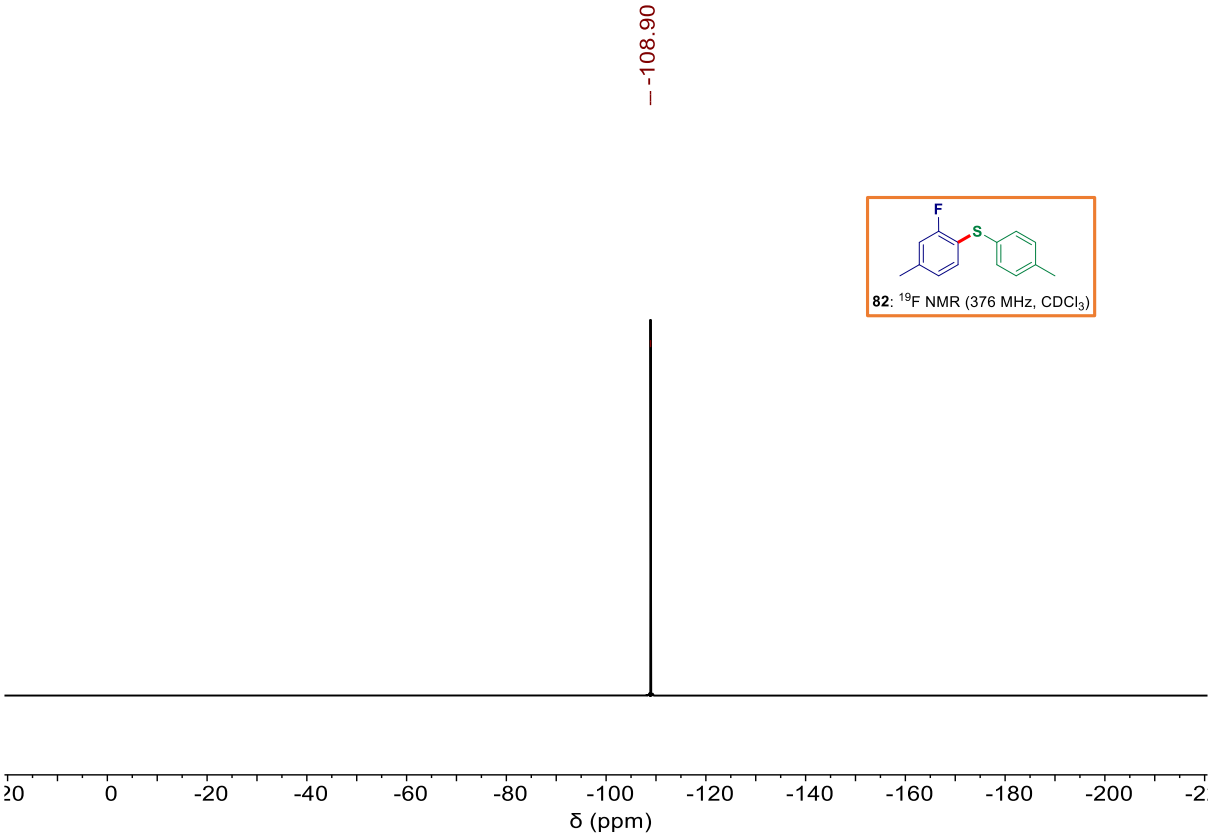

-113.88
80: 19F NMR (376 MHz, CDCl3)
00 180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -2
δ (ppm)

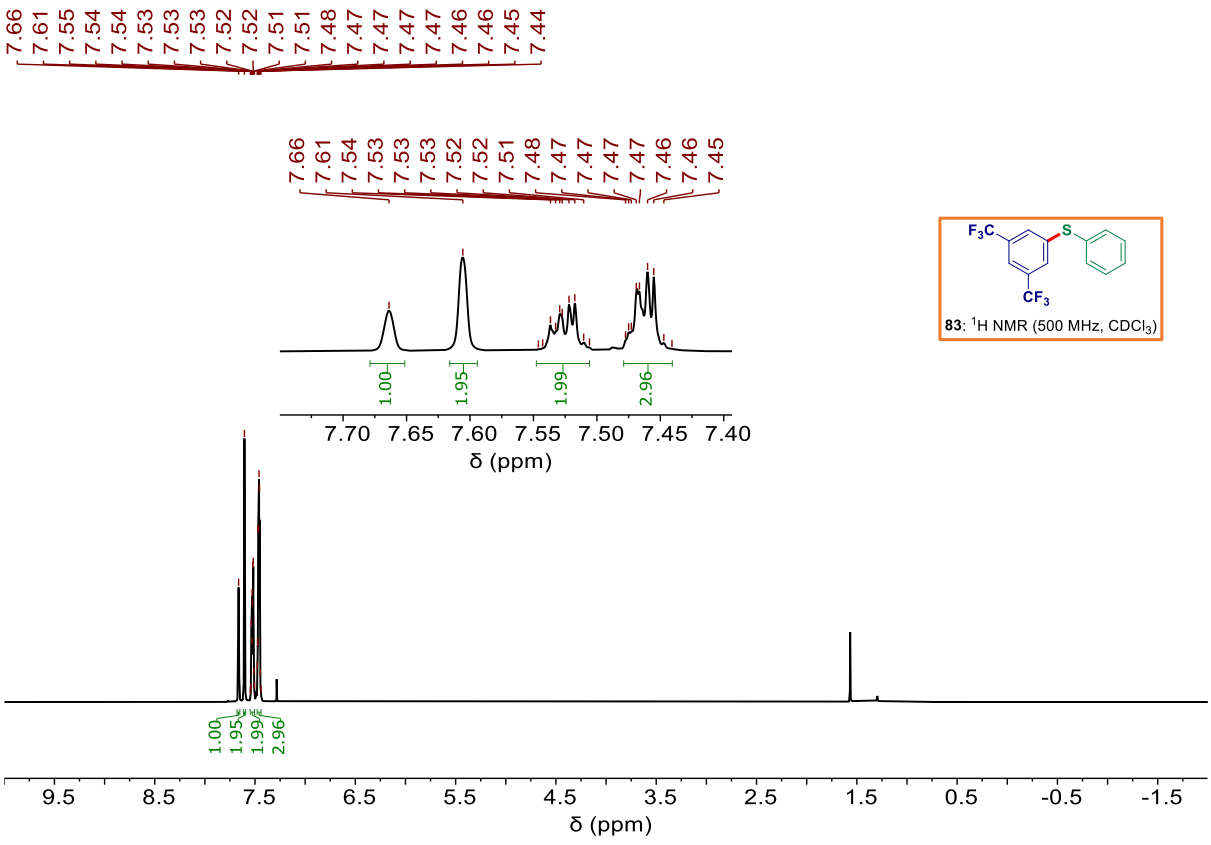

9.93 7.77 7.76 7.76 7.75 7.72 7.72 7.71 7.71 7.71 7.70 7.69 7.69 7.53 7.53 7.52 7.52 7.51 7.50 7.49 7.46 7.46 7.45 7.44 7.43 7.42 7.42 7.41 7.41 7.38 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32
7.76 7.76 7.75 7.72 7.71 7.71 7.69 7.69 7.52 7.51 7.50 7.46 7.44 7.43 7.42 7.42 7.41 7.41 7.38 7.36 7.36 7.35 7.34 7.34 7.33
2.06 1.03 3.08 3.09
7.80 7.70 7.60 7.50 7.40 7.30 7.20
δ (ppm)
OHC
S
81: ^{1}H NMR (400 MHz, $CDCl_3$)
1.00 2.06 1.03 3.08 3.09
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)

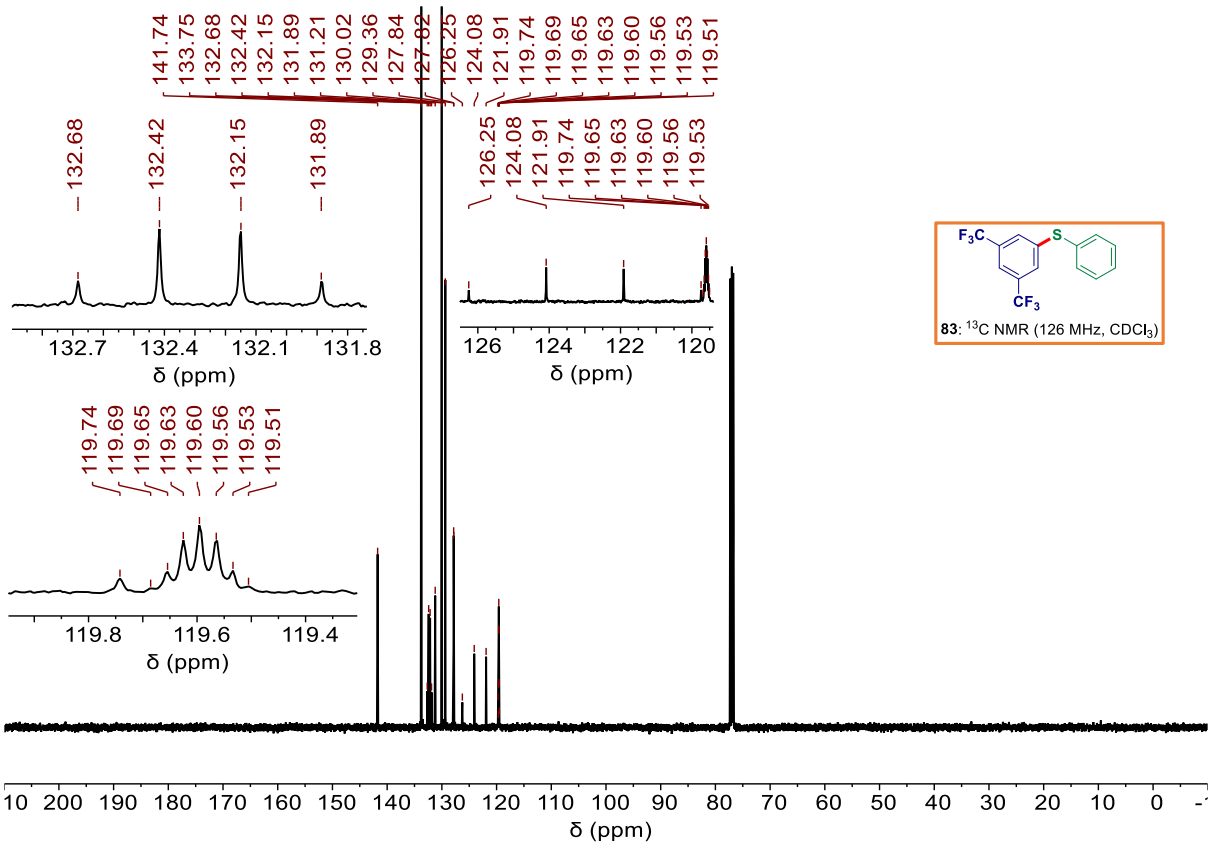

191.74
138.88 137.25 135.42 133.75 132.59 130.71 129.80 129.68 128.26 127.72
138.88 137.25 135.42 133.75 132.59 130.71 129.80 129.68 128.26 127.72
139 137 135 133 131 129 127
δ (ppm)
OHC
S
81: ^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.41
7.40
7.36
7.34
7.33
7.32
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.19
6.96
6.96
6.93
6.91
6.91
2.36
3.14
2.95
2.00
3.00
δ (ppm)
82: 1H NMR (400 MHz, CDCl3)

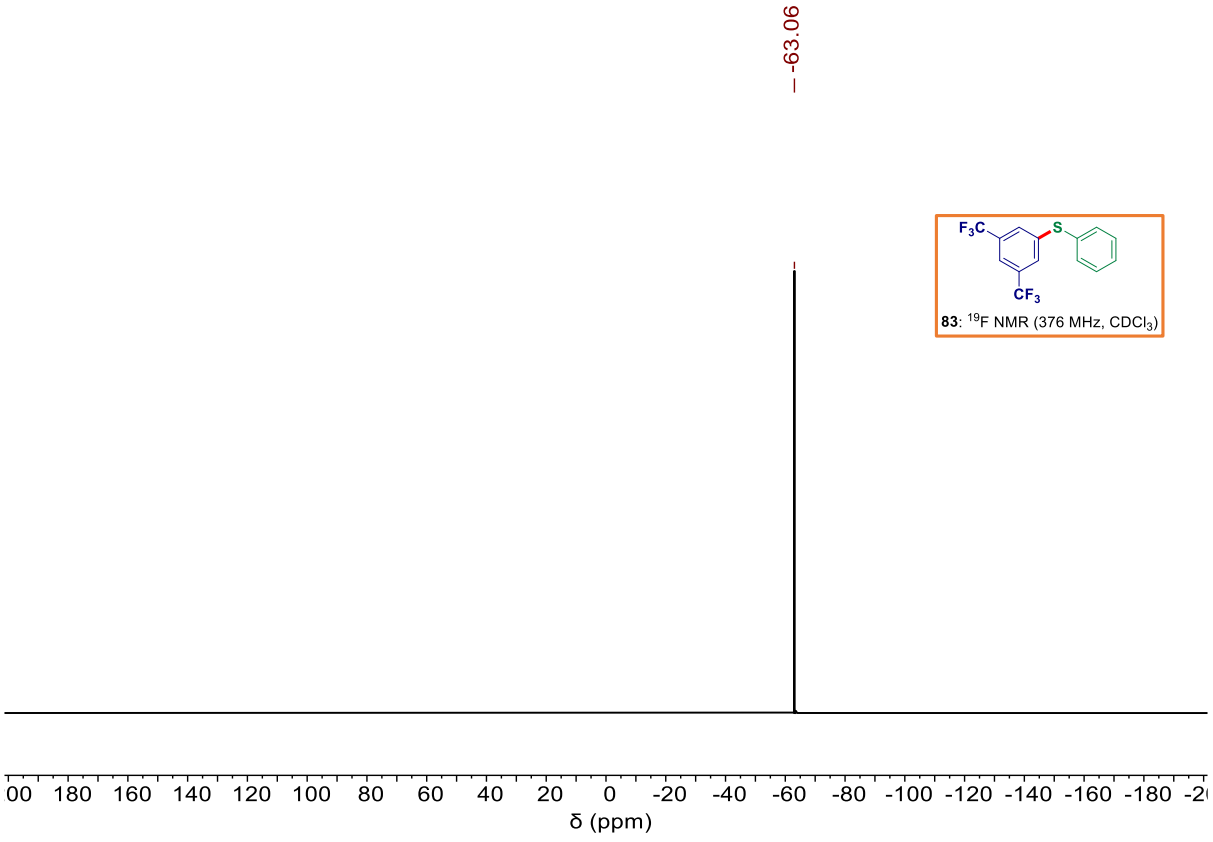

162.99
160.53
141.19
141.11
135.68
134.70
131.72
131.03
129.62
129.19
126.70
125.69
118.15
117.97
116.94
116.72
21.25
δ (ppm)
82: 13C NMR (101 MHz, CDCl3)


-108.90
F
S
82: 19F NMR (376 MHz, CDCl3)
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
δ (ppm)

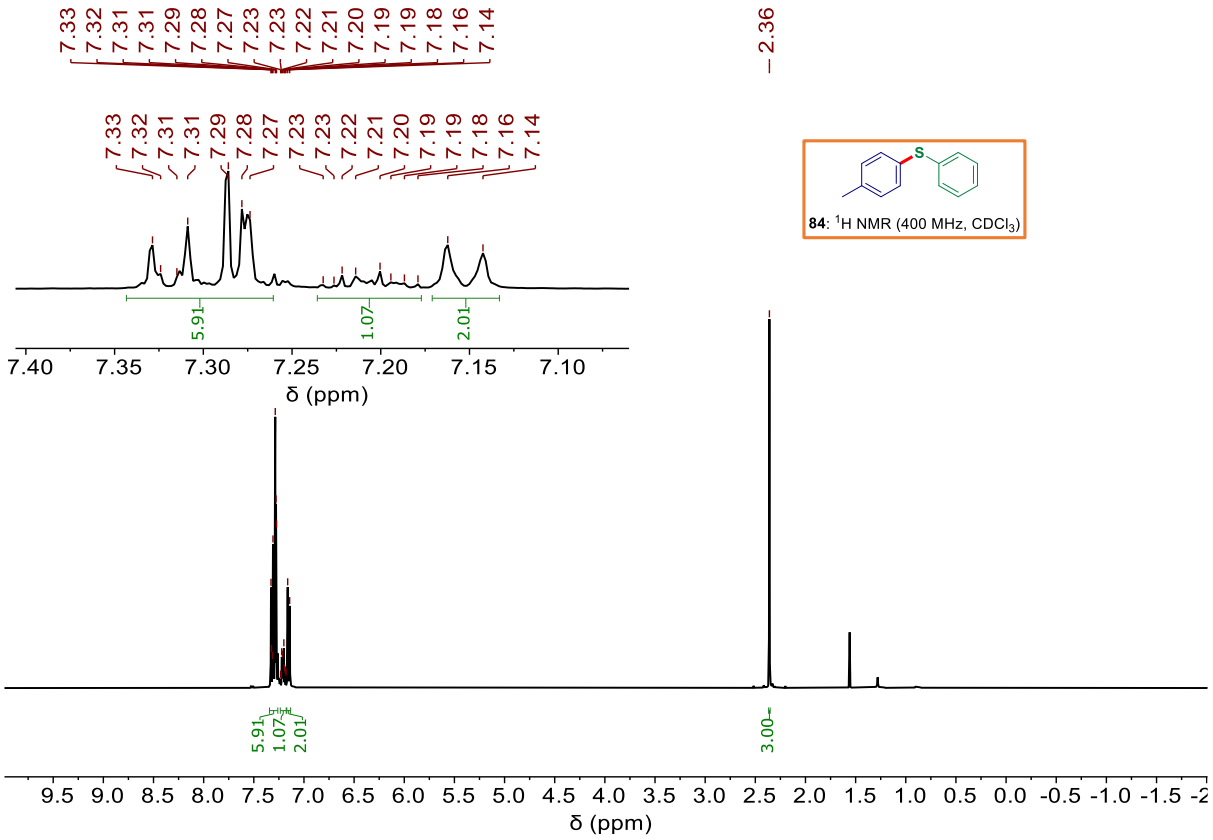

7.66
7.61
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.51
7.51
7.48
7.47
7.47
7.47
7.47
7.46
7.46
7.45
7.44
F3C
S
CF3
83: 1H NMR (500 MHz, CDCl3)
1.00
1.95
1.99
2.96
7.70
7.65
7.60
7.55
7.50
7.45
7.40
δ (ppm)
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
δ (ppm)

