Supporting Information

Sustainable and Highly Controlled Aryl Couplings Revealed by Systematic Assessment of Photoactivatable Linkers

Veit G. Haensch,[a] Toni Neuwirth,[a] Alexander Bergner,[a] Jakob Bruhnke,[a] Florian Kloss,[b] and Christian Hertweck*[a,c]

a) Department of Biomolecular Chemistry, Leibniz Institute for Natural Product Research and Infection Biology (HKI) Beutenbergstr. 11a, 07745 Jena (Germany)
E-mail: christian.hertweck@leibniz-hki.de
b) Transfer Group Antiinfectives Leibniz Institute for Natural Product Research and Infection Biology (HKI), 07745 Jena (Germany)
c) Faculty of Biological Sciences, Friedrich Schiller University Jena, 07743 Jena (Germany)

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Experimental Procedures

General synthesis procedures

All reagents were obtained from commercial suppliers (Sigma Aldrich, TCI, Alfa Aesar, etc.) and used without further purification, unless otherwise explained. Some reactions were performed under inert gas (argon) by using the Schlenk technique and dried solvents. Dichloromethane (DCM), acetonitrile (MeCN), methanol (MeOH) and chloroform were used from a solvent purification system (Innovative Technologies). Open column chromatographic separations were executed on silica gel (Kieselgel 60, 15–40 µm, Merck KGaA). Reaction progresses were monitored by thin layer chromatography (TLC) (silica gel on aluminum sheets 20 × 20 cm with fluorescent indicator 254 nm, Merck KGaA), GC-MS or HPLC-(HR)MS.

Thin film photoreactor: Photoreactions were performed on a self-made photoreactor made from a milled aluminum block (16.9 × 31.9 × 0.03 cm, reaction volume ~15 mL) covered with a quartz glass slide. A SIMDOS 02 dosing pump from KNF was connected to the photoreactor via FEP (fluorinated ethylene propylene) tubes. A Herolab UVT-40 S UV illuminator equipped with 6 Philips TUV 15 W/G15 T8 tubes (UV-C lamp, total power 90 W, 44 $W \cdot m^{-2}$ at 245–260 nm or 118 $W \cdot m^{-2}$ at 245–260 nm without the glass cover, peak at 254 nm) or 6 Sankyo-Denki G15T8E tubes (UV-B lamp, total power 90 W, 75 $W \cdot m^{-2}$ at 270–370 nm, peak at 305–310 nm) was used as the UV light source to illuminate the samples from above. A cryostat attached to the aluminum block allowed the temperature to be controlled. Air bubbles from the pump were prevented from reaching the photoreactor by a small container. Flow rates (0.5–10 $mL \cdot min^{-1}$) were selected during reaction optimization.

Tubular photoreactor: Reactive solutions that could attack the aluminum of the thin film reactor were exposed to UV light in a self-made tubular photoreactor made of FEP tubing (0.8 mm inner diameter, 1.6 mm outer diameter, Bola S 1815-04, reaction volume ~3.5 mL). A Sigma T 2201 UV illuminator (model no.: 16-3102) equipped with 4 Philips TUV 15 W/G15 T8 (UV-C lamp, 25.5 mm outer diameter) was used as the UV light source to illuminate the samples. The FEP tube (~7 m) was wrapped (~70 times) around a quartz tube (32±0.64 mm outer diameter, 1.7±0.17 mm wall thickness 420±0.1 mm length), in which one light source was located. A SIMDOS 02 dosing pump from KNF was attached to the photoreactor with FEP tubes. Samples were either dissolved in the solvent or introduced through a three-way valve downstream of the pump. Flow rates (0.5–2 $mL \cdot min^{-1}$) were selected during reaction optimization. The quartz tube was insulated from heat transfer from the light source by a FEP tube (1 mm outer diameter, perforated several times and with compressed air flowing through it). This reactor was used for the synthesis of **2c**.

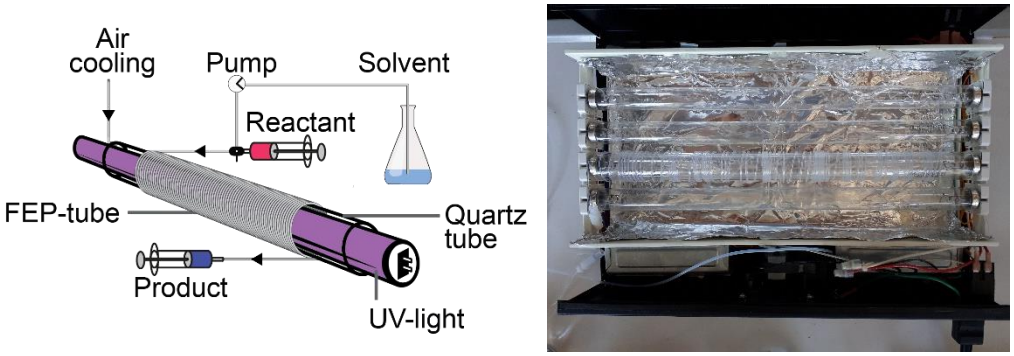


Figure S1: Schematic drawing and photo of tubular photoreactor (without protective cover).

Flask photoreactor: A Renkforce UV-30 LED-strip (5 m, 150 × 5050 SMD LEDs, 24 W, ~395 nm) was wrapped (~12 times) around a beaker (2 L, inner diameter 13 cm, borosilicate 3.3) so that flasks inside the beaker were evenly exposed to the light. The beaker was placed on a magnetic stirring plate. The temperature was maintained at ambient temperature with a fan. This reactor was used for the synthesis of **1ac**.

Figure S2: Picture of the flask photoreactor.

General analytical procedures

NMR: All 1D (^{1}H, ^{13}C, ^{31}P, DEPT) and 2D NMR (^{1}H-^{1}H COSY, HSQC, HMBC) were recorded in deuterated solvents using a Bruker AVANCE II 300, AVANCE III 500 or 600 MHz instrument equipped with Bruker Cryo Platform. The chemical shifts are reported in ppm relative to the solvent residual signal (^{1}H: δ ($CHCl_3$) = 7.26 ppm, δ (CH_2Cl_2) = 5.32 ppm, δ (D_2O) = 4.79 ppm, δ (MeOH) = 3.31 ppm, δ (DMSO) = 2.50 ppm, δ (MeCN) = 1.94 ppm. ^{13}C: δ ($CDCl_3$) = 77.16 ppm, δ (CD_2Cl_2) = 53.84 ppm, δ (MeOD) = 49.00 ppm, δ (DMSO-d_6) = 39.52 ppm, δ (CD_3CN) = 1.32 ppm or 118.26 ppm.[1] The following abbreviations are used for multiplicities of resonance signals: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, br = broad.

GC-MS: GC-MS analysis was performed using a Trace 1310 GC (Thermo Fisher Scientific) coupled with a TSQ 9000 electron impact (EI)-triple quad mass spectrometer (thermo scientific). A 4 mm SSL GC inlet glass liner with glass wool (P/N 453A1305) and a BPX5 capillary column (30 m, 0.25 mm inner diameter, 0.25 µm film) from Trajan (SGE) was used. The column was operated with helium carrier gas (1.5 mL·min^{-1}) and split injection (split ratio 1:10). The injector temperature was set to 200 °C, the MS transfer line was set to 300 °C, and the ion source temperature was set to 200 °C. The GC temperature profile was as follows: 40 °C for 0–1 min, heating to 100 °C over 1–3 min (30 °C·min^{-1}), heating to 300 °C over 3–24 min (10 °C·min^{-1}). Total ion current (TIC) values were recorded in the mass range of 45–500 amu, with a scan time of 0.2 sec. and a MS delay of 3 min. 1 µL samples in CH_2Cl_2, MeOH, MeCN, $CHCl_3$ or tetrahydrofuran were injected.

The National Institute of Standards and Technology (NIST) Mass Spectra Search Program version 2.4 (dated March 25, 2020) was used for comparison of the EI-MS spectra.

LC-MS: LC-MS measurements were performed using Q Exactive Orbitrap High Performance Benchtop LC-MS with electrospray ion source and Accela HPLC system (Thermo Fisher Scientific, Bremen) or Ultimate3000 UHPLC system (Thermo Fisher Scientific, Bremen), or LTQ Velos Ion Trap Benchtop LC-MS with electrospray ion source and Surveyor HPLC system (Thermo Fisher Scientific, Bremen).

HPLC conditions using Q Exactive: An Accucore C18 column (2.1 × 100 mm, 2.6 µm, Thermo Fisher) was used with gradient elution as follows: MeCN (0.1% (*v*/*v*) HCOOH)/H_2O (0.1% (*v*/*v*) HCOOH) initially at 5:95, reaching 2:98 over 10 min, then maintaining 2:98 for 4 min. The flow rate was 0.2 mL·min^{-1} and injection volume was 3 µL.

UHPLC conditions using Q Exactive: An Accucore C18 column (2.1 × 100 mm, 2.6 µm, Thermo Fisher) was used with gradient elution as follows: MeCN (0.1% (*v*/*v*) HCOOH)/H_2O (0.1% (*v*/*v*) HCOOH) initially at 5:95, reaching 2:98 over 10 min, then maintaining 2:98 for 4 min. The flow rate was 0.2 mL·min^{-1} and injection volume was 3 µL.

UHPLC conditions using Q Exactive: An Accucore C18 column (2.1 × 100 mm, 2.6 µm, Thermo Fisher) was used with gradient elution as follows: MeCN (0.1% (*v*/*v*) HCOOH)/H_2O (0.1% (*v*/*v*) HCOOH) initially at 5:95, reaching 2:98 over 7 min, then maintaining 2:98 for 3 min. The flow rate was 0.2 mL·min^{-1} and injection volume was 3 µL.

HPLC conditions using LTQ: A C18 column (Phenomenex Kinetex XB-C18, 2.6 µm, 100 × 3 mm) was used with gradient elution as follows: MeCN (0.1% (*v*/*v*) HCOOH)/H_2O (0.1% (*v*/*v*) HCOOH) initially at 10:90 for 1 min, reaching 100:0 over 8 min, maintaining 100:0 for 4 min. The flow rate was 0.6 mL·min^{-1} and injection volume was 5 µL.

Particle size measurement was performed with the Bettersizer S3 Plus with dynamic image analysis.

Detection of byproducts

Detection of methylamine with TrCl by GC-MS

A triphenylmethyl chloride (TrCl) solution (10 mg TrCl in 1 mL MeCN) was prepared. A methylamine solution ($MeNH_2$ in MeOH (2 µL, 40%) in 600 µL MeCN) was prepared.
Sulfonamide **1c** (1.0 mg) was dissolved in MeCN (600 µL) in a fused silica NMR tube and irradiated with a 254 nm hand lamp for 1 h. This crude solution was mixed with the TrCl solution (60 µL) at room temperature for 1 h and measured by GC-MS. As a positive control, the $MeNH_2$ solution (30 µL) was mixed with the TrCl solution (3 µL) at room temperature for 1 h and measured by GC-MS. As a negative control, an irradiated solution of sulfonamide **1c** was measured by GC-MS, which showed no corresponding peak.

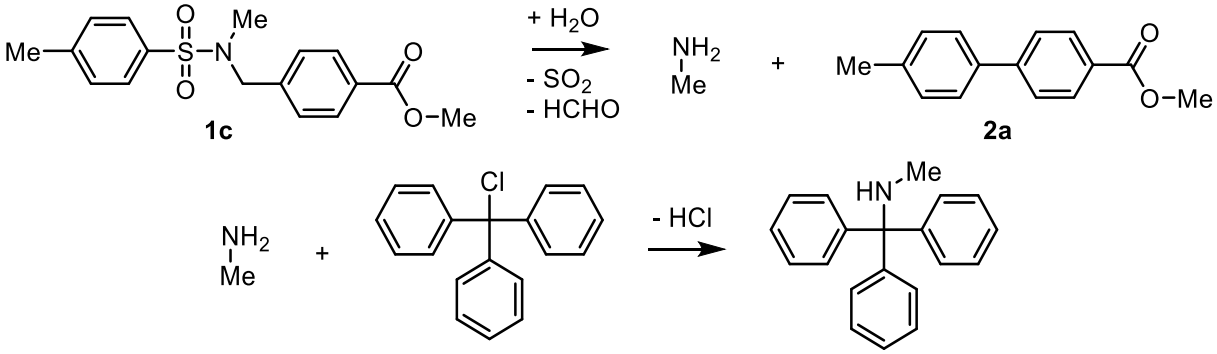


Figure S3: Photosplicing of compound **1c** with the formation of $MeNH_2$, and the reaction of $MeNH_2$ with TrCl.

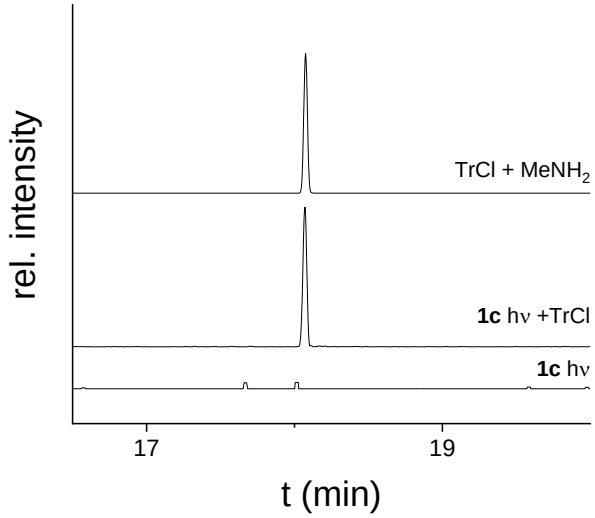


Figure S4: GC-MS measurement with EIC (*m*/*z* = 273.15, 500 ppm window) of **1c**, irradiated **1c** with TrCl, and TrCl with $MeNH_2$.

Detection of $TsNH_2$ by GC-MS

Sulfonamide **1d** (2.5 mg) was dissolved in MeCN-d_3 (600 µL) and irradiated with a 254 nm hand lamp for 2 h. The crude mixture was analyzed by GC-MS. Tosyl amide ($TsNH_2$) was detected and compared with an analytical standard. As a negative control, the not irradiated sulfonamide **1d** was measured by GC-MS, which showed no corresponding peak.

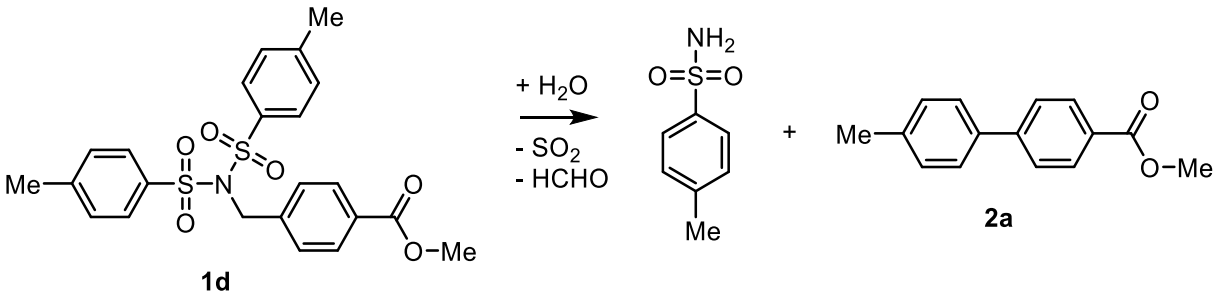


Figure S5: Photosplicing of compound **1d** with the formation of $TsNH_2$.

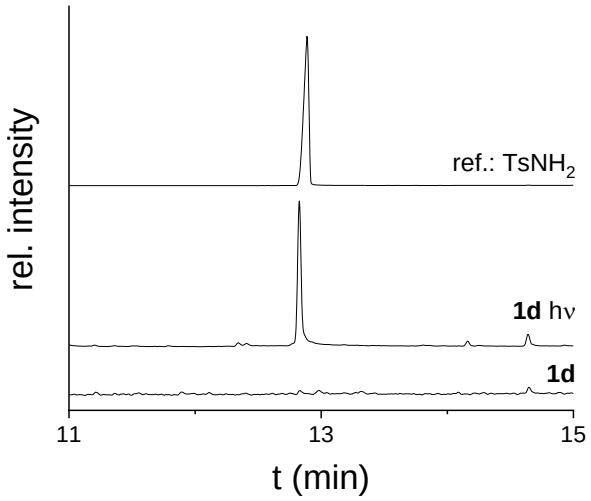


Figure S6: GC-MS measurement with TIC (*m*/*z* = 171.04, 500 ppm window) of **1d**, irradiated **1d**, and $TsNH_2$.

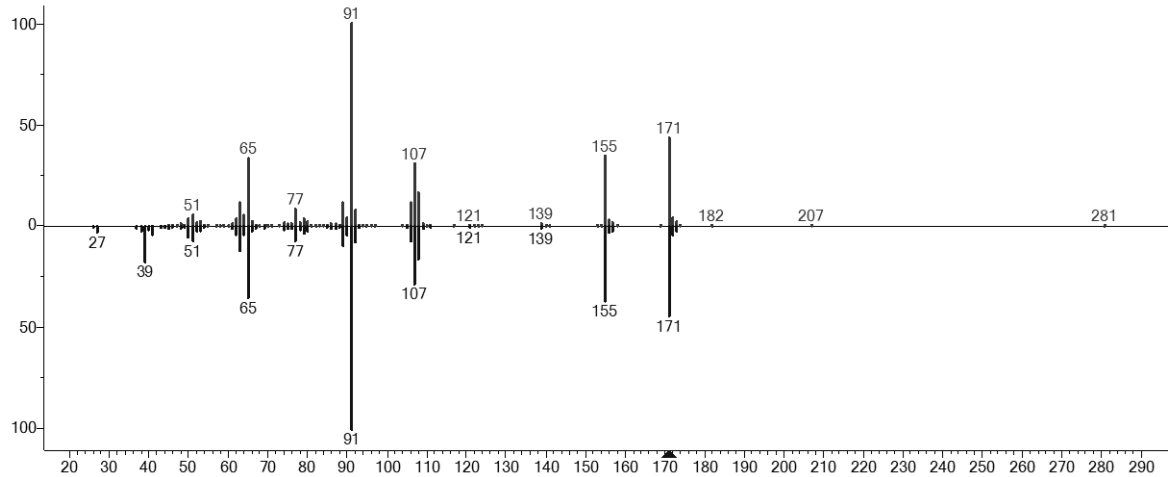


Figure S7: Comparison of EI-MS spectrum of $TsNH_2$ from the photoreaction of **1d** (top) with that of authentic $TsNH_2$ taken from the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

Detection of ethene by NMR

A solution of sulfone **1h** (2.0 mg) was dissolved in MeCN-d_3 (600 µL) in a well-sealed NMR tube made of quartz glass. The NMR tube was irradiated with a 254 nm hand lamp for 2 h. ^{1}H, ^{13}C and HSQC spectra were recorded.

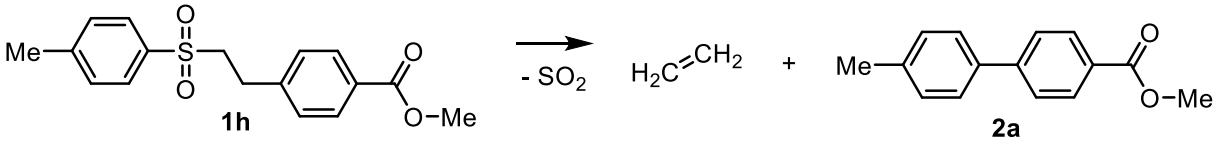


Figure S8: Photosplicing of compound **1h** with the formation of ethylene.

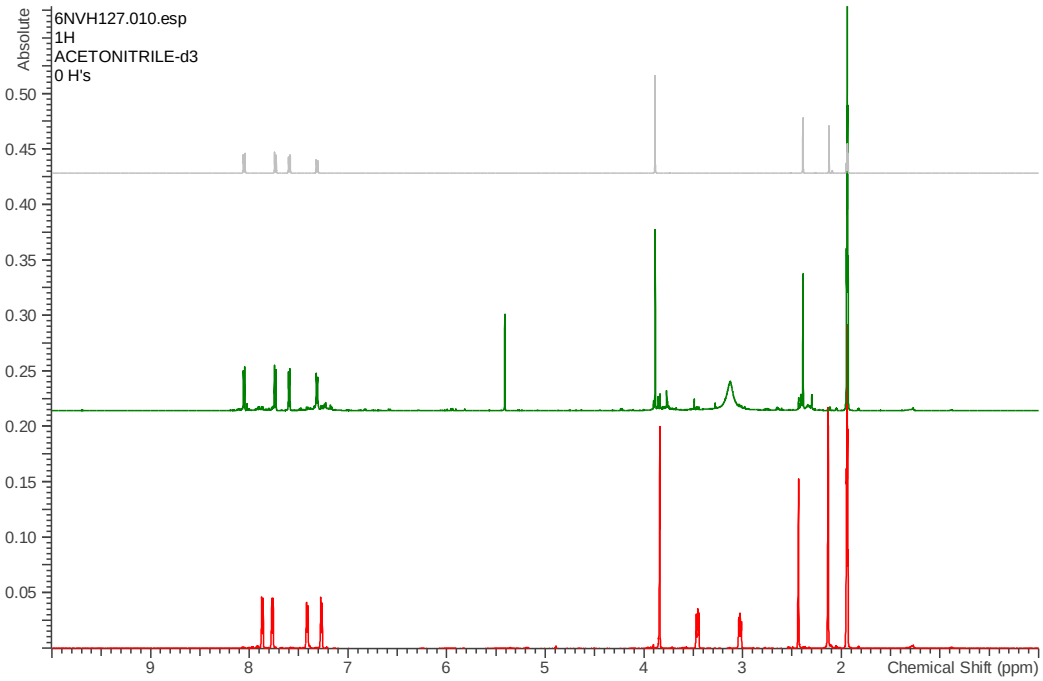


Figure S9: ^{1}H-NMR spectra of sulfone **1h** (bottom, red), irradiated sulfone **1h** (2 h with 254 nm, crude, middle, green), and the biphenyl **2a** (reference, top, grey) in MeCN-d_3 at 600 MHz and 298 K.

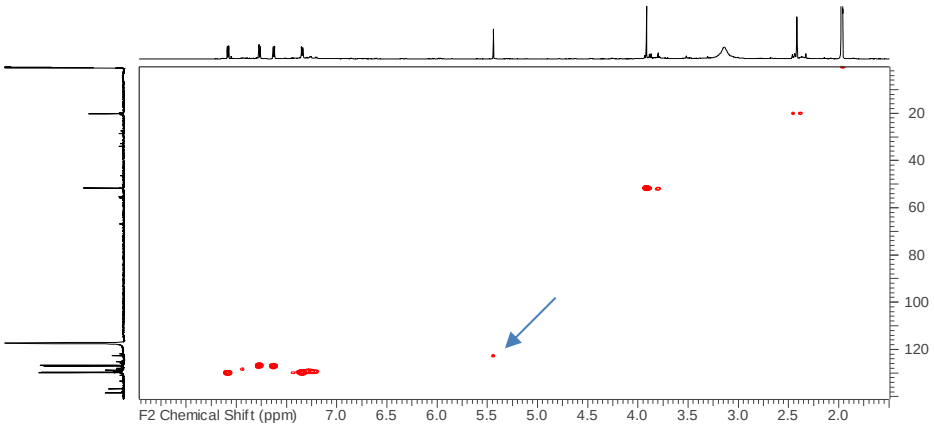


Figure S10: HSQC of irradiated sulfone **1h** with cross peak that corresponds to ethene (blue arrow) in MeCN-d_3 at 600 MHz and 298 K.

Detection of acetone with DNPH by HPLC-HRMS

Sulfonamide **1i** (19.8 mg) was dissolved in MeOH (20 mL) and irradiated on the thin film photoreactor with a flow rate of 1 mL·min^{-1}. The fraction containing the crude photoproduct (60 mL) was collected and 1 mL was mixed with a solution of DNPH (saturated solution in MeCN, 100 µL) at room temperature and measured after 24 h by HPLC-HRMS. As a positive control, acetone in MeCN was mixed with DNPH. As a negative control, irradiated sulfonamide **1i** was measured, which showed no corresponding peak.

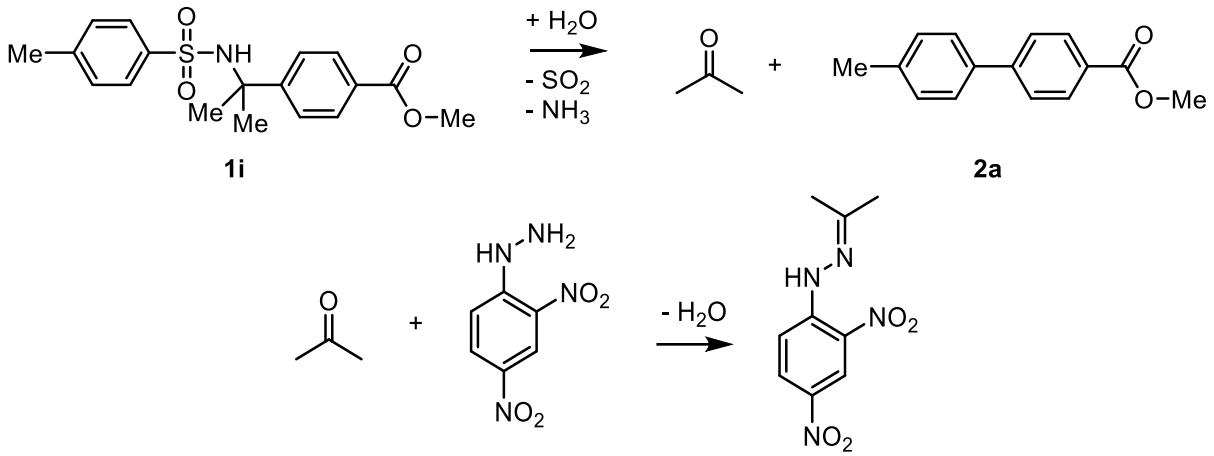


Figure S11: Photosplicing of compound **1i** and the reaction of acetone with DNPH.

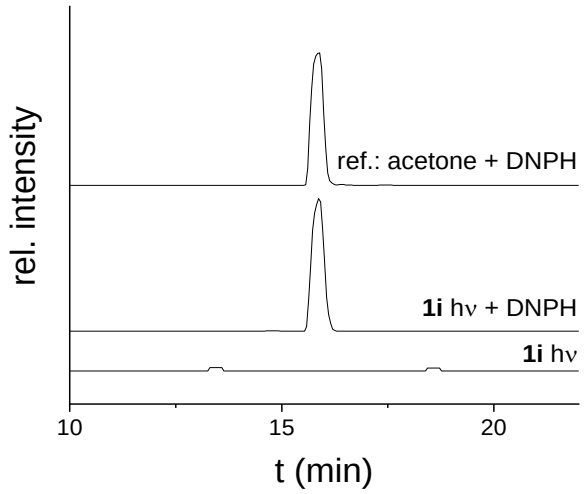


Figure S12: HPLC-HRMS measurement with EIC (ESI$^+$, $C_9H_{11}N_4O_4^+$ *m/z* = 239.0775, 5 ppm window) of irradiated **1i**, irradiated **1i** with DNPH, and acetone with DNPH. The wavelength maximum for both compounds is λ_{max} = 365 nm.

Detection of ethene with bromine by GC-MS

A solution of thioether **1v** (4.4 mg) was dissolved in MeCN-d_3 (700 µL) in an NMR tube made of quartz glass, then degassed with argon. The NMR tube was irradiated with a 254 nm hand lamp for 4 h. A solution of bromine (0.2 g) in DCM (2 mL) was prepared. DCM (100 µL), the bromine solution (10 µL) and the irradiated solution of thioether **1v** (10 µL) were mixed and stored at room temperature for 30 min. The mixture was analyzed by GC-MS. As a negative control, DCM (100 µL) was mixed with the irradiated solution of thioether **1v** (10 µL) and analyzed by GC-MS, which showed no corresponding peak. A solution of 1,2-dibromoethane in DCM as an analytical reference was analyzed by GC-MS as a positive control. The EI-MS spectra of 1,2-dibromoethane and the new compound from irradiated thioether **1v** and bromine were compared.

This method is more sensitive than the direct measurement by NMR. The characteristic singlet in ^{1}H NMR was detected but the concentration of ethene was too low for a meaningful ^{13}C NMR. The NMR tube should be well sealed to minimize the volatilization of ethylene.

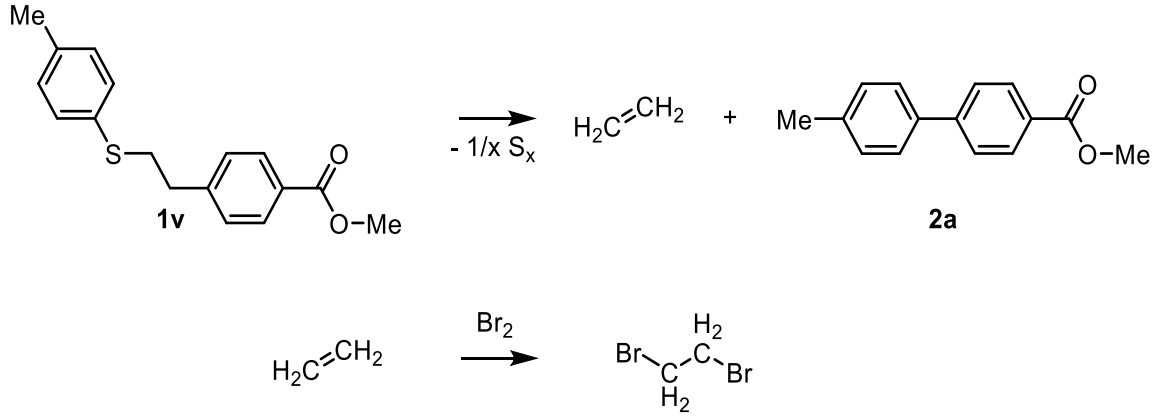


Figure S13: Photosplicing of compound **1v** with the formation of ethylene next to biphenyl **2a**. Ethylene reacts with bromine in a second step to form 1,2-dibromoethane, which was analyzed by GC-MS.

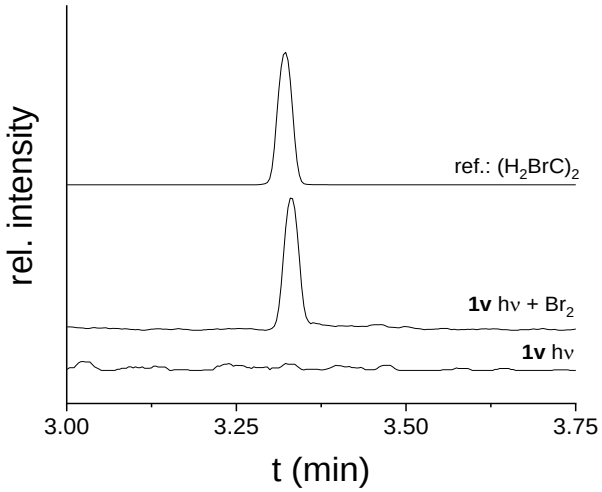


Figure S14: GC-MS measurement with EIC traces (*m/z* = 187.9, 500 ppm window) of 1,2-dibromoethane (positive control), irradiated thioether **1v** with bromine, and irradiated thioether **1v** without bromine (negative control).

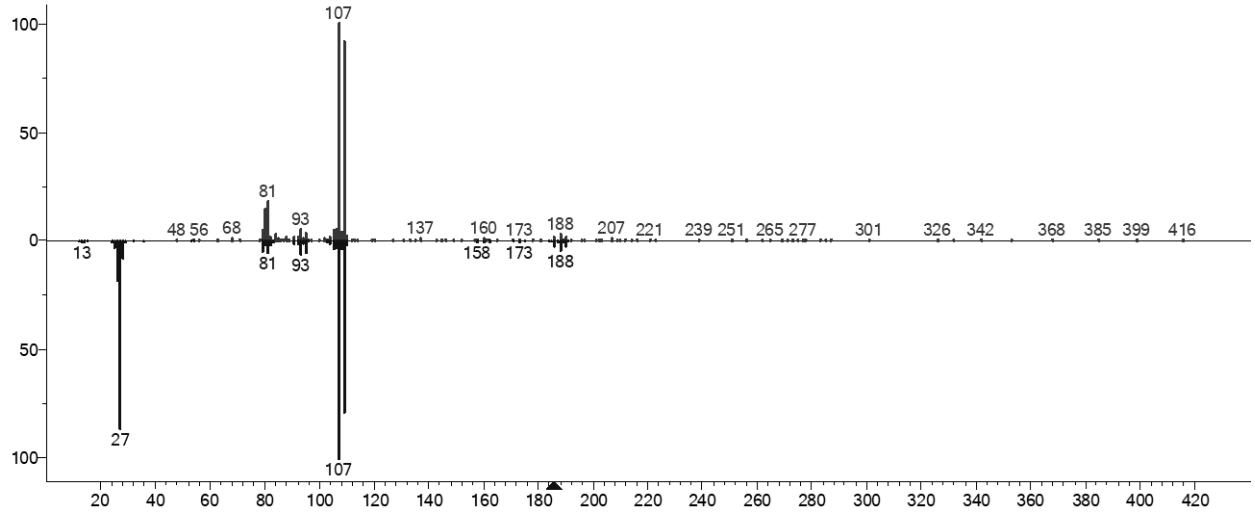


Figure S15: Comparison of EI-MS spectra of 1,2-dibromoethane from the reaction of ethene with bromine (top) with the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

Detection of sulfur with phenylmagnesium bromide by GC-MS

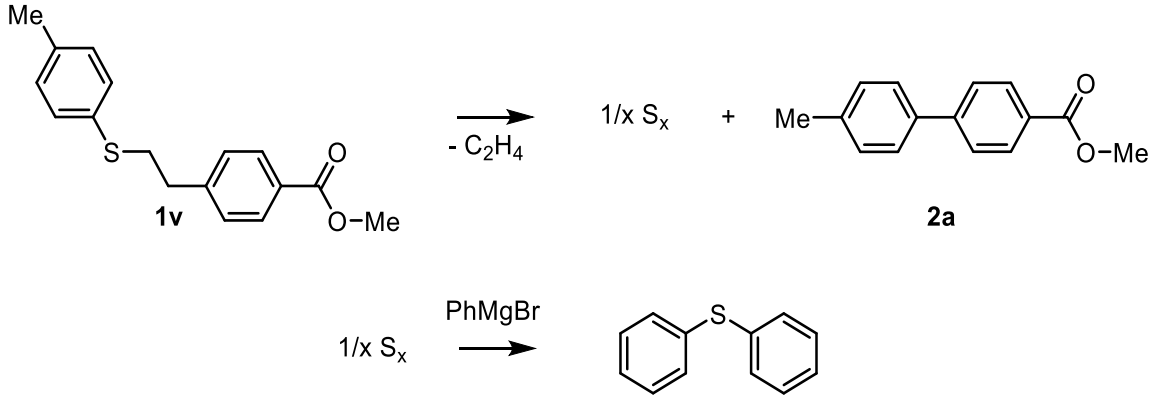


Figure S16: Photosplicing of compound **1v** with the formation of sulfur next to biphenyl **2a**. Sulfur reacts with phenylmagnesium bromide in a second step to form diphenylsulfide, which was analyzed by GC-MS.

A solution of thioether **1v** (1 mg) in MeOH (1 mL) was irradiated with UV-C light (254 nm) in the tubular photoreactor with a flow rate of 1 mL·min^{-1}. The fraction containing the photoproducts was collected and the solvent was evaporated under reduced pressure. The solid residue was further dried under reduced pressure (< 1 mbar) to remove all volatile products. The residue was dissolved in a solution of PhMgBr in THF (1 M, 200 µL) and directly measured by GC-MS. Traces of elemental sulfur (< 0.1 mg) were dissolved in a solution of PhMgBr in THF (1 M, 200 µL) and directly measured by GC-MS as a positive control. A solution of irradiated thioether **1v** was used as a negative control and measured by GC-MS.