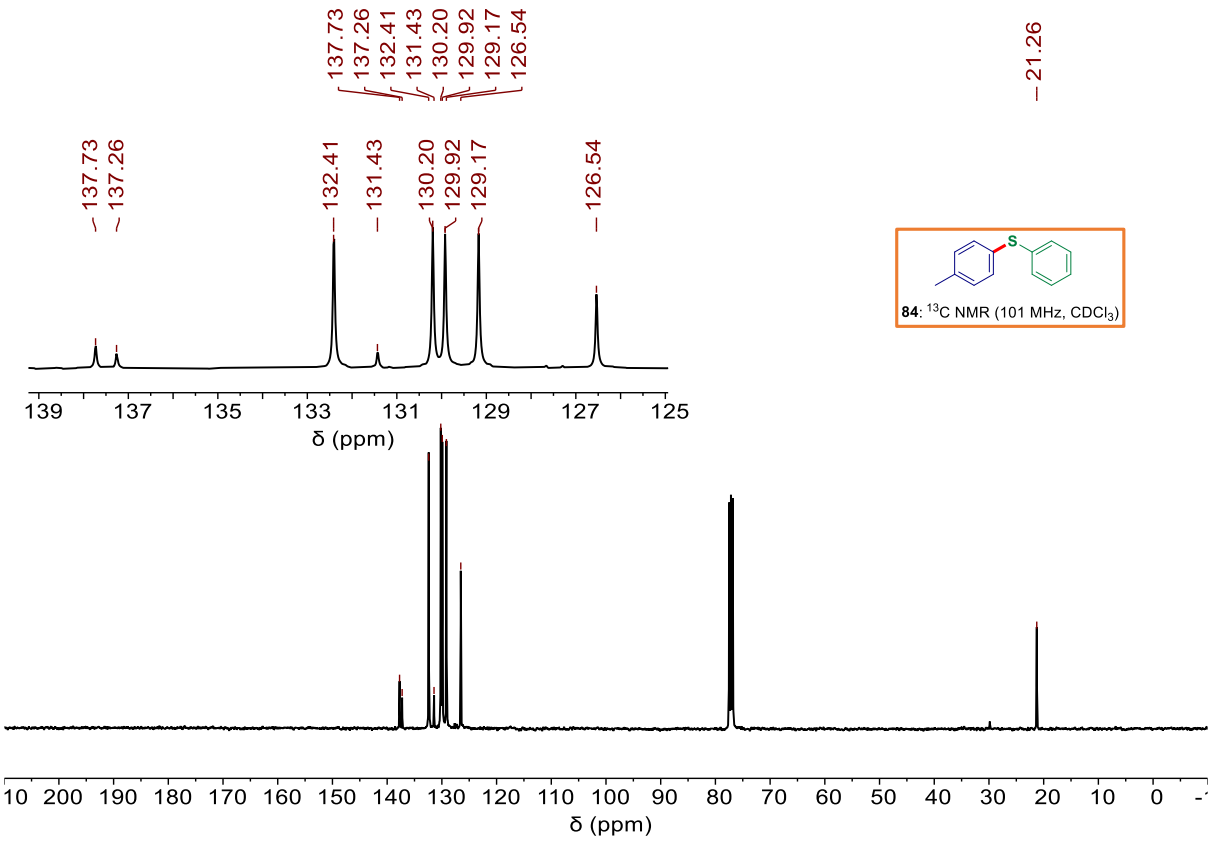


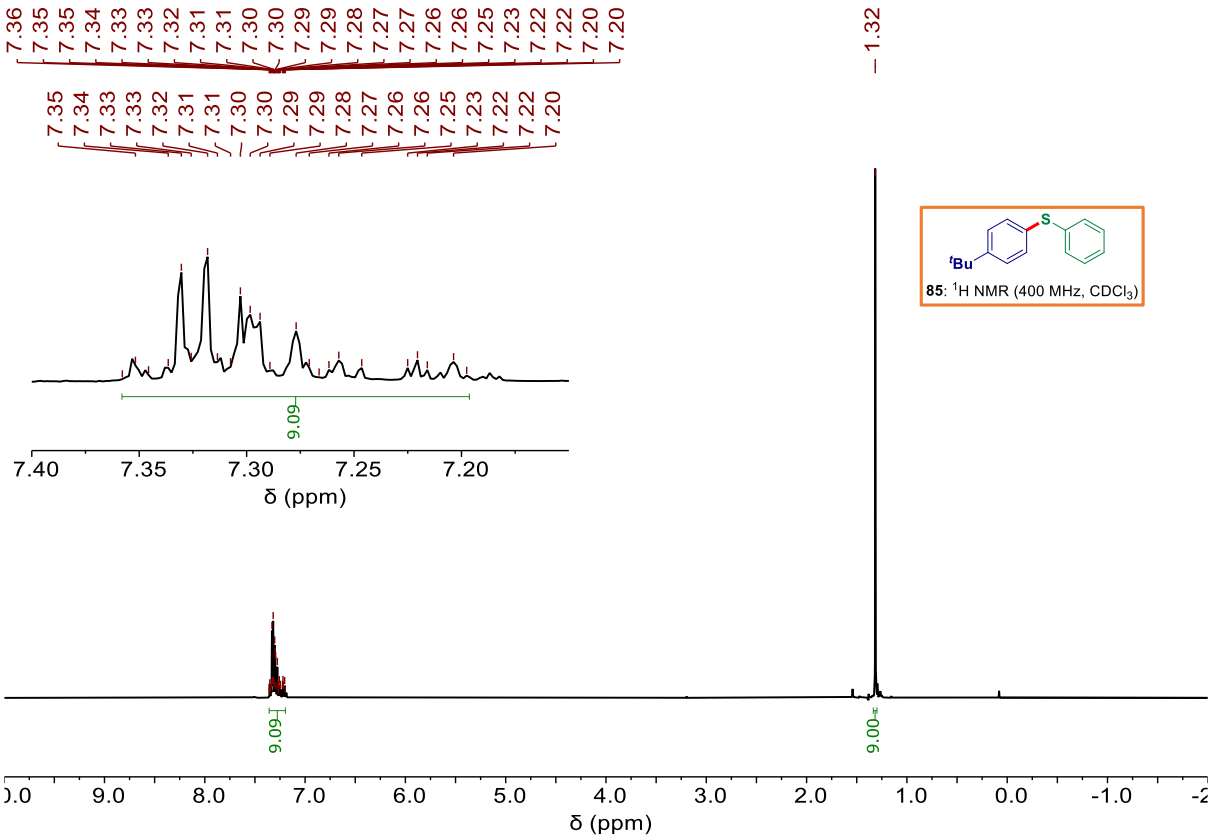
83: ^{13}C NMR (126 MHz, $CDCl_3$)

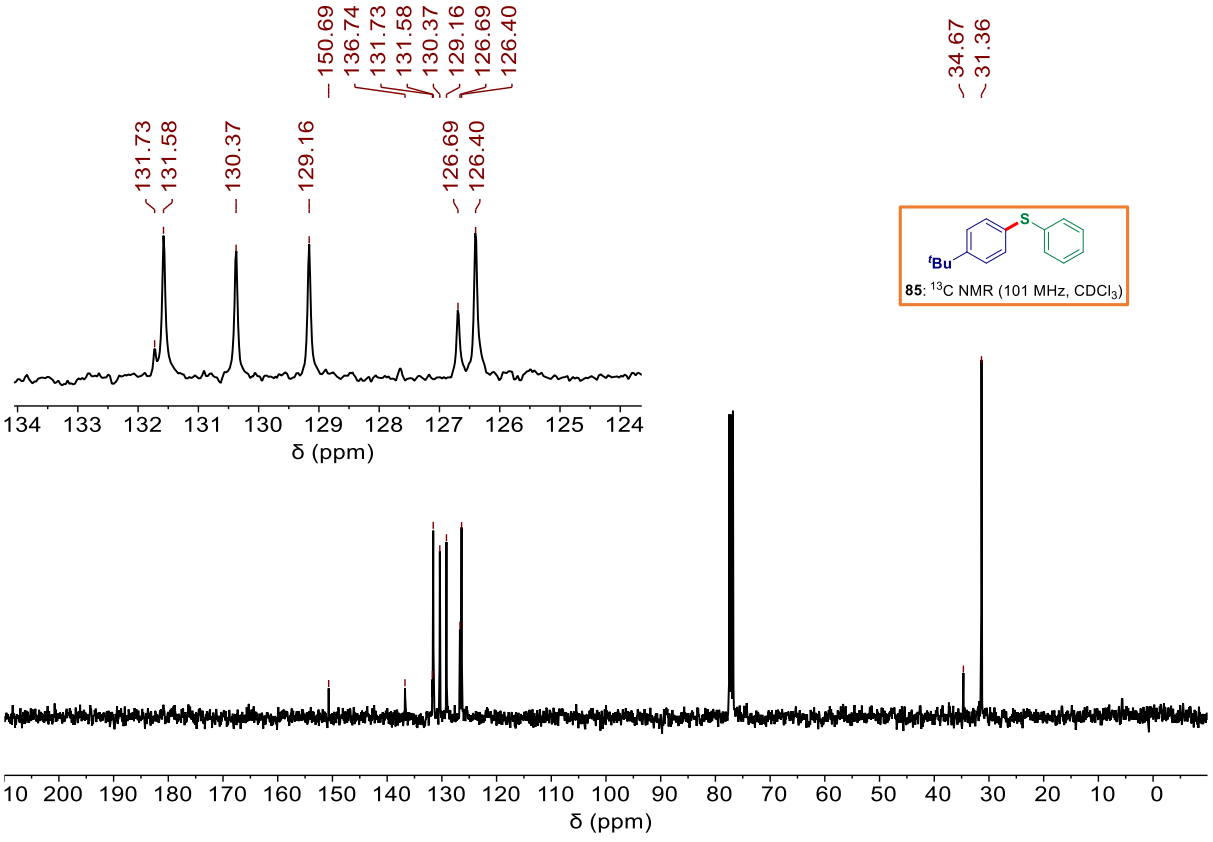


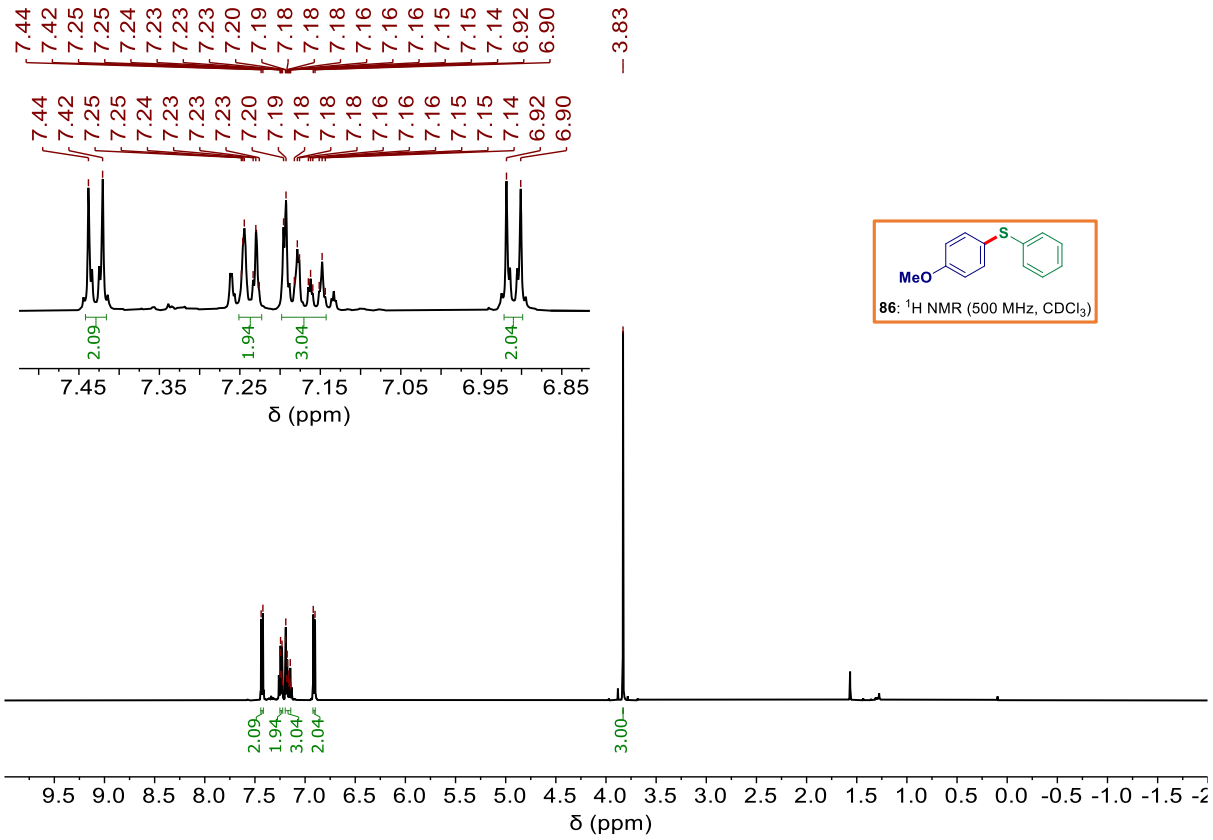
83: ^{19}F NMR (376 MHz, $CDCl_3$)

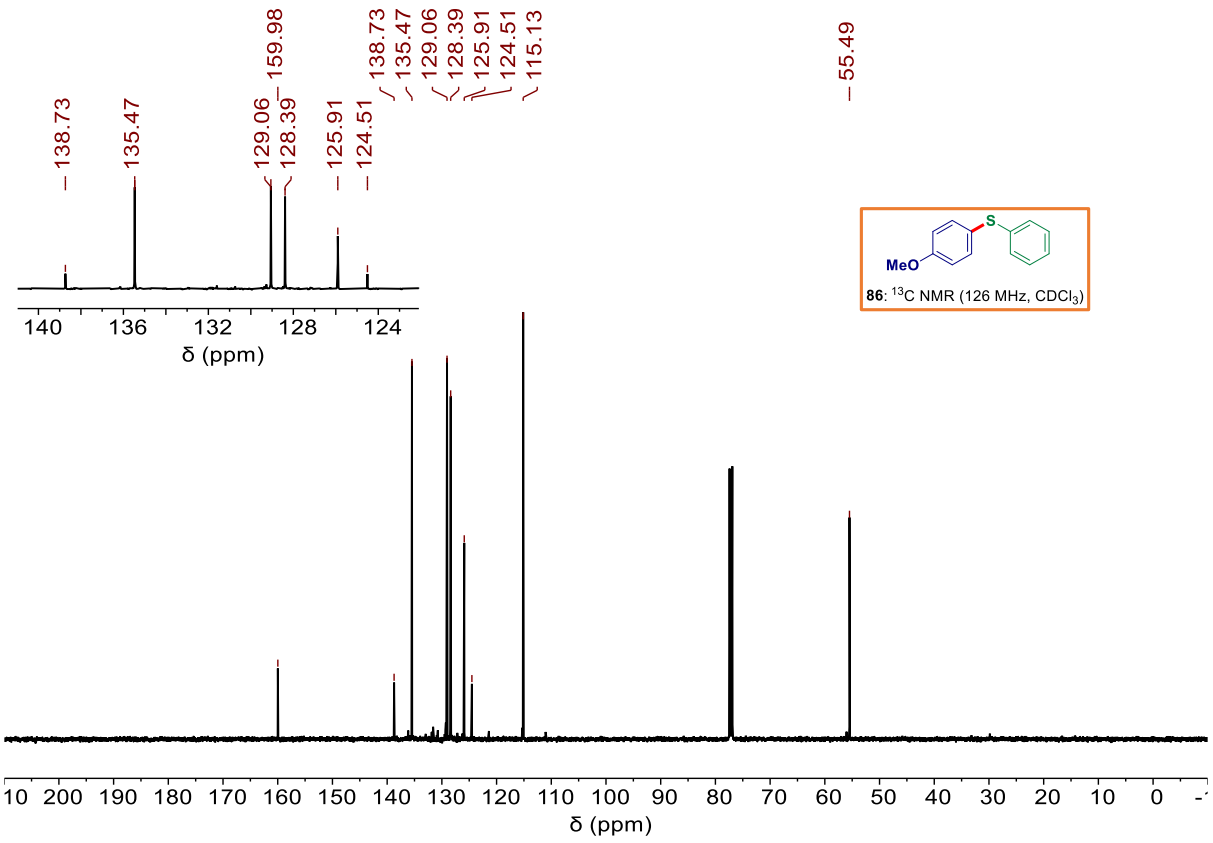

7.33
7.32
7.31
7.31
7.29
7.28
7.27
7.23
7.23
7.22
7.21
7.20
7.19
7.19
7.18
7.16
7.14
2.36
5.91
1.07
2.01
3.00
7.40 7.35 7.30 7.25 7.20 7.15 7.10
δ (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
δ (ppm)
84: 1H NMR (400 MHz, CDCl3)