Elemental sulfur reacts with an excess of phenyl magnesium bromide to form diphenyl sulfide. The EI-MS spectra of diphenyl sulfide (NIST database) and the two new compounds that formed after the addition of PhMgBr solution to sulfur or the irradiated thioether **1v** were compared.

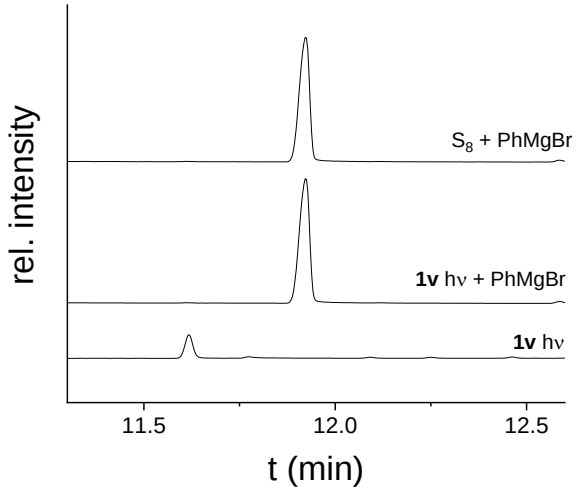


Figure S17: TIC traces from GC-MS measurement of sulfur with an excess phenyl magnesium bromide (positive control), irradiated thioether **1v** with phenyl magnesium bromide, and irradiated thioether **1v** without phenyl magnesium bromide (negative control).

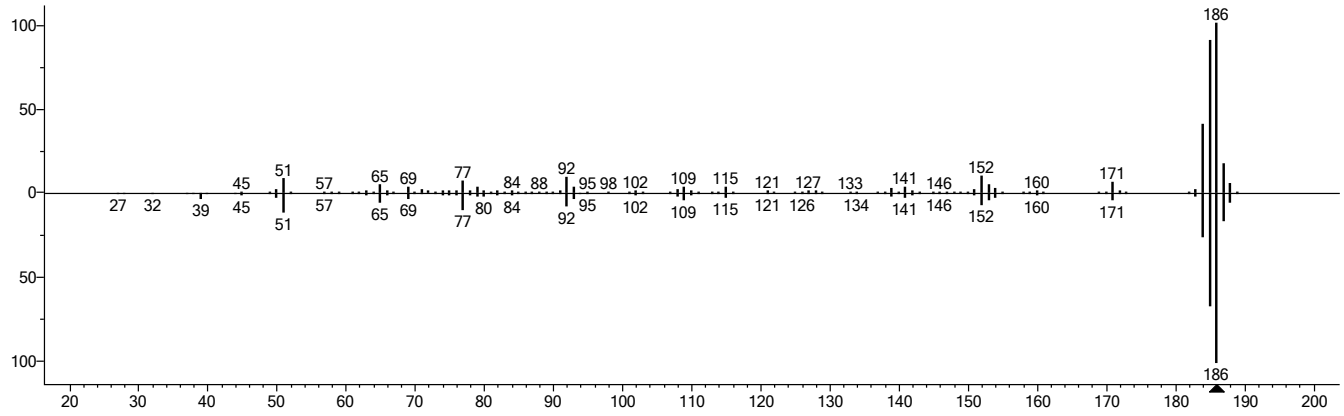


Figure S18: Comparison of EI-MS spectra of the new peak that formed after the reaction of crude irradiated **1v** with phenyl magnesium bromide (top) with diphenyl sulfide from the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

*Preparation of a suspension of **1a** in water*

General procedure: sulfonamide **1a** (20 mg) was dissolved in MeCN (2 mL) and poured into an aqueous solution (8 mL distilled H_2O and 100 µL Tween 20 (11% *v*/*v*)) under vigorous stirring to give a stable suspension. A typical solution was analyzed with a particle size analyzer to give the following distribution: D10: 3.7 µm, D50: 10.4 µm, D90: 26.3 µm. A light microscope showed the crystalline character of the particles.

Linker derivates with at least two methylene groups

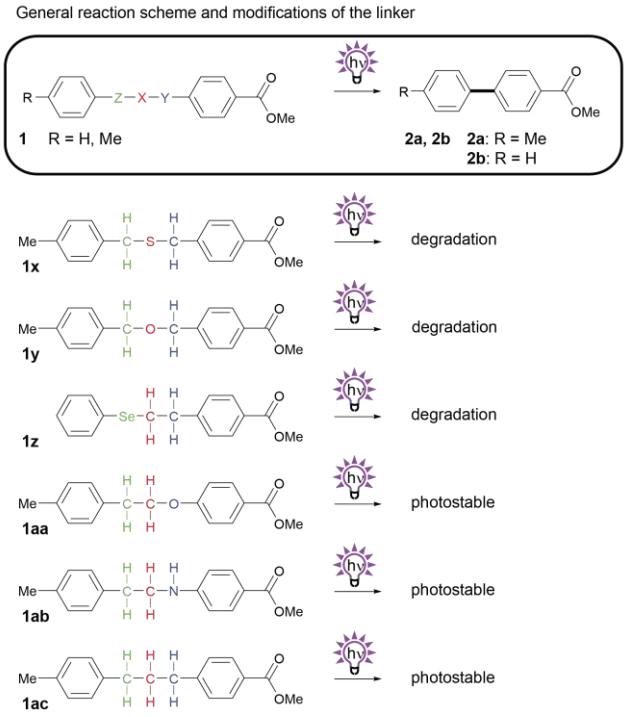


Figure S19: Investigation of the photochemistry of compounds with at least two methylene groups in the linker. General reaction scheme and structures of derivatives (**1x** to **1ac**). Sulfur is in the middle of the linker without the direct linkage to a phenyl residue (**1x**), oxygen is in the middle of the linker without the direct linkage to a phenyl residue (**1y**), selenium is in the linker with a direct linkage to a phenyl residue (**1z**), oxygen is in the linker with a direct linkage to a phenyl residue (**1aa**), nitrogen is in the linker with a direct linkage to a phenyl residue (**1ab**) and a pure linker of carbon (**1ac**). In none of these examples was biphenyl detected after irradiation.

Linker derivates with non-flexible linker, without an attached π-system and a photolabile linker.

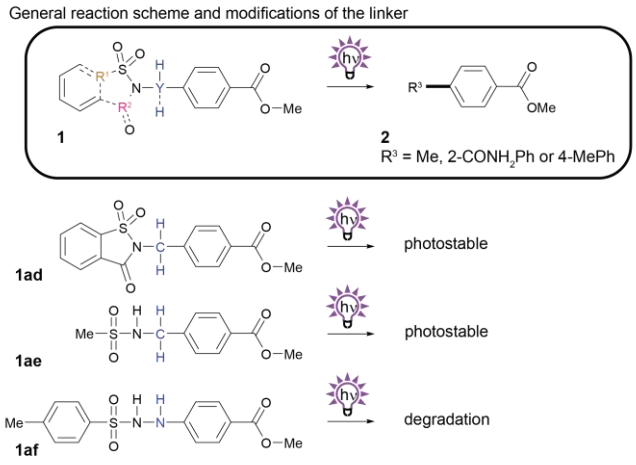
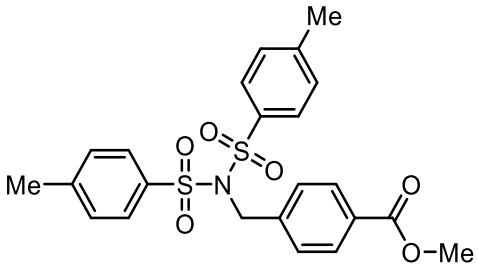


Figure S20: Control experiments for general photosplicing rules. General reaction scheme and structures of derivatives with a non-flexible linker (**1ad**), a linker without a phenyl residue on both sides (**1ae**), and a photolabile linker with a phenyl hydrazine part (**1af**).

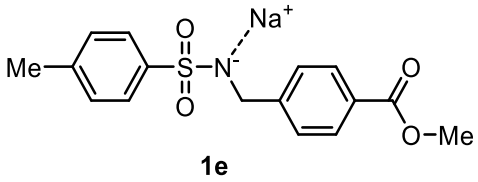
Chemical synthesis procedures for linker studies

1a, **1b**, **1c,** and **1i** are known compounds.[2, 3]



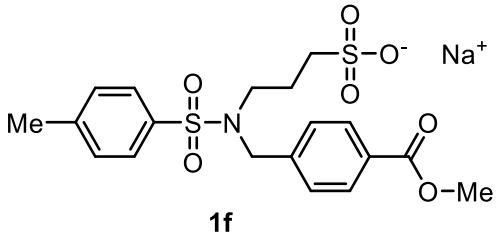
1d

*Compound **1d.*** Methyl 4-(((4-methyl-*N*-tosylphenyl)sulfonamido)methyl)benzoate. A solution of tosyl chloride (238.3 mg, 1.25 mmol, 2.58 eq.), methyl 4-(aminomethyl)benzoate hydrochloride (**1a**, 100.8 mg, 0.5 mmol, 1 eq.) and DMAP (214 mg, 1.75 mmol, 3.5 eq.) in DCM (2 mL) was prepared and stirred at room temperature. After 24 h, tosyl chloride (100 mg) and DMAP (100 mg) were added. After 48 h, tosyl chloride (200 mg) was added. After 72 h, DCM (3 mL) was added and the solution was sequentially washed with water (3 mL), aqueous hydrochloric acid (1 M, 3 mL), saturated $NaHCO_3$ solution (3 mL), and water (3 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by silica column chromatography (DCM, SiO_2, Rf 0.5) to give the title product (97.2 mg, 0.21 mmol, 41%) and sulfonamide **1a** (69.6 mg, 0.22 mmol, 44%) as a white solid.
^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) δ ppm 2.42 (s, 6 H), 3.94 (s, 3 H), 4.93 (s, 2 H), 7.23 (d, *J* = 7.96 Hz, 4 H), 7.42 (d, *J* = 8.48 Hz, 2 H), 7.66–7.70 (m, 4 H), 7.91 (d, *J* = 7.70 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C) δ ppm 21.6 (s, 2 C), 51.7 (s, 1 C), 52.2 (s, 1 C), 128.2 (s, 4 C), 128.8 (s, 2 C), 129.5 (s, 4 C), 129.6 (s, 2 C), 129.7 (s, 1 C), 136.8 (s, 2 C), 140.0 (s, 1 C), 144.9 (s, 2 C), 166.7 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{23}H_{24}NO_6S_2^+$: 474.1040; found: 474.1044. HRMS (ESI$^-$) calcd. for $C_{23}H_{22}NO_6S_2^-$: 472.0894; found: 472.0885.



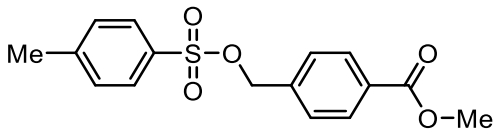
1e

*Compound **1e.*** Sodium (4-(methoxycarbonyl)benzyl)(tosyl)amide. A solution of methyl 4-(((4-methylphenyl)sulfonamido)methyl)benzoate (**1a**) (200 mg, 0.63 mmol, 1 eq) in MeOH (4 mL) was prepared and a solution of 30% NaOMe in MeOH (113 mg 120 µL, 3.3 mmol, 1 eq.) was added. The mixture was heated to 60 °C for 15 min and cooled to room temperature. The solvent was removed under reduced pressure, and the solid was dried under reduced pressure to yield the title product as large crystals (212 mg, 0.62 mmol, 99%).
^{1}H NMR (300 MHz, DMSO-d_6, 27 °C) δ ppm 2.37 (s, 3 H), 3.84 (s, 3 H), 4.03 (s, 2 H), 7.35 (d, *J* = 8.22 Hz, 2 H), 7.39 (d, *J* = 8.22 Hz, 2 H), 7.64–7.75 (m, 2 H), 7.84–7.89 (m, 2 H). ^{13}C NMR (75 MHz, DMSO-d_6, 27 °C) δ ppm 21.39 (s, 1 C), 40.16 (s, 1 C), 46.33 (s, 1 C), 52.53 (s, 1 C), 126.99 (s, 2 C), 128.17 (s, 2 C), 128.79 (s, 1 C), 129.54 (s, 2 C), 130.02 (s, 2 C), 138.49 (s, 1 C), 142.94 (s, 1 C), 144.19 (s, 1 C), 166.52 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{16}H_{18}NO_4S^+$: 320.0951; found: 320.0942. HRMS (ESI$^-$) calcd. for $C_{16}H_{16}NO_4S^-$: 318.0806; found: 318.0801.



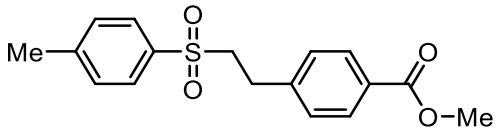
1f

*Compound **1f.*** Sodium 3-((*N*-(4-(methoxycarbonyl)benzyl)-4-methylphenyl)sulfonamido)propane-1-sulfonate. A solution of sodium (4-(methoxycarbonyl)benzyl)(tosyl)amide (**1e**, 206.4 mg, 0.60 mmol, 1 eq.) in DMSO (2 mL) was prepared and 1,3-propansultone (73.7 mg, 0.60 mmol, 1 eq.) was added and the reaction was monitored by TLC (cyclohexane:ethyl acetate, 2:1) until no protonated starting material (**1a**, SiO_2, Rf 0.3) was detected. After 1.5 h, the solvent was removed under reduced pressure to give the title compound (261.2 mg, 0.56 mmol, 93%) without further purification.
^{1}H NMR (300 MHz, D_2O, 27°C) δ ppm 1.78 (quin, *J* = 7.45 Hz, 2 H), 2.41 (s, 3 H), 2.63–2.70 (m, 1 H), 3.32 (t, *J* = 7.19 Hz, 2 H), 3.91 (s, 3 H), 4.42 (s, 2 H), 7.40 (br d, *J* = 8.48 Hz, 2 H), 7.42 (br d, *J* = 7.96 Hz, 2 H), 7.70 (d, *J* = 8.22 Hz, 2 H), 7.93 (d, *J* = 8.48 Hz, 2 H). ^{13}C NMR (75 MHz, D_2O, 27 °C) δ ppm 20.66 (s, 1 C), 23.20 (s, 1 C), 47.75 (s, 1 C), 48.13 (s, 1 C), 51.63 (s, 1 C), 52.63 (s, 1 C), 126.99 (s, 2 C), 128.25 (s, 2 C), 128.88 (s, 1 C), 129.73 (s, 2 C), 130.10 (s, 2 C), 134.39 (s, 1 C), 142.27 (s, 1 C), 145.26 (s, 1 C), 169.09 (s, 1 C). HRMS (ESI^-) calcd. for $C_{19}H_{24}NO_7S_2^+$: 442.0989; found: 442.0982. HRMS (ESI^-) calcd. for $C_{19}H_{22}NO_7S_2^-$: 440.0843; found: 440.0841.



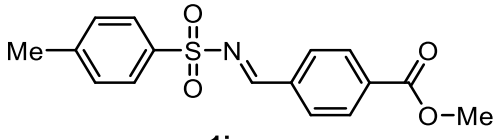
1g

*Compound **1g.*** Methyl 4-((tosyloxy)methyl)benzoate. A solution of methyl 4-(hydroxymethyl)benzoate (174 mg, 1.05 mmol, 1 eq), *N*,*N*-diisopropylethylamine (163 mg, 1.26 mmol, 219 µL, 1.2 eq) and catalytic amounts of DMAP (~2 mg) in DCM (3 mL) was prepared, then tosyl chloride (200 mg, 1.05 mmol, 1 eq.) was added. The reaction progress was monitored by TLC. After 45 min, the crude reaction mixture was directly subjected to column chromatography (DCM, SiO_2, Rf 0.60) to give the title product as a white crystalline solid (107 mg, 0.33 mmol, 32%).
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ ppm 2.46 (s, 3 H), 3.93 (s, 3 H), 5.12 (s, 2 H), 7.32–7.37 (m, 2 H), 7.33 (br s, 2 H), 7.82 (br d, *J* = 8.24 Hz, 2 H), 8.00 (br d, *J* = 8.24 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ ppm 21.66 (s, 1 C), 52.25 (s, 1 C), 70.80 (s, 1 C), 127.97 (s, 2 C), 127.98 (s, 2 C), 129.89 (s, 2 C), 129.94 (s, 2 C), 130.60 (s, 1 C), 132.99 (s, 1 C), 138.28 (s, 1 C), 145.11 (s, 1 C), 166.50 (s, 1 C). HRMS (ESI^+) calcd. for $C_{16}H_{17}O_5S^+$: 321.0791; found: 321.0795. HRMS (ESI^-) calcd. for $C_{16}H_{15}O_5S^-$: 319.0646; found: 319.0652.



1h

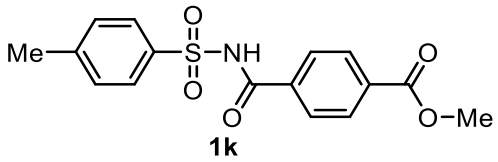
*Compound **1h.*** Methyl 4-(2-tosylethyl)benzoate. A solution of methyl 4-(2-bromoethyl)benzoate (155 mg, 64 mmol, 1.14 eq) and sodium 4-methylbenzenesulfinate (100 mg, 0.56 mmol, 1 eq) in dimethylformamide (2 mL) was prepared. The solution was stirred at 100 °C for 1 h and then poured into water (10 mL). The precipitate was washed with water (2 × 2 mL) and dried under vacuum to give the title product as a white powder (117.7 mg, 0.37 mmol, 66%).
^{1}H NMR (300 MHz, $CDCl_3$, 21 °C) δ ppm 2.5 (s, 3 H), 3.1–3.1 (m, 2 H), 3.3–3.4 (m, 2 H), 3.9 (s, 3 H), 7.2 (d, *J* = 8.48 Hz, 2 H), 7.4 (d, *J* = 7.71 Hz, 2 H), 7.8 (d, *J* = 7.55 Hz, 2 H), 7.9–8.0 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 21 °C) δ ppm 21.7 (s, 1 C), 28.9 (s, 1 C), 52.1 (s, 1 C), 57.1 (s, 1 C), 128.1 (s, 2 C), 128.4 (s, 2 C), 128.9 (s, 1 C), 130.1 (s, 2 C), 130.1 (s, 2 C), 135.9 (s, 1 C), 142.8 (s, 1 C), 145.0 (s, 1 C), 166.7 (s, 1 C). HRMS (ESI^+) calcd. for $C_{17}H_{19}O_4S^+$: 319.0999; found: 319.0997. HRMS (ESI^-) calcd. for $C_{17}H_{17}O_4S^-$: 317.0853; found: 317.0858.



1j

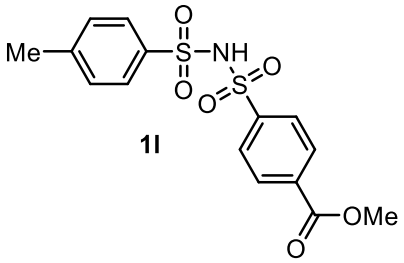
*Compound **1j.*** Methyl 4-((tosylimino)methyl)benzoate. A solution of 4-methylbenzenesulfonamide (8.65 g, 51 mmol, 1 eq.) and methyl 4-formylbenzoate (9.03 g, 55 mmol, 1.09 eq.) in toluene (125 mL) was prepared. P_4O_{10} (21.3 g, 75 mmol, 1.49 eq.) was added and the solution was refluxed under an argon atmosphere for 1 h. Then all solid components were removed by hot filtration under inert conditions. Upon cooling to room temperature crystals of the product formed. The supernatant was removed, and the crystalline solid was washed several times with pentane. The off-white product was dried under reduced pressure to give the title product (10.7 g,

33.5 mmol, 66%). Hint: the product is very sensitive towards hydrolysis in solution but can be stored as a solid under argon at -20 °C in a well-sealed flask.
^{1}H NMR (300 MHz, $CDCl_3$, 21 °C) δ ppm 2.46 (s, 3 H), 3.96 (s, 3 H), 7.38 (d, *J* = 7.96 Hz, 2 H), 7.90–7.93 (m, 2 H), 7.99–8.02 (m, 2 H), 8.13–8.17 (m, 2 H), 9.08 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) δ ppm 21.71 (s, 1 C), 52.64 (s, 1 C), 128.29 (s, 2 C), 129.94 (s, 2 C), 130.14 (s, 2 C), 131.04 (s, 2 C), 134.59 (s, 1 C), 135.32 (s, 1 C), 135.89 (s, 1 C), 145.00 (s, 1 C), 165.91 (s, 1 C), 168.87 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{16}H_{16}NO_4S^+$: 318.0795; found: 318.0793.



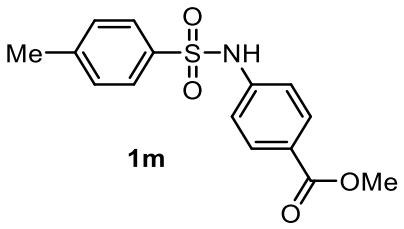
1k

Compound ***1k.*** Methyl 4-(tosylcarbamoyl)benzoate. A solution of 4-methylbenzenesulfonamide (516.6 mg, 3 mmol, 1 eq.), DMAP (1.8 mg, 15 µmol, 0.5 mol-%) and triethylamine (799.6 mg, 1045 µL, 7.5 mmol, 2.5 eq.) in ethyl acetate (6 mL) was prepared. A solution of methyl-4-(chlorcarbonyl)benzoate (655.4 mg, 3.3 mmol, 1.1 eq.) in toluene (2.64 mL) was added slowly and stirred at 55 °C for 1 h. Then the reaction mixture was diluted with ethyl acetate (40 mL) and washed with water (10 mL), hydrochloric acid (10 mL, 2 M), Na_2CO_3 solution (10 mL, saturated) and NaCl solution (20 mL, saturated). The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was recrystallized from water/ethanol (*v*/*v* = 1/1) and dried under reduced pressure to give the title product as white crystals (847.2 mg, 2.54 mmol, 85%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ ppm 2.46 (s, 3 H), 3.94 (s, 3 H), 7.38 (d, *J* = 7.96 Hz, 2 H), 7.88–7.92 (m, 2 H), 8.04–8.07 (m, 2 H), 8.07–8.10 (m, 2 H), 9.57 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ ppm 21.76 (s, 1 C), 52.61 (s, 1 C), 127.96 (s, 2 C), 128.72 (s, 2 C), 129.73 (s, 2 C), 130.02 (s, 2 C), 134.30 (s, 1 C), 134.90 (s, 1 C), 135.15 (s, 1 C), 145.55 (s, 1 C), 163.72 (s, 1 C), 165.91 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{16}H_{16}NO_5S^+$: 334.0744; found: 334.0740. HRMS (ESI$^-$) calcd. for $C_{16}H_{14}NO_5S^-$: 332.0598; found: 322.0601.



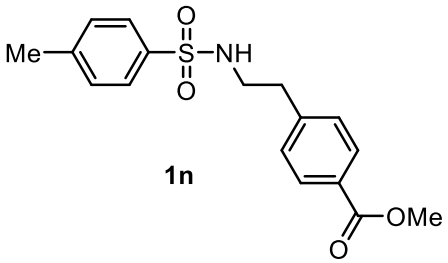
1l

Compound ***1l.*** Methyl 4-(*N*-tosylsulfamoyl)benzoate. A solution of 4-methylbenzensulfonamide (99 mg, 0.58 mmol, 1 eq.), methyl-4-(chlorsulfonyl)benzoate (203 mg, 0.87 mmol, 1,5 eq.) and *N*,*N*-diisopropylethylamine (0.93 g, 1.3 mL, 7.46 mmol, 12 eq.) in MeCN (10 mL) was prepared and stirred at 80 °C for 12 h. Then the reaction mixture was diluted with ethyl acetate (20 mL) and washed with hydrochloric acid (20 mL, 2 M), Na_2CO_3 solution (10 mL, saturated) and NaCl solution (20 mL, saturated). The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was recrystallized from ethyl acetate and dried under reduced pressure to give the title compound as white crystals (165 mg, 0,45 mmol, 77%).
^{1}H NMR (500 MHz, DMSO-d_6, 27 °C) δ ppm 2.30–2.33 (s, 3 H), 3.86–3.90 (m, 3 H), 7.10–7.18 (m, 2 H), 7.47–7.55 (m, 2 H), 7.74 (d, *J* = 7.36 Hz, 2 H), 7.88–7.97 (m, 2 H). ^{13}C NMR (126 MHz, DMSO-d_6, 27 °C) δ ppm 21.30 (s, 1 C), 52.81 (s, 1 C), 126.64 (s, 2 C), 127.00 (s, 2 C), 128.73 (s, 2 C), 129.30 (s, 2 C), 131.07 (s, 1 C), 140.26 (s, 1 C), 143.84 (s, 1 C), 151.03 (s, 1 C), 166.15 (s, 1 C). HRMS (ESI$^-$) calcd. for $C_{15}H_{14}NO_6S_2^-$: 368,0268; found: 368,0261.



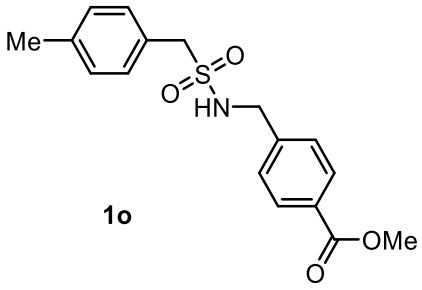
1m

*Compound **1m.*** Methyl 4-((4-methylphenyl)sulfonamido)benzoate. A solution of methyl 4-aminobenzoate (95 mg, 0.63 mmol, 1.2 eq.) and 4-methylbenzensulfonylchlorid (100 mg, 0.52 mmol, 1 eq.) in dimethylformamide (2 mL) was prepared and stirred at 60 °C for 30 min. Then the solution was poured into water (15 mL) and the precipitate was washed with water (2 × 5 mL) and dried under reduced pressure to give the title product as a white powder (8.4 mg, 0.03 mmol, 5%).
^{1}H NMR (600 MHz, $CDCl_3$, 27 °C) δ ppm 2.39 (s, 3 H), 3.88 (s, 3 H), 6.98 (s, 1 H), 7.13 (d, *J* = 8.71 Hz, 2 H), 7.25 (d, *J* = 8.39 Hz, 2 H) 7.73 (d, *J* = 8.30 Hz, 2 H), 7.92 (d, *J* = 8.67 Hz, 2 H). ^{13}C NMR (151 MHz, $CDCl_3$, 29 °C) δ ppm 21.53 (s, 1 C), 52.06 (s, 1 C), 119.14 (s, 2 C), 126.35 (s, 1 C), 127.27 (s, 2 C), 129.84 (s, 2 C), 131.10 (s, 2 C), 135.89 (s, 1 C), 140.92 (s, 1 C), 144.41 (s, 1 C), 166.33 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{15}H_{16}NO_4S^+$: 306.0795; found: 306.0787. HRMS (ESI$^-$) calcd. for $C_{15}H_{14}NO_4S^-$: 304.0649; found: 304.0647.



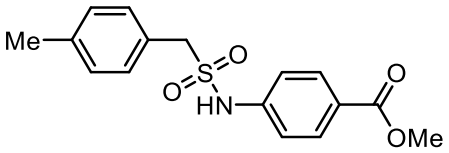
1n

*Compound **1n.*** Methyl-4-(2-((4-methylphenyl)sulfonamido)ethyl)benzoate. A solution of 4-methylbenzensulfonylchlorid (190.6 mg, 1 mmol, 1 eq.), methyl-4-(aminoethyl)benzoate hydrochloride (215.7 mg, 1 mmol, 1 eq.) and *N*,*N*-diisopropylethylamine (284.4 mg, 383.2 µL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was prepared and stirred at room temperature for 1 h. Then ethyl acetate (40 mL) was added, and the solution was washed with water (20 mL), hydrochloric acid (20 mL, 1 M) and NaCl solution (20 mL, saturated). The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was recrystallized from water/ethanol (*v*/*v* = 1/1) and dried under reduced pressure to give the title compound as white crystals (274 mg, 0,82 mmol, 82%).
^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) δ ppm 2.43–2.46 (m, 3 H), 2.85 (t, *J* = 6.94 Hz, 2 H), 3.26 (q, *J* = 6.94 Hz, 2 H), 3.92–3.94 (m, 3 H), 4.61 (br s, 1 H), 7.17 (d, *J* = 7.36 Hz, 2 H), 7.30 (d, *J* = 7.48 Hz, 2 H), 7.70 (d, *J* = 7.84 Hz, 2 H), 7.92–7.96 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C) δ ppm 21.49 (s, 1 C), 35.90 (s, 1 C), 43.84 (s, 1 C), 52.09 (s, 1 C), 127.03 (s, 2 C), 128.70 (s, 1 C), 128.77 (s, 2 C), 129.73 (s, 2 C), 129.95 (s, 2 C), 136.77 (s, 1 C), 143.15 (s, 1 C), 143.53 (s, 1 C), 166.83 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{20}NO_4S^+$: 334.1108; found: 334.1107. HRMS (ESI$^-$) calcd. for $C_{17}H_{18}NO_4S^-$: 332.0962; found: 332.0964.



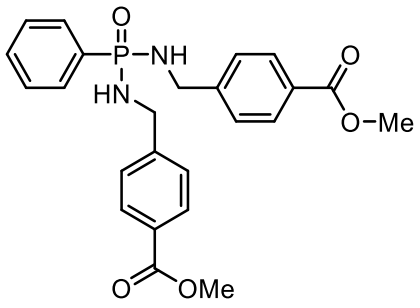
1o

*Compound **1o.*** Methyl 4-(((*p*-tolylmethyl)sulfonamido)methyl)benzoate. A solution of *p*-tolylmethanesulfonyl chloride (100 mg, 0.49 mmol, 1 eq.), methyl 4-(aminomethyl)benzoate hydrochloride (120 mg, 0.59 mmol, 1.2 eq.) and *N*,*N*-diisopropylethylamine (126 mg, 1.66 µL, 0.98 mmol, 2 eq.) in DCM (2 mL) was prepared and stirred at room temperature for 1 h. Then the mixture was directly subjected to column chromatography (DCM with 1% MeOH, SiO_2, Rf 0.33) to give the title product as a white solid (3.3 mg, 0.01 mmol, 2%).
^{1}H NMR (300 MHz, $CDCl_3$, 22 °C) δ ppm 2.37 (s, 3 H), 3.93 (s, 3 H), 4.19 (d, *J* = 5.91 Hz, 2 H), 4.23 (s, 2 H), 4.46 (br d, *J* = 5.14 Hz, 1 H), 7.16–7.21 (m, 2 H), 7.21–7.26 (m, 2 H), 7.36 (m, *J* = 8.48 Hz, 2 H), 7.98–8.05 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 22 °C) δ ppm 21.23 (s, 1 C), 47.26 (s, 1 C), 52.23 (s, 1 C), 59.21 (s, 1 C), 125.94 (s, 1 C), 127.78 (s, 2 C), 129.63 (s, 2 C), 129.86 (s, 1 C), 130.08 (s, 2 C), 130.47 (s, 2 C), 138.93 (s, 1 C), 142.00 (s, 1 C), 166.67 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{20}NO_4S^+$: 334.1108; found: 334.1104. HRMS (ESI$^-$) calcd. for $C_{17}H_{18}NO_4S^-$: 332.0962; found: 332.0965.



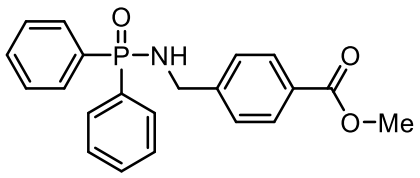
1p

Compound ***1p.*** Methyl 4-((*p*-tolylmethyl)sulfonamido)benzoate. A solution of *p*-tolylmethanesulfonyl chloride (100 mg, 0.49 mmol, 1 eq.), methyl 4-aminobenzoate (81 mg, 0.54 mmol, 1.1 eq.) and *N*,*N*-diisopropylethylamine (76 mg, 100 µL, 0.59 mmol, 1.2 eq.) in DCM (2 mL) was prepared and stirred for 2 h at room temperature. Then *p*-tolylmethanesulfonyl chloride (50 mg, 0.24 mmol, 0.5 eq.) was added and the mixture was stirred for 18 h. The reaction mixture was washed with water (2 mL) and hydrochloric acid (2 mL, 1 M), filtered and dried over Na_2SO_4. The crude product was purified by column chromatography (DCM with 2% MeOH, SiO_2, Rf 0.48) to give the title product as a white solid (7 mg, 0.02 mmol, 5%).
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ ppm 2.35 (s, 3 H), 3.93 (s, 3 H), 4.35 (s, 2 H), 6.52 (s, 1 H), 7.10 (d, *J* = 7.30 Hz, 2 H), 7.13–7.17 (m, 4 H), 8.02 (dt, *J* = 8.47, 1.93 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ ppm 21.19 (s, 1 C), 52.14 (s, 1 C), 57.66 (s, 1 C), 117.90 (s, 2 C), 125.05 (s, 1 C), 126.02 (s, 1 C), 129.66 (s, 2 C), 130.63 (s, 2 C), 131.39 (s, 2 C), 139.30 (s, 1 C), 141.38 (s, 1 C), 166.33 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{16}H_{18}NO_4S^+$: 320.0951; found: 320.0949. HRMS (ESI$^-$) calcd. for $C_{16}H_{16}NO_4S^-$: 318.0806; found: 318.0802.



1q

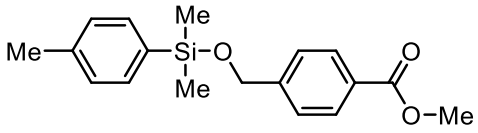
Compound ***1q.*** Dimethyl 4,4'-(((phenylphosphoryl)bis(azanediyl))bis(methylene))dibenzoate. A solution of phenylphosphonic dichloride (200 mg, 145 µL, 1.03 mmol, 1 eq.), methyl-4-(aminoethyl)benzoate hydrochloride (455 mg, 2.26 mmol, 2.2 eq.) and *N*,*N*-diisopropylethylamine (597 mg, 742 µL, 4.62 mmol, 4.5 eq) in DCM (2 mL) was prepared and stirred at room temperature for 30 min. Then the mixture was directly subjected to column chromatography (DCM with 5% MeOH, SiO_2, Rf 0.27) to give the title compound (421.6 mg, 0.94 mmol, 91%).
^{1}H NMR (500 MHz, MeCN-d_3, 27 °C) δ ppm 3.86 (s, 6 H), 4.00 (br s, 2 H), 4.08–4.15 (m, 4 H), 7.40 (br d, *J* = 8.09 Hz, 4 H), 7.45 (td, *J* = 7.36, 3.20 Hz, 2 H), 7.49–7.56 (m, 1 H), 7.81 (br dd, *J* = 12.28, 7.32 Hz, 2 H), 7.88 (d, *J* = 8.16 Hz, 4 H). ^{13}C NMR (126 MHz, MeCN-d_3, 27 °C) δ ppm 44.97 (s, 2 C), 52.97 (s, 2 C), 128.72 (s, 4 C), 129.66 (d, *J* = 13.30 Hz, 2 C), 130.10 (s, 2 C), 130.60 (s, 4 C), 132.74 (d, *J* = 2.88 Hz, 1 C), 132.86 (d, *J* = 9.66 Hz, 2 C), 135.15 (d, *J* = 151.84 Hz, 1 C), 147.95 (d, *J* = 5.39 Hz, 2 C), 167.94 (s, 2 C). ^{31}P NMR (203 MHz, MeCN-d_3, 27 °C) δ ppm 20.08 (s, 1 P). HRMS (ESI$^+$) calcd. for $C_{24}H_{26}N_2O_5P^+$: 453.1574; found: 453.1575. HRMS (ESI$^-$) calcd. for $C_{24}H_{24}N_2O_5P^-$: 451.1428; found: 451.1425.