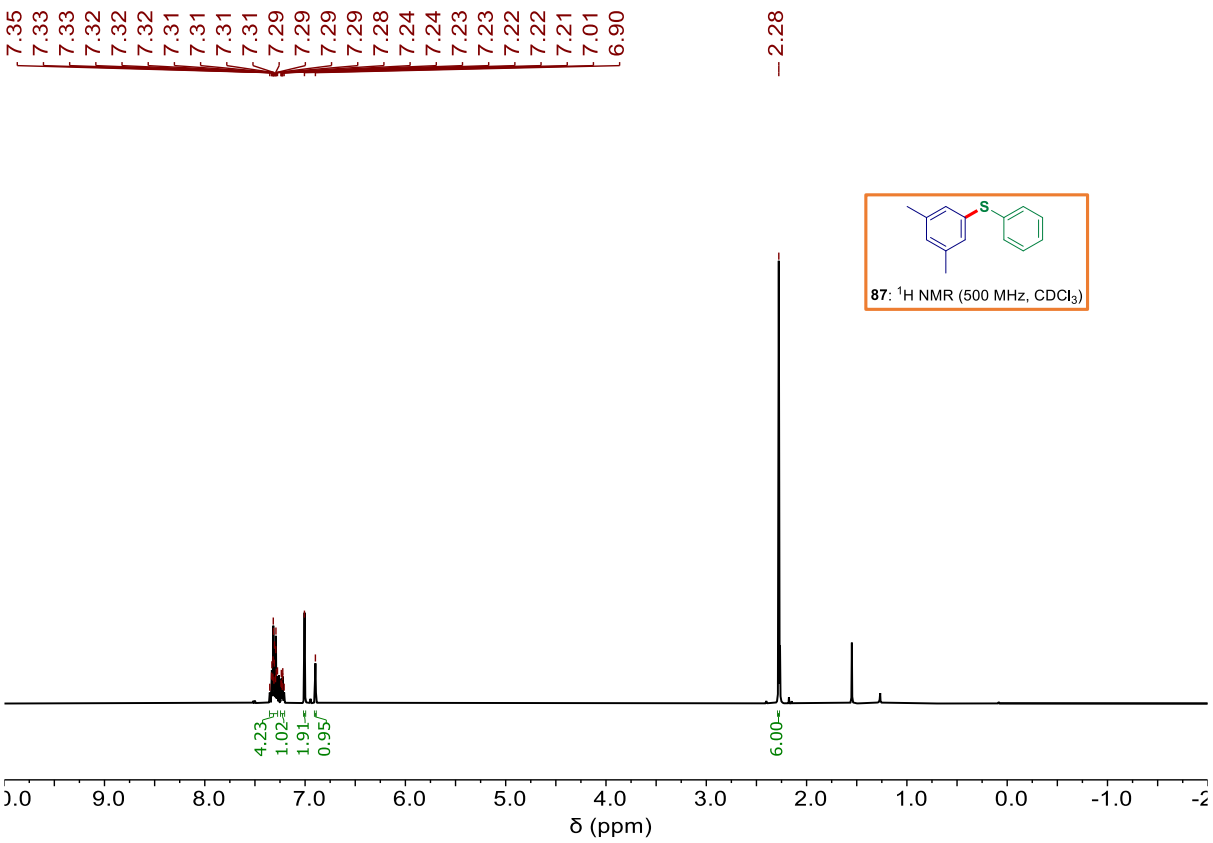

137.73
137.26
132.41
131.43
130.20
129.92
129.17
126.54
21.26
139 137 135 133 131 129 127 125
δ (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)
84: 13C NMR (101 MHz, CDCl3)

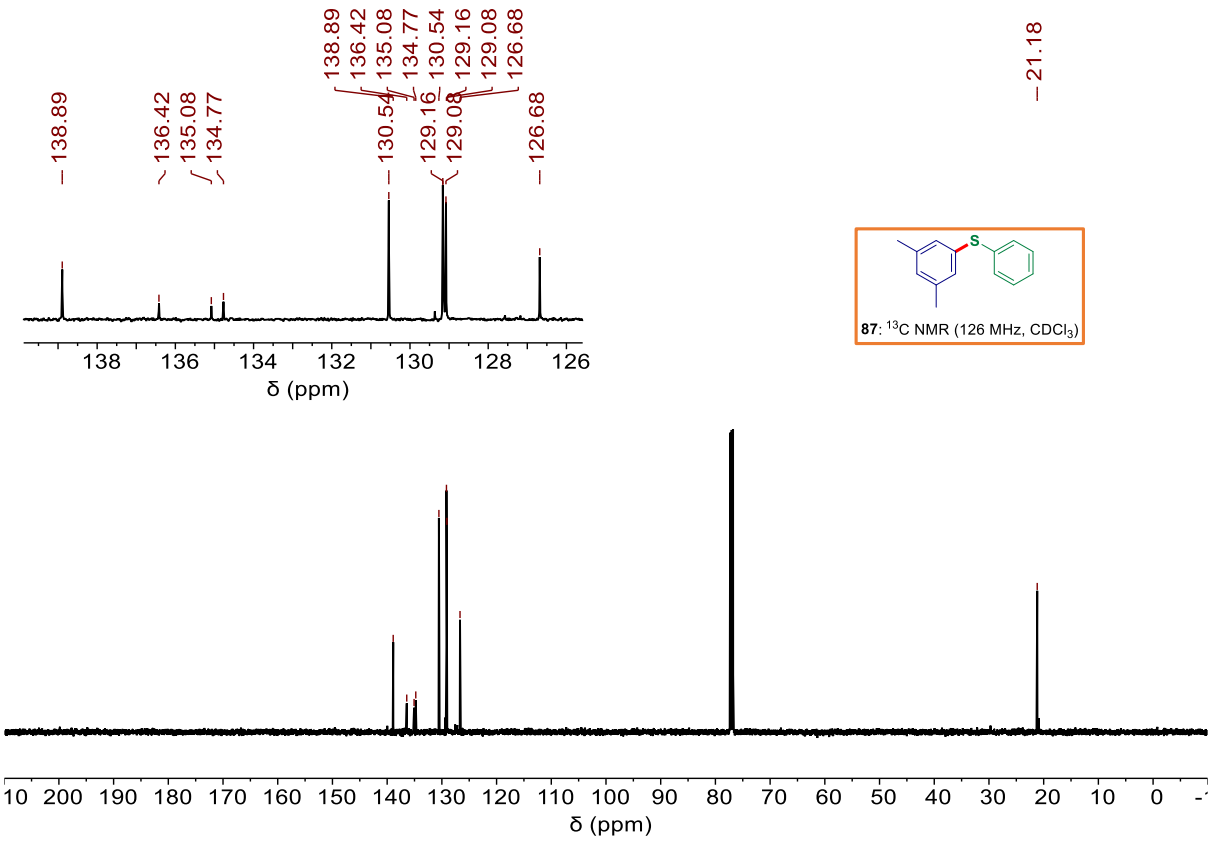

7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.23 7.22 7.22 7.20 7.20
1.32
tBu
S
85: 1H NMR (400 MHz, CDCl3)
9.09
9.09
9.00
δ (ppm)

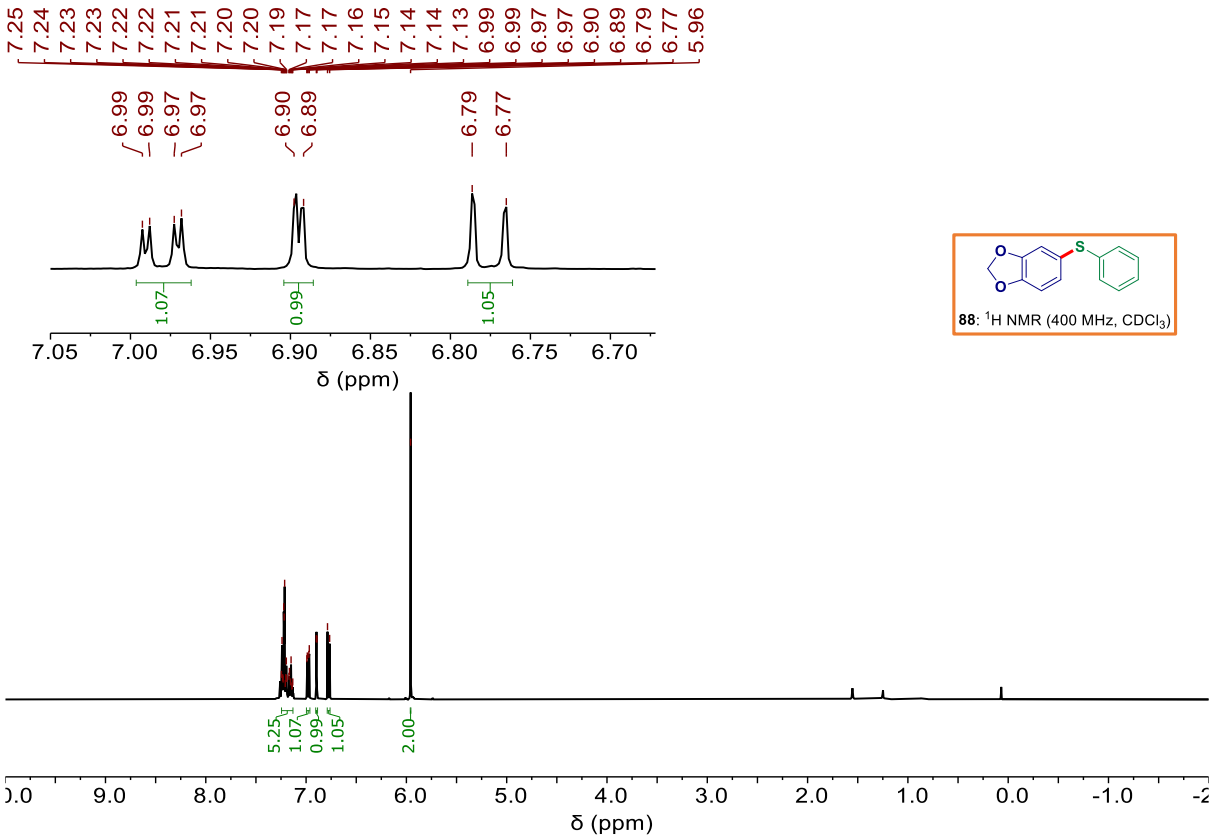

150.69 136.74 131.73 131.58 130.37 129.16 126.69 126.40
34.67 31.36
131.73 131.58 130.37 129.16 126.69 126.40
tBu
S
85: 13C NMR (101 MHz, CDCl3)
δ (ppm)


7.44 7.42 7.25 7.25 7.24 7.23 7.23 7.23 7.20 7.19 7.18 7.18 7.18 7.16 7.16 7.16 7.15 7.15 7.14 6.92 6.90
3.83
2.09 1.94 3.04 2.04
7.45 7.35 7.25 7.15 7.05 6.95 6.85
δ (ppm)
MeO
S
86: 1H NMR (500 MHz, CDCl3)
2.09 1.94 3.04 2.04
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
δ (ppm)

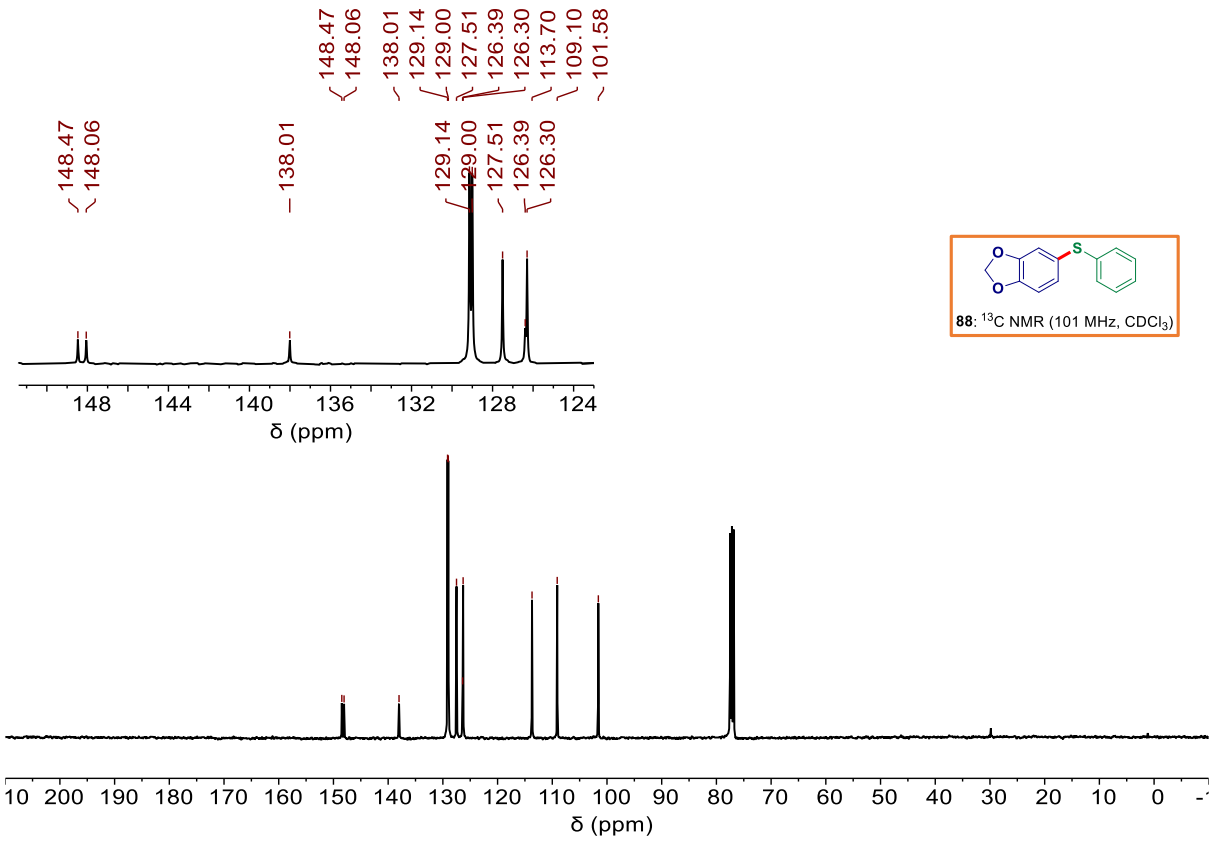

138.73 135.47 129.06 128.39 125.91 124.51 159.98 138.73 135.47 129.06 128.39 125.91 124.51 115.13
55.49
140 136 132 128 124
δ (ppm)
MeO
S
86: 13C NMR (126 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


7.35
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.31
7.29
7.29
7.29
7.29
7.28
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.01
6.90
2.28
87: 1H NMR (500 MHz, CDCl3)
4.23
1.02
1.91
0.95
6.00
δ (ppm)

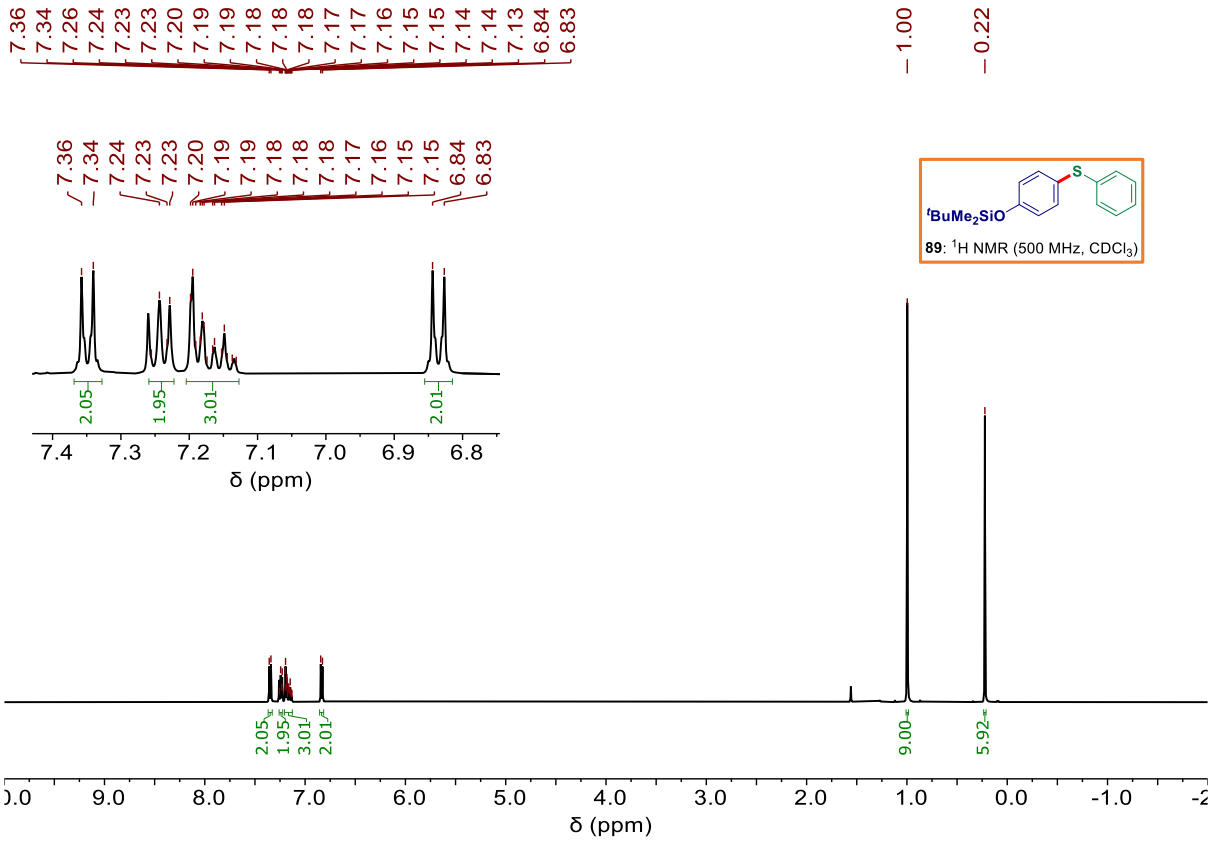

138.89
136.42
135.08
134.77
130.54
129.16
129.08
126.68
21.18
87: 13C NMR (126 MHz, CDCl3)
δ (ppm)

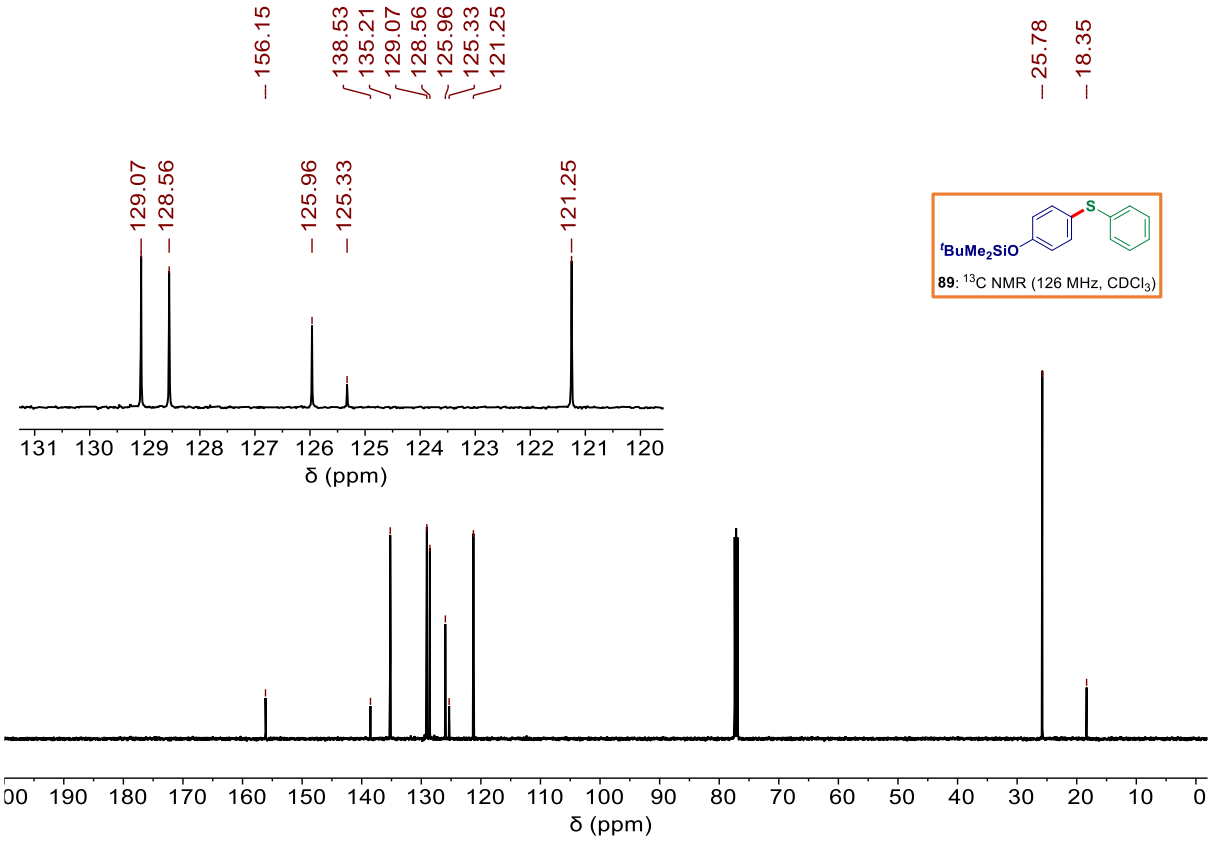


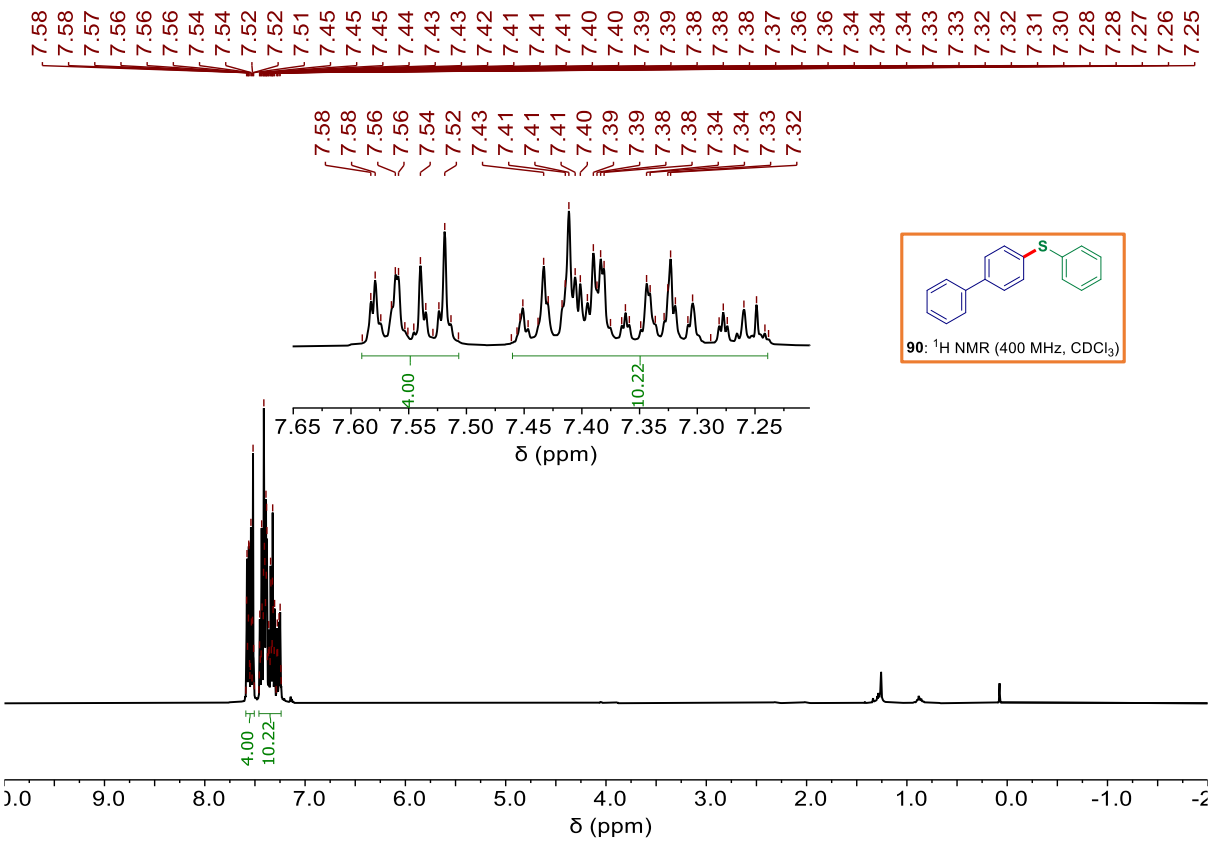
88: ^{1}H NMR (400 MHz, $CDCl_3$)

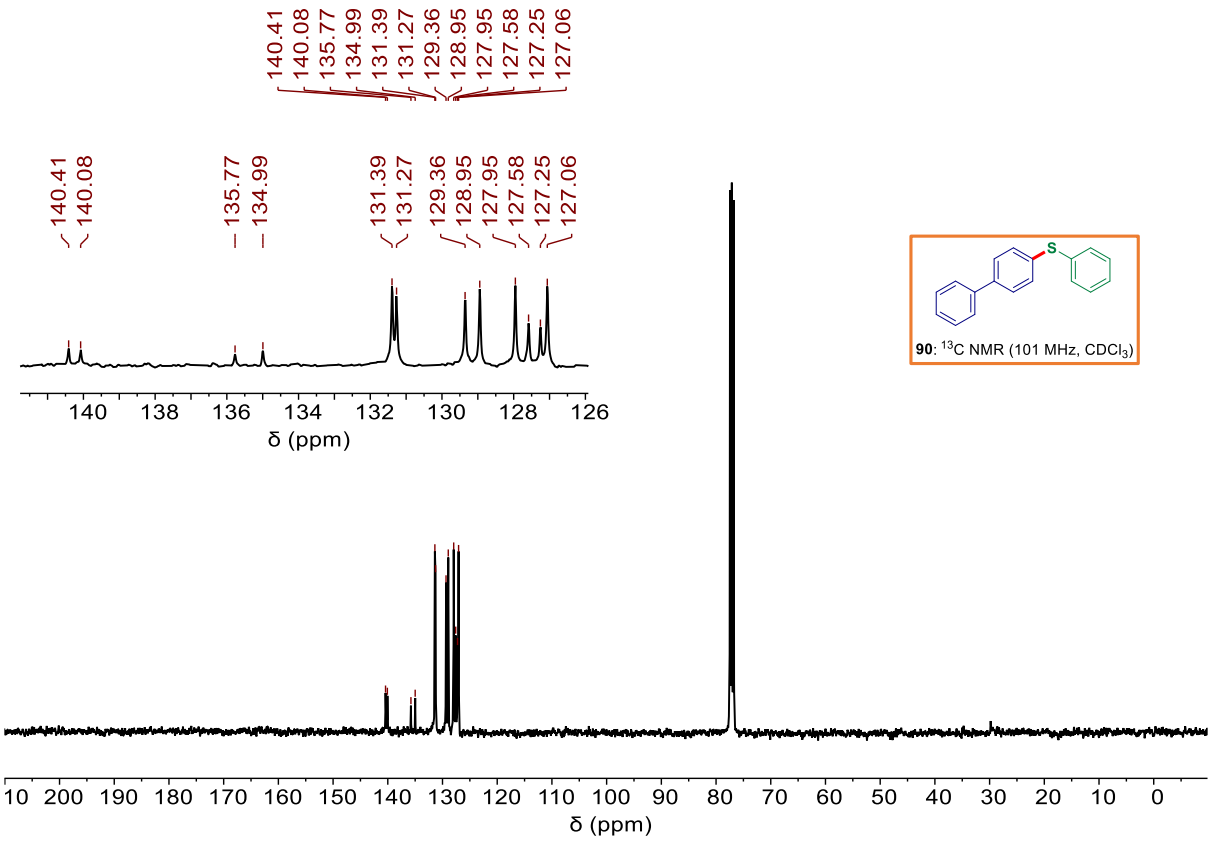


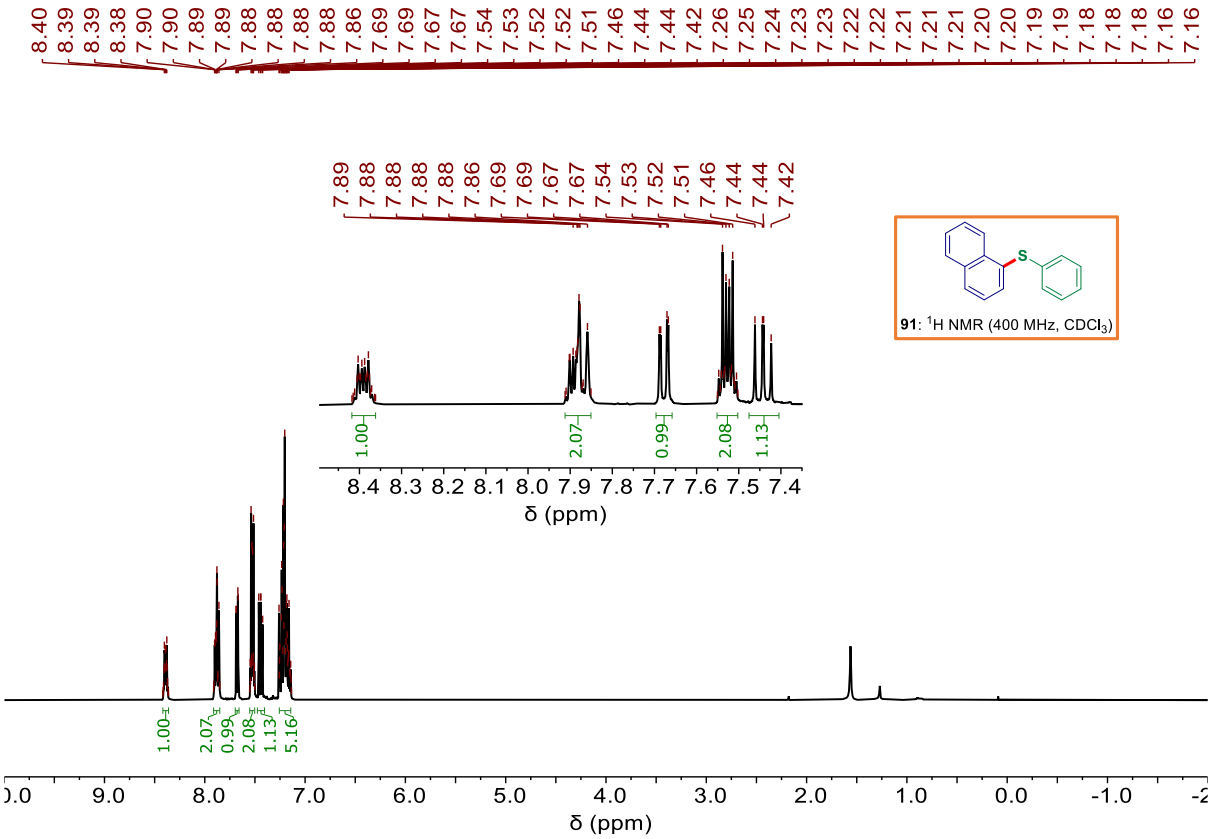
88: ^{13}C NMR (101 MHz, $CDCl_3$)

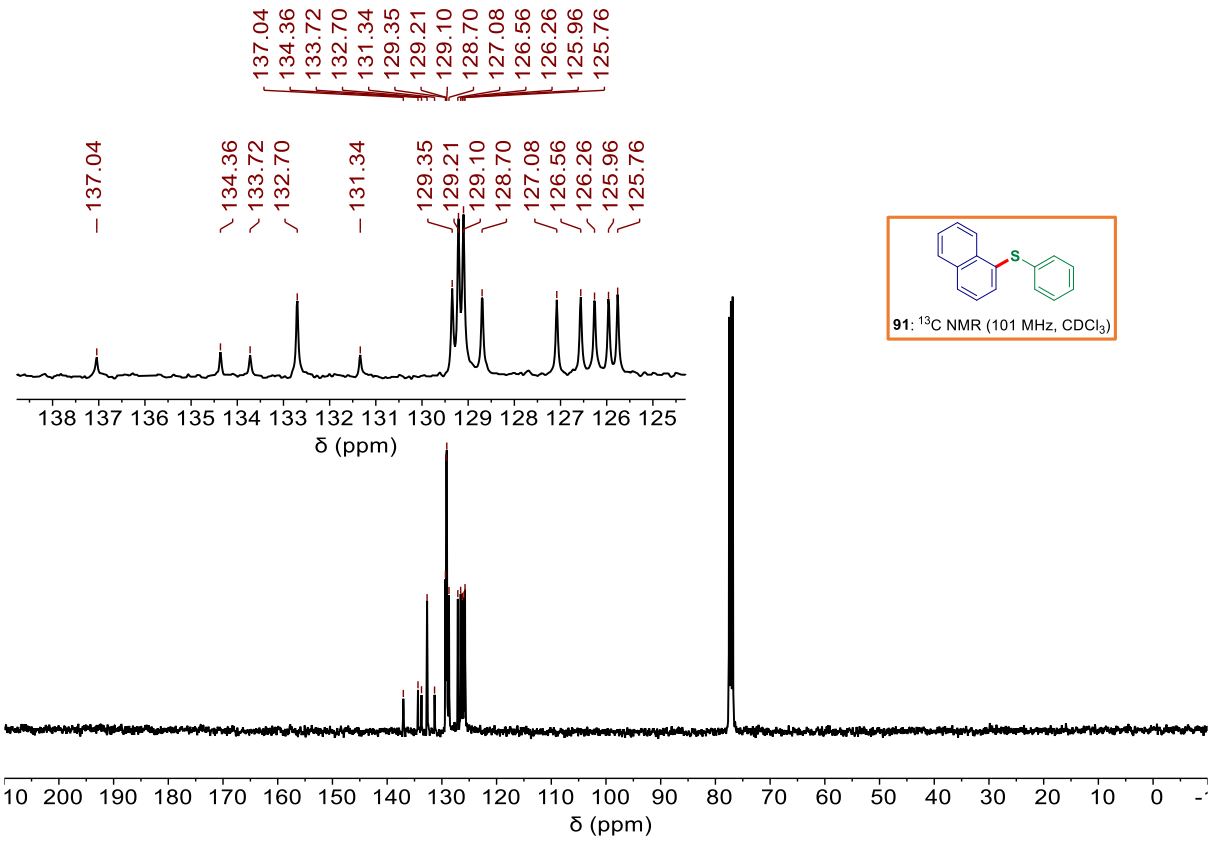

7.36
7.34
7.26
7.24
7.23
7.23
7.20
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.13
6.84
6.83
1.00
0.22
tBuMe2SiO
S
89: 1H NMR (500 MHz, CDCl3)
2.05
1.95
3.01
2.01
9.00
5.92
δ (ppm)