1r

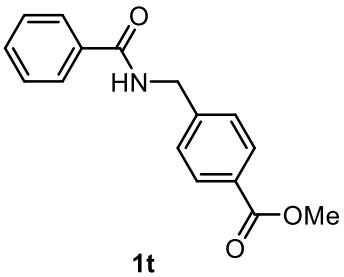
Compound ***1r.*** Methyl 4-(((diphenylphosphoryl)amino)methyl)benzoate. A solution of diphenylphosphinic chloride (100 mg, 79 µL, 0.42 mmol, 1 eq.), methyl-4-(aminoethyl)benzoate hydrochloride (85 mg, 0.42 mmol, 1 eq.) and *N*,*N*-diisopropylethylamine (131 mg,

177 µL, 1.01 mmol, 2.4 eq.) was dissolved in DCM (3 mL) and stirred at room temperature for 1 h. Then the solution was washed with hydrochloric acid (2 mL,1 M), $NaHCO_3$ solution (2 mL, saturated) and NaCl solution (2 mL, saturated). The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography (DCM acetone 7:3, SiO_2, Rf 0.40) to give the title compound (107 mg, 0.29 mmol, 70%).
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ ppm 3.81 (br d, *J* = 5.95 Hz, 1 H), 3.85 (s, 3 H), 4.10–4.14 (m, 2 H), 7.37–7.42 (m, 6 H), 7.42–7.48 (m, 2 H), 7.85–7.91 (m, 4 H), 7.93 (d, *J* = 8.24 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ ppm 44.41 (s, 1 C), 52.04 (s, 1 C), 127.54 (s, 2 C), 128.58 (d, *J* = 13.30 Hz, 4 C), 129.11 (s, 1 C), 129.83 (s, 2 C), 132.14 (d, *J* = 129.50 Hz, 2 C), 131.96 (d, *J* = 3.01 Hz, 2 C), 132.11 (d, *J* = 9.79 Hz, 4 C), 145.05 (d, *J* = 7.78 Hz, 1 C), 166.83 (s, 1 C). ^{31}P NMR (203 MHz, $CDCl_3$, 27 °C) δ ppm 24.20 (s, 1 P). HRMS (ESI^+) calcd. for $C_{21}H_{21}NO_3P^+$: 366.1254; found: 366.1243. HRMS (ESI^-) calcd. for $C_{21}H_{19}NO_3P^-$: 364.1108; found: 364.1106.



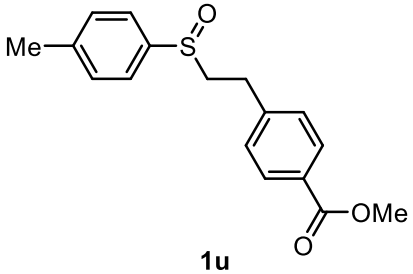
1s

Compound ***1s.*** Methyl 4-(((dimethyl(*p*-tolyl)silyl)oxy)methyl)benzoate. A solution of chlorodimethyl(*p*-tolyl)silane (100 mg, 0.54 mmol, 1 eq.), methyl 4-(hydroxymethyl)benzoate (90 mg, 0.54 mmol. 1 eq.) and *N*,*N*-diisopropylethylamine (84 mg, 113 µL, 0.84 mmol, 1.2 eq.) in DCM (2 mL) was prepared and stirred at room temperature for 30 min. The mixture was directly subjected to column chromatography (DCM, SiO_2, Rf 0.9) and dried under vacuum to give the title product as a colorless oil (127.6 mg, 0.41 mmol, 75%).
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 0.33 (s, 6 H), 2.37 (s, 3 H), 3.94 (s, 3 H), 4.80 (s, 2 H), 7.19 (d, *J* = 7.45 Hz, 2 H), 7.42–7.50 (m, 4 H), 7.99–8.13 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 0.93 (s, 2 C), 21.47 (s, 1 C), 52.08 (s, 1 C), 64.73 (s, 1 C), 126.45 (s, 2 C), 128.48 (s, 2 C), 129.39 (s, 1 C), 129.85 (s, 2 C), 133.06 (s, 2 C), 136.34 (s, 1 C), 139.04 (s, 1 C), 145.89 (s, 1 C), 166.90 (s, 1 C). HRMS (ESI^-) calcd. for $C_{18}H_{21}O_3Si^-$: 313.1265; found: 313.1281.



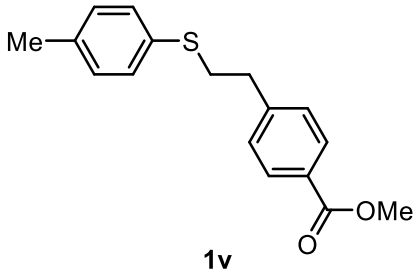
1t

Compound ***1t.*** Methyl 4-(benzamidomethyl)benzoate. A solution of benzoyl chloride (63.4 mg, 0.45 mmol, 51 µL, 1 eq.), methyl 4-(aminomethyl)benzoate hydrochloride (100 mg, 0.50 mmol, 1.1 eq) in DCM (3 mL) was prepared and *N*,*N*-diisopropylethylamine (70 mg, 0.54 mmol, 92 µL, 1.2 eq) was added and stirred for 12 h. The organic phase was sequentially washed with water (3 mL), aqueous hydrochloric acid (1 M, 3 mL), and water (3 mL), then dried with sodium sulfate, filtered and the solvent was evaporated. The crude product was purified by silica column chromatography ($CHCl_3$/ethyl acetate, *v*/*v* = 9/1, SiO_2, Rf 0.29) to yield the title product (92.8 mg, 0.3 mmol, 67%).
^{1}H NMR (300 MHz, $CDCl_3$, 24 °C) δ ppm 3.92 (s, 3 H), 4.71 (d, *J* = 5.91 Hz, 2 H), 6.68 (br s, 1 H), 7.39–7.43 (m, 2 H), 7.43–7.49 (m, 2 H), 7.49–7.56 (m, 1 H), 7.79–7.86 (m, 2 H), 8.01 (d, *J* = 7.55 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ ppm 43.69 (s, 1 C), 52.14 (s, 1 C), 127.00 (s, 2 C), 127.59 (s, 2 C), 128.66 (s, 2 C), 129.37 (s, 1 C), 130.03 (s, 2 C), 131.73 (s, 1 C), 134.11 (s, 1 C), 143.50 (s, 1 C), 166.82 (s, 1 C), 167.49 (s, 1 C). HRMS (ESI^+) calcd. for $C_{16}H_{16}NO_3^+$: 270.1125; found: 270.1124.



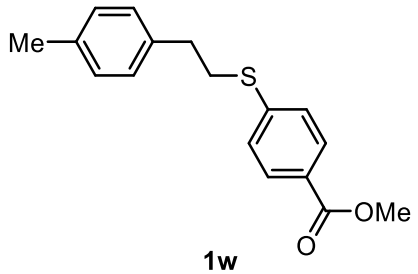
1u

Compound ***1u.*** Methyl 4-(2-(*p*-tolylsulfinyl)ethyl)benzoate. A solution of methyl 4-(2-(*p*-tolylthio)ethyl)benzoate (**1v**, 33.3 mg, 0.12 mmol, 1 eq.) in MeOH (4 mL) was prepared and H_2O_2 (30% solution in water, 330 µL, 370 µL, 3.26 mmol, 28 eq.) was added dropwise. The reaction was stirred at room temperature overnight and the solution was concentrated under a stream of argon to 1 mL. Then brine (5 mL) and DCM (5 mL) were added, and the water phase was extracted two additional times with DCM (3 mL). The combined organic extracts were dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (DCM: ethyl acetate 1:1, SiO_2, Rf 0.6) to give the title product (30.4 mg, 0.1 mmol, 86%) as a white solid.
^{1}H NMR (300 MHz, $CDCl_3$, 21 °C) δ ppm 2.44 (s, 3 H), 2.90–3.00 (m, 1 H), 3.03–3.10 (m, 2 H), 3.10–3.20 (m, 1 H), 3.91 (s, 3 H), 7.24–7.28 (m, 2 H), 7.35 (d, *J* = 7.96 Hz, 2 H), 7.52–7.56 (m, 2 H), 7.97 (d, *J* = 7.54 Hz, 2 H).^{13}C NMR (75 MHz, $CDCl_3$, 21 °C) δ ppm 21.39 (s, 1 C), 28.05 (s, 1 C), 52.06 (s, 1 C), 57.51 (s, 1 C), 124.06 (s, 2 C), 128.57 (s, 2 C), 128.63 (s, 1 C), 130.00 (s, 2 C), 130.02 (s, 2 C), 139.80 (s, 1 C), 141.72 (s, 1 C), 144.15 (s, 1 C), 166.79 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{19}O_3S^+$: 303.1049; found: 303.1043.



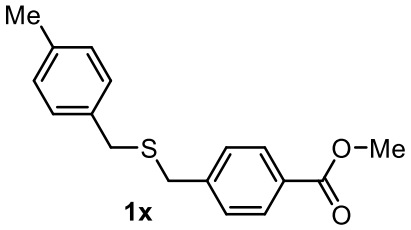
1v

Compound ***1v.*** Methyl 4-(2-(*p*-tolylthio)ethyl)benzoate. Method A: A solution of 4-methylbenzenethiol (100 mg, 0.81 mmol, 1 eq.), methyl 4-(2-bromoethyl)benzoate (215 mg, 0.89 mmol, 1.1 eq.) and *N*,*N*-diisopropylethylamine (114 mg, 151 µL, 0.89 mmol, 1.1 eq.) in DCM (1 mL) was prepared and stirred for 1.5 h at room temperature. The mixture was subjected to column chromatography (ethyl acetate/cyclohexane *v*/*v* = 1/9, SiO_2, Rf 0.48) to give the title compound as a white solid (191.1 mg, 0.67 mmol, 83%).
Method B: 4-Methylbenzenethiol (100 mg, 0.81 mmol, 1.1 eq.) and methyl 4-vinylbenzoate (119 mg, 0.73 mmol, 1 eq) were mixed, sonicated for 1 minute at 40 °C in a water bath, then left at room temperature for 1.5 h. The mixture was subjected to column chromatography (ethyl acetate/cyclohexane *v*/*v* = 1/9, SiO_2, Rf 0.48) to give the title compound as a white solid (154.2 mg, 0.54 mmol, 74%).
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 2.35 (s, 3 H), 2.93–2.99 (m, 2 H), 3.12–3.18 (m, 2 H), 3.93 (s, 3 H), 7.13–7.16 (m, 2 H), 7.25–7.28 (m, 2 H), 7.28–7.32 (m, 2 H), 7.97–8.00 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 21.04 (s, 1 C), 35.56 (s, 1 C), 35.72 (s, 1 C), 52.03 (s, 1 C), 128.38 (s, 1 C), 128.59 (s, 2 C), 129.80 (s, 2 C), 129.80 (s, 2 C), 130.46 (s, 2 C), 132.06 (s, 1 C), 136.53 (s, 1 C), 145.64 (s, 1 C), 166.98 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{19}O_2S^+$: 287.1100; found: 287.1100.



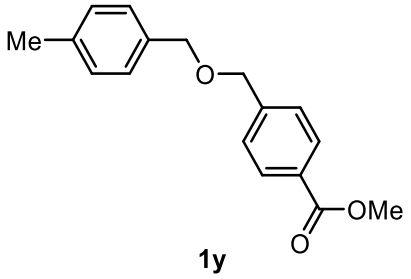
1w

Compound ***1w.*** Methyl 4-((4-methylphenethyl)thio)benzoate. Methyl 4-mercaptobenzoate (123.5 mg, 0.73 mmol, 1 eq.) was dissolved in MeOH (2 mL) and a solution of 30% NaOMe in MeOH (132 mg 140 µL, 0.73 mmol, 1 eq) was added. Then 1-(2-bromoethyl)-4-methylbenzene (161 mg, 123 µL, 0.80 mmol, 1.1 eq) was added and the solution was stirred for 12 h at room temperature. The mixture was cooled to -30 °C and the product was separated by filtration to give large crystals, which were then washed with ice-cold MeOH and dried under reduced pressure to give the title product (159 mg 0.55 mmol, 75%).
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 2.34 (s, 3 H), 2.92–2.98 (m, 2 H), 3.20–3.26 (m, 2 H), 3.91 (s, 3 H), 7.10–7.16 (m, 2 H), 7.12–7.16 (m, 2 H), 7.29–7.34 (m, 2 H), 7.91–7.98 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 21.03 (s, 1 C), 33.71 (s, 1 C), 34.71 (s, 1 C), 52.02 (s, 1 C), 126.53 (s, 2 C), 126.79 (s, 1 C), 128.34 (s, 2 C), 129.27 (s, 2 C), 129.94 (s, 2 C), 136.23 (s, 1 C), 136.66 (s, 1 C), 143.84 (s, 1 C), 166.77 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{19}O_2S^+$: 287.1100; found: 287.1098. HRMS (ESI$^-$) calcd. for $C_{17}H_{17}O_2S^-$: 285.0955; found: 285.0953.



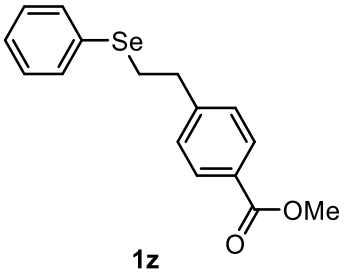
1x

*Compound **1x.*** Methyl 4-(((4-methylbenzyl)thio)methyl)benzoate. A solution of *p*-tolylmethanethiol (51 mg, 0.36 mmol, 1 eq.), methyl 4-(bromomethyl)benzoate (89 mg, 0.38 mmol, 1.05 eq) and K_2CO_3 (100 mg, 0.72 mmol, 2 eq.) in dimethylformamide (2 mL) was prepared and stirred at room temperature. After 3 h, the reaction mixture was poured into water (25 mL). The precipitate was filtered washed with water (2 × 10 mL) and dried under reduced pressure to give the title product as a white solid (89 mg, 0.31 mmol, 86%).
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C) δ ppm 2.36 (s, 3 H), 3.58 (s, 2 H), 3.64 (s, 2 H), 3.94 (s, 3 H), 7.13–7.19 (m, 4 H), 7.36–7.38 (m, 2 H), 8.00–8.02 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$, 27 °C) δ ppm 21.10 (s, 1 C), 35.28 (s, 1 C), 35.36 (s, 1 C), 52.08 (s, 1 C), 128.86 (s, 1 C), 128.89 (s, 2 C), 129.02 (s, 2 C), 129.23 (s, 2 C), 129.79 (s, 2 C), 134.61 (s, 1 C), 136.78 (s, 1 C), 143.74 (s, 1 C), 166.92 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{19}O_2S^+$: 287.1100; found: 287.1095.



1y

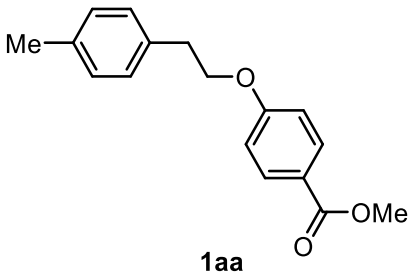
*Compound **1y.*** Methyl 4-(((4-methylbenzyl)oxy)methyl)benzoate. A solution of 1-(bromomethyl)-4-methylbenzene (100 mg, 0.54 mmol, 1 eq.), methyl 4-(hydroxymethyl)benzoate (134 mg, 0.81 mmol, 1.5 eq.) and K_2CO_3 (150 mg, 1.08 mmol, 2 eq.) in MeCN (2 mL) was prepared and stirred at 55 °C for 24 h. Then the organic solvent was evaporated, and the residue was dissolved in water (2 mL) and DCM (2 mL). The organic phase was washed with NaOH (2 × 2 mL, 1 M) and water (2 mL), then evaporated under reduced pressure. The crude product was purified by column chromatography (DCM, SiO_2, Rf 0.5) to give the title product as a white solid (36.4 mg, 0.13 mmol, 25%).
^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) δ ppm 2.38 (s, 3 H), 3.94 (s, 3 H), 4.56 (s, 2 H), 4.61 (s, 2 H), 7.17–7.23 (m, 2 H), 7.25–7.31 (m, 2 H), 7.45 (d, *J* = 8.48 Hz, 2 H), 8.04 (d, *J* = 7.77 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C) δ ppm 21.20 (s, 1 C), 52.11 (s, 1 C), 71.26 (s, 1 C), 72.38 (s, 1 C), 127.29 (s, 2 C), 127.95 (s, 2 C), 129.17 (s, 2 C), 129.32 (s, 1 C), 129.72 (s, 2 C), 134.83 (s, 1 C), 137.57 (s, 1 C), 143.73 (s, 1 C), 167.01 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{19}O_3^+$: 271.1329; found: 271.1327.



1z

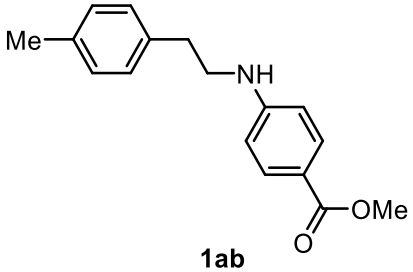
*Compound **1z.*** Methyl 4-(2-(phenylselanyl)ethyl)benzoate. A solution of benzeneselenol (100 mg, 68 µL, 0.63 mmol, 1.3 eq.), methyl 4-(2-bromoethyl)benzoate (119 mg, 0.49 mmol, 1 eq.) and *N*,*N*-diisopropylethylamine (126 mg, 170 µL, 0.98 mmol, 2 eq.) in DCM (2 mL) was prepared and stirred at room temperature for 13 h. Then the reaction mixture was directly subjected to column chromatography (DCM, SiO_2, Rf 0.78) to give the title product as a white solid (114.6 mg, 0.36 mmol, 73%).
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ ppm 3.01–3.12 (m, 2 H), 3.12–3.22 (m, 2 H), 3.93 (s, 3 H), 7.27 (d, *J* = 8.32 Hz, 2 H), 7.28–7.33 (m, 1 H), 7.28–7.33 (m, 2 H), 7.50–7.56 (m, 2 H), 7.99 (d, *J* = 8.24 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$, 42 °C) δ ppm 28.14 (s, 1 C), 36.57 (s, 1 C), 51.94 (s, 1 C), 127.07 (s, 2 C), 128.43 (s, 2 C), 128.48 (s, 1 C), 129.12 (s, 1 C), 129.84 (s, 2 C), 129.91 (s, 1 C), 132.93

(s, 2 C), 146.26 (s, 1 C), 166.95 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{16}H_{17}O_2Se^+$: 321.0388; found: 321.0390. HRMS (ESI$^-$) calcd. for $C_{16}H_{15}O_2Se^-$: 319.0243; found: 319.0246.



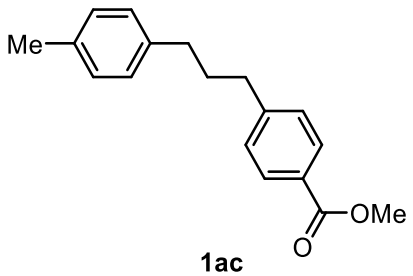
1aa

Compound ***1aa.*** Methyl 4-(4-methylphenethoxy)benzoate. A solution of 1-(2-bromoethyl)-4-methylbenzene (100 mg, 0.50 mmoL, 1 eq.), methyl 4-hydroxybenzoate (92 mg, 0.60 mmol, 1.2 eq), and *N*,*N*-diisopropylethylamine (84 mg, 114 µL, 0.65 mmol, 1.3 eq.) in DCM (3 mL) was prepared and stirred at room temperature for 1 h. Then Cs_2CO_3 (164 mg, 0.5 mmol, 1 eq.) was added and the solution was stirred at room temperature for 5 days. The mixture was subjected to column chromatography (DCM, SiO_2, Rf 0.48) to give the title product as a colorless oil, which crystallized after some days (32.4 mg, 0.12 mmol, 24%).
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 2.36 (s, 3 H), 3.10 (t, *J* = 7.06 Hz, 2 H), 3.90 (s, 3 H), 4.21 (t, *J* = 7.06 Hz, 2 H), 6.90–6.95 (m, 2 H), 7.14–7.22 (m, 4 H), 7.97–8.02 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 21.05 (s, 1 C), 35.22 (s, 1 C), 51.83 (s, 1 C), 68.98 (s, 1 C), 114.14 (s, 2 C), 122.59 (s, 1 C), 128.88 (s, 2 C), 129.26 (s, 2 C), 131.59 (s, 2 C), 134.74 (s, 1 C), 136.21 (s, 1 C), 162.64 (s, 1 C), 166.87 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{19}O_3^+$: 271.1329; found: 271.1327.



1ab

Compound ***1ab.*** Methyl 4-((4-methylphenethyl)amino)benzoate. A solution of methyl 4-aminobenzoate (100 mg, 0.66 mmol, 1 eq) and 1-(2-bromoethyl)-4-methylbenzene (145 mg, 0.73 mmol, 111 µL, 1.1 eq) and *N*,*N*-diisopropylethylamine (171 mg, 230 µL, 1.32 mmol, 2 eq) was prepared and stirred at 50 °C overnight. The next day, 1-methyl-4-(2-(methylsulfonyl)ethyl)benzene (50 mg, 0.25 mmol, 0.38 eq) was added and stirred for 4 h. The mixture was subjected to column chromatography (DCM, SiO_2, Rf 0.42) to give the title product (80 mg, 0.30 mmol, 45%) as a white solid.
1H NMR (500 MHz, $CDCl_3$, 27 °C) δ ppm 2.36 (s, 3 H), 2.92 (t, J = 6.97 Hz, 2 H), 3.46 (t, J = 7.02 Hz, 2 H), 3.87 (s, 3 H), 4.07–4.32 (m, 1 H), 6.56–6.59 (m, 2 H), 7.12–7.14 (m, 2 H), 7.14–7.17 (m, 2 H), 7.87–7.90 (m, 2 H). 13C NMR (126 MHz, $CDCl_3$, 27 °C) δ ppm 21.03 (s, 1 C), 34.81 (s, 1 C), 44.48 (s, 1 C), 51.51 (s, 1 C), 111.64 (s, 2 C), 118.49 (s, 1 C), 128.62 (s, 2 C), 129.40 (s, 2 C), 131.58 (s, 2 C), 135.59 (s, 1 C), 136.21 (s, 1 C), 151.71 (s, 1 C), 167.30 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{17}H_{20}NO_2^+$: 270.1489; found: 270.1484.

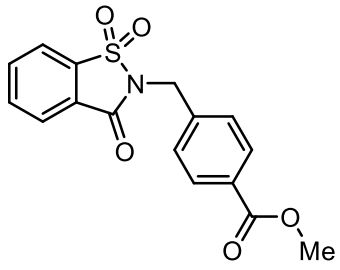


1ac

Compound ***1ac.*** Methyl 4-(3-(*p*-tolyl)propyl)benzoate: The irradiation was performed under nitrogen atmosphere with degassed solvents in analogy to Lima *et al*.[4] A solution of 4,4,5,5-tetramethyl-2-(4-methylbenzyl)-1,3,2-dioxaborolane (101 mg, 0.44 mmol, 1 eq.),

methyl 4-vinylbenzoate (279 mg, 1.74 mmol, 4 eq.), DMAP (30 mg, 0.24 mmol, 0.55 eq.) and [4,4'-bis(tert-butyl)-2,2'-bipyridine]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate (25 mg, 0.022 mmol, 0.05 eq.) in MeOH:acetone (1:1, 10 mL) was prepared. The solution was irradiated with a 395 nm UV LED in the flask photoreactor for 6 h. Then the solvent was removed under reduced pressure, and volatile products were removed under vacuum (< 1 mbar) at 70 °C water bath temperature. The crude product was purified by column chromatography (DCM, SiO_2, Rf 0.83) to give the title product as a colorless oil (22 mg, 0.82 mmol, 19%).

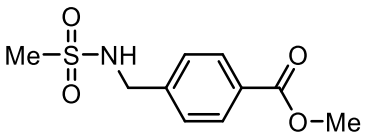
^{1}H NMR (300 MHz, CD_2Cl_2, 21 °C) δ ppm 1.95–2.01 (m, 2 H), 2.35 (s, 3 H), 2.61–2.68 (m, 2 H), 2.71–2.76 (m, 2 H), 3.91 (s, 3 H), 7.09–7.16 (m, 4 H), 7.31 (d, *J* = 8.48 Hz, 2 H), 7.97 (d, *J* = 7.38 Hz, 2 H). ^{13}C NMR (75 MHz, CD_2Cl_2, 21 °C) δ ppm 20.70 (s, 1 C), 32.86 (s, 1 C), 34.89 (s, 1 C), 35.41 (s, 1 C), 51.82 (s, 1 C), 127.83 (s, 1 C), 128.24 (s, 2 C), 128.50 (s, 2 C), 128.94 (s, 2 C), 129.48 (s, 2 C), 135.28 (s, 1 C), 138.99 (s, 1 C), 148.10 (s, 1 C), 166.92 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{18}H_{21}O_2^+$: 269.1536; found: 269.1532.



1ad

*Compound **1ad.*** Methyl 4-((1,1-dioxido-3-oxobenzo[*d*]isothiazol-2(3*H*)-yl)methyl)benzoate. A solution of benzo[*d*]isothiazol-3(2*H*)-one 1,1-dioxide (235 mg, 1.28 mmol, 1 eq.) and NaOH (51 mg, 1.28 mmol, 1 eq.) in water (3 mL) was prepared and stirred for a few minutes at room temperature until it became clear. The solvent was evaporated under reduced pressure and the organic residue was dried under vacuum. Then it was dissolved in dimethylformamide and heated to 120 °C for 5 min and methyl 4-(bromomethyl)benzoate (235 mg, 1.03 mmol, 0.8 eq.) was added. After 45 min, the solution was poured into cold water (30 mL). The resulting white precipitate was filtered and washed with water (3 × 10 mL) and MeOH (2 × 5 mL), then dried under reduced pressure to give the title product (222.8 mg, 0.67 mmol, 66%).

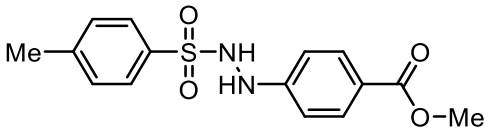
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 3.92 (s, 3 H), 4.97 (s, 2 H), 7.58 (d, *J* = 7.57 Hz, 2 H), 7.88 (td, *J* = 7.06, 1.54 Hz, 1 H), 7.83–7.93 (m, 1 H), 7.94–7.98 (m, 1 H), 8.02–8.06 (m, 2 H), 8.06–8.10 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 42.23 (s, 1 C), 52.16 (s, 1 C), 121.13 (s, 1 C), 125.37 (s, 1 C), 127.17 (s, 1 C), 128.51 (s, 2 C), 130.05 (s, 2 C), 130.08 (s, 1 C), 134.46 (s, 1 C), 134.98 (s, 1 C), 137.74 (s, 1 C), 139.43 (s, 1 C), 158.90 (s, 1 C), 166.63 (s, 1 C). HRMS (ESI$^-$) calcd. for $C_{16}H_{12}NO_5S^-$: 330.0442; found: 330.0448.



1ae

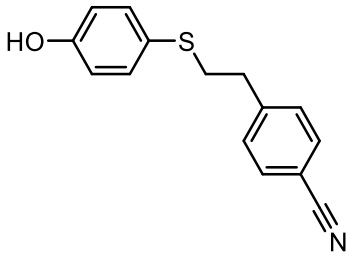
*Compound **1ae.*** Methyl 4-(methylsulfonamidomethyl)benzoate. A solution of methyl 4-(aminomethyl)benzoate hydrochloride (100 mg, 0.50 mmol, 1 eq.), methanesulfonyl chloride (56.8 mg, 38 µL, 0.5 mmol, 1 eq.) and *N*,*N*-diisopropylethylamine (141 mg, 186 µL, 1.09 mmol, 2.2 eq.) in DCM (3 ml) was prepared. After 10 min, the solution was sequentially washed with water (3 mL), hydrochloric acid (1.5 mL, 1 m) and brine (1.5 mL). The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM with 5% MeOH, SiO_2, Rf 0.46) to give the title compound as a white solid (102.8 mg, 0.42 mmol, 85%).

^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) δ ppm 2.91 (s, 3 H), 3.94 (s, 3 H), 4.40 (d, *J* = 6.26 Hz, 2 H), 5.03 (br t, *J* = 5.91 Hz, 1 H), 7.42–7.47 (m, 2 H), 8.02–8.07 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$, 23 °C) δ ppm 41.22 (s, 1 C), 46.76 (s, 1 C), 52.25 (s, 1 C), 127.72 (s, 2 C), 129.93 (s, 1 C), 130.17 (s, 2 C), 141.89 (s, 1 C), 166.67 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{10}H_{14}NO_4S^+$: 244.0638; found: 244.0634. HRMS (ESI$^-$) calcd. for $C_{10}H_{12}NO_4S^-$: 242.0493; found: 242.0487.



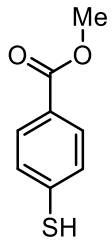
1af

Compound ***1af.*** Methyl 4-(2-tosylhydrazineyl)benzoate. A solution of 4-methylbenzenesulfonyl chloride (190.7 mg, 1 mmol, 1 eq.), methyl 4-hydrazineylbenzoate (202.6 mg, 1 mmol, 1 eq.) and *N*,*N*-diisopropylethylamine (284.4 mg, 383.2 µL, 2.2 mmol, 2.2 eq.) in DCM (4 mL) was prepared and stirred at room temperature for 12 h. Then the solution was sequentially washed with hydrochloric acid (5 mL; 1 M) and brine (5 mL) and the organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was recrystallized from water/ethanol (*v*/*v* = 1/1), washed with DCM, and dried under reduced pressure to give the title product (56.8 mg, 0.18 mmol, 18%, orange crystals).
^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) δ ppm 2.42 (s, 3 H), 3.86 (s, 3 H), 5.99 (br s, 1 H), 6.37 (s, 1 H), 6.72 (d, *J* = 7.91 Hz, 2 H), 7.24–7.32 (m, 2 H), 7.69–7.82 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$, 23 °C) δ ppm 21.60 (s, 1 C), 51.77 (s, 1 C), 112.10 (s, 2 C), 122.44 (s, 1 C), 128.22 (s, 2 C), 129.83 (s, 2 C), 131.09 (s, 2 C), 134.30 (s, 1 C), 144.92 (s, 1 C), 150.08 (s, 1 C), 166.78 (s, 1 C). HRMS (ESI^+) calcd. for $C_{15}H_{17}N_2O_4S^+$: 321.0904; found: 321.0903. HRMS (ESI^-) calcd. for $C_{15}H_{15}N_2O_4S^-$: 319.0747; found: 319,0758.



1ag

Compound ***1ag.*** 4-(2-((4-Hydroxyphenyl)thio)ethyl)benzonitrile. 4-Mercaptophenol (100 mg, 0.79 mmol, 1.1 eq) and 4-vinylbenzonitrile (93 mg, 0.72 mmol, 1 eq) were mixed, sonicated, and heated to 40 °C. After 1 h at room temperature, the reaction mixture was subjected to column chromatography (ethyl acetate/cyclohexane *v*/*v* = 9/1 to 1:1, SiO_2, Rf 0.75 (ethyl acetate/cyclohexane *v*/*v* = 1/1)) to give the title product as a white solid (89.6 mg, 0.35 mmol, 49%).
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 2.90–2.96 (m, 2 H), 3.04–3.10 (m, 2 H), 5.35 (s, 1 H), 6.82 (d, *J* = 8.73 Hz, 2 H), 7.26–7.30 (m, 2 H), 7.30–7.34 (m, 2 H), 7.59 (d, *J* = 8.22 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 35.85 (s, 1 C), 36.78 (s, 1 C), 110.19 (s, 1 C), 116.22 (s, 2 C), 118.93 (s, 1 C), 125.60 (s, 1 C), 129.43 (s, 2 C), 132.27 (s, 2 C), 133.94 (s, 2 C), 145.86 (s, 1 C), 155.45 (s, 1 C). HRMS (ESI^-) calcd. for $C_{15}H_{12}NOS^-$: 254.0645; found: 254.0641.

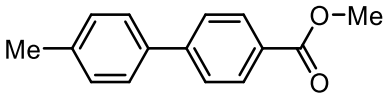


1ah

Compound ***1ah.*** Methyl 4-mercaptobenzoate. A solution of 4-mercaptobenzoic acid (1 g, 6.5 mmol, 1 eq.) in MeOH (25 mL) was cooled to -10 °C and thionyl chloride (1.04 g, 635 µL, 8.76 mmol, 1.3 eq.) was added dropwise under strong stirring. The solution was warmed to room temperature and stirred for 2.5 h. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography (DCM/cyclohexane *v*/*v* = 9/1, SiO_2, Rf 0.53) to give the title product (498 mg, 3 mmol, 46%).
^{1}H NMR (300 MHz, $CDCl_3$, 27 °C) δ ppm 3.62 (s, 1 H), 3.91 (s, 3 H), 7.30 (dt, *J* = 7.96, 1.80 Hz, 2 H), 7.90 (dt, *J* = 8.22, 1.80 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, 27 °C) δ ppm 52.08 (s, 1 C), 127.15 (s, 1 C), 128.13 (s, 2 C), 130.23 (s, 2 C), 138.33 (s, 1 C), 166.62 (s, 1 C). HRMS (ESI^+) calcd. for $C_8H_9O_2S^+$: 169.0318; found: 169.0316. HRMS (ESI^-) calcd. for $C_8H_7O_2S^-$: 167.0172; found: 167.0159.

Irradiation of linker derivatives

General procedure for the synthesis of a biphenyl (**2a**–**2c)**: A solution of the precursor (**1a**–**1ag**) in MeOH, EtOH, H_2O or MeCN at a concentration of 1 to 2 mg·mL^{-1} was prepared. The solution was irradiated in the thin film photoreactor at 254 nm (normal light intensity with 44 W·m^{-2} unless otherwise stated) at a flow rate of 1 mL·min^{-1} (dwell time ~15 min unless otherwise stated). The fraction containing the photoproducts was collected and analyzed by HPLC-MS, GC-MS or TLC. The solvent was evaporated, and the photoproduct was purified by column chromatography.
Compounds are considered photostable if the dominant peak in HPLC-MS measurements after irradiation is the parent material and only minor amounts of other photoproducts appear. No detectable amounts of biphenyl were formed for any of the photostable or photolabile compounds.
Small amounts of residual moisture in the solvents (usually 0.02–0.03%) are sufficient for the formation of hydrolysis products.
2a and **2b** are known compounds.[2, 3]



2a

Irradiation of sulfonamide **1d.** A solution of **1d** (20.54 mg, 0.043 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (8.2 mg, 0.036 mmol, 84%).

Irradiation of water-soluble sulfonamide **1f.** A solution of **1f** (20.2 mg, 0.044 mmol) was dissolved in H_2O (10 mL) and irradiated in the photoreactor with a flow of 2 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (3.7 mg, 0.016 mmol, 38%).

Irradiation of sulfonester **1g.** A solution of **1g** (18.9 mg, 0.062 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (4.1 mg, 0.018 mmol, 29%).

Irradiation of sulfon **1h.** A solution of **1h** (20 mg, 0.063 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (1.9 mg, 0.008 mmol, 13%).

Irradiation of acylsufonamid **1k.** A solution of **1k** (24.9 mg, 0.075 mmol) was dissolved in MeOH (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (5 mg, 0.022 mmol, 30%).