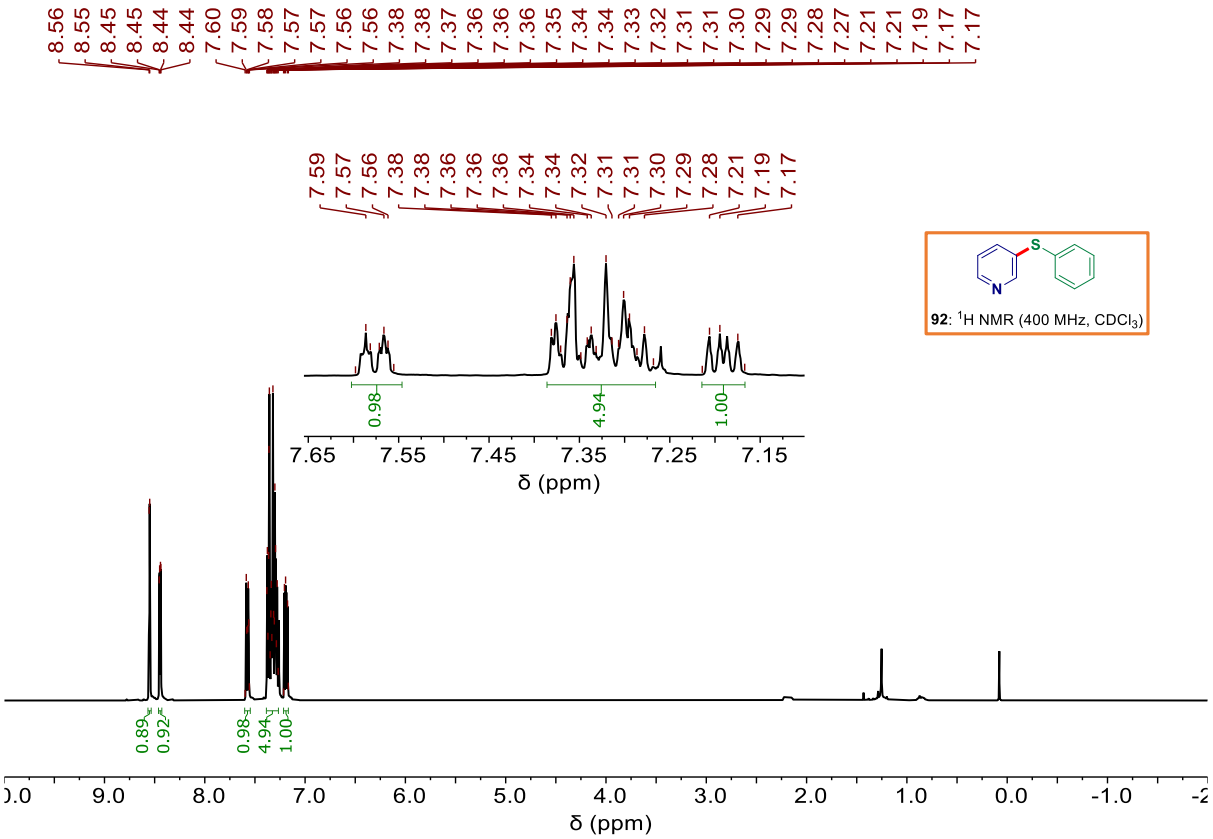

156.15
138.53
135.21
129.07
128.56
125.96
125.33
121.25
25.78
18.35
tBuMe2SiO
S
89: 13C NMR (126 MHz, CDCl3)
δ (ppm)

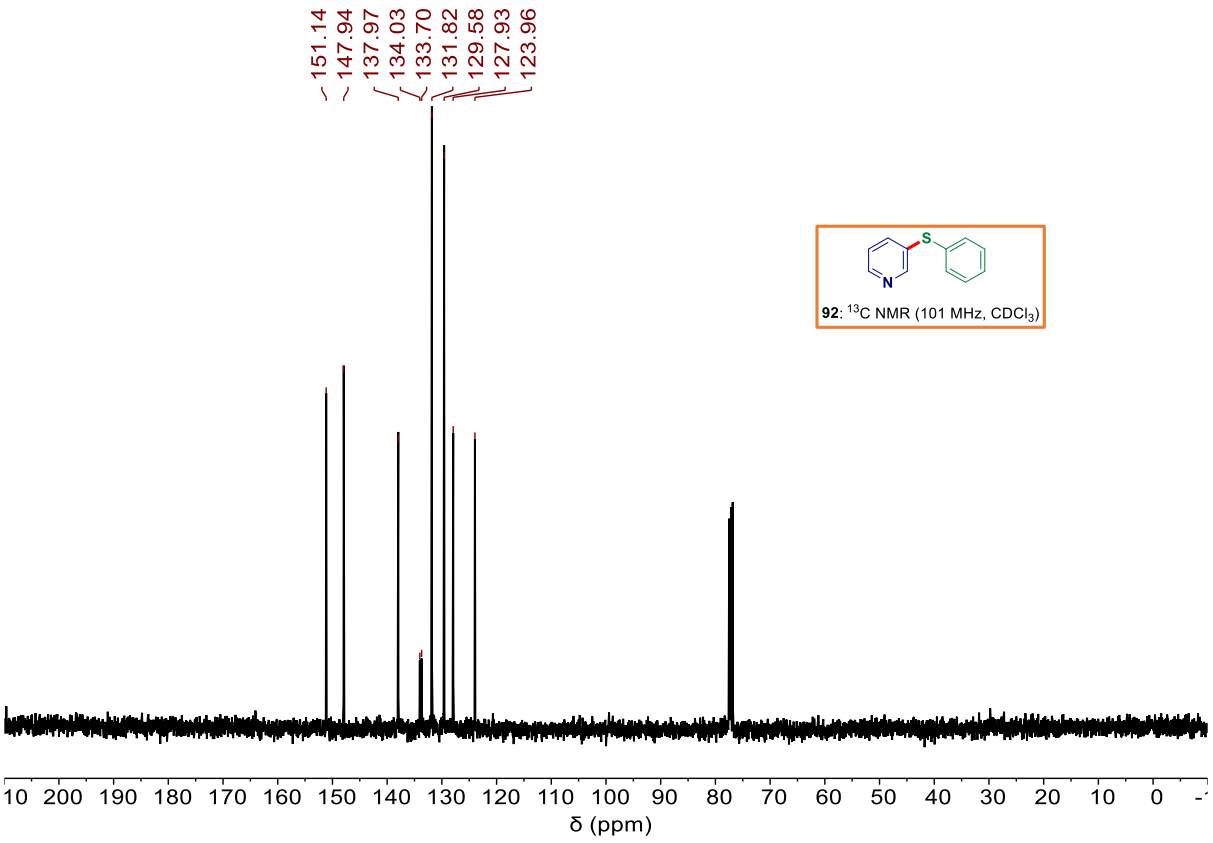

7.58 7.58 7.57 7.56 7.56 7.56 7.54 7.54 7.52 7.52 7.51 7.45 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.28 7.28 7.27 7.26 7.25
7.58 7.58 7.56 7.56 7.54 7.52 7.43 7.41 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.34 7.34 7.33 7.32
4.00
10.22
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
δ (ppm)
90: 1H NMR (400 MHz, CDCl3)
4.00
10.22
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

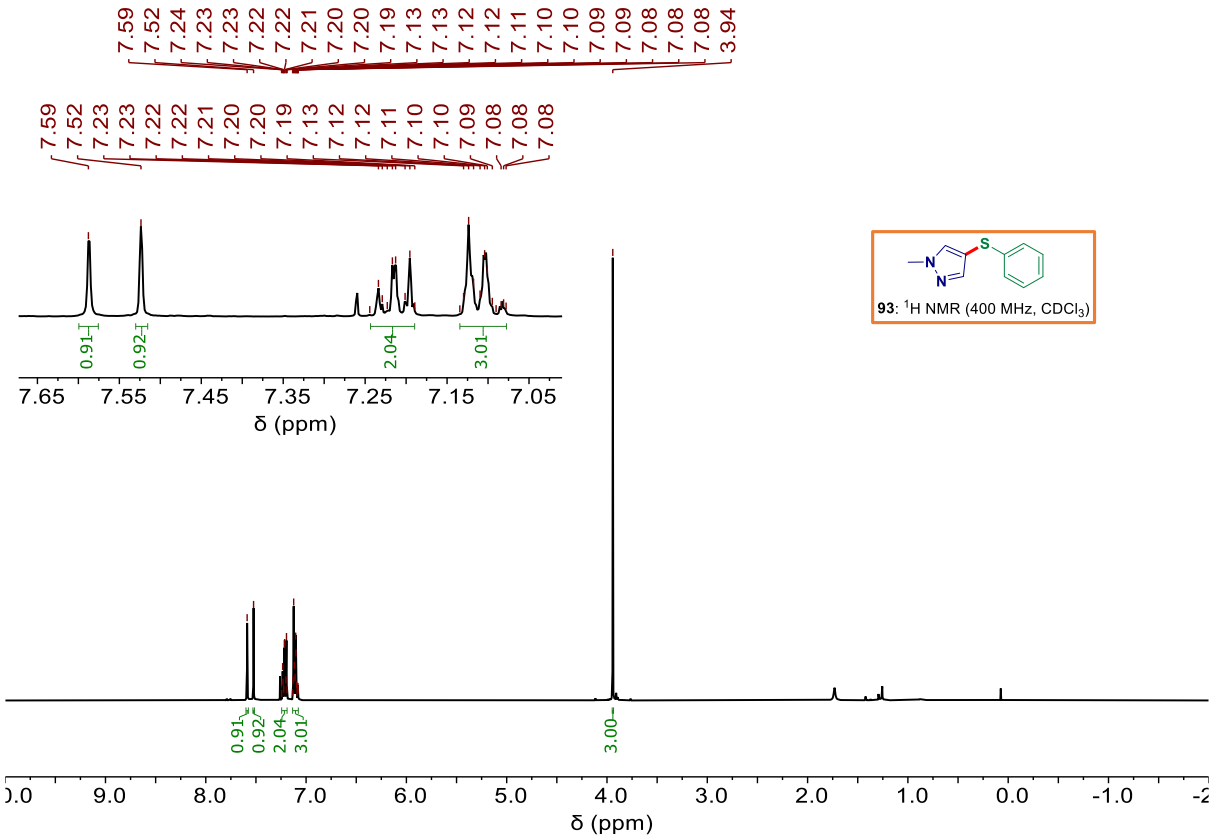

140.41 140.08 135.77 134.99 131.39 131.27 129.36 128.95 127.95 127.58 127.25 127.06
140.41 140.08 135.77 134.99 131.39 131.27 129.36 128.95 127.95 127.58 127.25 127.06
140 138 136 134 132 130 128 126
δ (ppm)
90: 13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

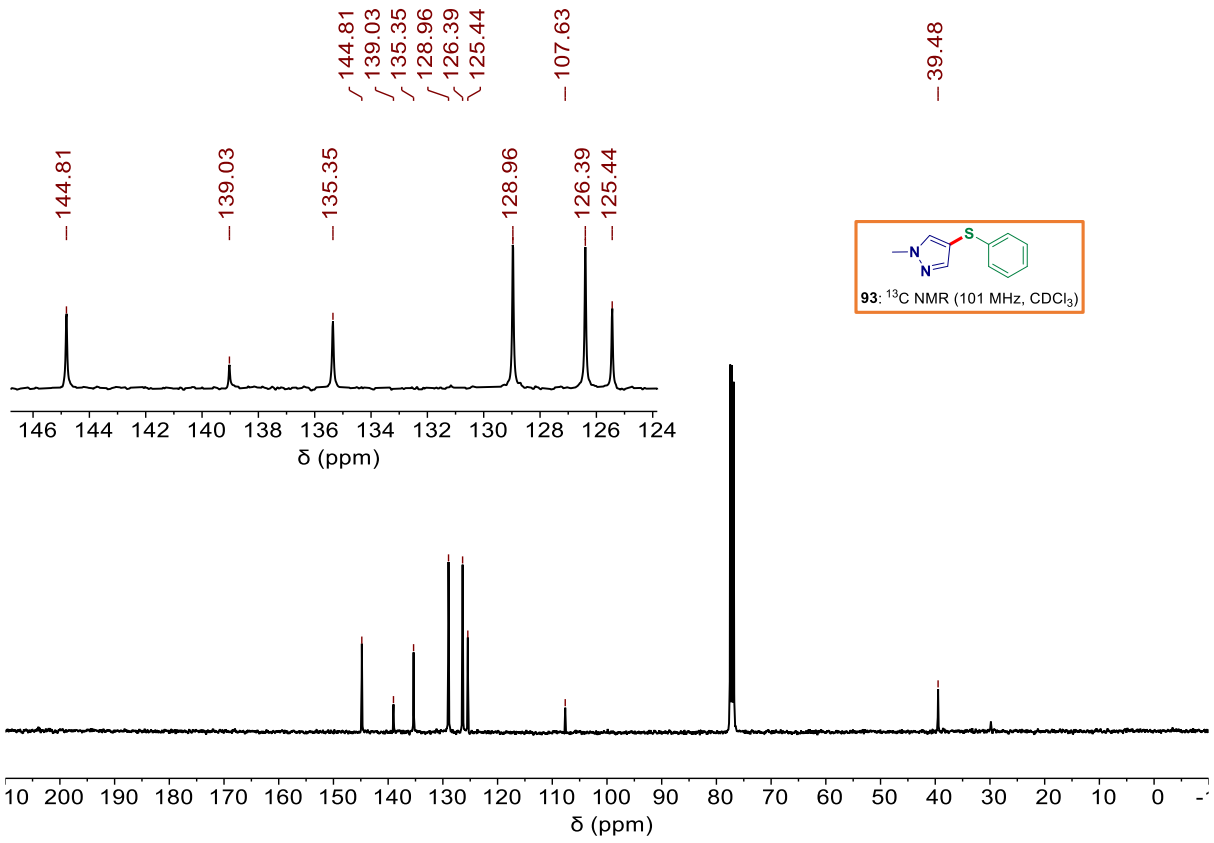

8.40 8.39 8.39 8.38 7.90 7.90 7.89 7.89 7.88 7.88 7.88 7.88 7.86 7.69 7.69 7.67 7.67 7.54 7.53 7.52 7.52 7.51 7.46 7.44 7.44 7.42 7.26 7.25 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.18 7.16 7.16
7.89 7.88 7.88 7.88 7.88 7.86 7.69 7.69 7.67 7.67 7.54 7.53 7.52 7.51 7.46 7.44 7.44 7.42
1.00 2.07 0.99 2.08 1.13
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
δ (ppm)
91: 1H NMR (400 MHz, CDCl3)
1.00 2.07 0.99 2.08 1.13 5.16
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

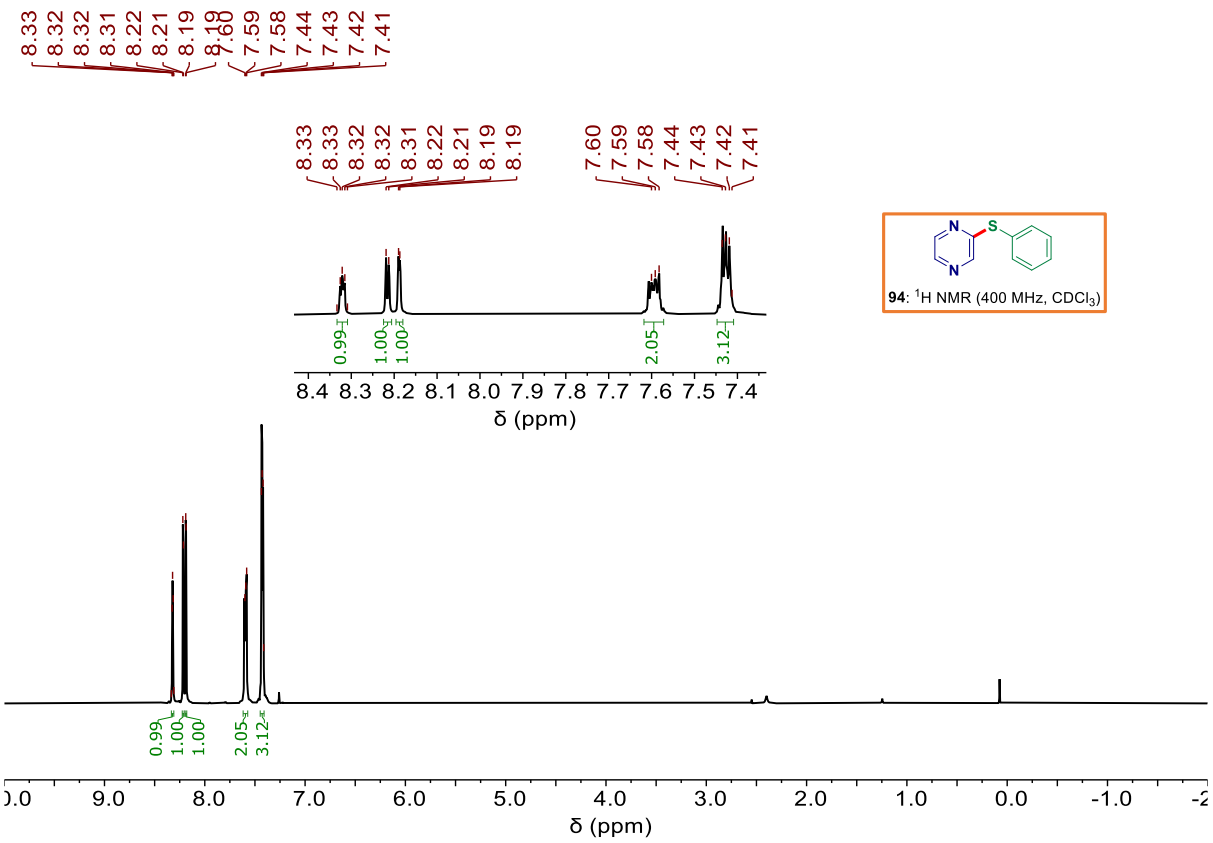

137.04 134.36 133.72 132.70 131.34 129.35 129.21 129.10 128.70 127.08 126.56 126.26 125.96 125.76
138 137 136 135 134 133 132 131 130 129 128 127 126 125
δ (ppm)
91: 13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

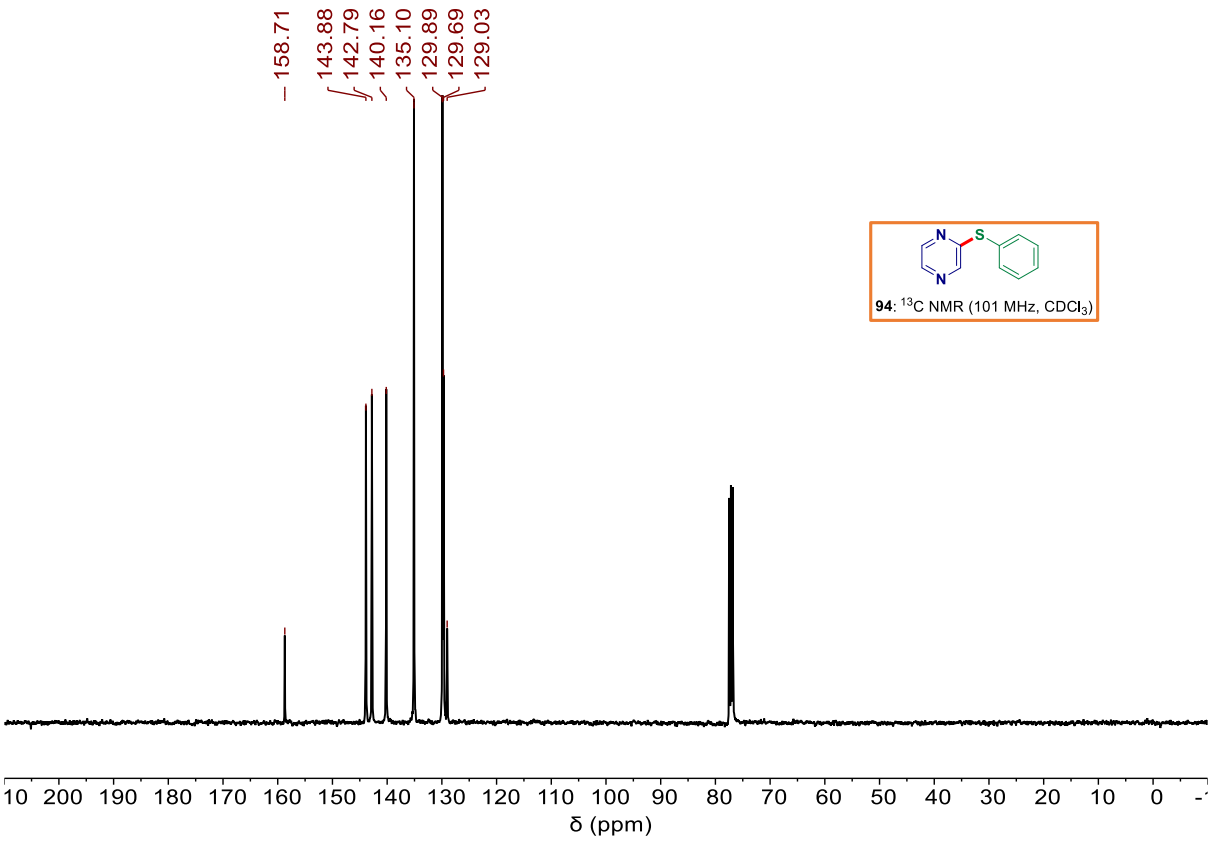

8.56 8.55 8.45 8.45 8.44 8.44 7.60 7.59 7.58 7.57 7.57 7.56 7.56 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.21 7.21 7.19 7.17 7.17
7.59 7.57 7.56 7.38 7.38 7.36 7.36 7.36 7.34 7.34 7.32 7.31 7.31 7.30 7.29 7.28 7.21 7.19 7.17
0.98 4.94 1.00
7.65 7.55 7.45 7.35 7.25 7.15
δ (ppm)
92: 1H NMR (400 MHz, CDCl3)
0.89 0.92 0.98 4.94 1.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

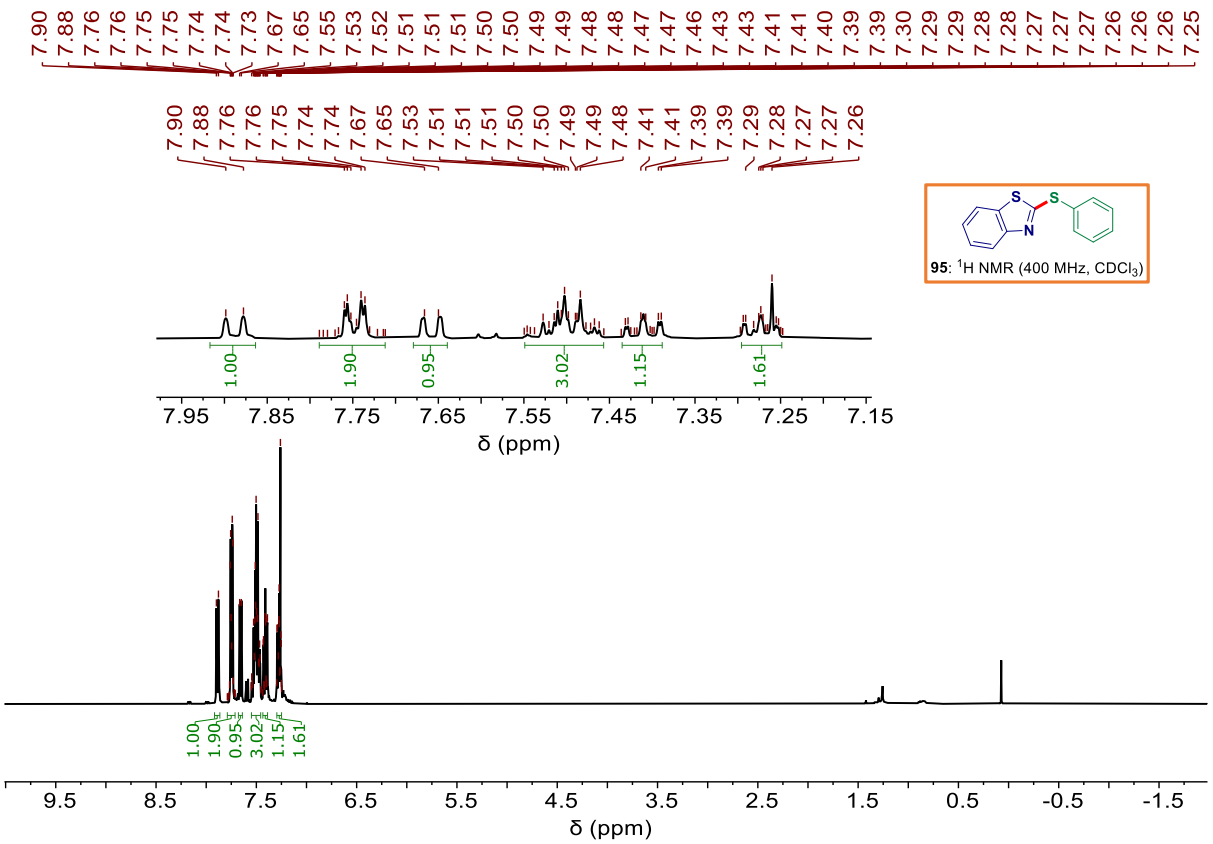

151.14 147.94 137.97 134.03 133.70 131.82 129.58 127.93 123.96
92: 13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

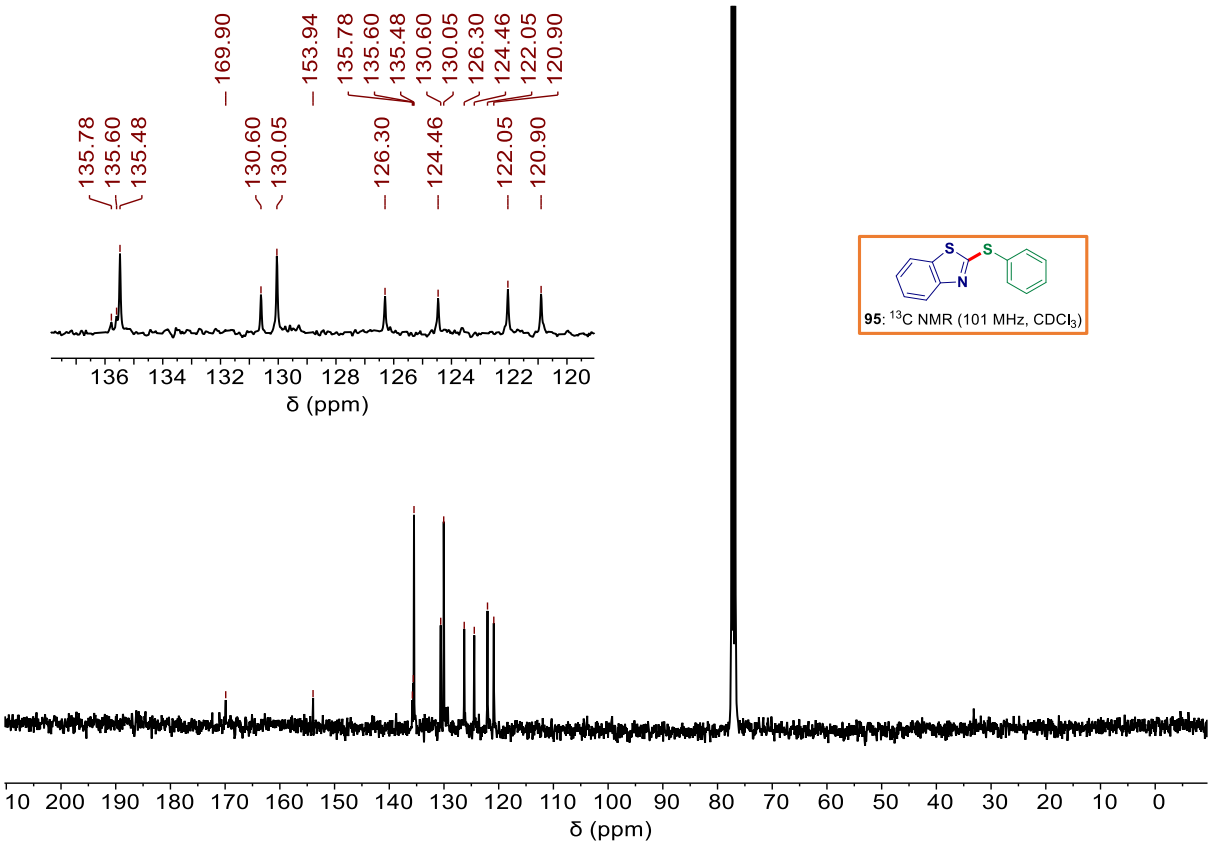

7.59 7.52 7.24 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.13 7.13 7.12 7.12 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.08 3.94
7.59 7.52 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.13 7.12 7.12 7.11 7.10 7.10 7.09 7.08 7.08 7.08
0.91 0.92 2.04 3.01
7.65 7.55 7.45 7.35 7.25 7.15 7.05
δ (ppm)
93: 1H NMR (400 MHz, CDCl3)
0.91 0.92 2.04 3.01 3.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)

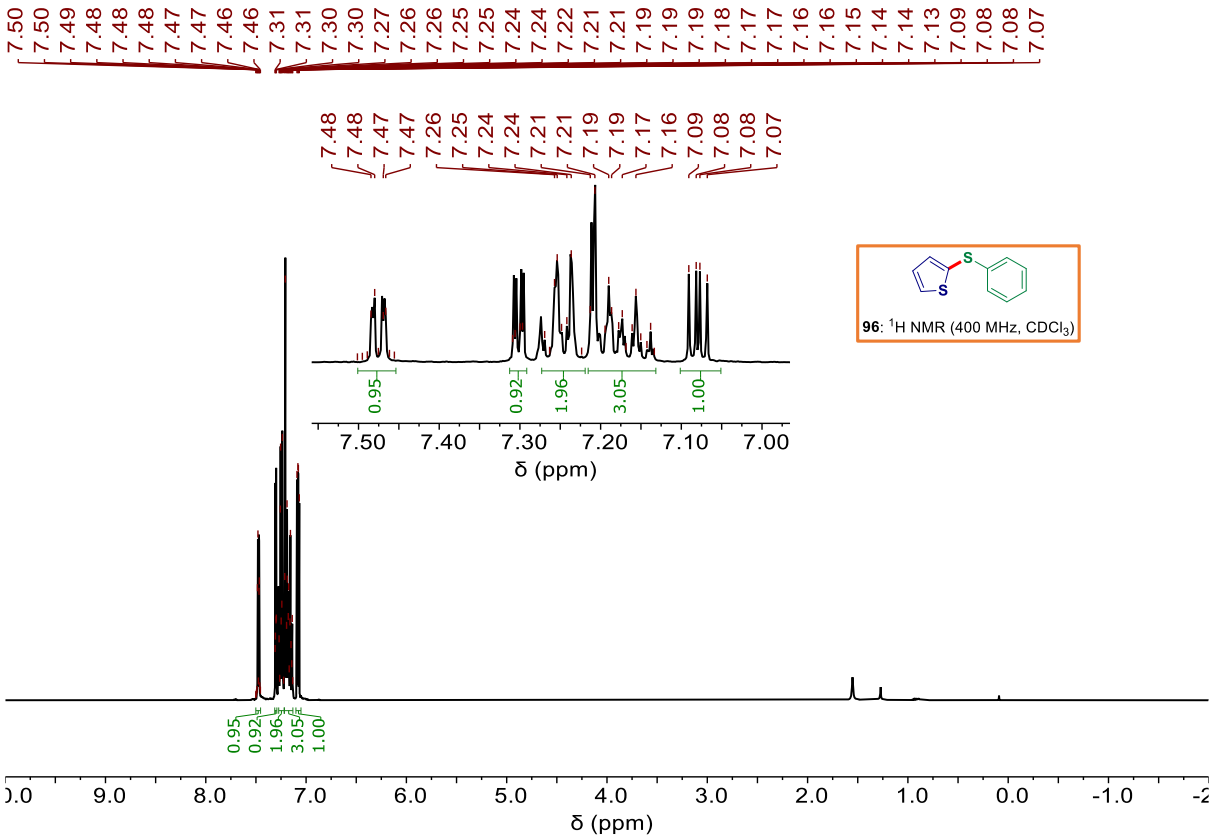

144.81 139.03 135.35 128.96 126.39 125.44 107.63 39.48
144.81 139.03 135.35 128.96 126.39 125.44
146 144 142 140 138 136 134 132 130 128 126 124
δ (ppm)
93: 13C NMR (101 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