Irradiation of bis-sulfonamid **1l.** A solution of **1l** (15 mg, 0.041 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected. **2a** was detected by HPLC-MS but the amount obtained was insufficient to purify.

Irradiation of sulfonamide **1n.** A solution of **1l** (22.1 mg, 0.069 mmol) was dissolved in MeOH (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (1.9 mg, 0.008 mmol, 12%).

Irradiation of phosphinic amide **1q**. A solution of **1q** (100.1 mg, 0.22 mmol) was dissolved in MeCN (50 mL) and irradiated in the photoreactor (high light intensity, 118 W·m^{-2}) with a flow of 0.5 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2b** was purified by column chromatography (0.9 mg, 0.004 mmol, 2%).

Irradiation of phosphonic amide **1r.** A solution of **1r** (20.6 mg, 0.056 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor without the glass cover with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected. **2b** was detected by HPLC-MS but the amount obtained was insufficient to purify.

Irradiation of sulfoxide **1u.** A solution of **1u** (20 mg, 0.066 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (2.3 mg, 0.010 mmol, 15%).

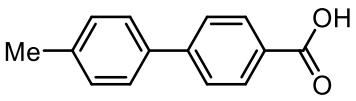
Irradiation of thioether **1v**. A solution of **1v** (19 mg, 0.066 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (7.3 mg, 0.032 mmol, 49%).
Alternative method: 4-Methylbenzenethiol (7.3 mg, 0.059 mmol, 1.4 eq.) and 4-vinylbenzonitrile (6.9 mg, 0.43 mmol, 1 eq.) were weighed into an Eppendorf tube, then centrifuged to the bottom. The mixture was melted in an ultrasonic bath (40 °C) and then stored for 1 h at room temperature. The crude mixture was dissolved in EtOH (10 mL) and irradiated in the photoreactor with UV-B light at a flow rate of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (5.2 mg, 0.023 mmol, 54%).

Irradiation of thioether **1w.** A solution of **1w** (10 mg, 0.035 mmol) was dissolved in MeCN (10 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (2.0 mg, 0.009 mmol, 25%).

Irradiation of sulfonamide **1a** suspension in water: Sulfonamide **1a** (19.9 mg, 0.062 mmol) was dissolved in MeCN (2 mL) and precipitated in water with Tween 20 (8 mL) and irradiated in the photoreactor with a flow of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure, and **2a** was purified by column chromatography (9.3 mg, 0.041 mmol, 66%).

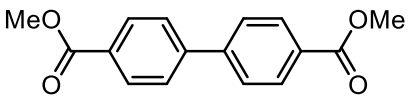
Irradiation of compound **1j**, **1m**, **1o**, **1p**, **1s**, **1t**, **1x, 1y, 1z**, **1aa**, **1ab**, **1ac**, **1ad** and **1af** using the general protocol did not produce any biphenyl and irradiation of compound **1ae** did not produce methyl 4-methylbenzoate.

Irradiation of compound **1e.**



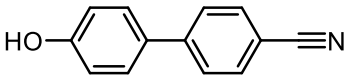
2c

*Compound **2c.*** 4'-methyl-[1,1'-biphenyl]-4-carboxylic acid. A solution of **1e** (10 mg, 29 µmol) in water (10 mL) and NaOH (0.25 mL, 2 M) was prepared, then sonicated until there was no more turbidity. The solution was irradiated at a wavelength of 254 nm and a flow rate of 0.5 mL·min^{-1} in the tubular photoreactor. The fraction containing the photoproducts was collected and the solvent was evaporated. The crude product was dissolved in MeOH (1 mL) and formic acid (100 µL), then the solvent was removed under reduced pressure. The crude product was purified by column chromatography (DCM with 1% MeOH, SiO_2, Rf 0.17) to yield the title product as a white solid (3.3 mg, 16 µmol, 53%).
^{1}H NMR (500 MHz, DMSO-d_6, 27 °C) δ ppm 2.35 (s, 3 H), 7.30 (d, J = 7.98 Hz, 2 H), 7.62 (d, J = 8.07 Hz, 2 H), 7.76 (d, J = 8.44 Hz, 2 H), 7.99 (d, J = 8.34 Hz, 2 H), 12.90 (br s, 1 H). ^{13}C NMR (126 MHz, DMSO-d_6, 28 °C) δ ppm 20.67 (s, 1 C), 126.44 (s, 2 C), 126.75 (s, 2 C), 129.27 (s, 1 C), 129.64 (s, 2 C), 129.90 (s, 2 C), 136.08 (s, 1 C), 137.75 (s, 1 C), 144.19 (s, 1 C), 167.11 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{14}H_{13}O_2^+$: 213.0910; found: 213.0909. HRMS (ESI$^-$) calcd. for $C_{14}H_{11}O_2^-$: 211.0765; found: 211.0759.



2d

*Compound **2d.*** Dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate. A solution of **1q** (100.1 mg, 0.22 mmol) was dissolved in MeCN (50 mL) and irradiated at 254 nm (high light intensity, 118 W·m^{-2}) in the thin film photoreactor with a flow rate of 0.5 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure and was subjected to column chromatography (DCM, SiO_2, Rf 0.3) to give **2d** (1.8 mg, 0.007 mmol, 3%). Extended exposure times due to a reduced flow rate and an increase in UV light intensity allowed the starting material to be completely transformed and sufficient material to be obtained for NMR studies.
^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C) δ ppm 3.91 (s, 6 H), 7.73 (d, *J* = 8.47 Hz, 4 H), 8.05–8.16 (m, 4 H). ^{13}C NMR (126 MHz, CD_2Cl_2, 20 °C) δ ppm 52.60 (s, 2 C), 127.67 (s, 4 C), 130.10 (s, 2 C), 130.44 (s, 4 C), 144.52 (s, 2 C), 166.98 (s, 2 C). HRMS (ESI$^+$) calcd. for $C_{16}H_{15}O_4^+$: 271.0965; found: 271.0964.



2e

*Compound **2e.*** 4'-Hydroxy-[1,1'-biphenyl]-4-carbonitrile. 4-Mercaptophenol (6 mg, 0.048 mmol, 1.2 eq.) and 4-vinylbenzonitrile (5.0 mg, 0.039 mmol, 1 eq.) were weighed into an Eppendorf tube, then centrifuged to the bottom. The mixture was melted in an ultrasonic bath (40 °C) and then stored for 1 h at room temperature. The crude mixture was dissolved in EtOH (10 mL) and irradiated in the photoreactor with UV-B light at a flow rate of 1 mL·min^{-1}. The fraction containing the photoproduct was collected, the solvent evaporated under reduced pressure and **2e** was purified by column chromatography (DCM with 5% MeOH, SiO_2, Rf 0.51) to give the title product (4.5 mg, 0.023 mmol, 60%).
^{1}H NMR (600 MHz, CD_2Cl_2, 27 °C) δ ppm 6.97–7.00 (m, 2 H), 7.54–7.58 (m, 2 H), 7.69–7.71 (m, 2 H), 7.73–7.76 (m, 2 H). ^{13}C NMR (151 MHz, CD_2Cl_2, 27 °C) δ ppm 110.13 (s, 1 C), 115.93 (s, 2 C), 118.98 (s, 1 C), 127.03 (s, 2 C), 128.57 (s, 2 C), 131.59 (s, 1 C), 132.58 (s, 2 C), 145.06 (s, 1 C), 156.50 (s, 1 C). HRMS (ESI$^+$) calcd. for $C_{13}H_{10}NO^+$: 196.0757; found: 196.0759. HRMS (ESI$^-$) calcd. for $C_{13}H_8NO^-$: 194.0611; found: 194.0603.

Study on the scope of the thiol-ene photosplicing at the analytical scale.
The depicted (Figure S21) styrene (~ 5 mg) and thiol (~ 5 mg or 5 µL) were weighed into four separate Eppendorf tubes and centrifuged to the bottom. The mixture was melted in an ultrasonic bath (40 °C) and then stored for 1 h at room temperature. The crude mixtures of **1ai, 1aj, 1ak** and **1al** were measured by GC-MS or HPLC-HRMS (Figure S23–S26, top). Each crude mixture was dissolved in MeOH (10 mL) and 1 mL of this solution was irradiated in the tubular photoreactor with UV-C light (254 nm) at a flow rate of 1 mL·min^{-1}. The fraction containing the photoproduct (Figure S22, **2f**, **2g**, **2h** and **2i**) was collected, filtered, and directly measured by GC-MS and HPLC-HRMS (Figure S23–S26, bottom).

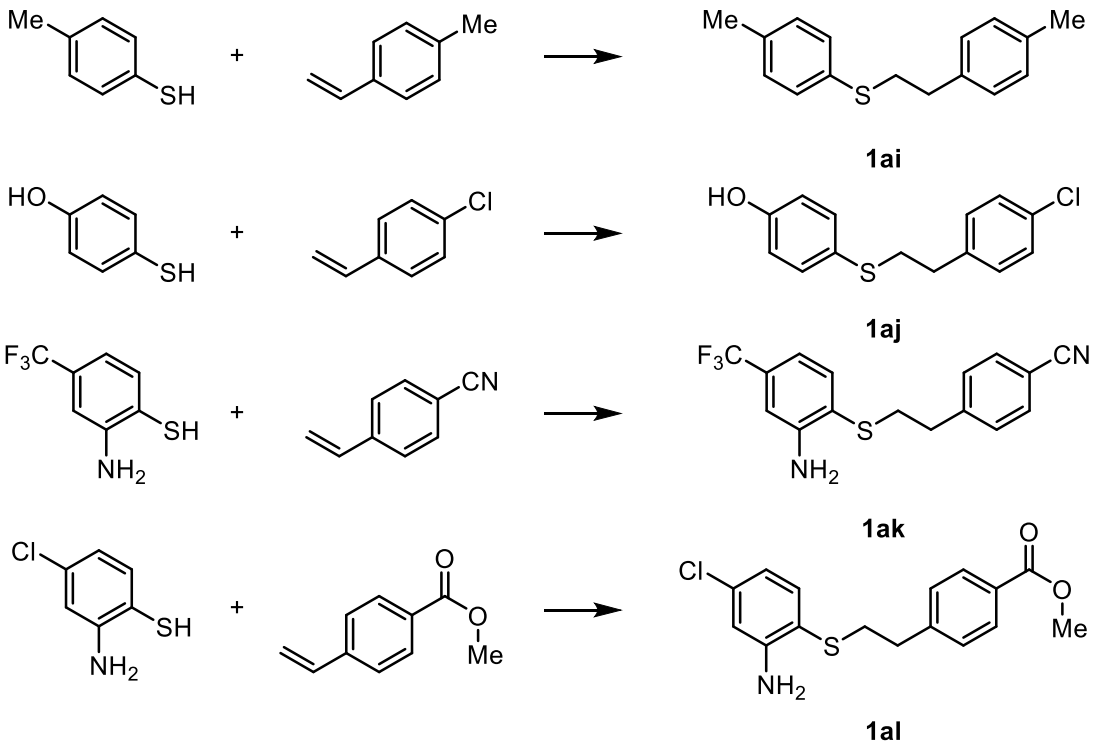


Figure S21: Reaction scheme of the thiol-ene reaction of a thiol and a styrene to give **1ai**, **1aj**, **1ak** and **1al**.

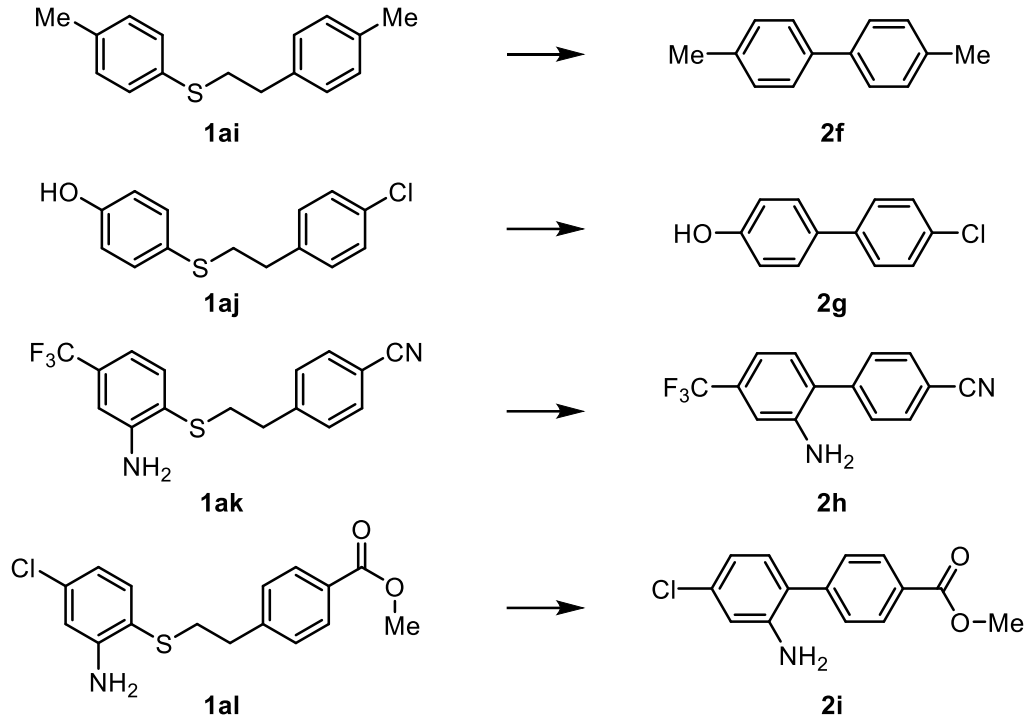


Figure S22: Reaction scheme of the photosplicing reaction of the crude thiol-ene addition product to give the corresponding biphenyl **2f**, **2g**, **2h** and **2i**.

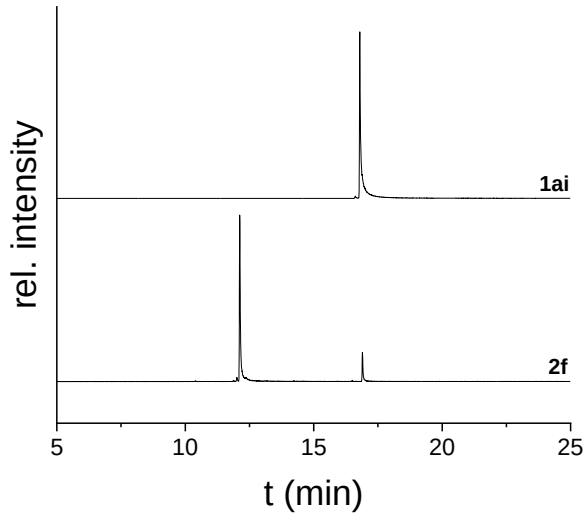


Figure S23: EIC traces of crude **1ai** (*m*/*z* = 242.1, 500 ppm window) and crude **2f** (*m*/*z* = 182.1, 500 ppm window) after irradiation by GC-MS.

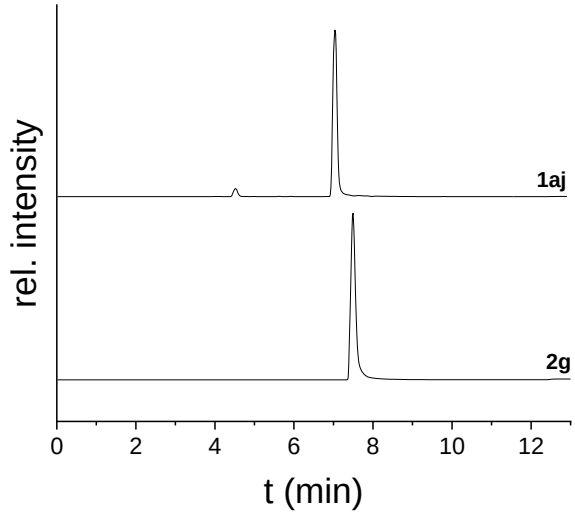


Figure S24: EIC traces of crude **1aj** (ESI^-, *m*/*z* = 263.0303, 5 ppm window) and crude **2g** (ESI^-, *m*/*z* = 203.0269, 5 ppm window) after irradiation by HPLC-HRMS.

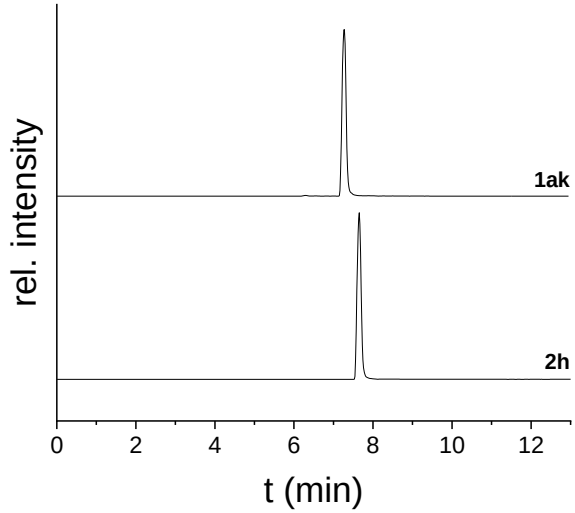


Figure S25: EIC traces of crude **1ak** (ESI^+, *m*/*z* = 323.0824, 5 ppm window) and crude **2h** (ESI^+, *m*/*z* = 263.0791, 5 ppm window) after irradiation by HPLC-HRMS.

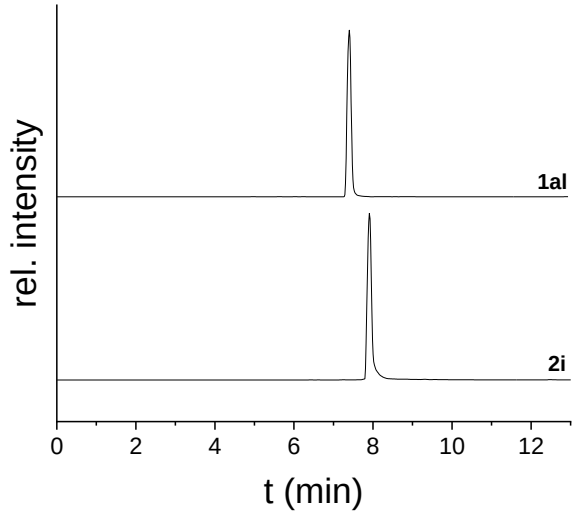


Figure S26: EIC traces of crude **1al** (ESI^+, *m*/*z* = 322.0663, 5 ppm window) and crude **2i** (ESI^+, *m*/*z* = 262.0629, 5 ppm window) after irradiation by HPLC-HRMS.

*Detection of side products after irradiation of **1v**.*

Compound **1v** (1 mg) was dissolved in MeOH (1 mL) and exposed to UV-C light (254 nm) in the tubular photoreactor at a flow rate of 1 mL·min^{-1}. The crude reaction mixture was analyzed by HPLC-HRMS and GC-MS.

Compound **3a** was detected by HPLC-HRMS (HRMS (ESI$^+$) calcd. for $C_{15}H_{13}O_3^+$: 241.0859; found: 241.0859) and was further characterized by NMR: ^{1}H NMR (500 MHz, $CDCl_3$, 22°C) δ ppm 3.99 (s, 3 H), 7.72–7.75 (m, 2 H), 7.80–7.84 (m, 2 H), 7.99–8.03 (m, 2 H), 8.16–8.20 (m, 2 H), 10.08–10.12 (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$, 23°C) δ ppm 52.30 (s, 1 C), 127.38 (s, 2 C), 127.94 (s, 2 C), 130.03 (s, 1 C), 130.11 (s, 2 C), 130.30 (s, 2 C), 135.81 (s, 1 C), 144.06 (s, 1 C), 145.91 (s, 1 C), 166.74 (s, 1 C), 191.78 (s, 1 C).

Compounds **3b**, **3c**, **3d** and **3e** were identified by GC-MS and comparison with the NIST database.

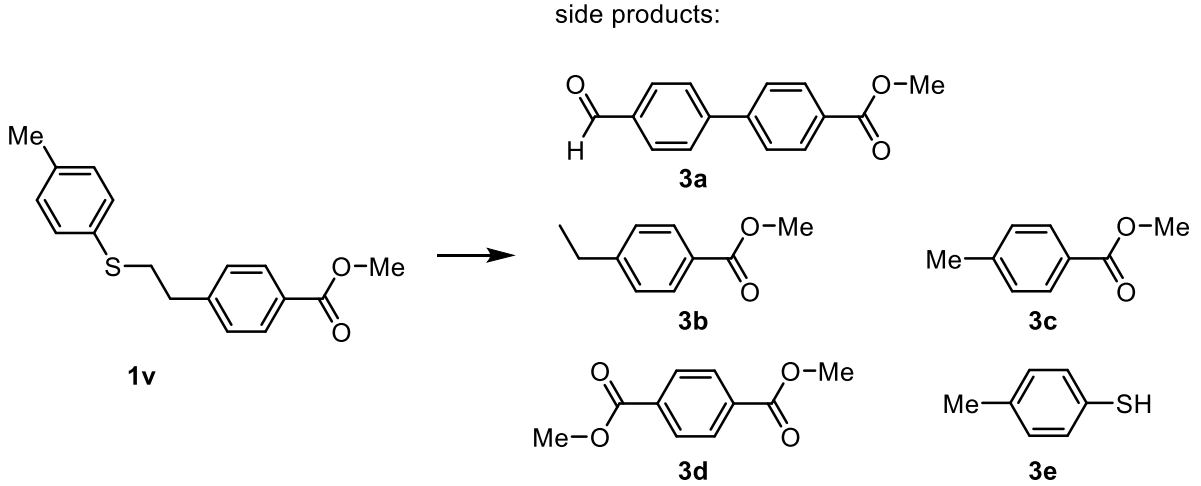


Figure S27: Structures of detected side products after the irradiation of compound **1v**.

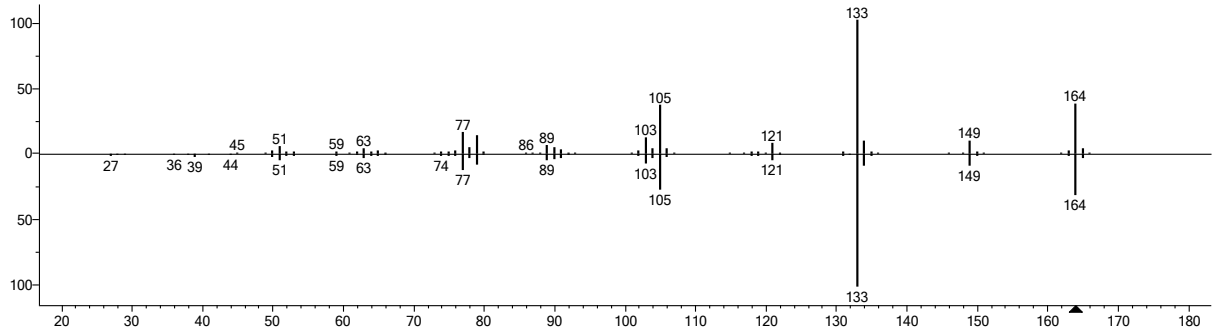


Figure S28: Comparison of EI-MS spectra of the side product with a retention time of 8.40 min from the irradiation of **1v** (top) with methyl 4-ethylbenzoate (**3b**) from the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

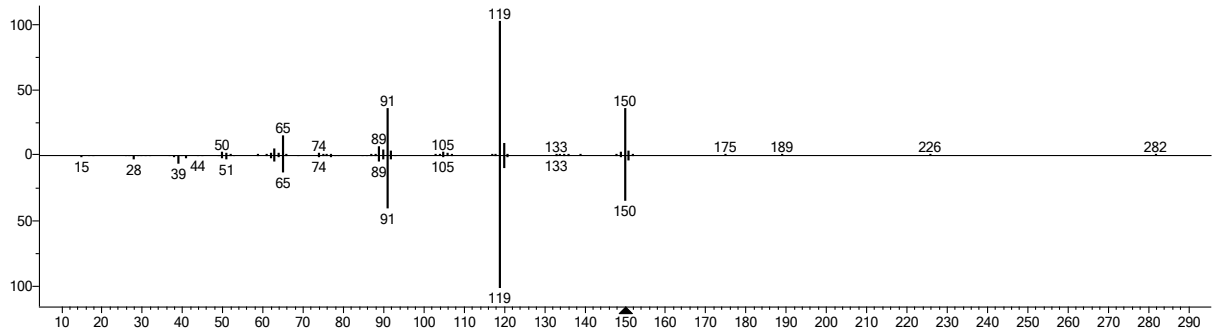


Figure S29: Comparison of EI-MS spectra of the side product with a retention time of 7.24 min from the irradiation of **1v** (top) with methyl 4-methylbenzoate (**3c**) from the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

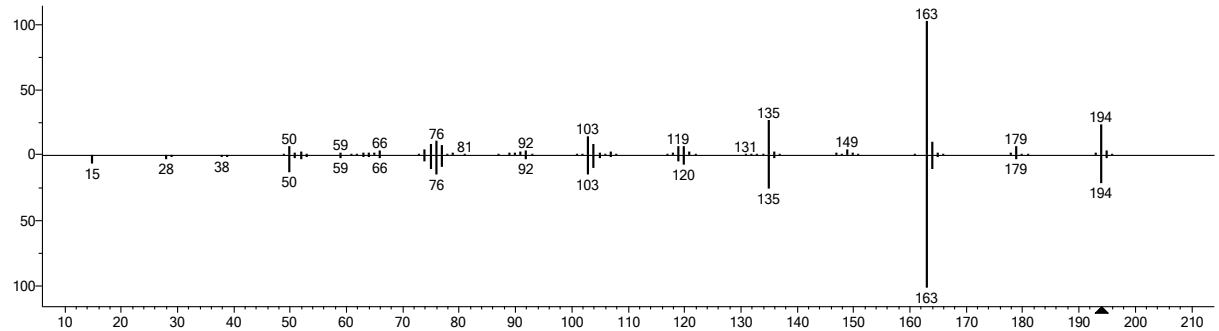


Figure S30: Comparison of EI-MS spectra of the side product with a retention time of 10.72 min from the irradiation of **1v** (top) with dimethyl terephthalate (**3d**) from the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

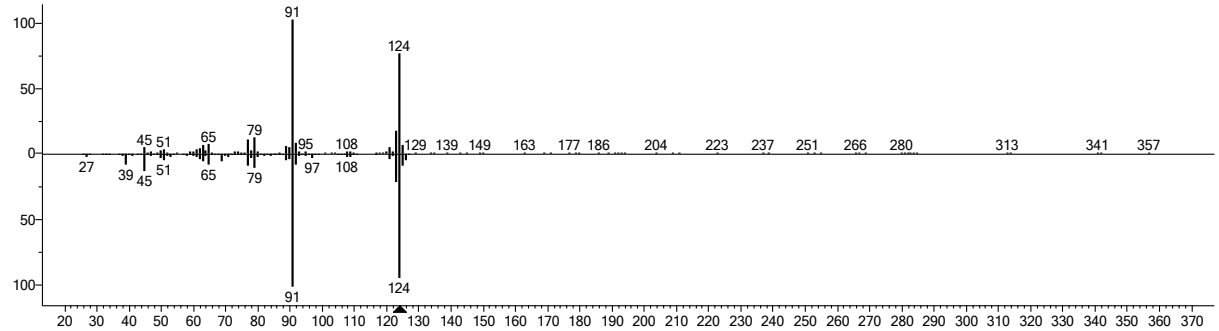


Figure S31: Comparison of EI-MS spectra of the side product with a retention time of 5.70 min from the irradiation of **1v** (top) with 4-methylbenzenethiol (**3e**) from the NIST database (bottom). The intensity of the mass-to-charge ratio (*m*/*z*) is given as a percentage.

References

1. G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
2. F. Kloss, T. Neuwirth, V. G. Haensch and C. Hertweck, *Angew. Chem., Int. Ed.*, 2018, **57**, 14476-14481.
3. V. G. Haensch, T. Neuwirth, J. Steinmetzer, F. Kloss, R. Beckert, S. Gräfe, S. Kupfer and C. Hertweck, *Chem. Eur. J.*, 2019, **25**, 16068-16073.
4. F. Lima, U. K. Sharma, L. Grunenberg, D. Saha, S. Johannsen, J. Sedelmeier, E. V. Van der Eycken and S. V. Ley, *Angew. Chem., Int. Ed.*, 2017, **56**, 15136-15140.

^{1}H and ^{13}C NMR Spectra

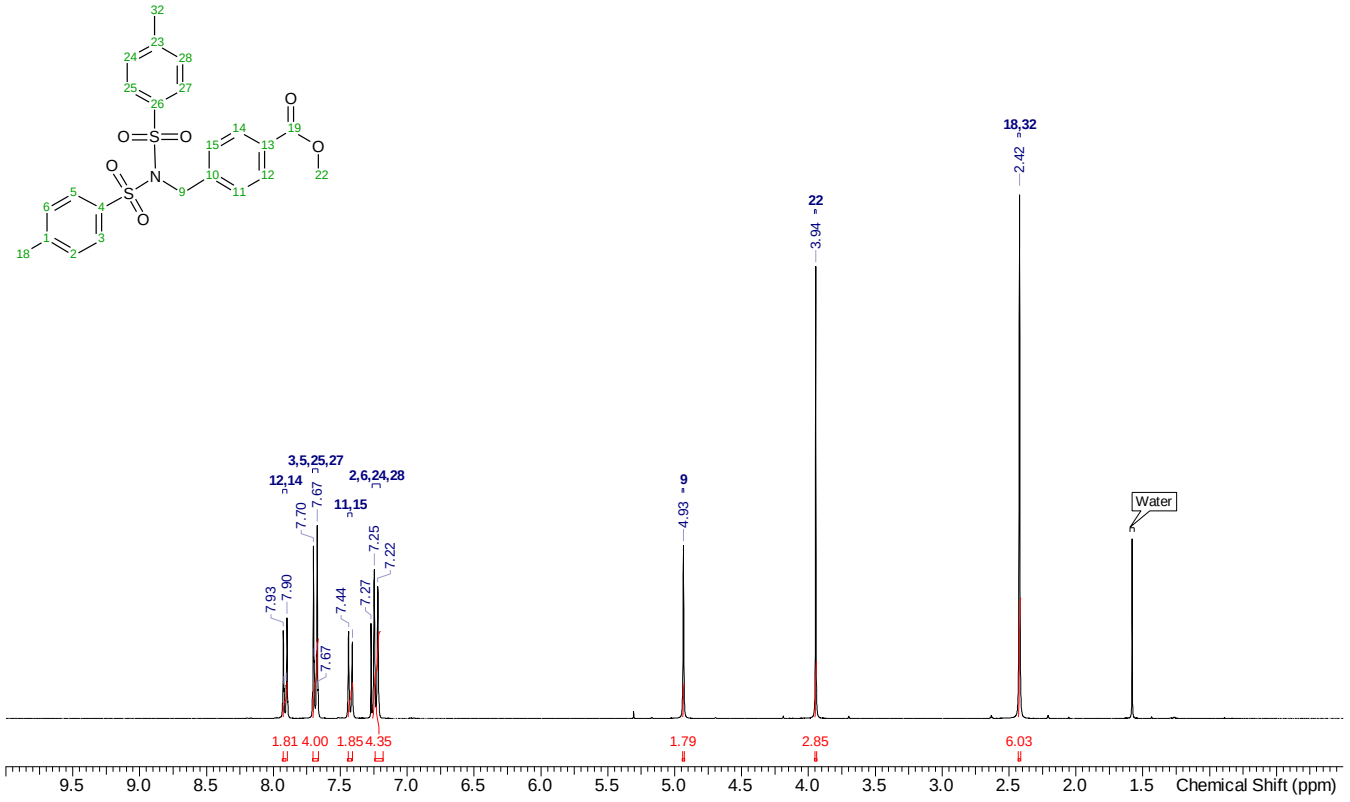


Figure S32: ^{1}H NMR spectrum of **1d**.

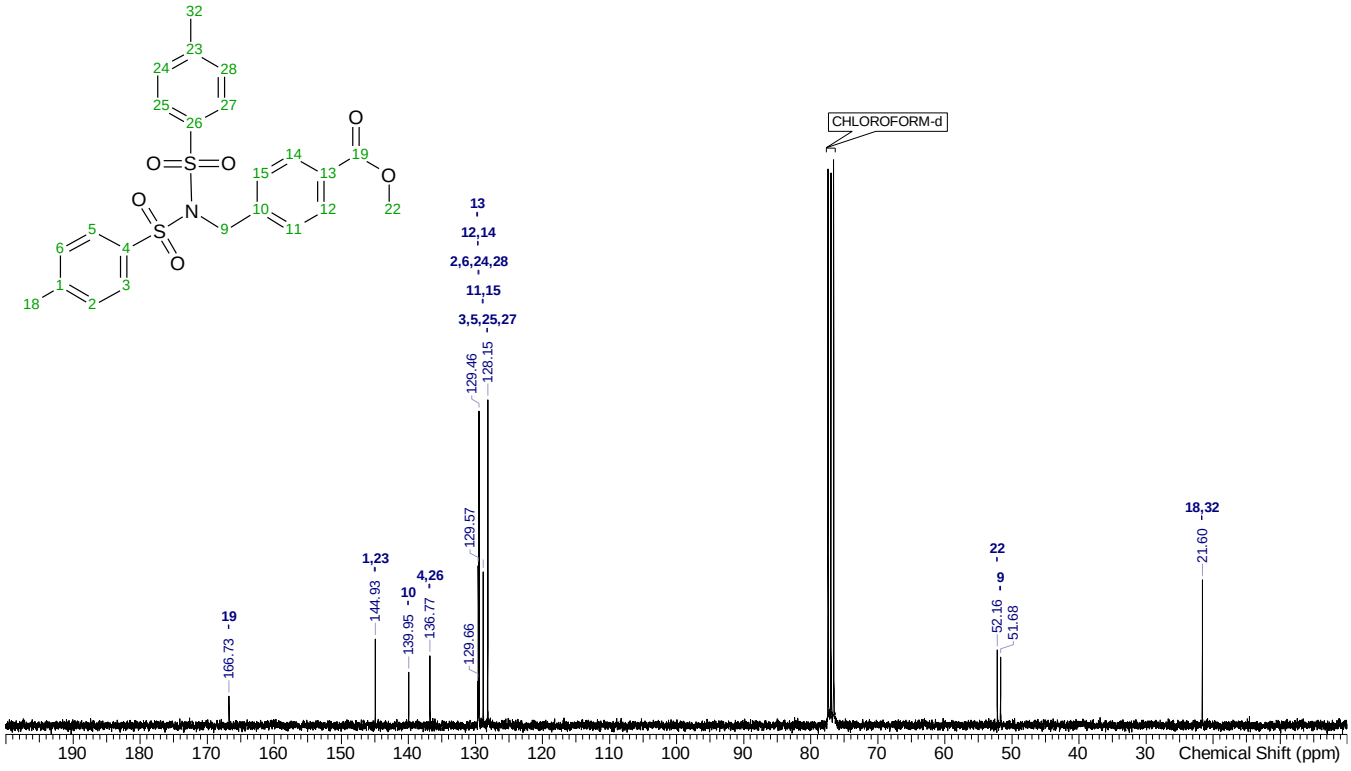


Figure S33: ^{13}C NMR spectrum of **1d.**

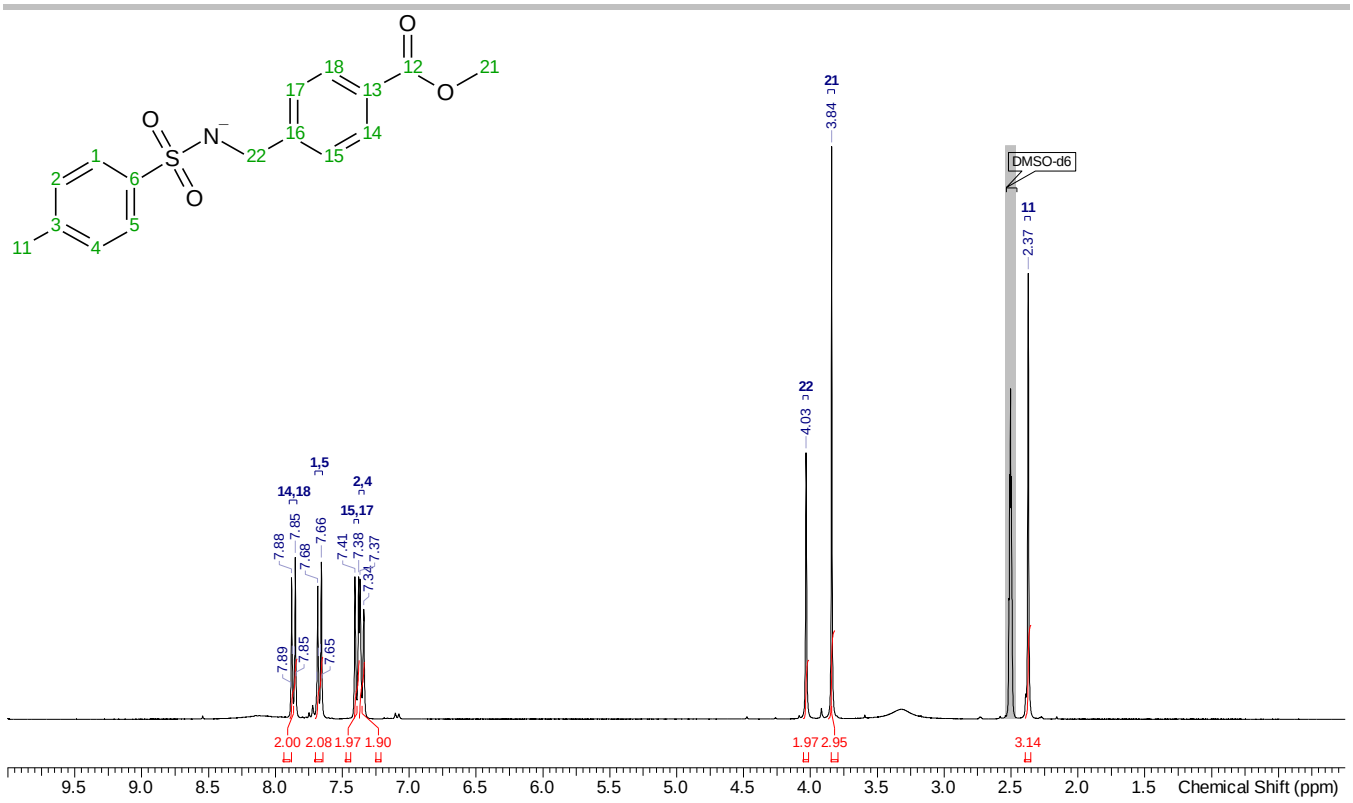


Figure S34: ^{1}H NMR spectrum of **1e**.