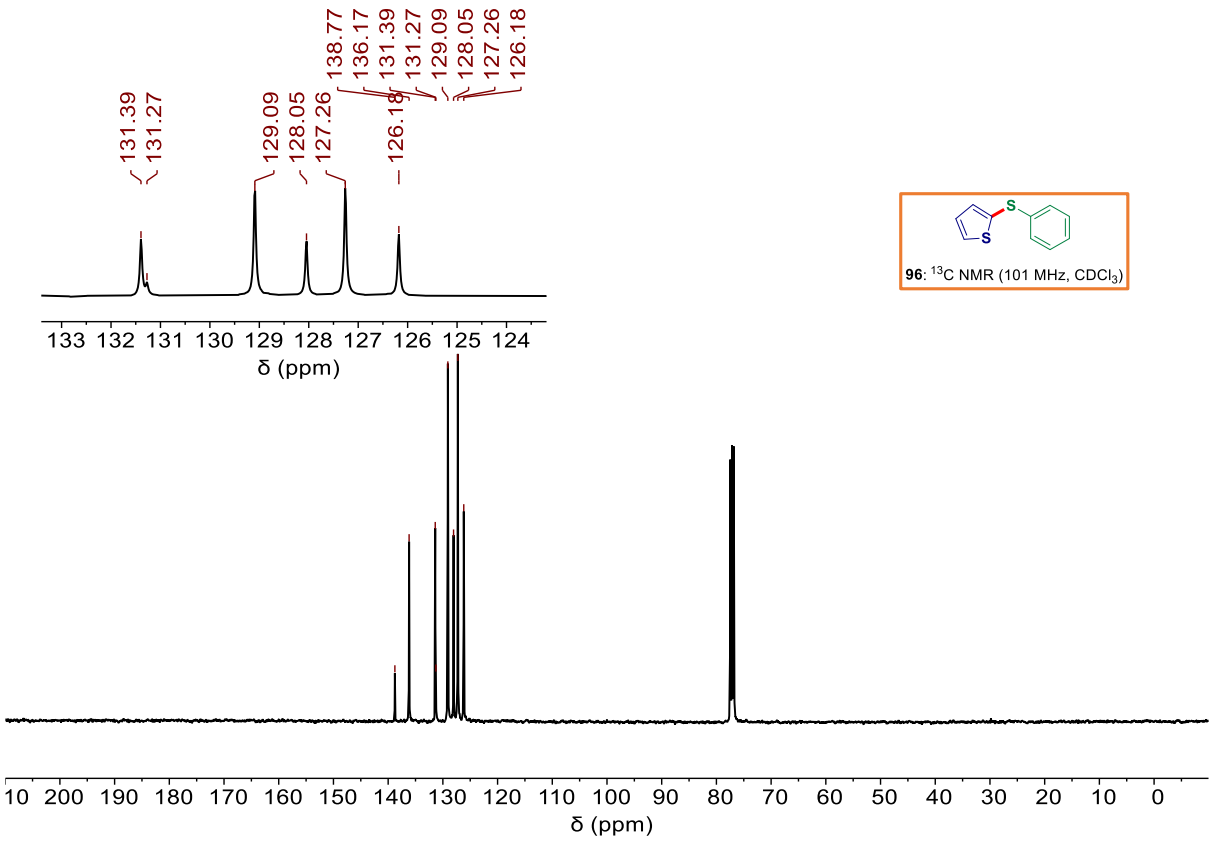

8.33
8.32
8.32
8.31
8.22
8.21
8.19
8.19
7.60
7.59
7.58
7.44
7.43
7.42
7.41
0.99
1.00
1.00
2.05
3.12
δ (ppm)
94: 1H NMR (400 MHz, CDCl3)

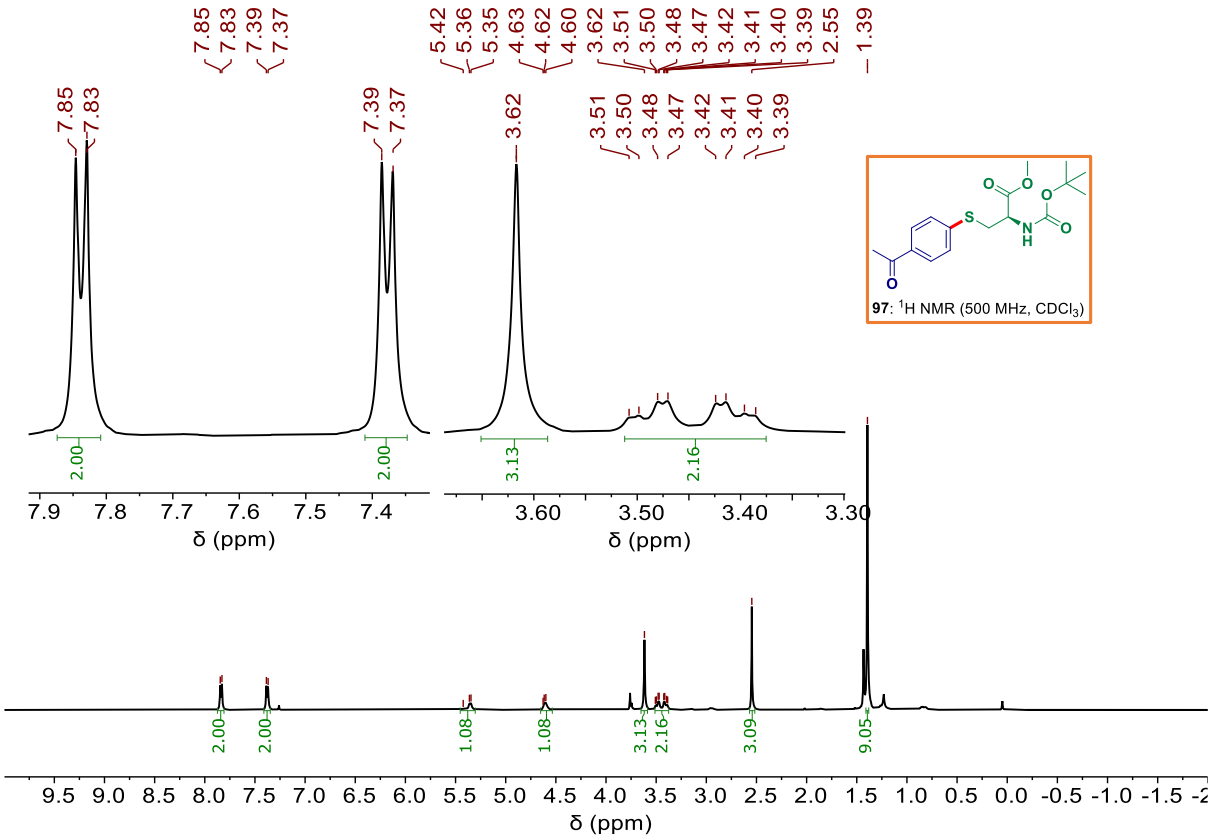

158.71
143.88
142.79
140.16
135.10
129.89
129.69
129.03
δ (ppm)
94: 13C NMR (101 MHz, CDCl3)

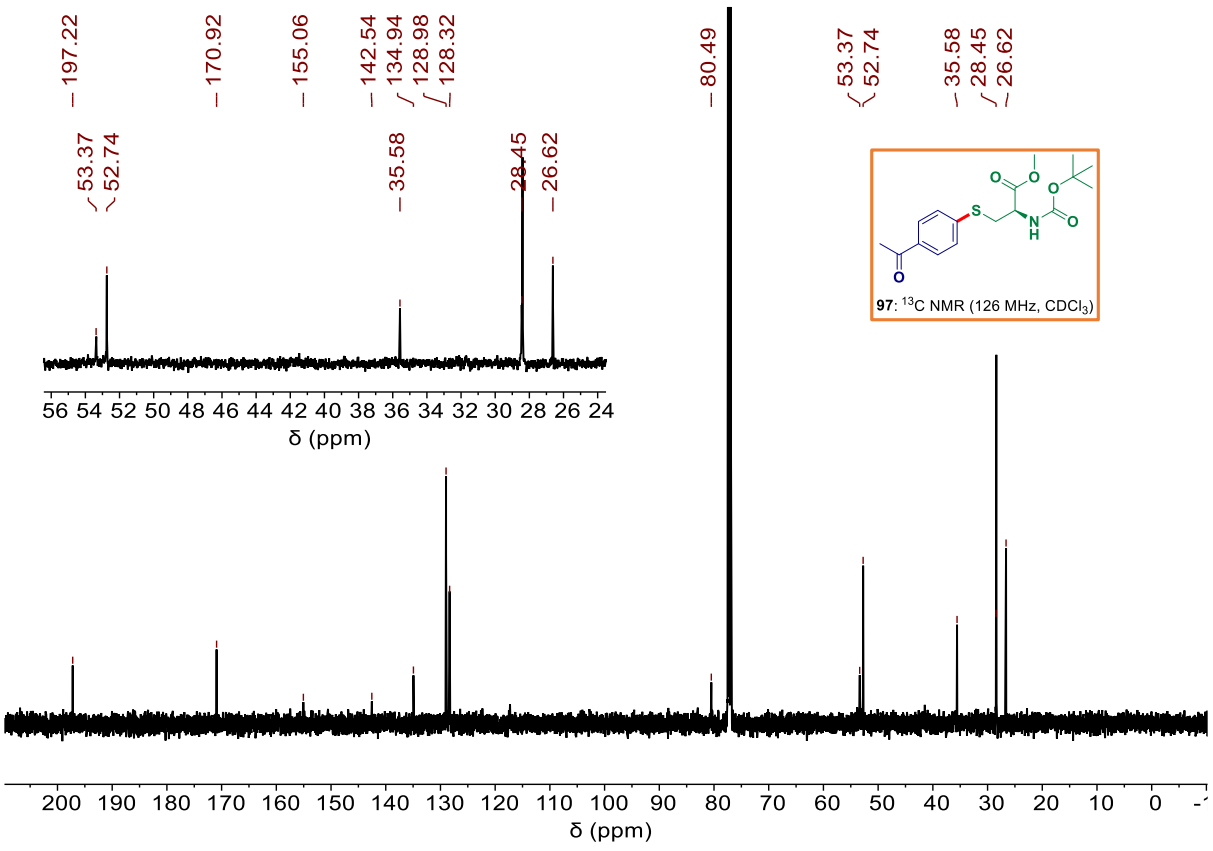

7.90 7.88 7.76 7.76 7.75 7.75 7.74 7.74 7.73 7.67 7.65 7.55 7.53 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.43 7.43 7.41 7.41 7.40 7.39 7.39 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25
7.90 7.88 7.76 7.76 7.75 7.74 7.74 7.67 7.65 7.53 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.41 7.41 7.39 7.39 7.29 7.28 7.27 7.27 7.26
95: 1H NMR (400 MHz, CDCl3)
1.00 1.90 0.95 3.02 1.15 1.61
7.95 7.85 7.75 7.65 7.55 7.45 7.35 7.25 7.15
δ (ppm)
1.00 1.90 0.95 3.02 1.15 1.61
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
δ (ppm)

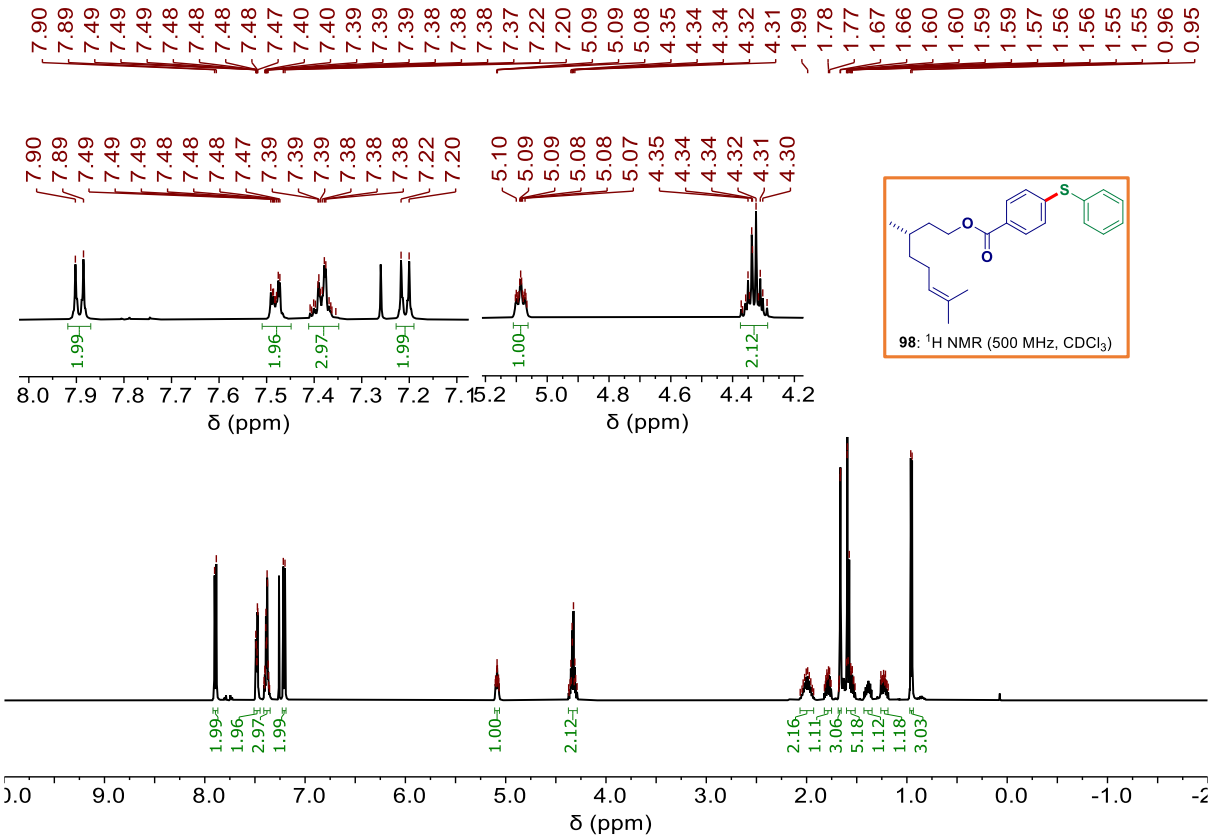

169.90 153.94 135.78 135.60 135.48 130.60 130.05 126.30 124.46 122.05 120.90
135.78 135.60 135.48 130.60 130.05 126.30 124.46 122.05 120.90
95: 13C NMR (101 MHz, CDCl3)
136 134 132 130 128 126 124 122 120
δ (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)

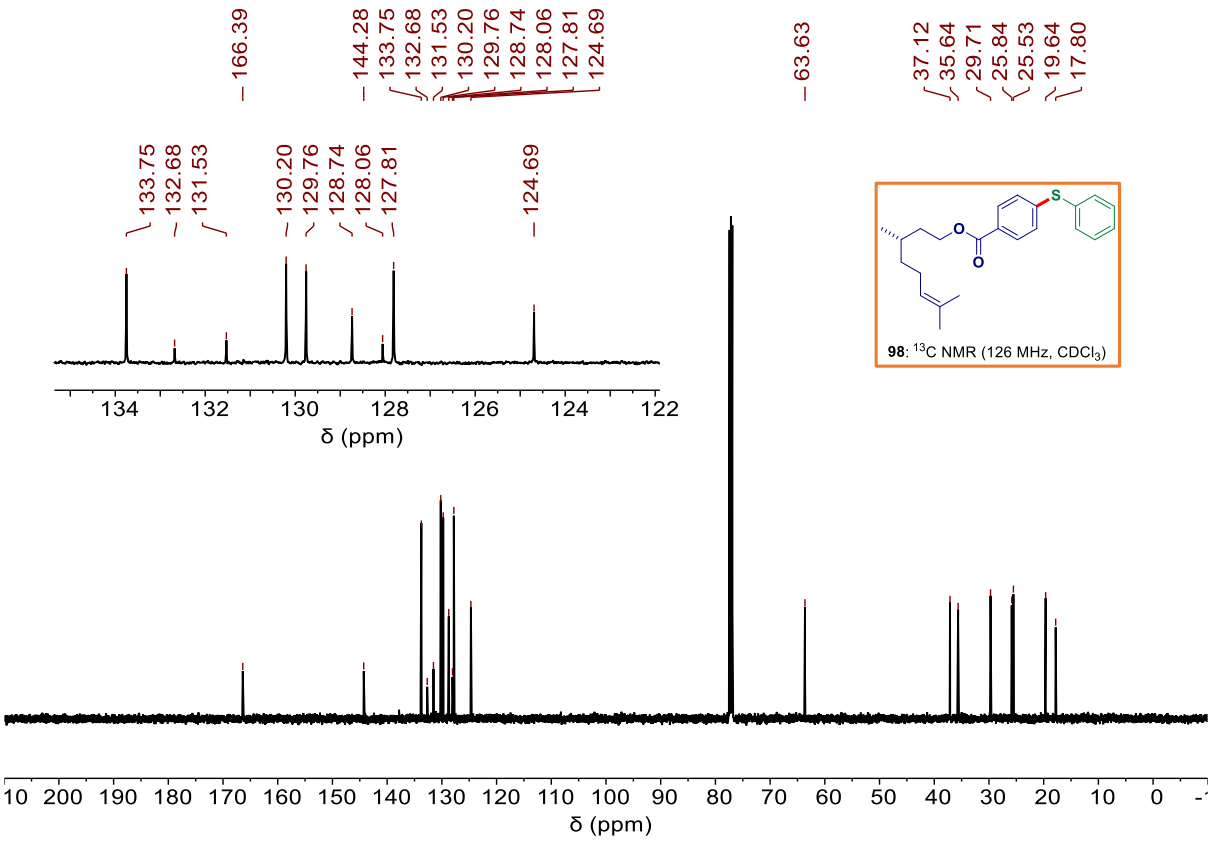

7.50 7.50 7.49 7.48 7.48 7.48 7.47 7.47 7.46 7.46 7.31 7.31 7.30 7.30 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.22 7.21 7.21 7.19 7.19 7.19 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.09 7.08 7.08 7.07
7.48 7.48 7.47 7.47 7.26 7.25 7.24 7.24 7.21 7.21 7.19 7.19 7.17 7.16 7.09 7.08 7.08 7.07
0.95 0.92 1.96 3.05 1.00
7.50 7.40 7.30 7.20 7.10 7.00
δ (ppm)
0.95 0.92 1.96 3.05 1.00
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
δ (ppm)
96: 1H NMR (400 MHz, CDCl3)

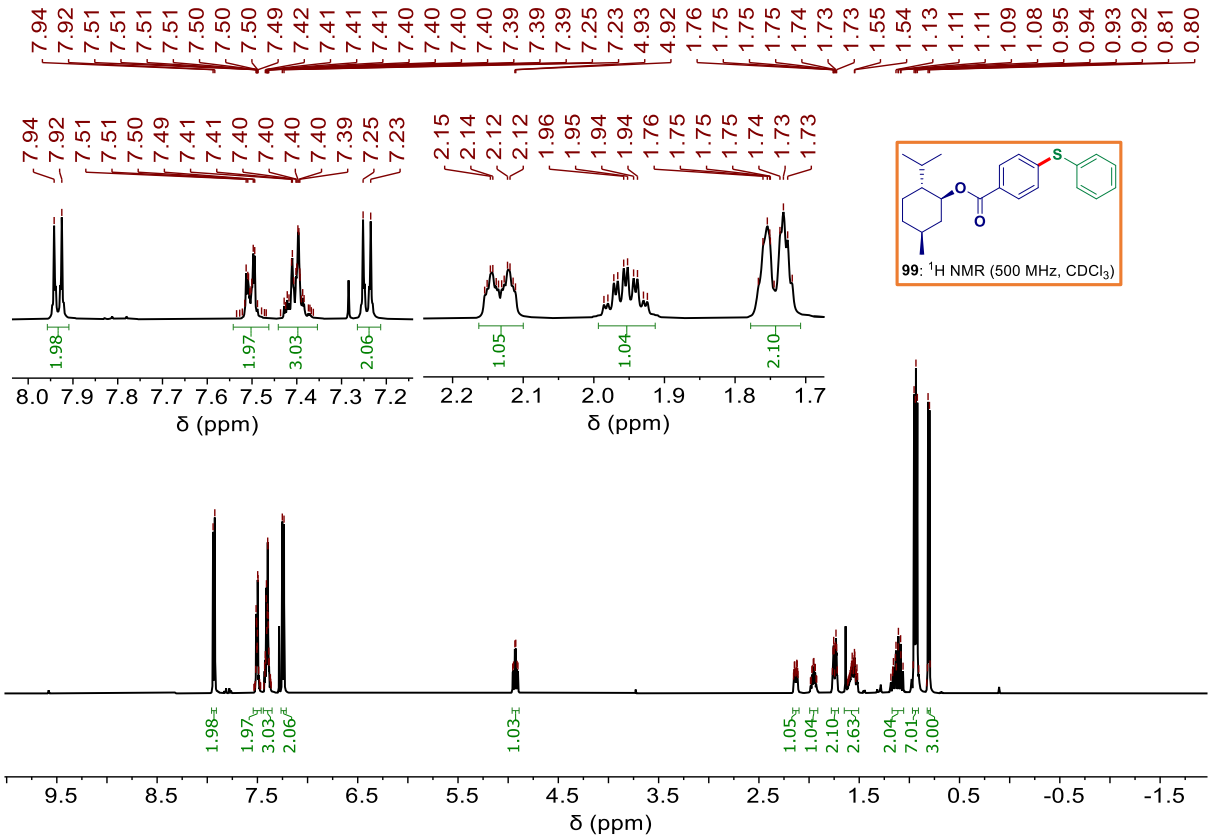

138.77 136.17 131.39 131.27 129.09 128.05 127.26 126.18
131.39 131.27 129.09 128.05 127.26 126.18
133 132 131 130 129 128 127 126 125 124
δ (ppm)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)
96: 13C NMR (101 MHz, CDCl3)

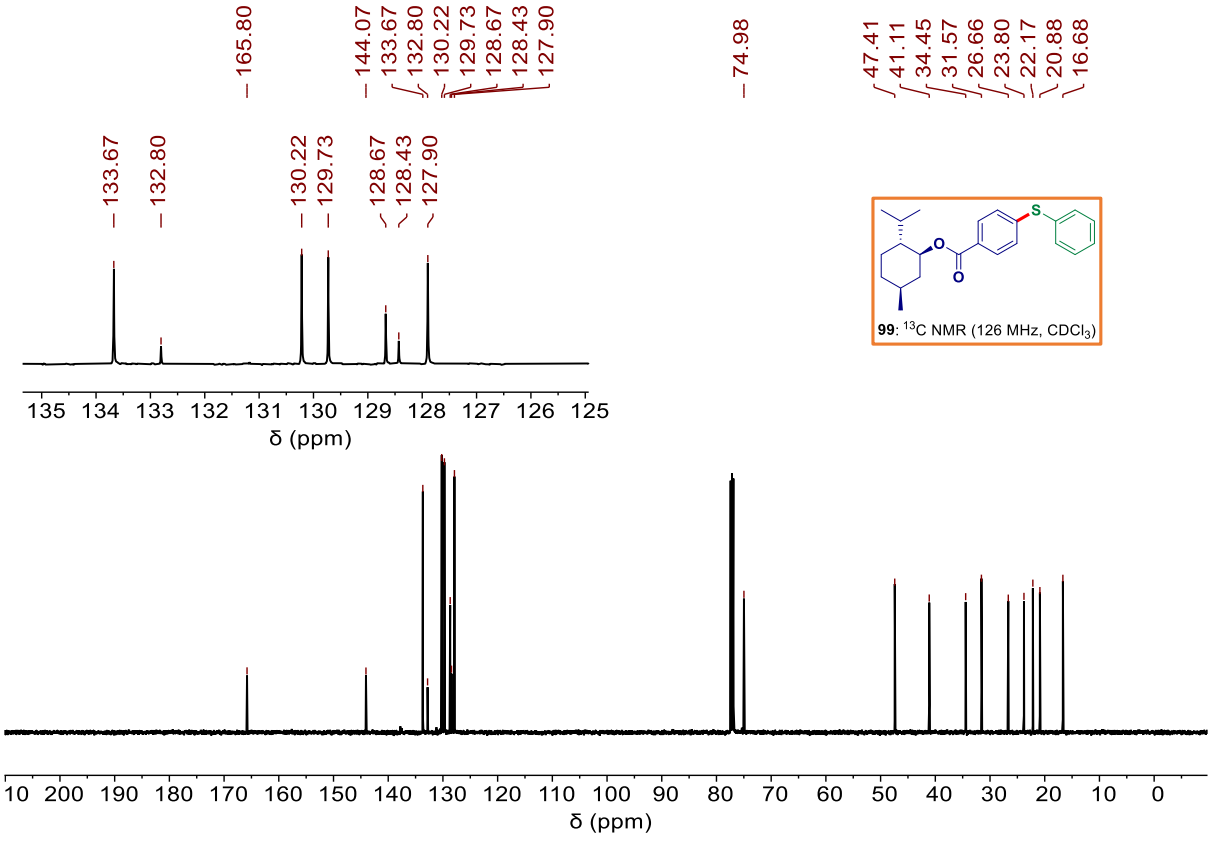

7.85
7.83
7.39
7.37
5.42
5.36
5.35
4.63
4.62
4.60
3.62
3.51
3.50
3.48
3.47
3.42
3.41
3.40
3.39
2.55
1.39
97: ^{1}H NMR (500 MHz, $CDCl_3$)
δ (ppm)

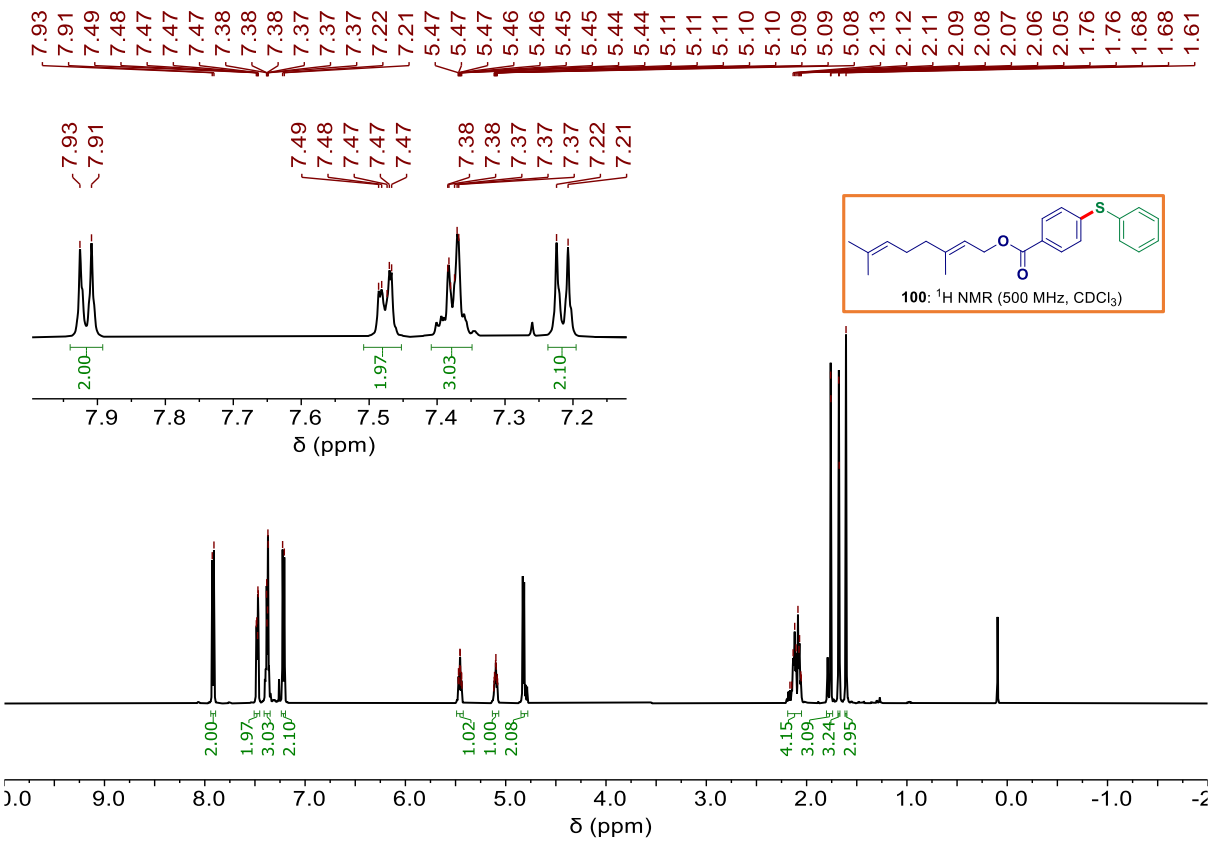

197.22
170.92
155.06
142.54
134.94
128.98
128.32
80.49
53.37
52.74
35.58
28.45
26.62
97: ^{13}C NMR (126 MHz, $CDCl_3$)
δ (ppm)

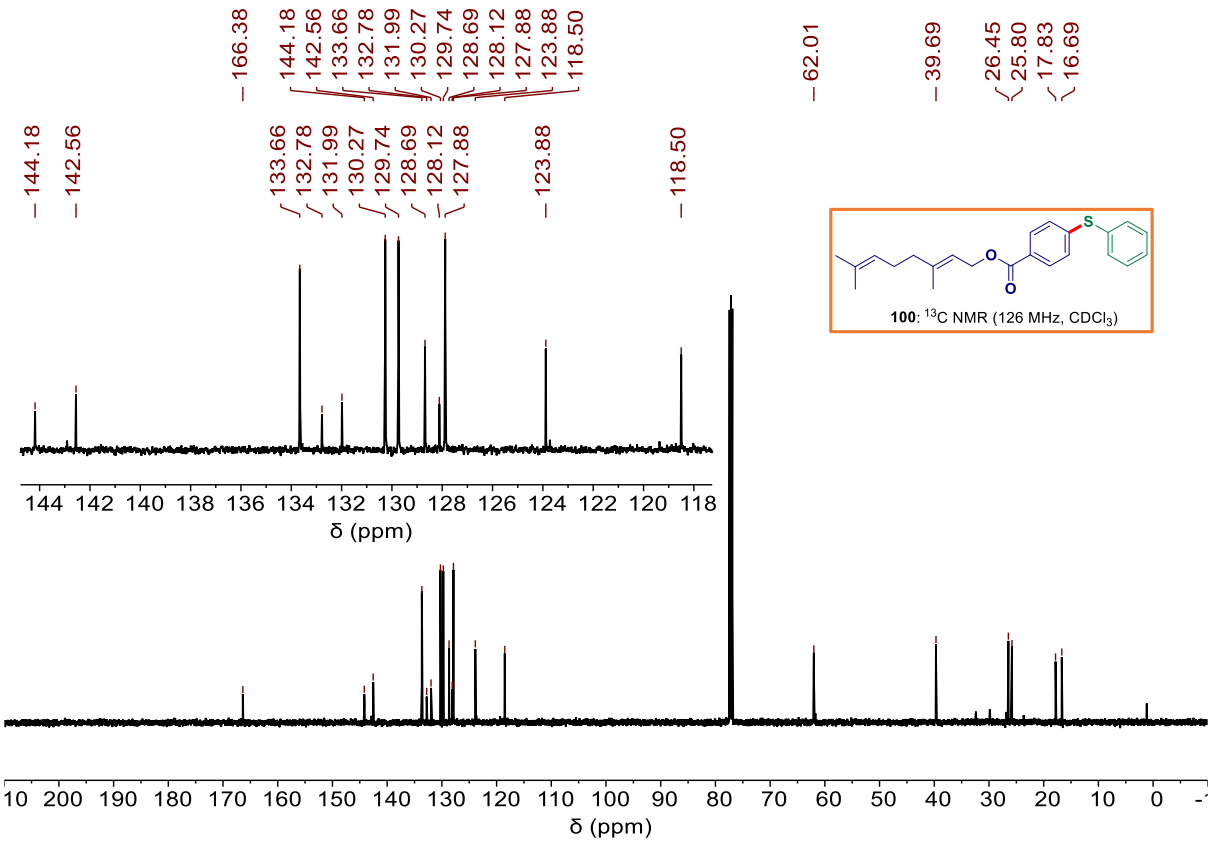

δ (ppm)
98: ^{1}H NMR (500 MHz, CDCl$_3$)


δ (ppm)
98: ^{13}C NMR (126 MHz, CDCl$_3$)


7.94 7.92 7.51 7.51 7.51 7.51 7.50 7.50 7.50 7.49 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.40 7.39 7.39 7.39 7.25 7.23 4.93 4.92 1.76 1.75 1.75 1.75 1.74 1.73 1.73 1.55 1.54 1.13 1.11 1.11 1.09 1.08 0.95 0.94 0.93 0.92 0.81 0.80
2.15 2.14 2.12 2.12 1.96 1.95 1.94 1.94 1.76 1.75 1.75 1.75 1.74 1.73 1.73
1.98 1.97 3.03 2.06 1.05 1.04 2.10
δ (ppm)
99: ^{1}H NMR (500 MHz, CDCl$_3$)
1.98 1.97 3.03 2.06 1.03 1.05 1.04 2.10 2.63 2.04 7.01 3.00
δ (ppm)


165.80 144.07 133.67 132.80 130.22 129.73 128.67 128.43 127.90 74.98 47.41 41.11 34.45 31.57 26.66 23.80 22.17 20.88 16.68
133.67 132.80 130.22 129.73 128.67 128.43 127.90
δ (ppm)
99: ^{13}C NMR (126 MHz, CDCl$_3$)
δ (ppm)


7.93 7.91 7.49 7.48 7.47 7.47 7.47 7.38 7.38 7.38 7.37 7.37 7.37 7.22 7.21 5.47 5.47 5.47 5.46 5.46 5.45 5.45 5.44 5.44 5.11 5.11 5.11 5.10 5.10 5.09 5.09 5.08 2.13 2.12 2.11 2.09 2.08 2.07 2.06 2.05 1.76 1.76 1.68 1.68 1.61
2.00 1.97 3.03 2.10
δ (ppm)
100: 1H NMR (500 MHz, CDCl3)
2.00 1.97 3.03 2.10 1.02 1.00 2.08 4.15 3.09 3.24 2.95
δ (ppm)


166.38 144.18 142.56 133.66 132.78 131.99 130.27 129.74 128.69 128.12 127.88 123.88 118.50 62.01 39.69 26.45 25.80 17.83 16.69
144.18 142.56 133.66 132.78 131.99 130.27 129.74 128.69 128.12 127.88 123.88 118.50
δ (ppm)
100: 13C NMR (126 MHz, CDCl3)
δ (ppm)