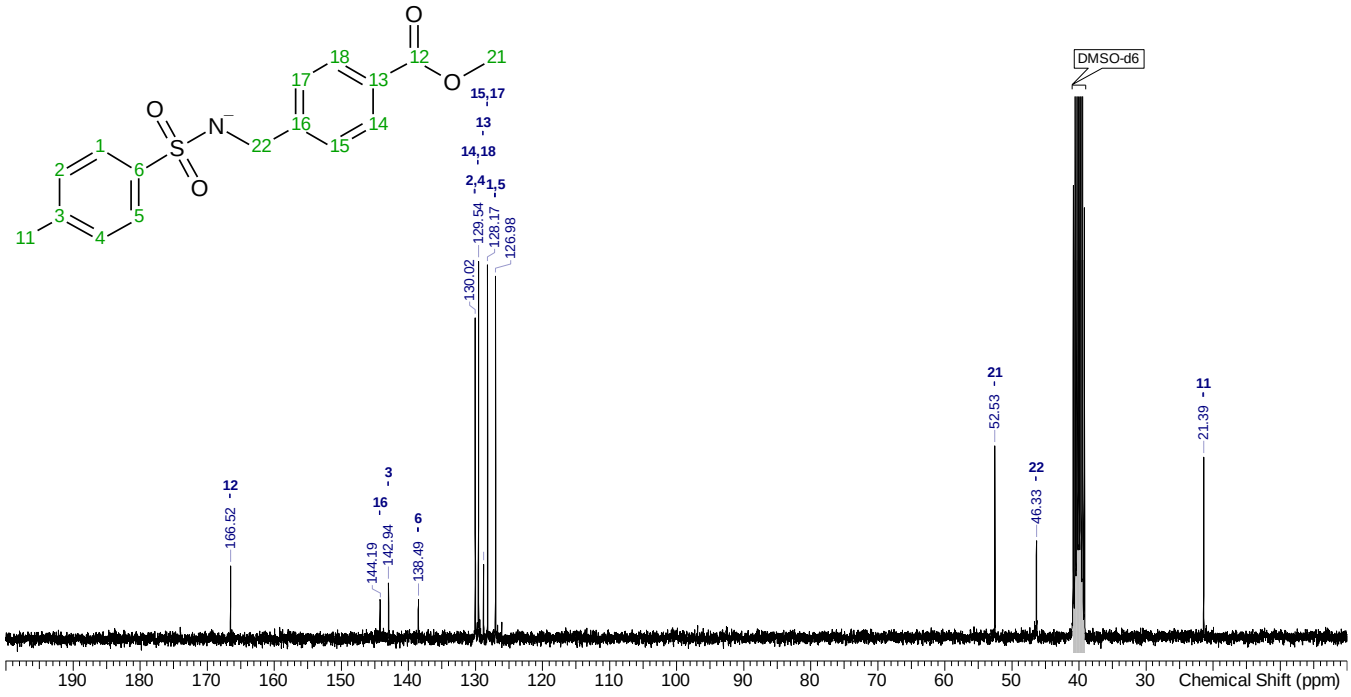


Figure S35: ^{13}C NMR spectrum of **1e.**

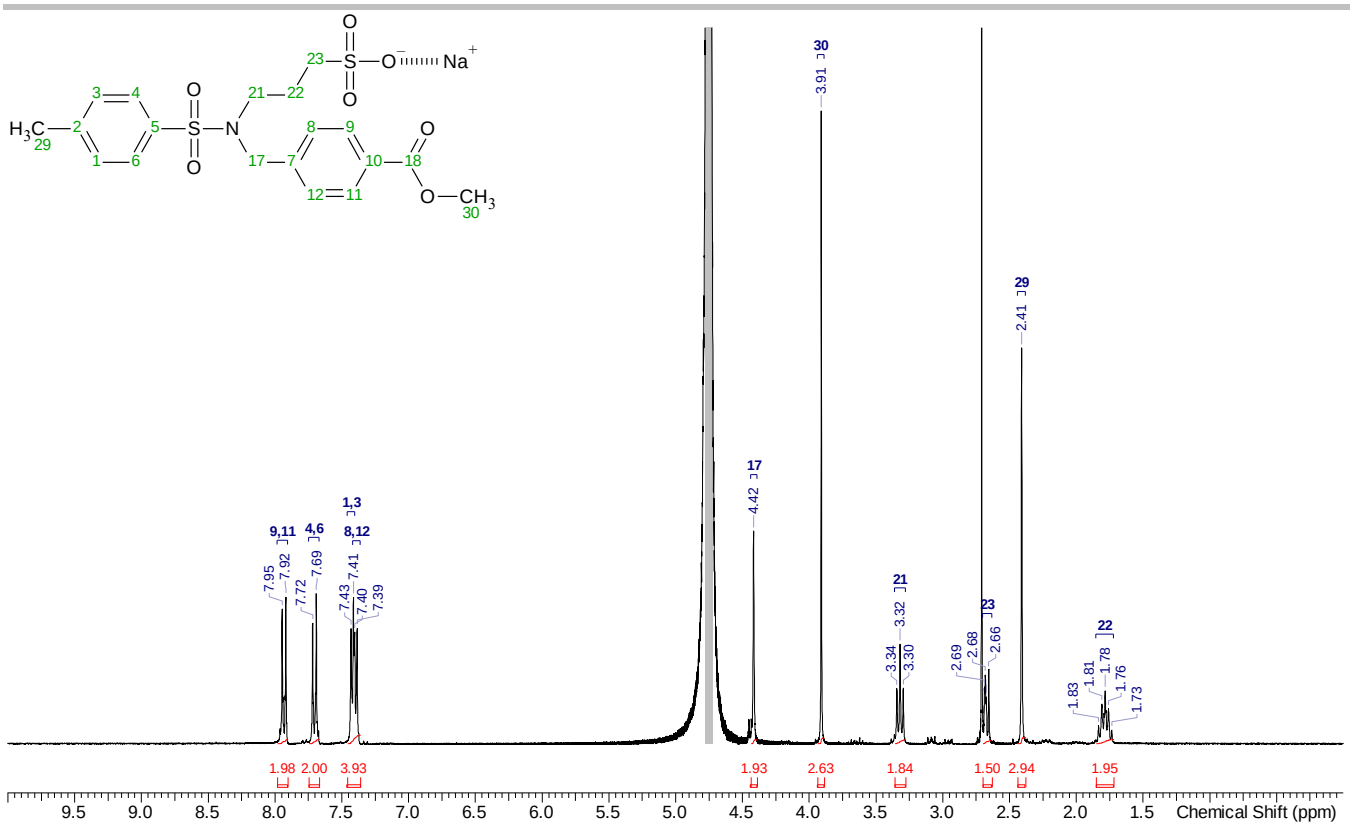


Figure S36: ^{1}H NMR spectrum of **1f**.

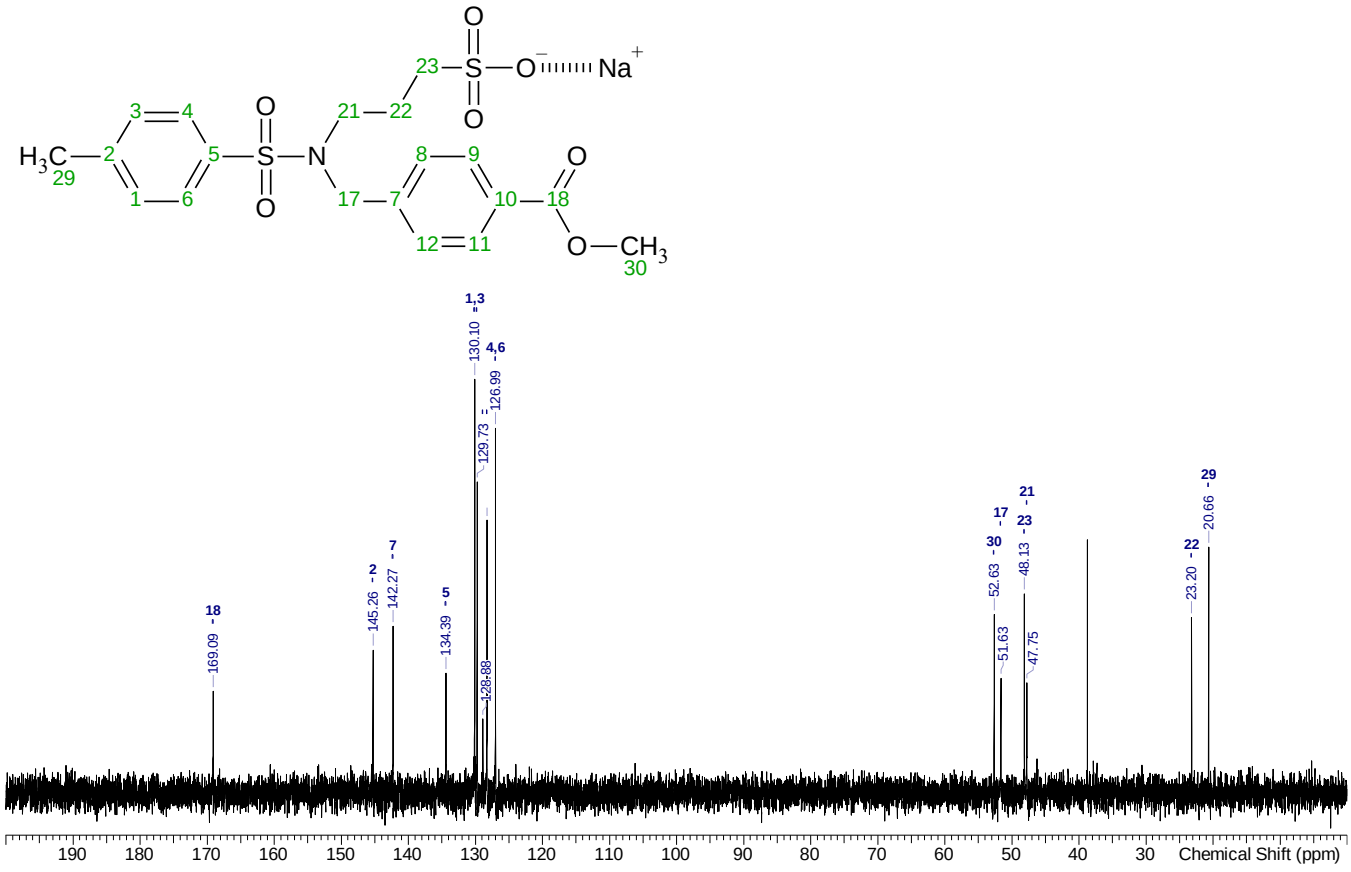


Figure S37: 13C NMR spectrum of 1f.

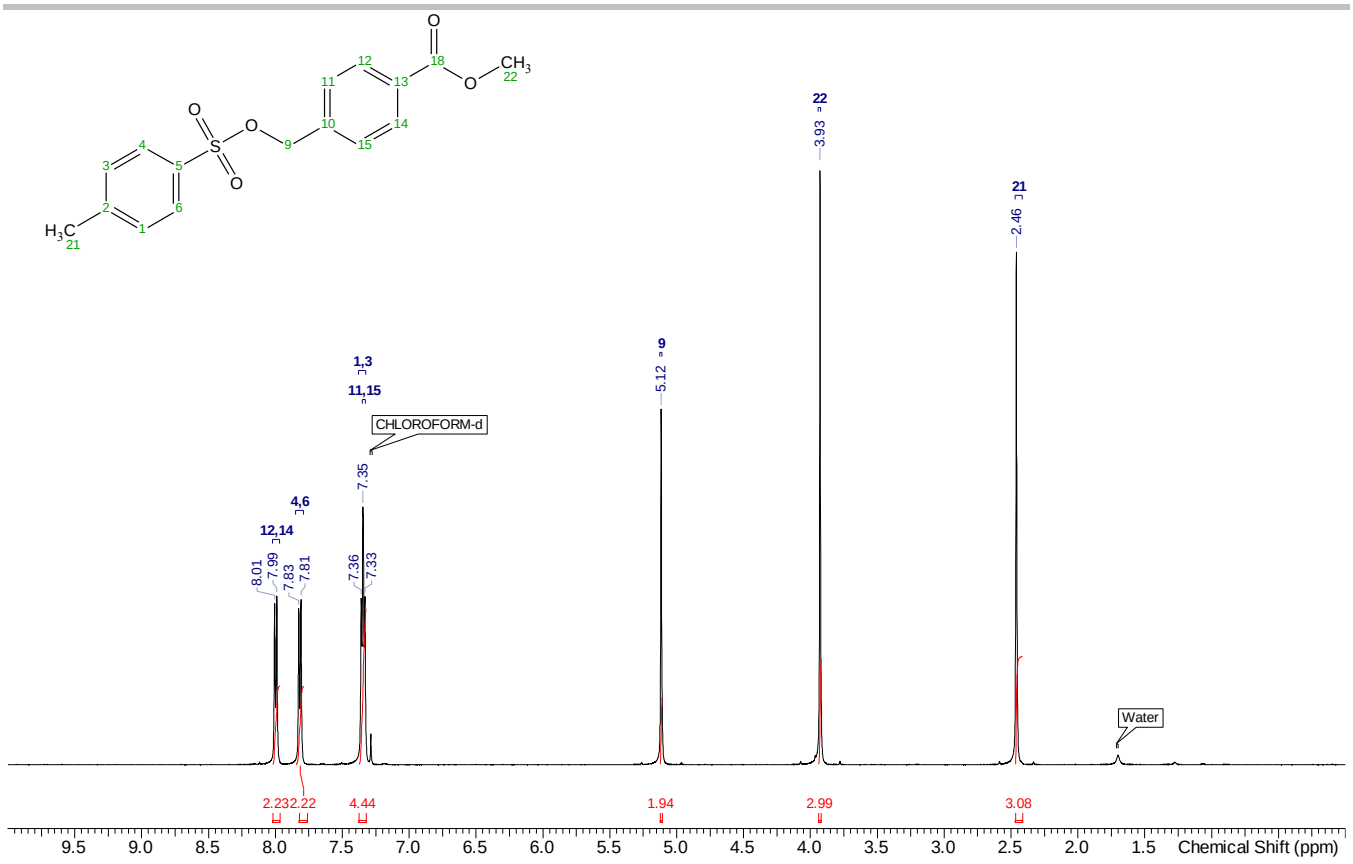


Figure S38: ^{1}H NMR spectrum of **1g**.

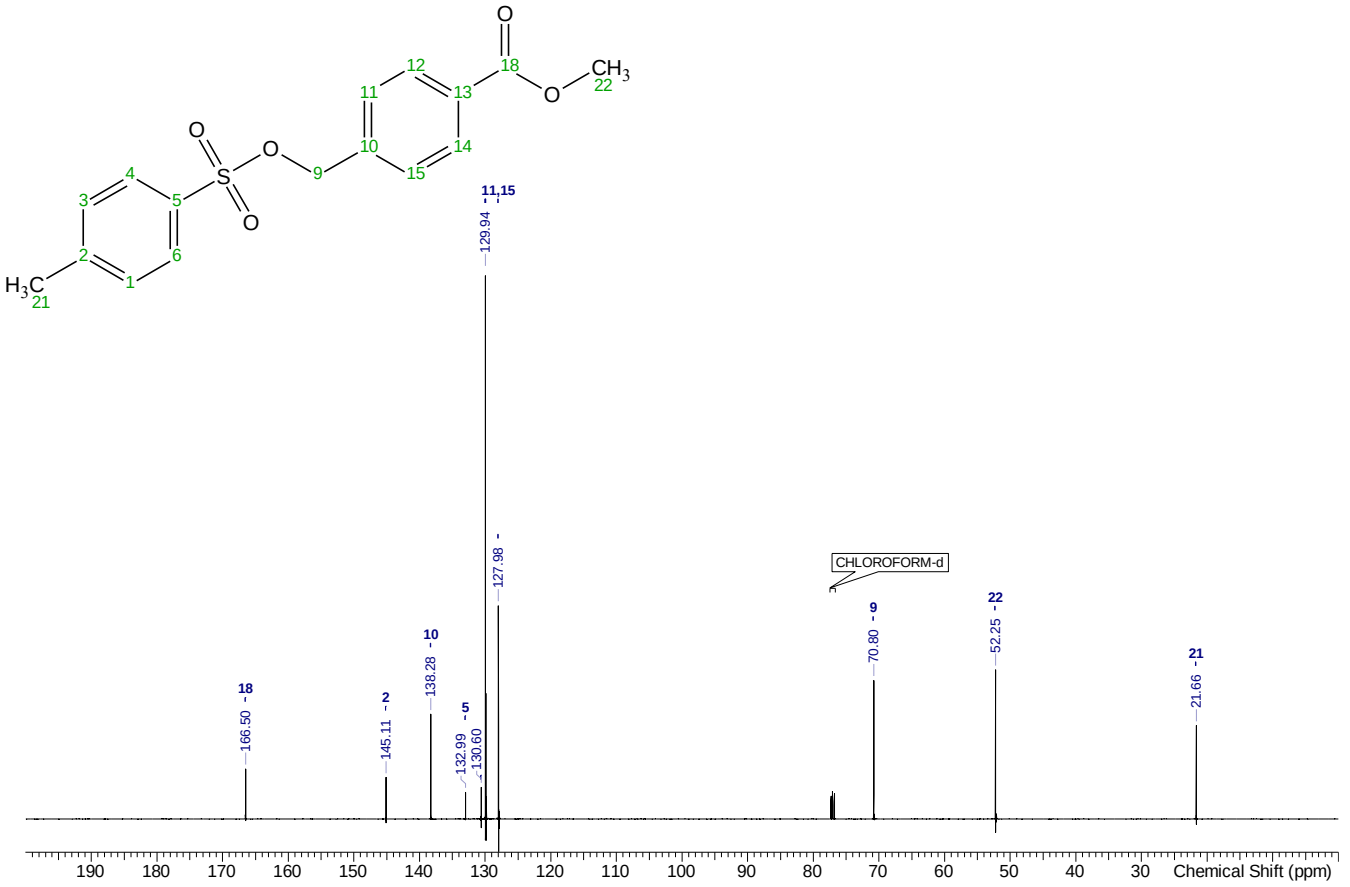


Figure S39: ^{13}C NMR spectrum of **1g.**

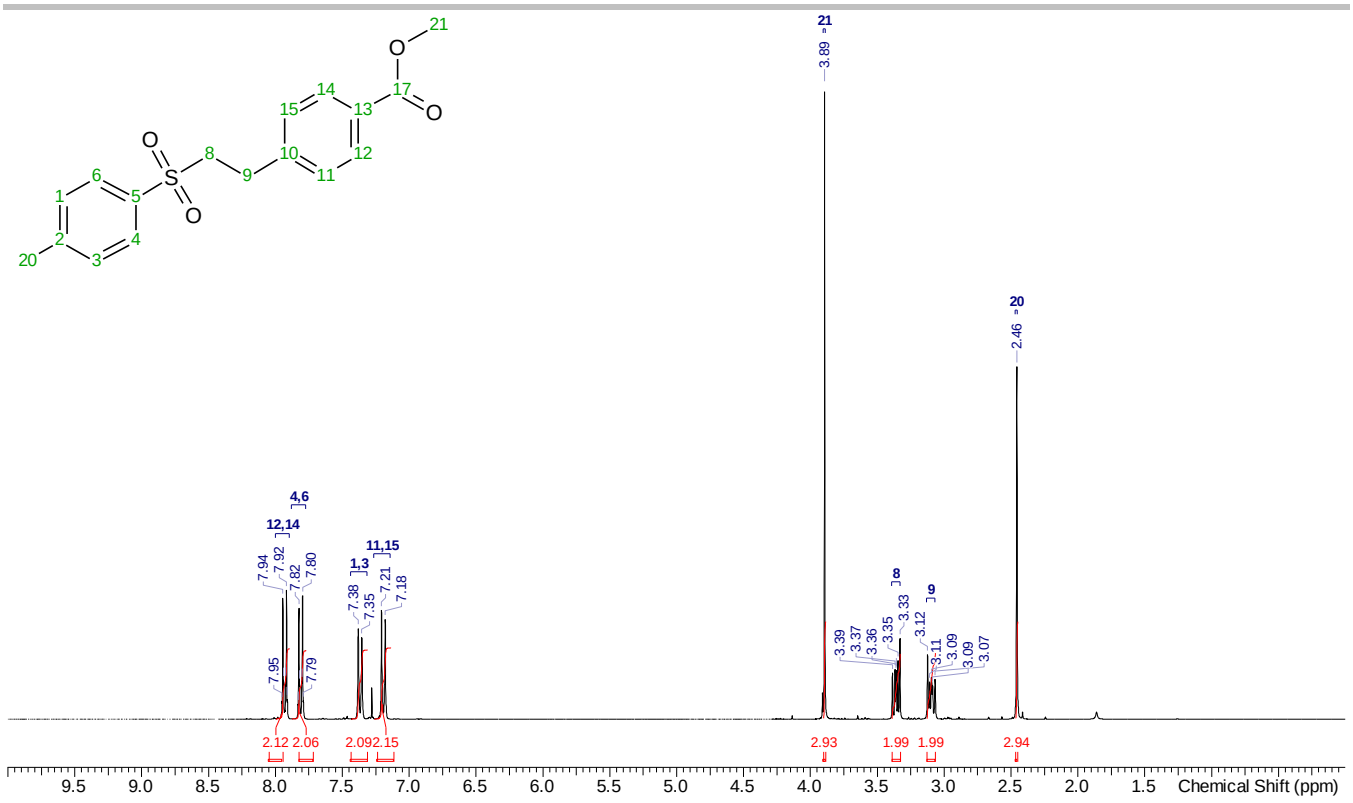


Figure S40: ^{1}H NMR spectrum of **1h**.

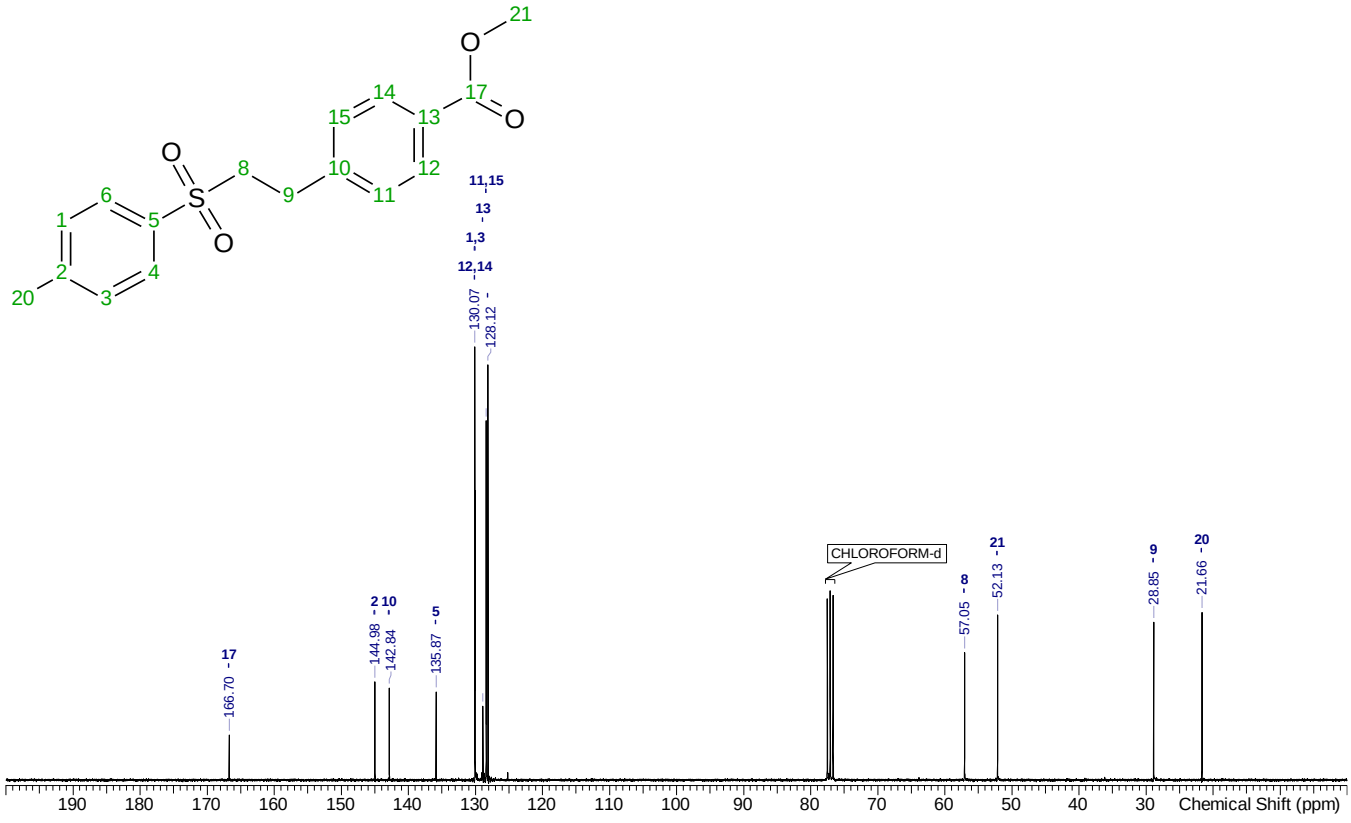


Figure S41: ^{13}C NMR spectrum of **1h.**

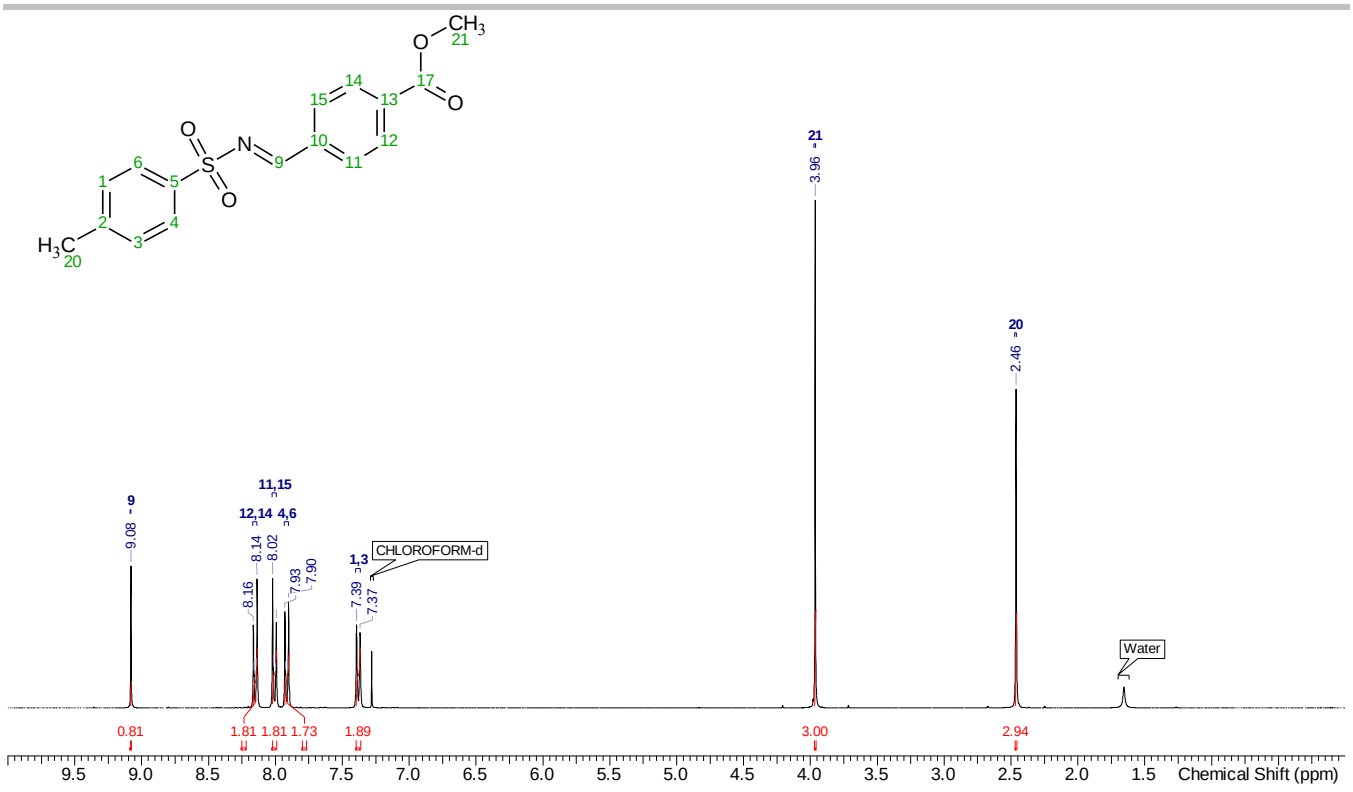


Figure S42: ^{1}H NMR spectrum of **1j**.

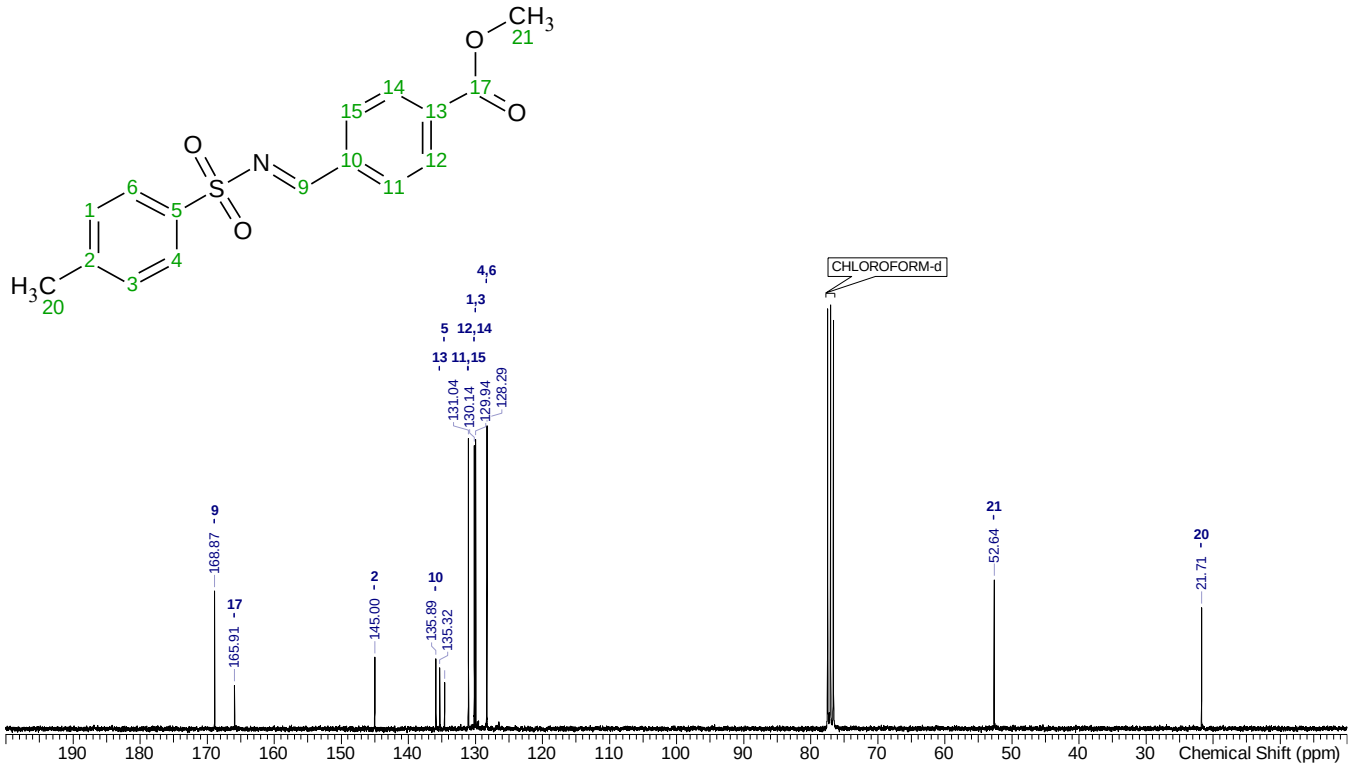


Figure S43: ^{13}C NMR spectrum of **1j.**

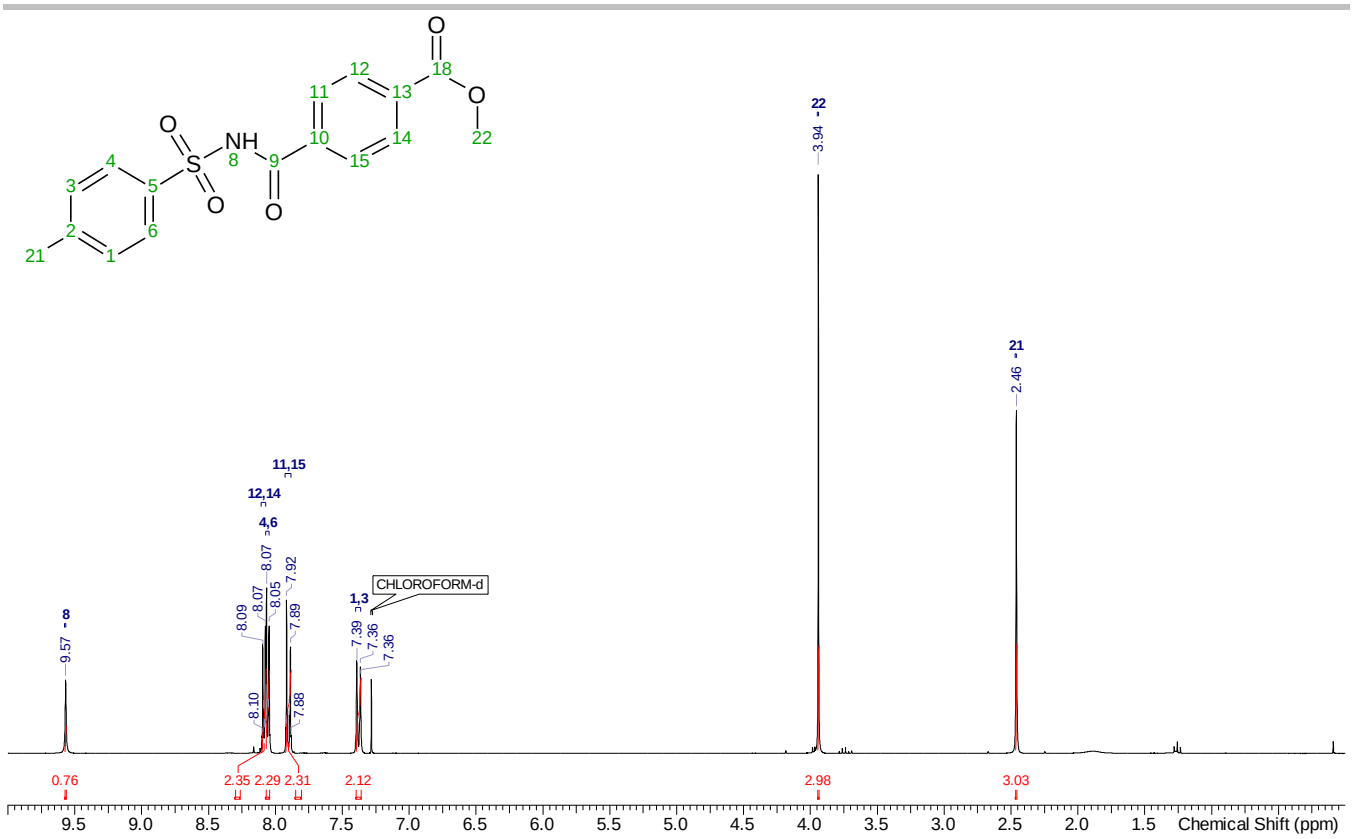


Figure S44: ^{1}H NMR spectrum of **1k**.

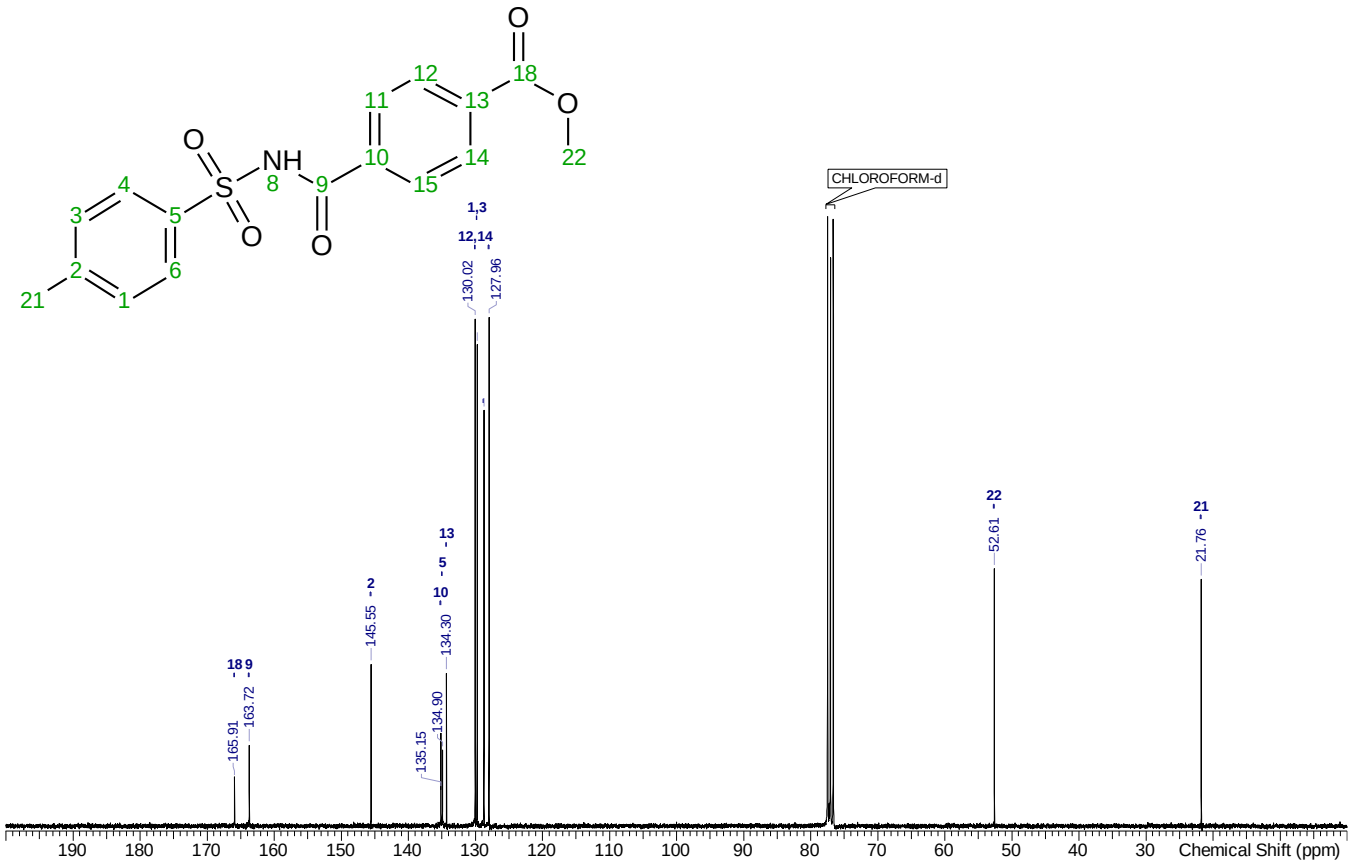


Figure S45: ^{13}C NMR spectrum of **1k.**

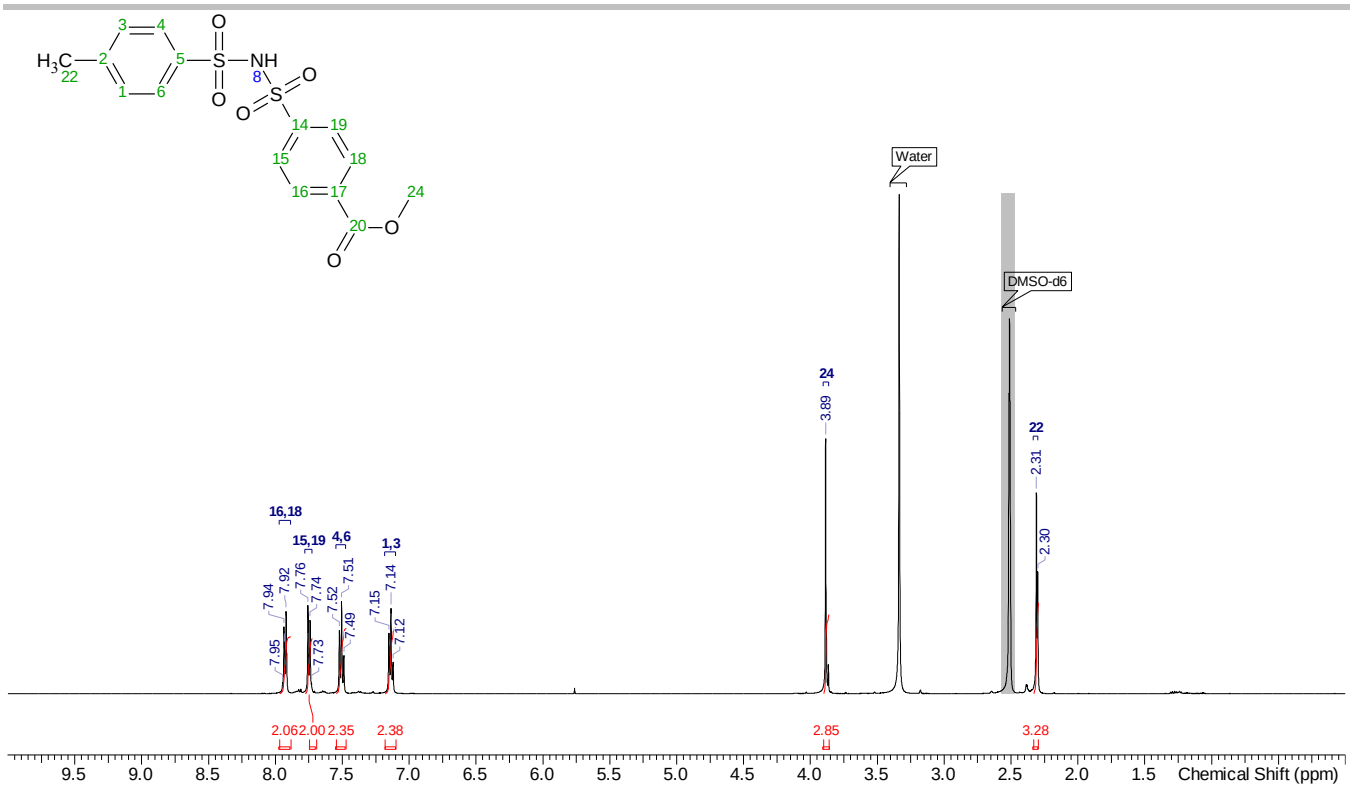


Figure S46: ^{1}H NMR spectrum of **1l**.

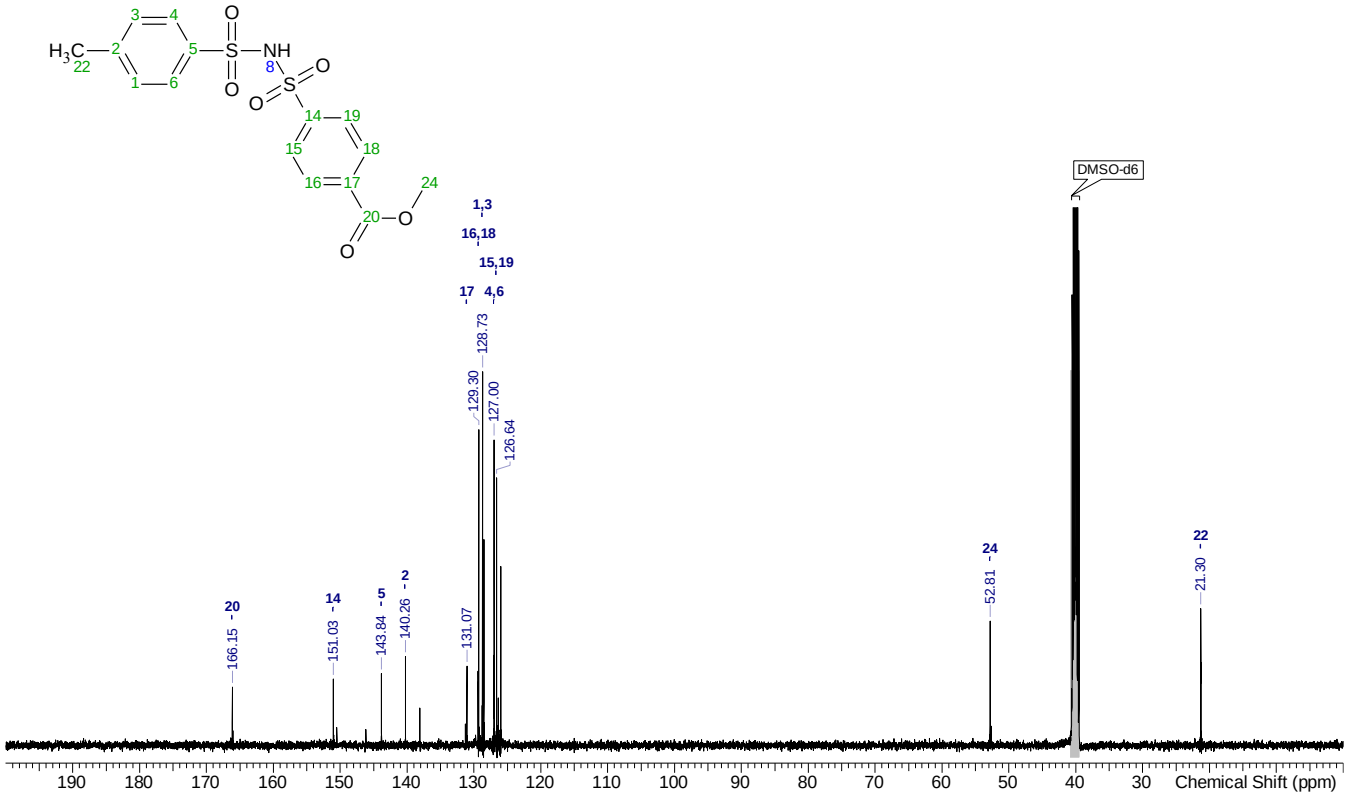


Figure S47: ^{13}C NMR spectrum of **1l.**

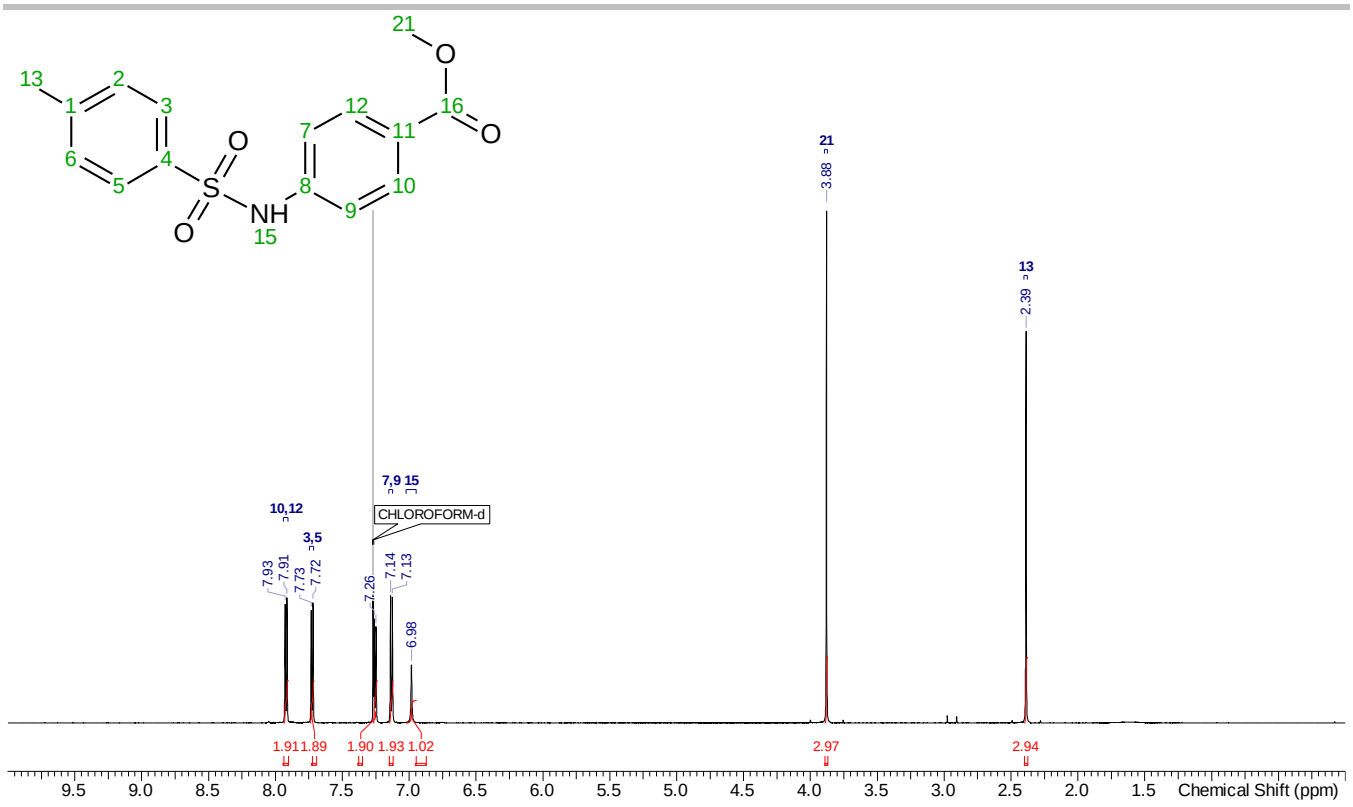


Figure S48: ^{1}H NMR spectrum of **1m**.

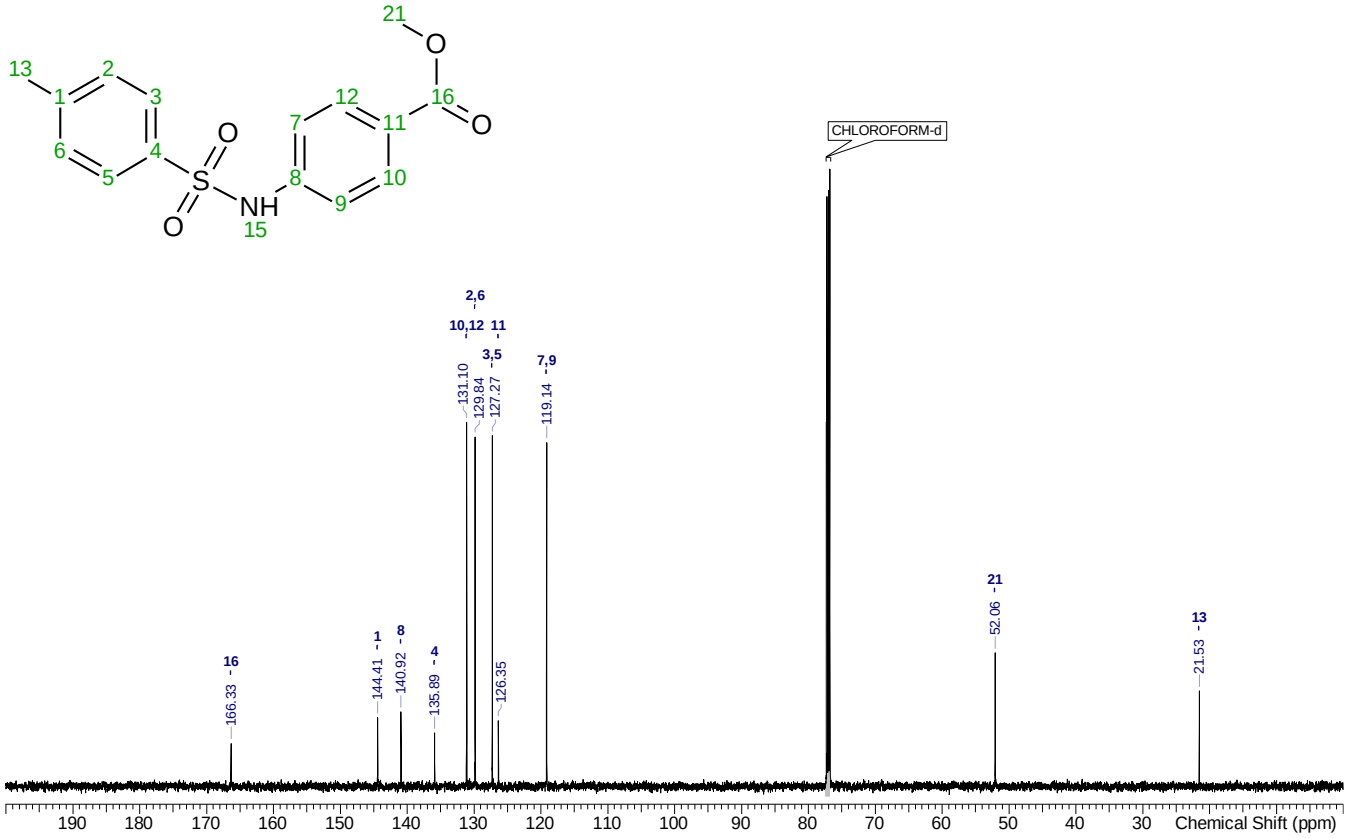


Figure S49: ^{13}C NMR spectrum of **1m.**

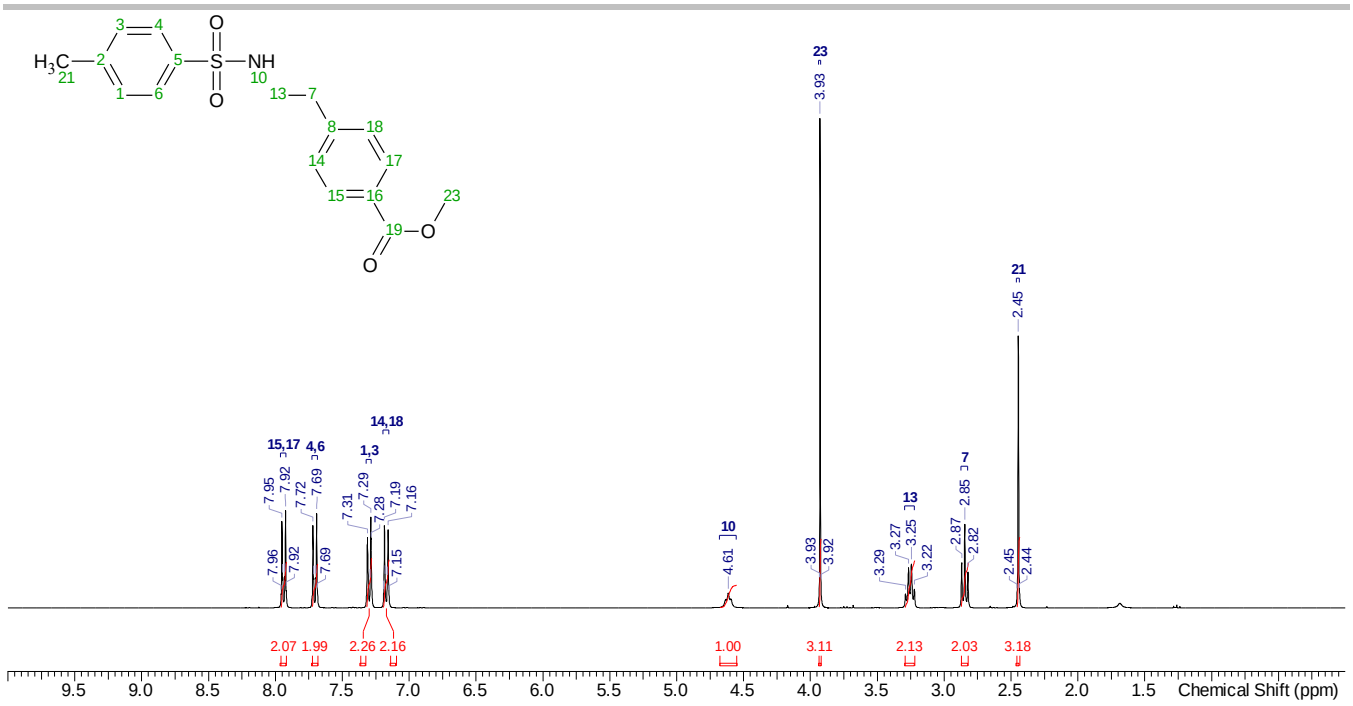


Figure S50: ^{1}H NMR spectrum of **1n**.

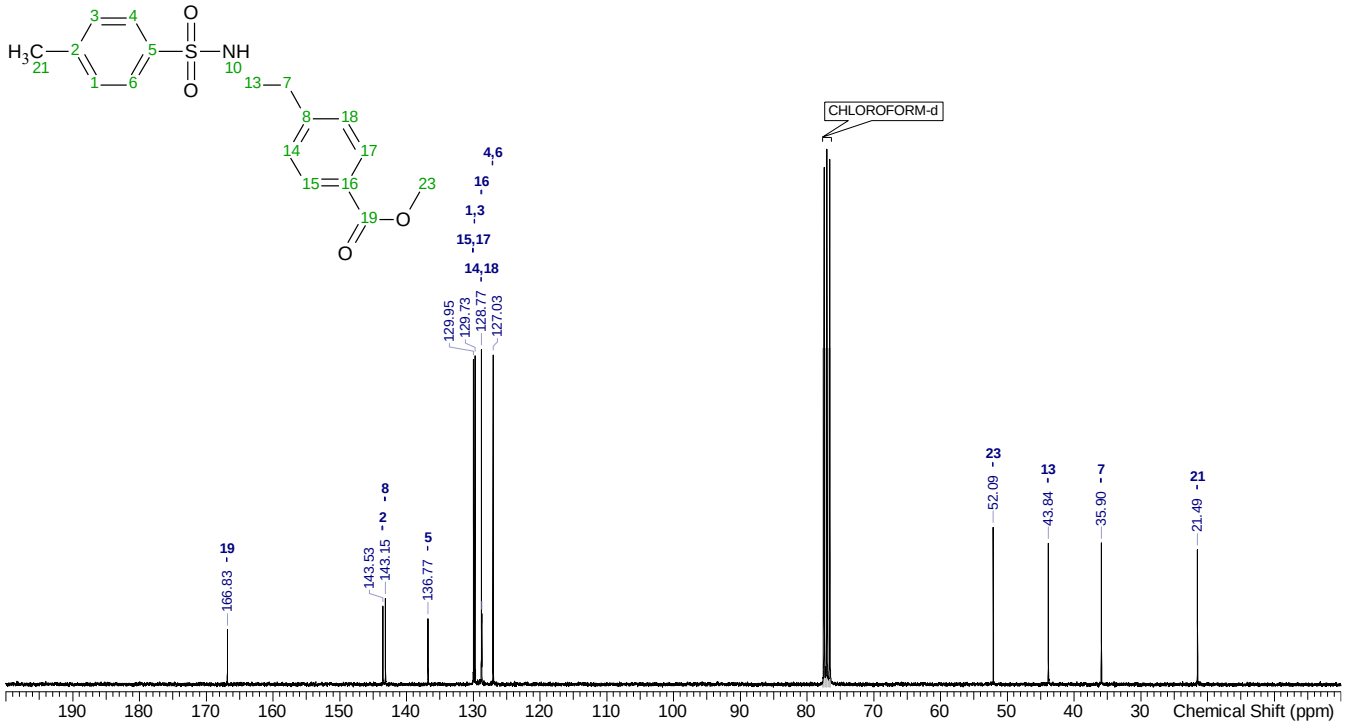


Figure S51: ^{13}C NMR spectrum of **1n.**

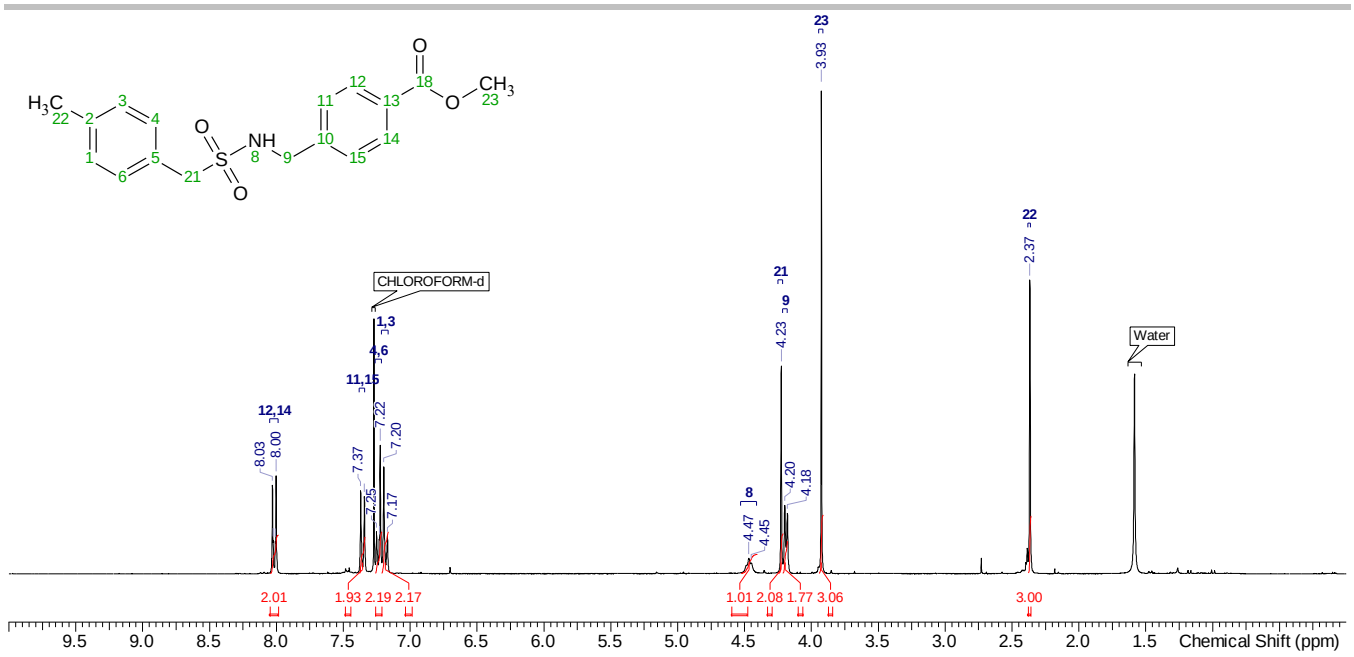


Figure S52: ^{1}H NMR spectrum of **1o**.

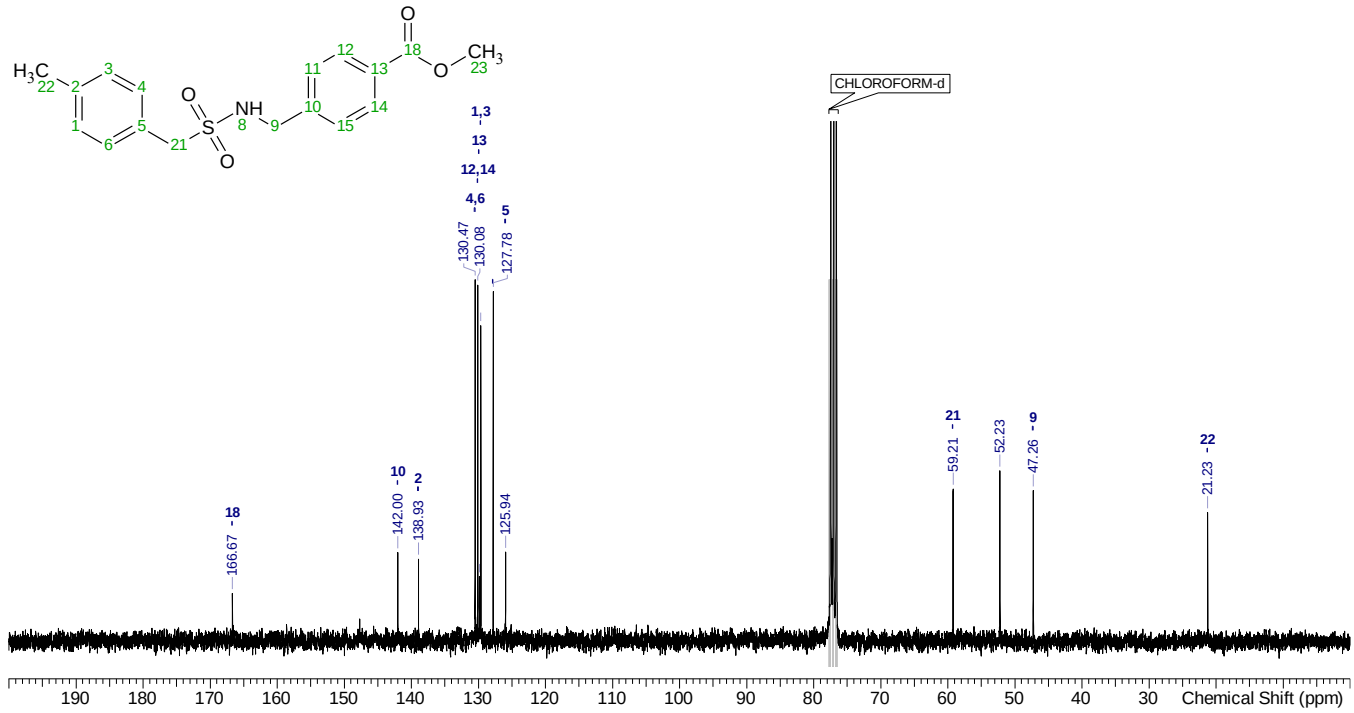


Figure S53: ^{13}C NMR spectrum of **1o.**

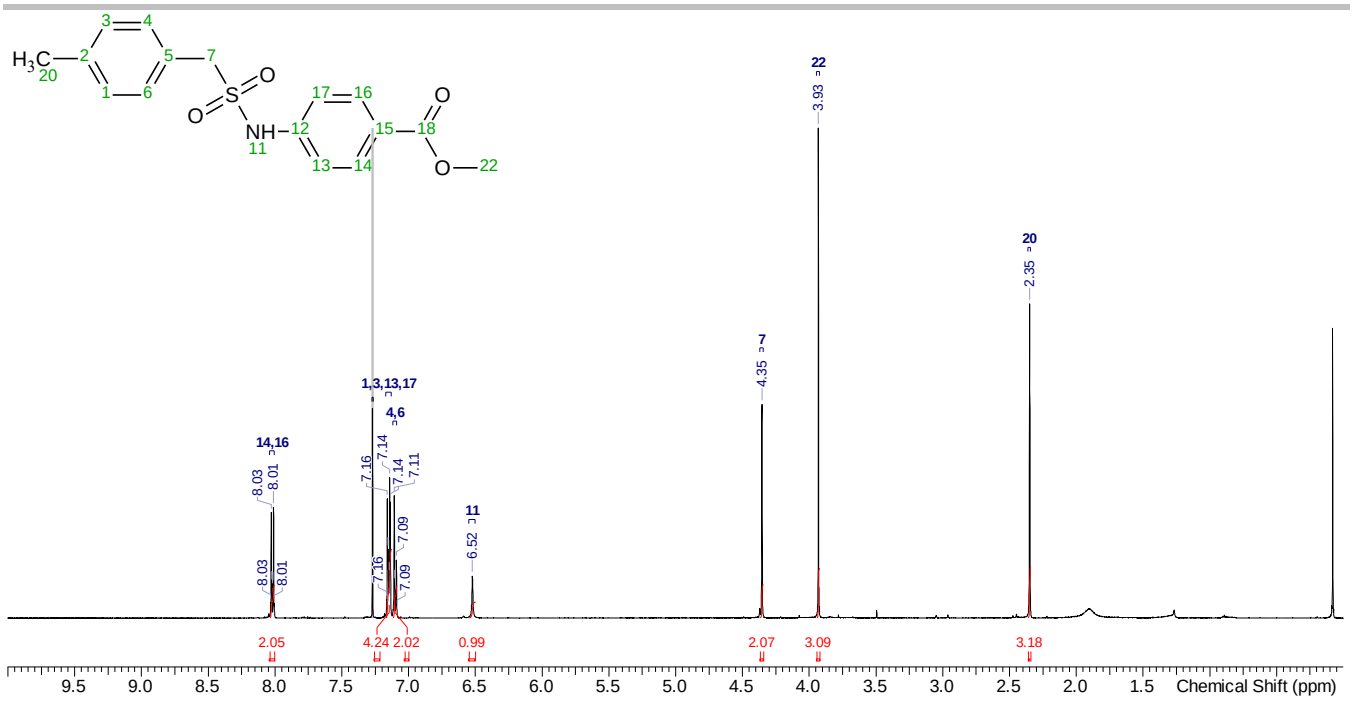


Figure S54: ^{1}H NMR spectrum of **1p**.

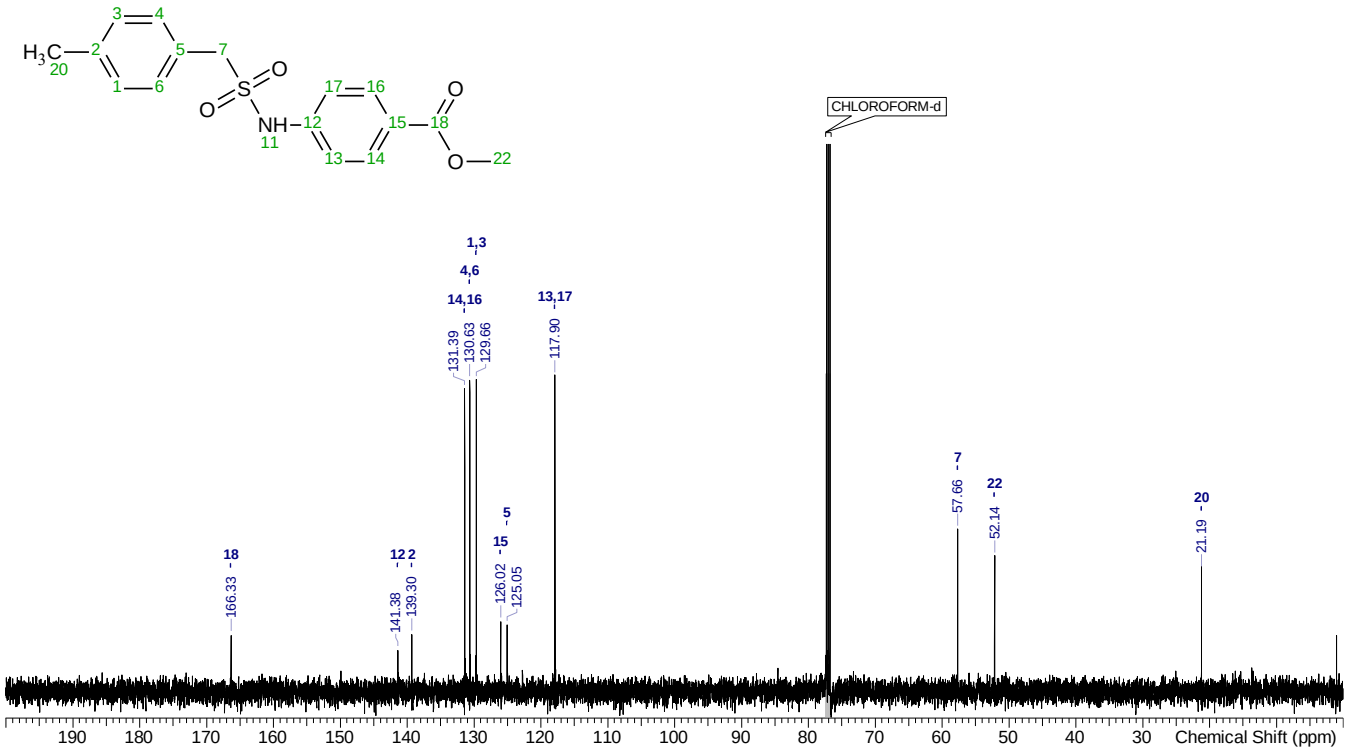


Figure S55: ^{13}C NMR spectrum of **1p.**

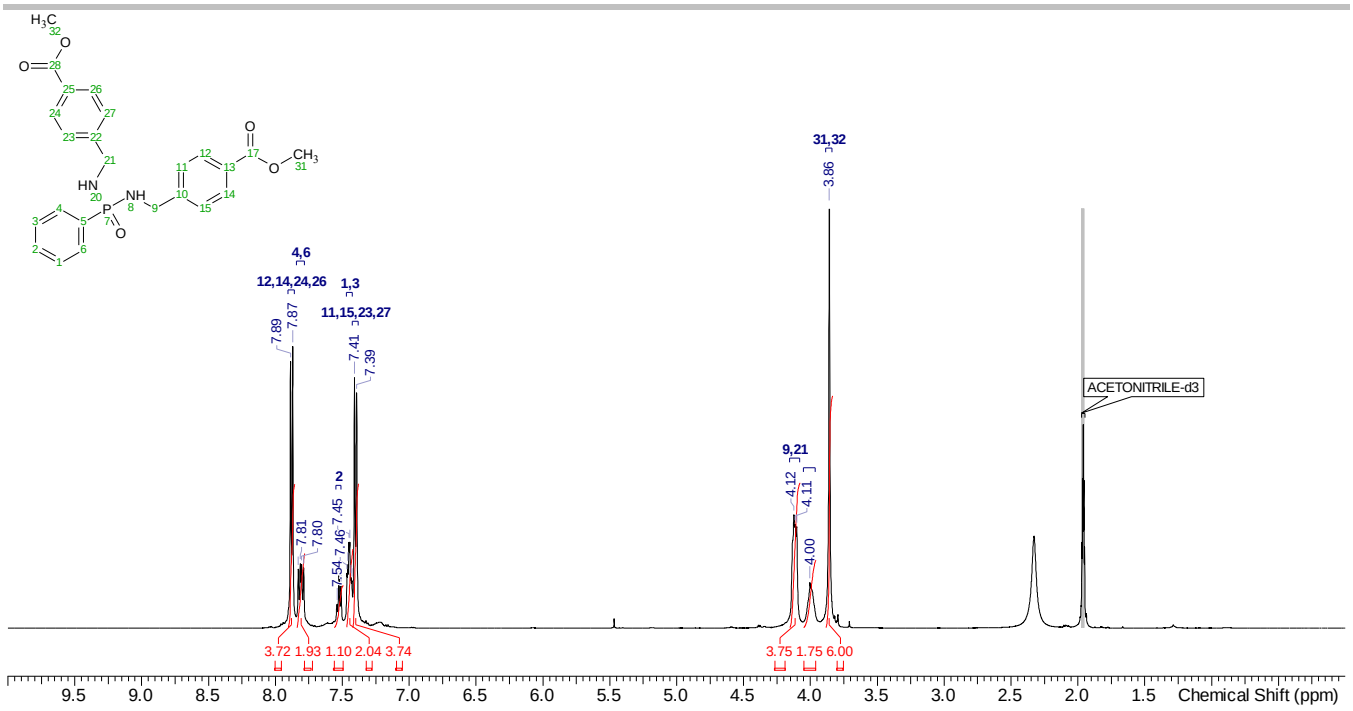


Figure S56: ^{1}H NMR spectrum of **1q**.

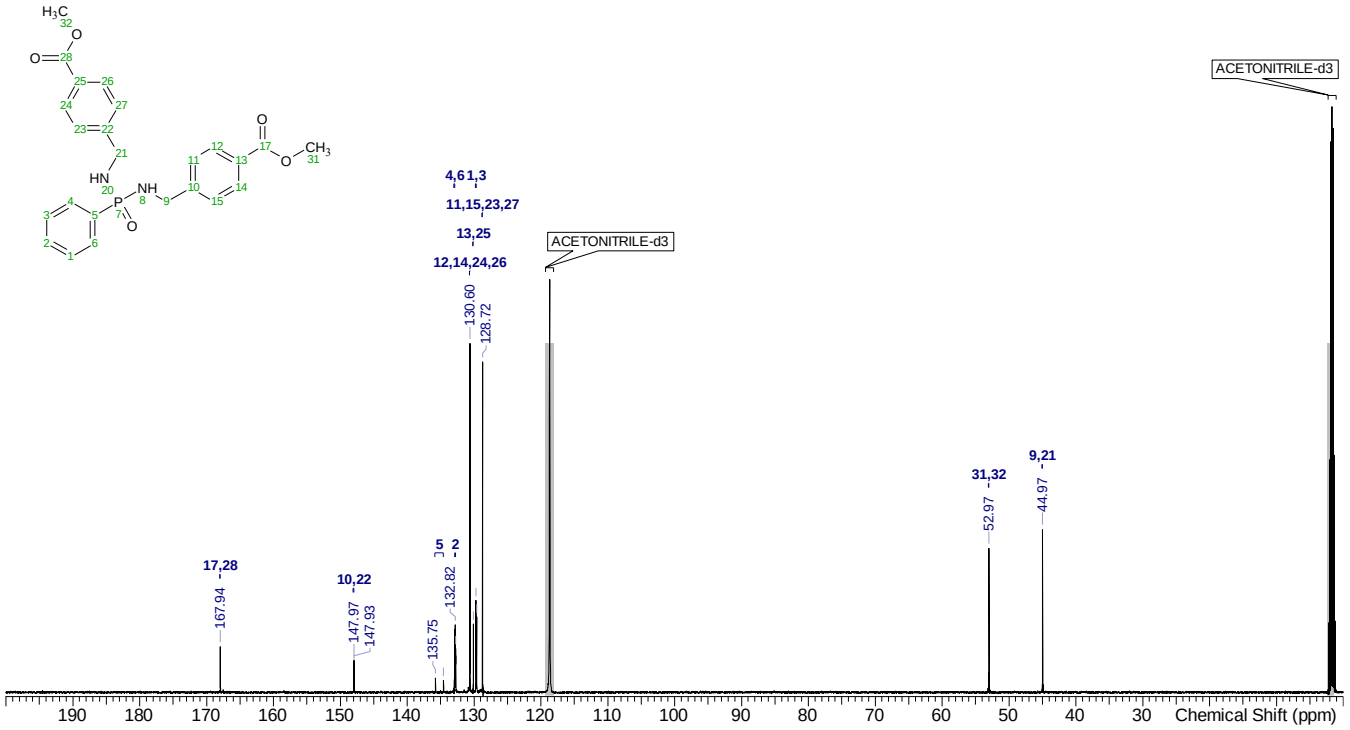


Figure S57: ^{13}C NMR spectrum of **1q.**

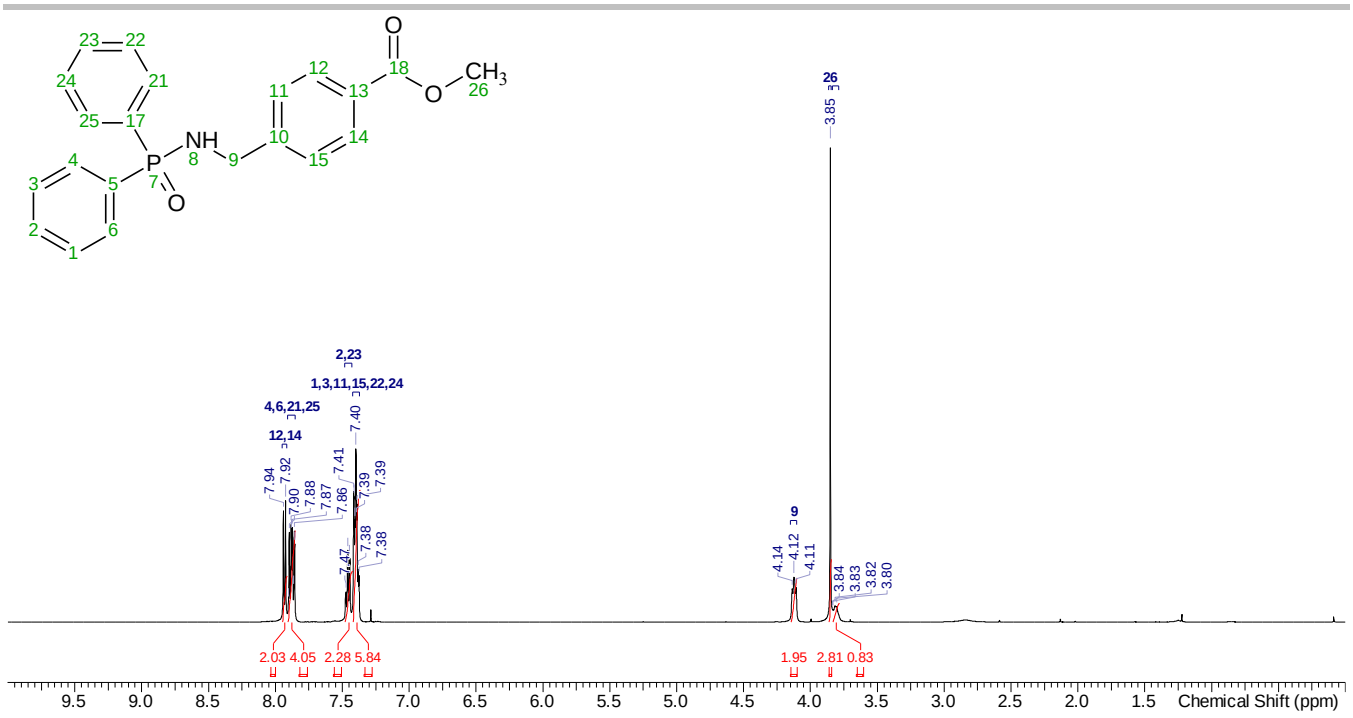


Figure S58: ^{1}H NMR spectrum of **1r**.

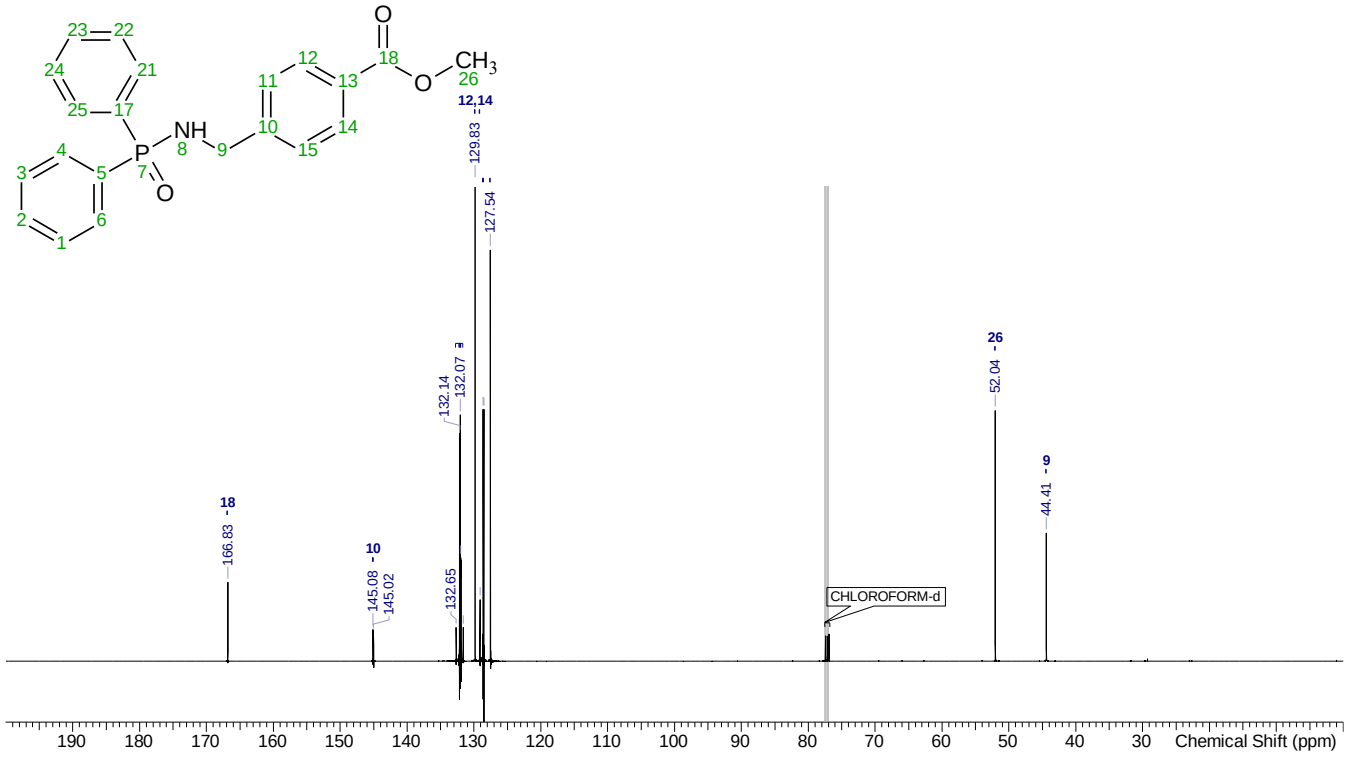


Figure S59: ^{13}C NMR spectrum of **1r.**

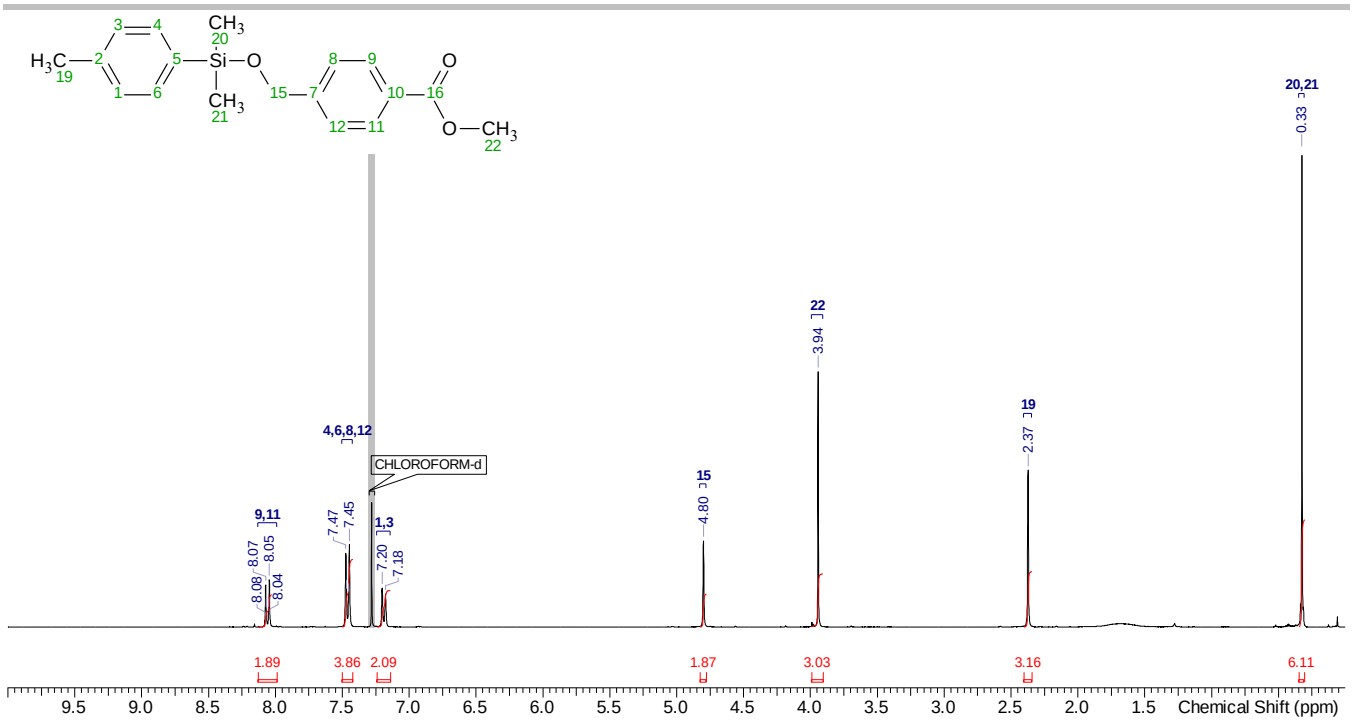


Figure S60: ^{1}H NMR spectrum of **1s**.

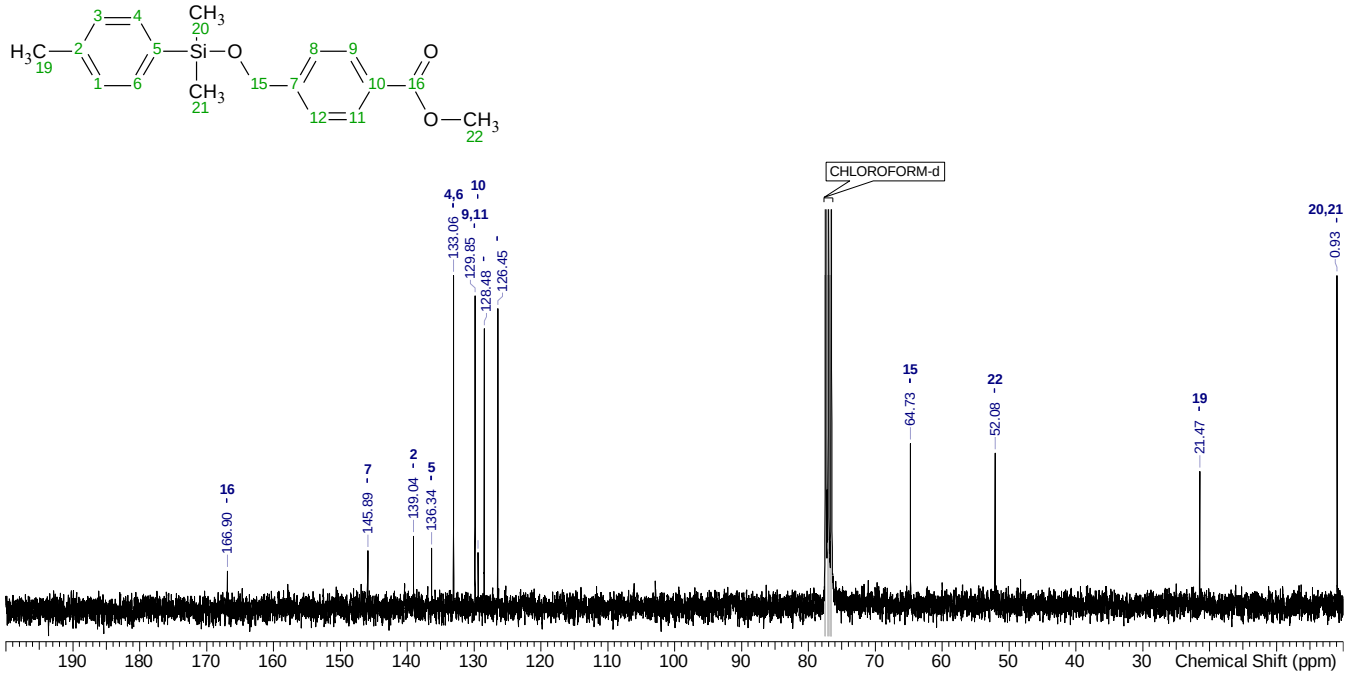


Figure S61: ^{13}C NMR spectrum of **1s.**

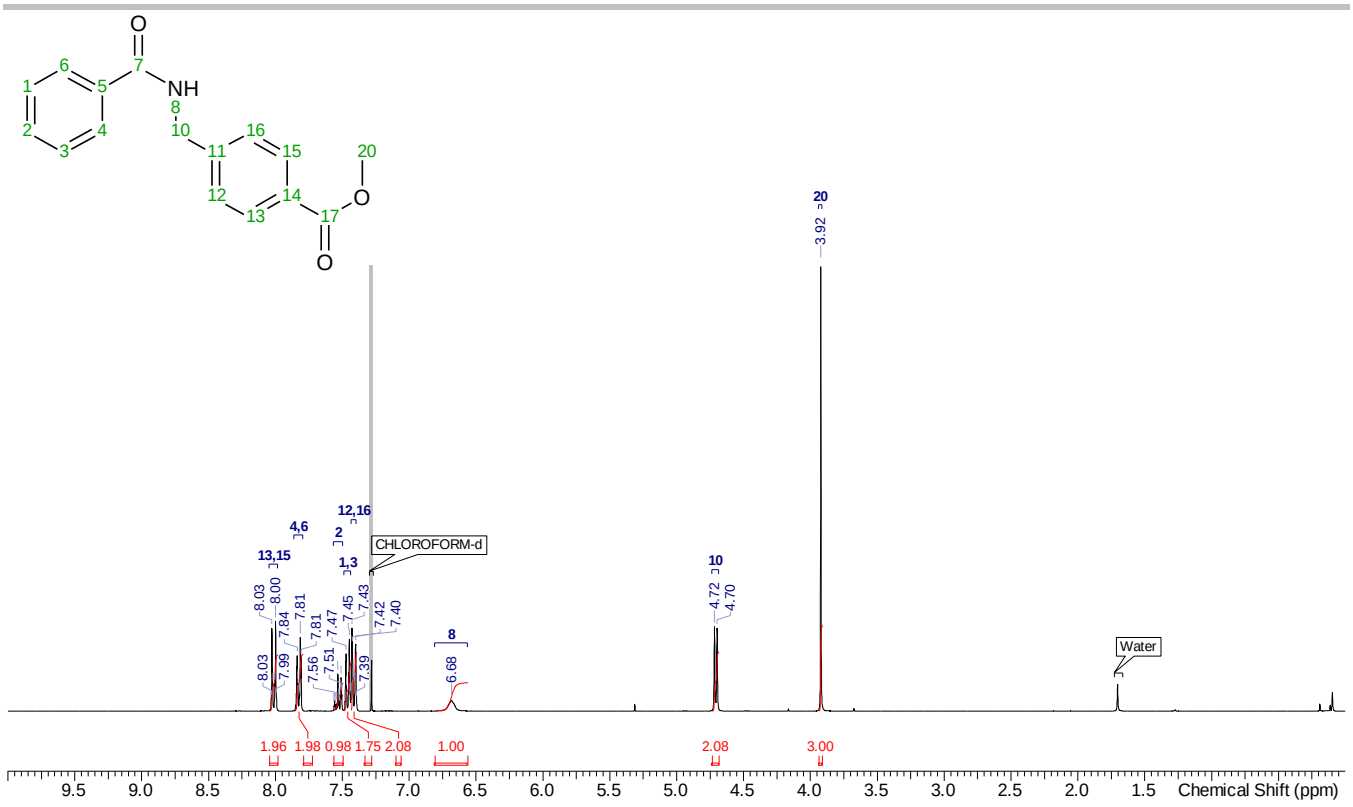


Figure S62: ^{1}H NMR spectrum of **1t**.

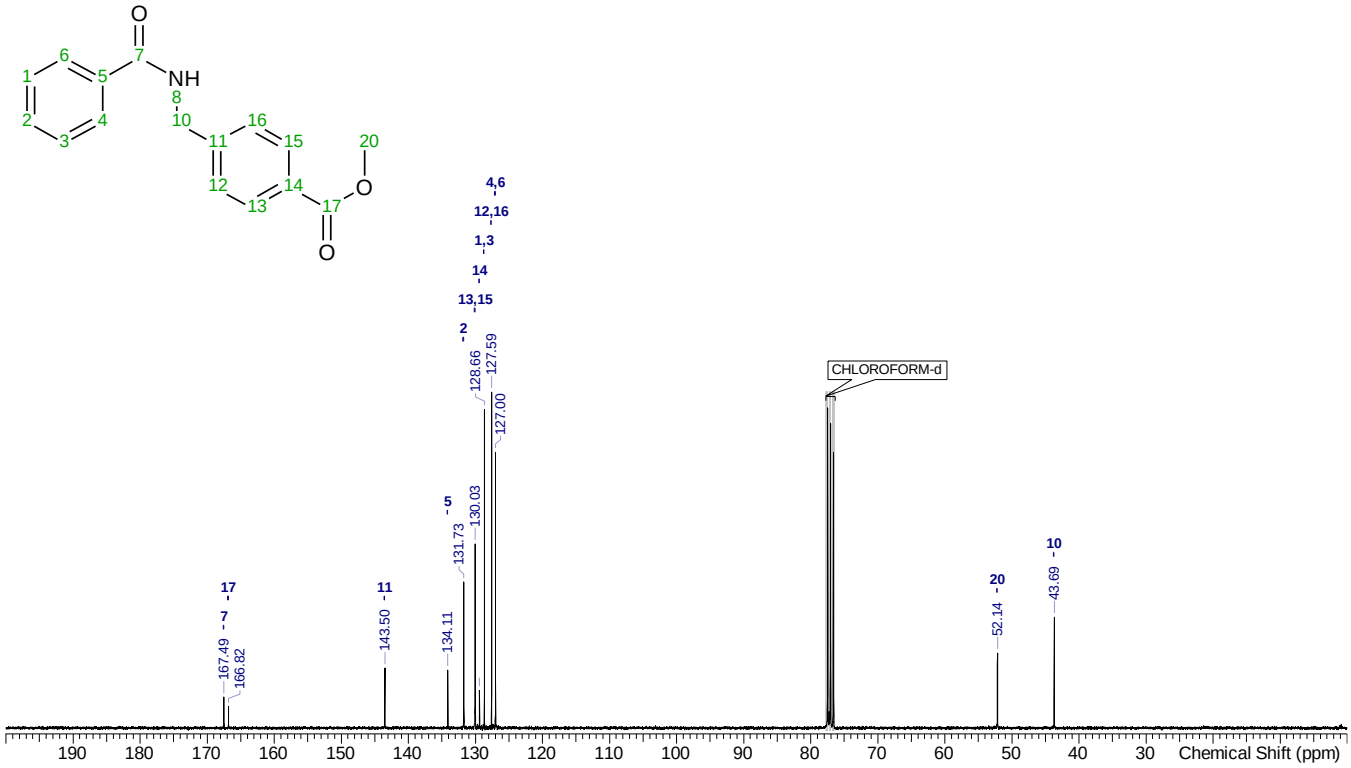


Figure S63: ^{13}C NMR spectrum of **1t.**

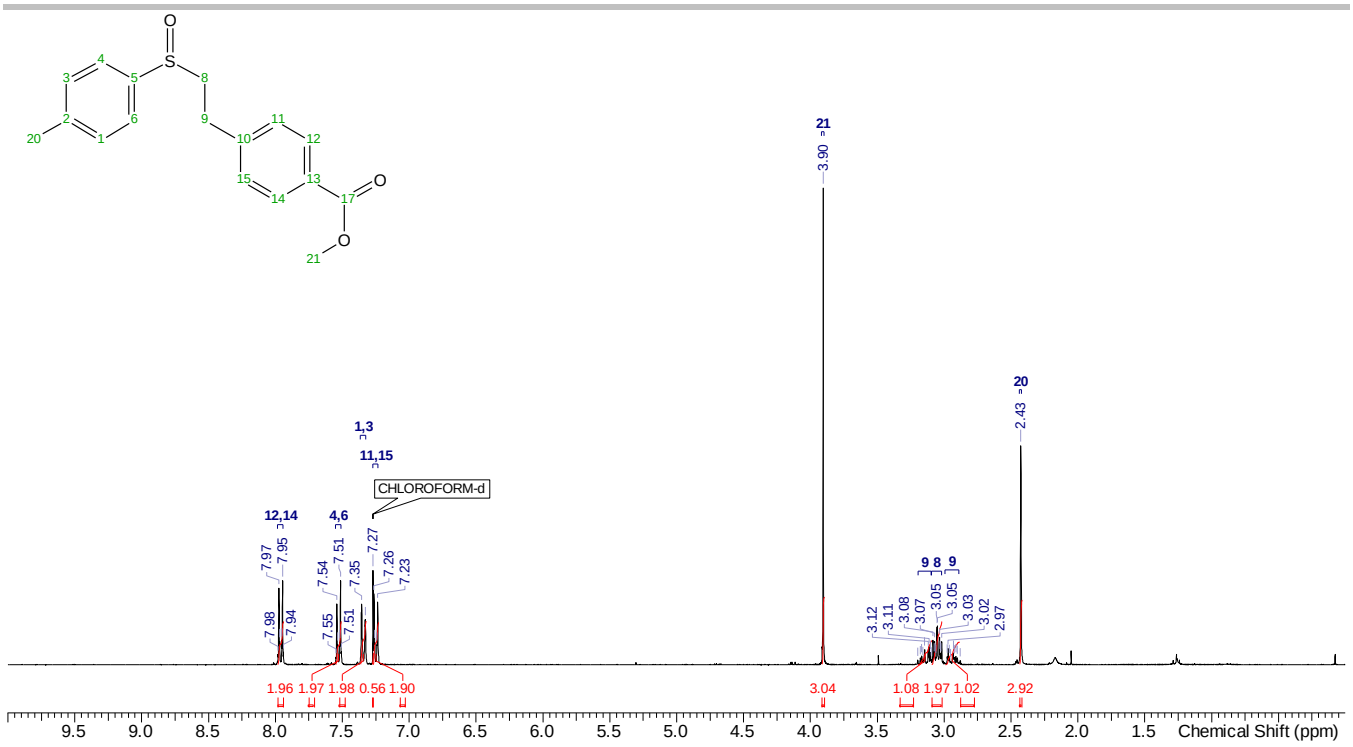


Figure S64: ^{1}H NMR spectrum of **1u**.

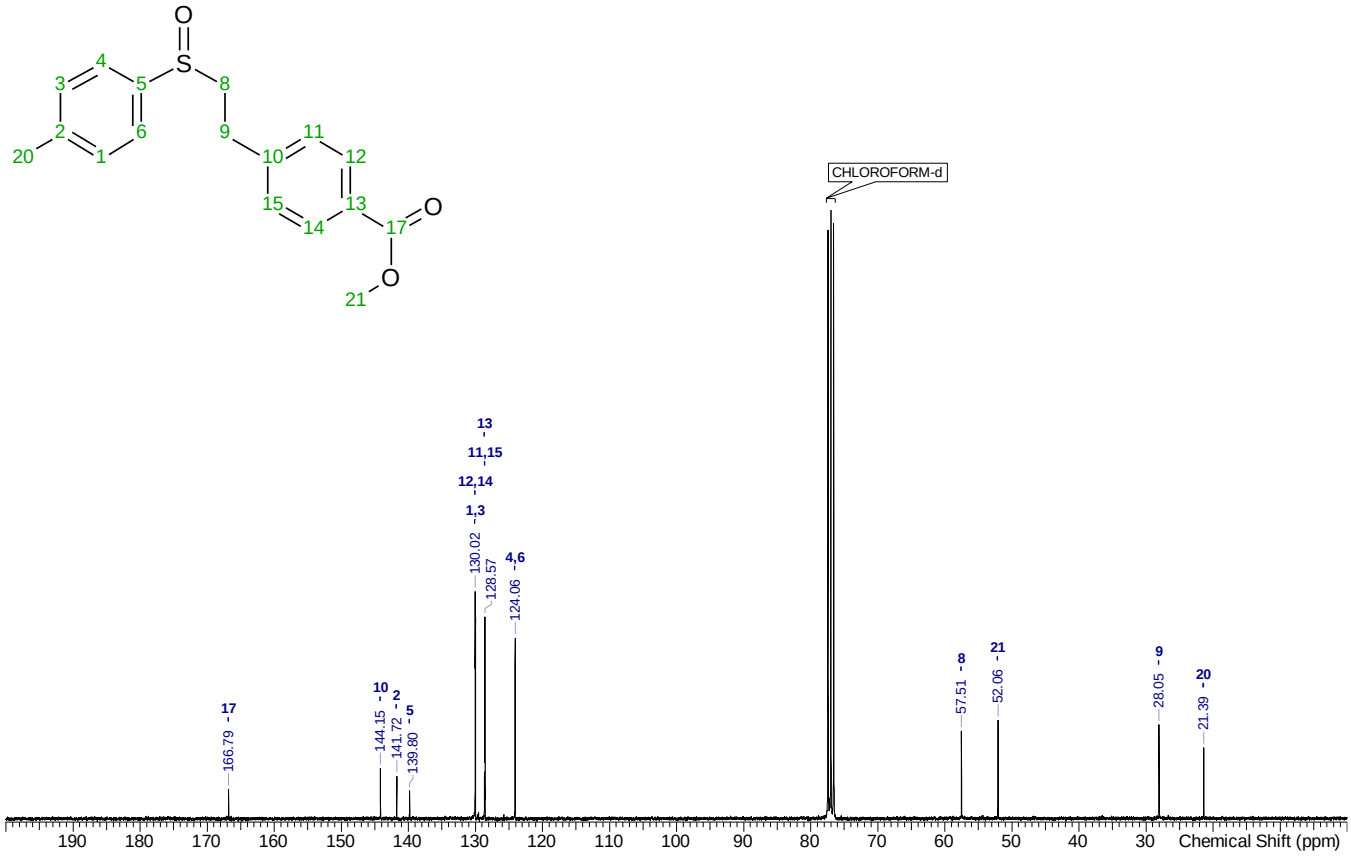


Figure S65: ^{13}C NMR spectrum of **1u.**

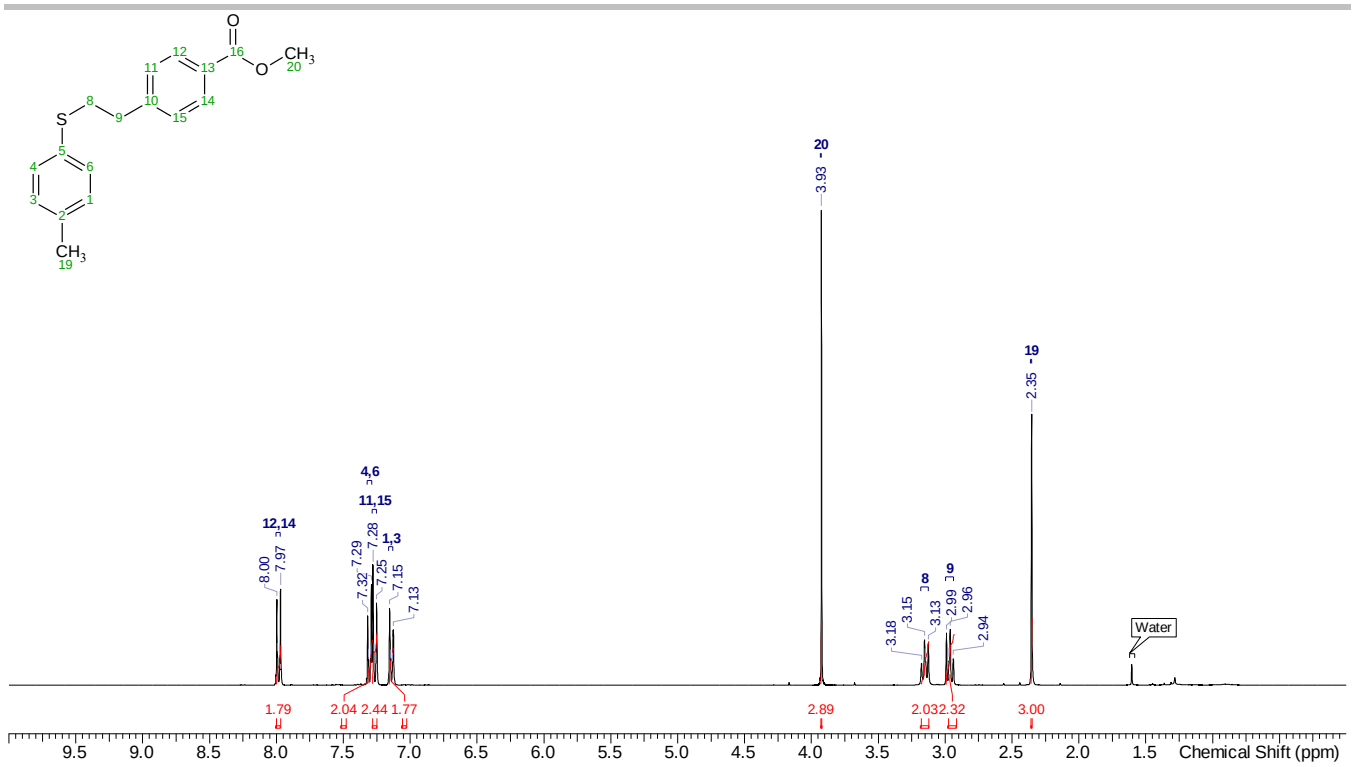


Figure S66: ^{1}H NMR spectrum of **1v**.

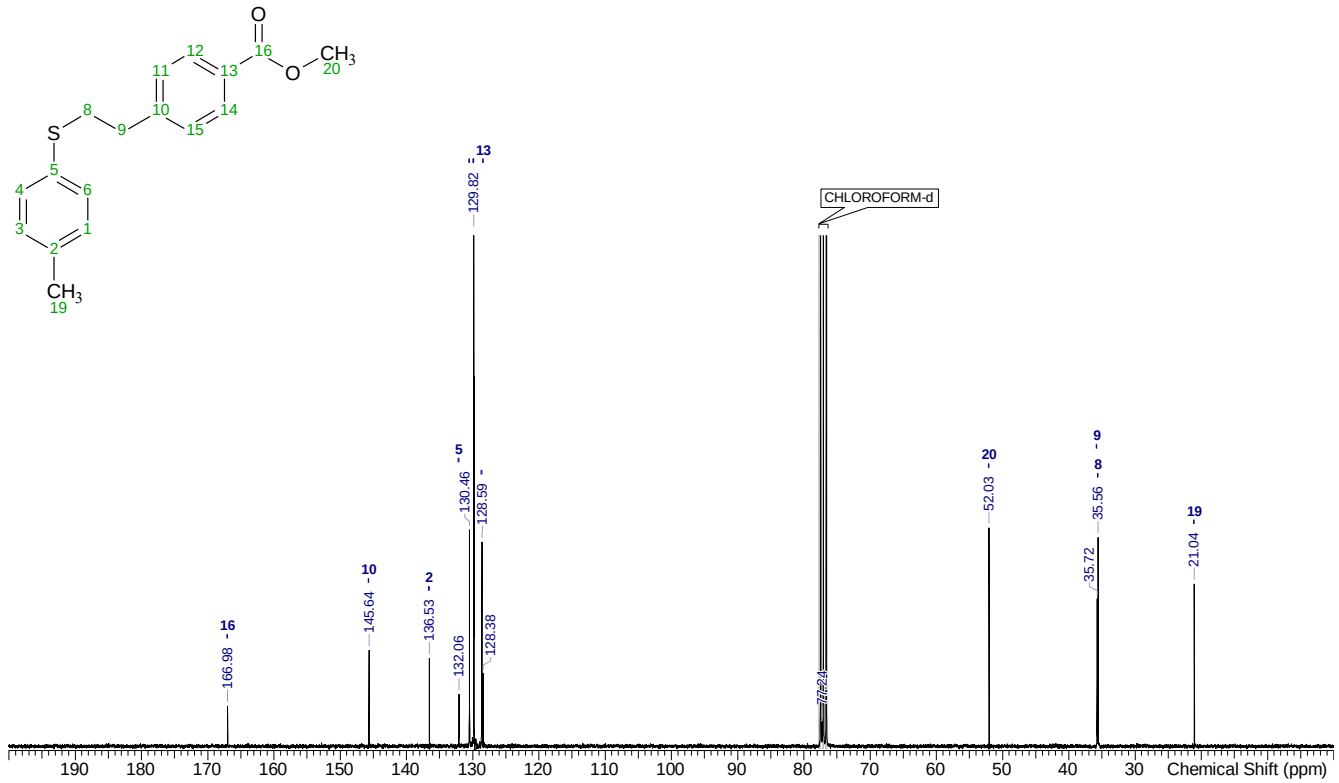


Figure S67: ^{13}C NMR spectrum of **1v.**

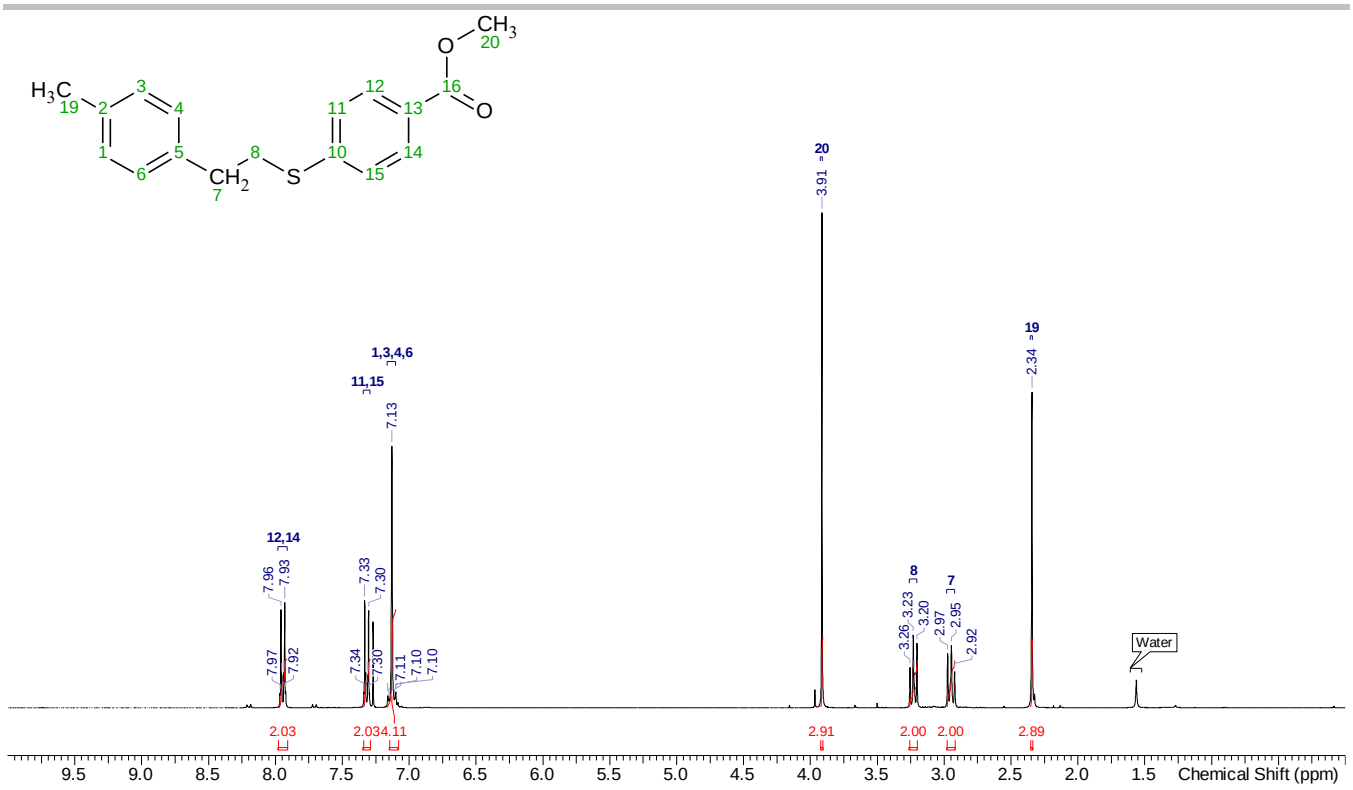


Figure S68: ^{1}H NMR spectrum of **1w**.

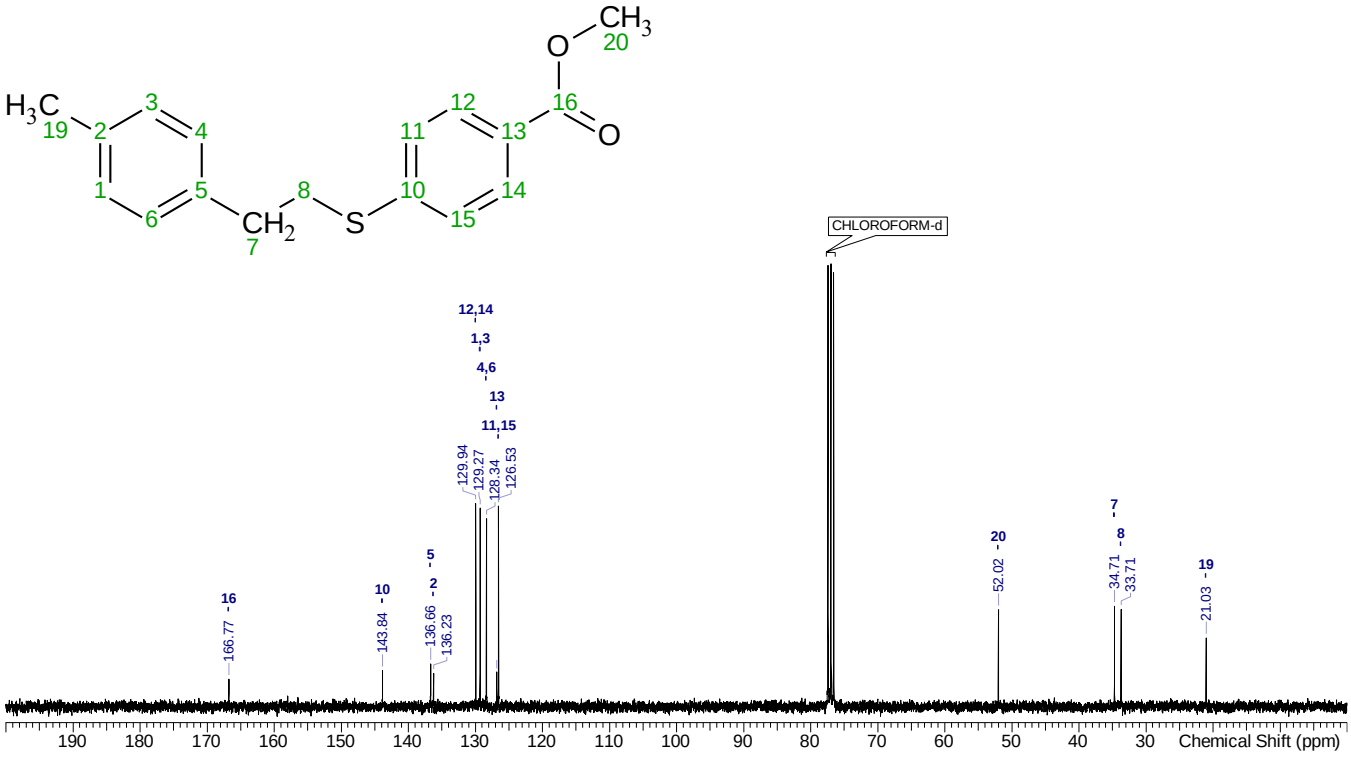


Figure S69: ^{13}C NMR spectrum of **1w.**

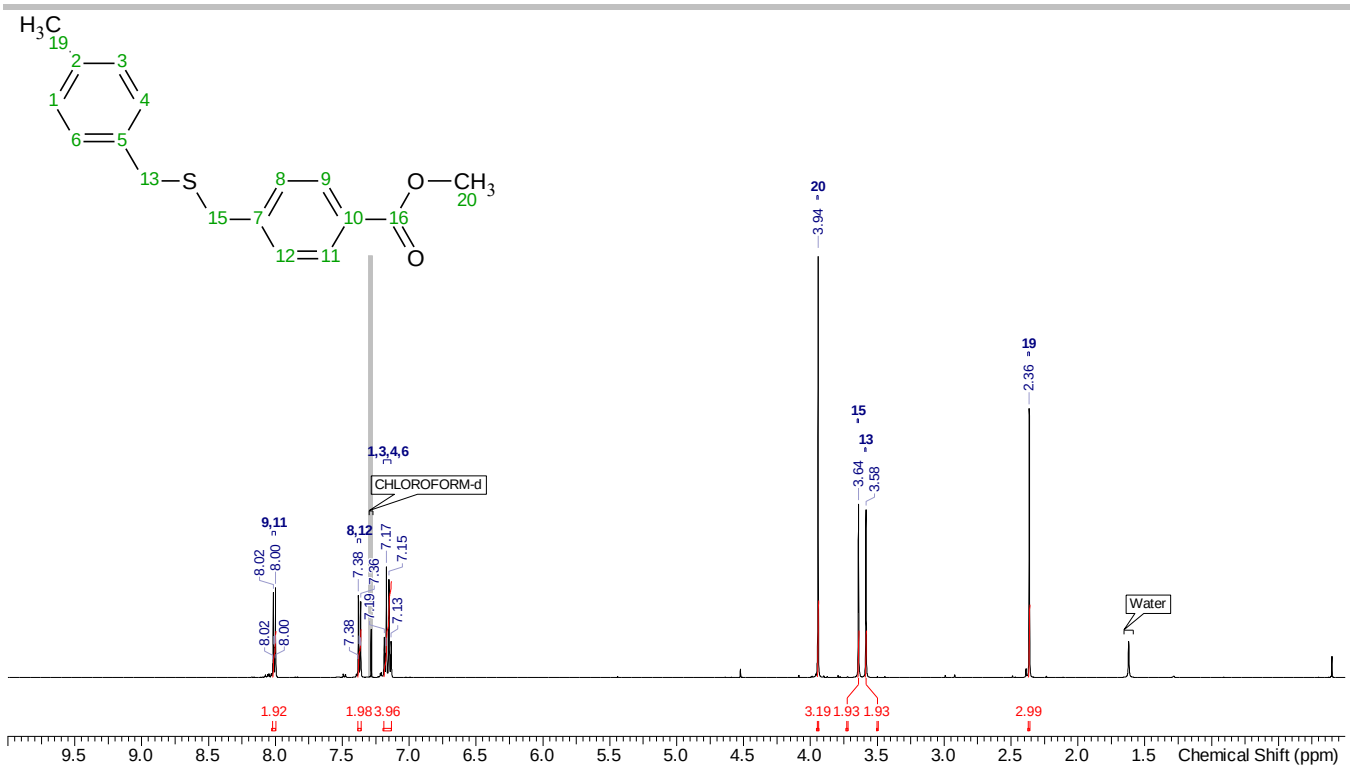


Figure S70: ^{1}H NMR spectrum of **1x**.

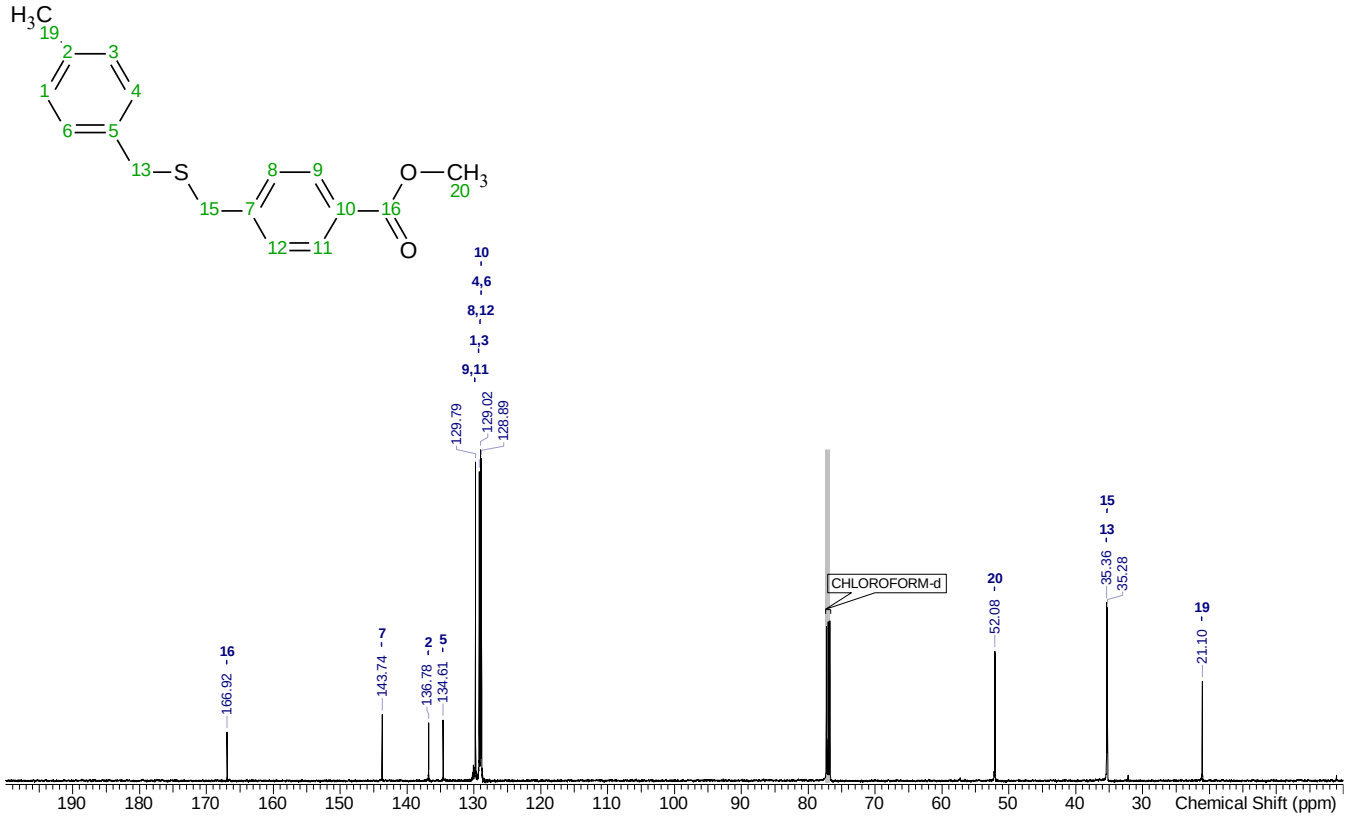


Figure S71: ^{13}C NMR spectrum of **1x.**

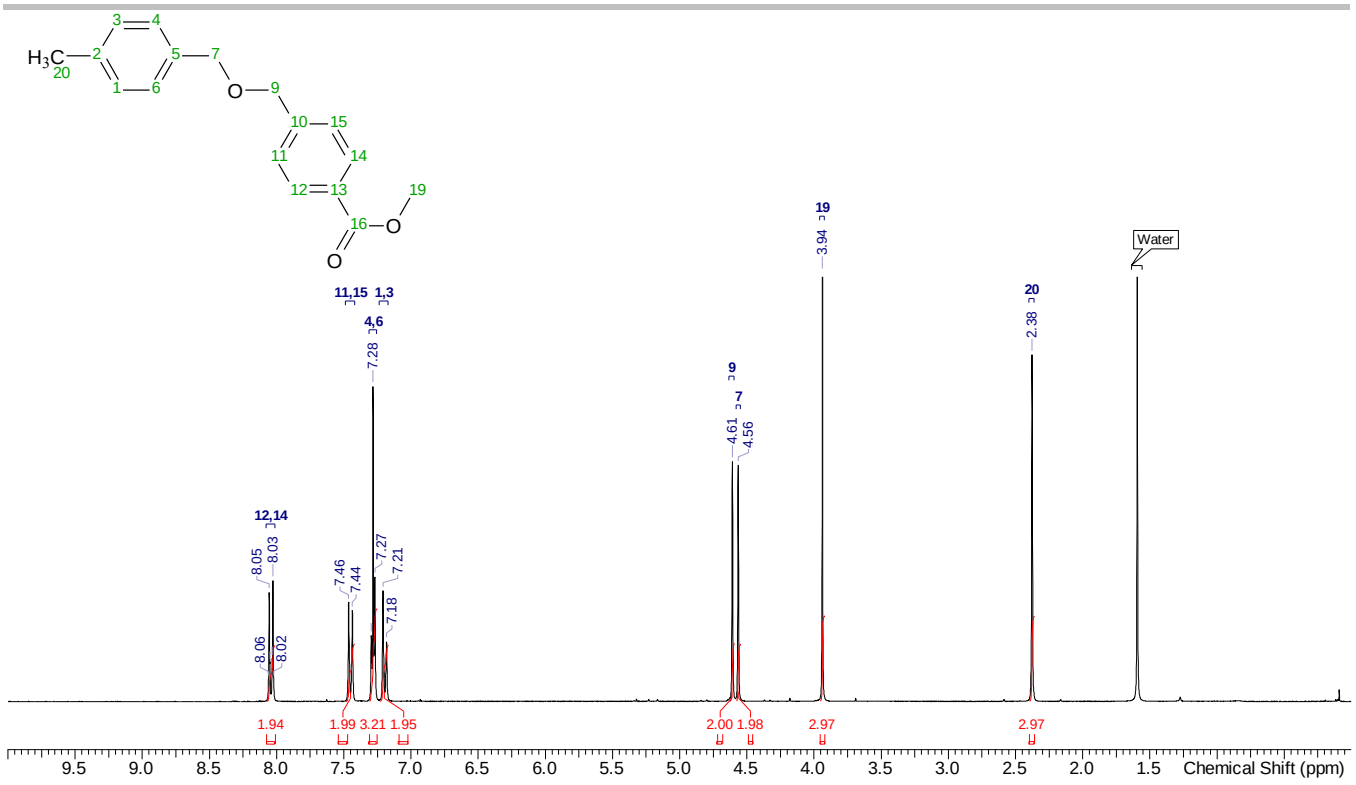


Figure S72: ^{1}H NMR spectrum of **1y**.

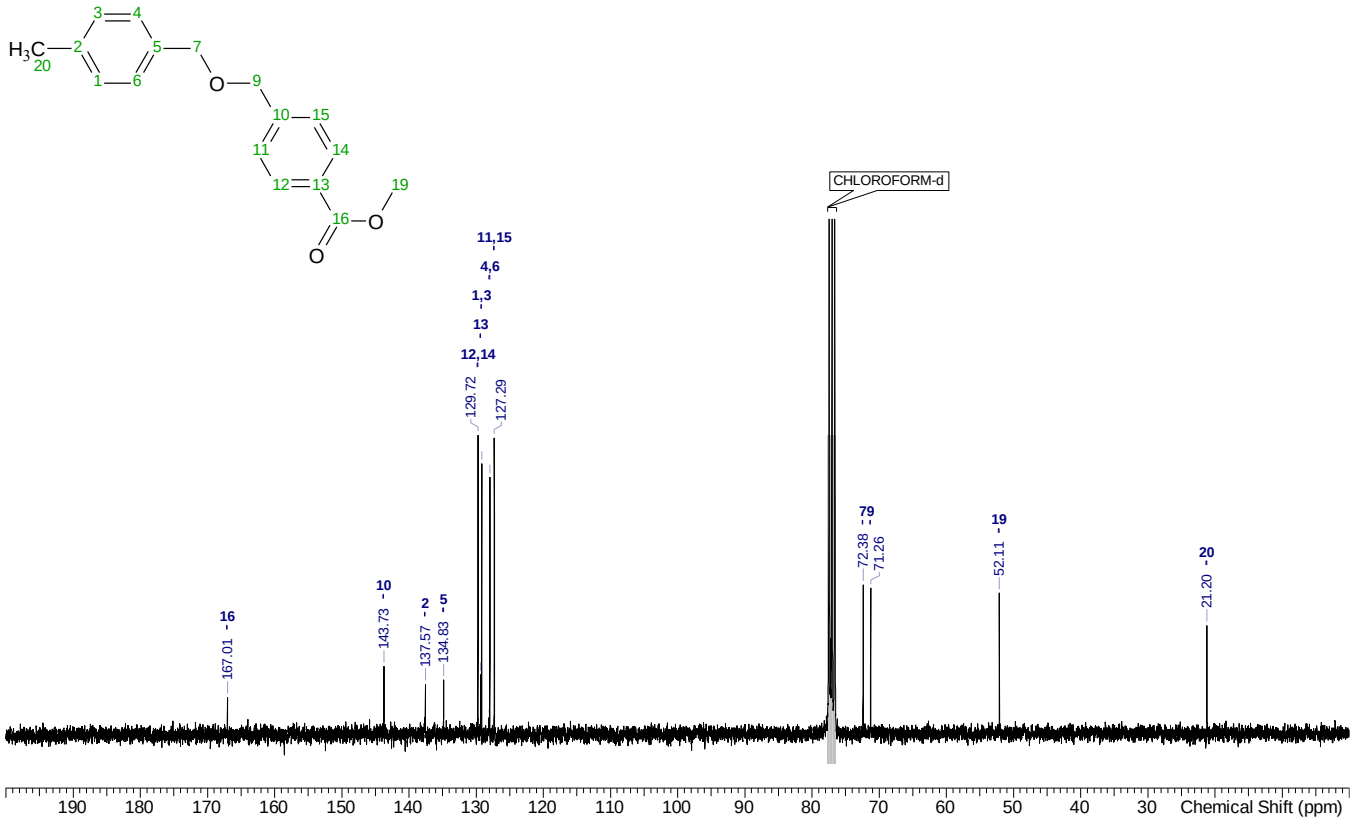


Figure S73: ^{13}C NMR spectrum of **1y.**

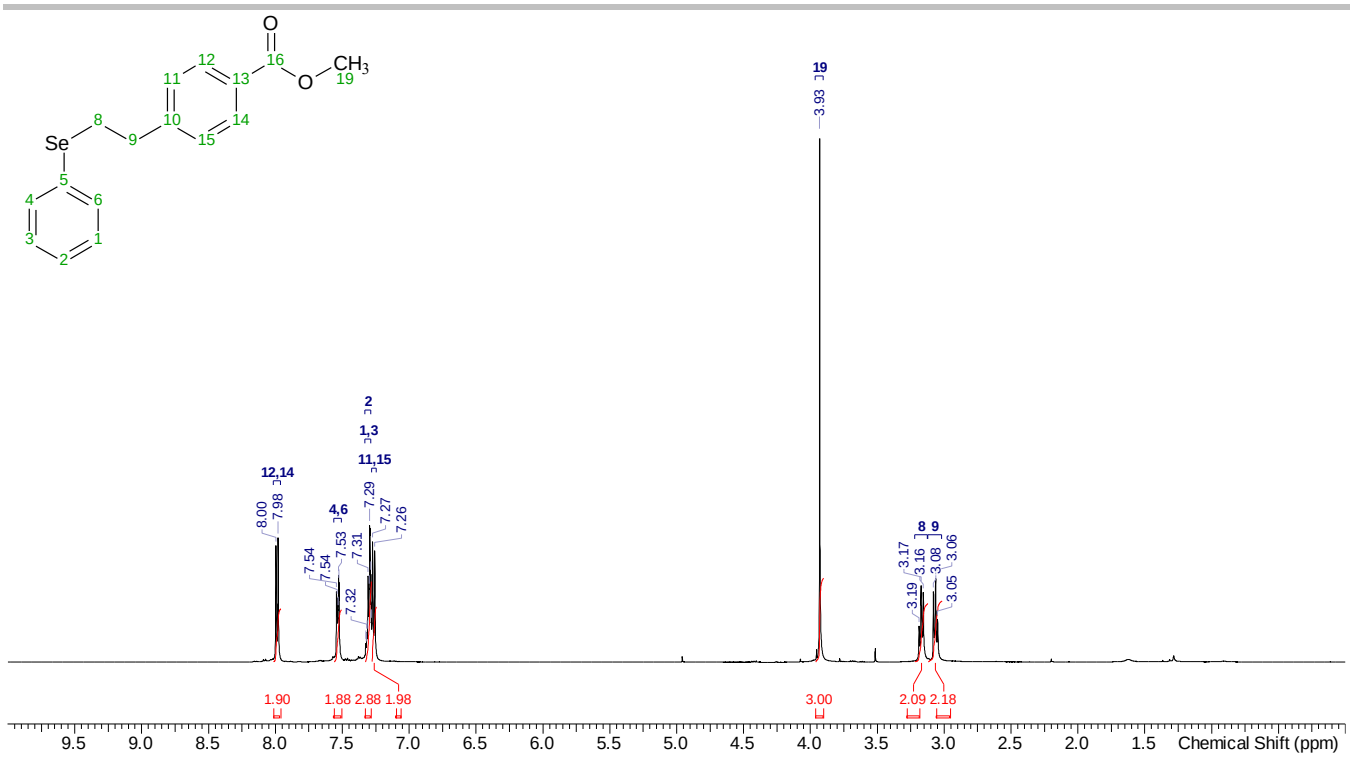


Figure S74: ^{1}H NMR spectrum of **1z**.

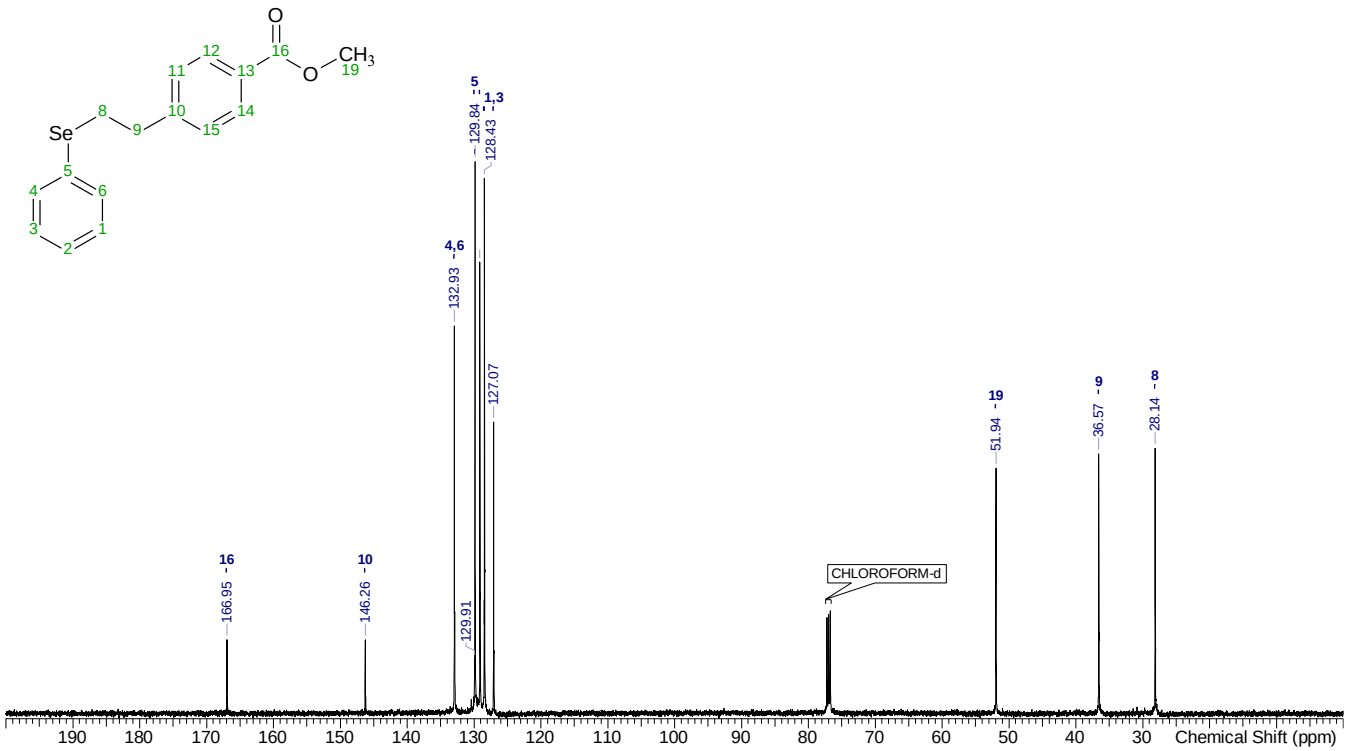


Figure S75: ^{13}C NMR spectrum of **1z.**

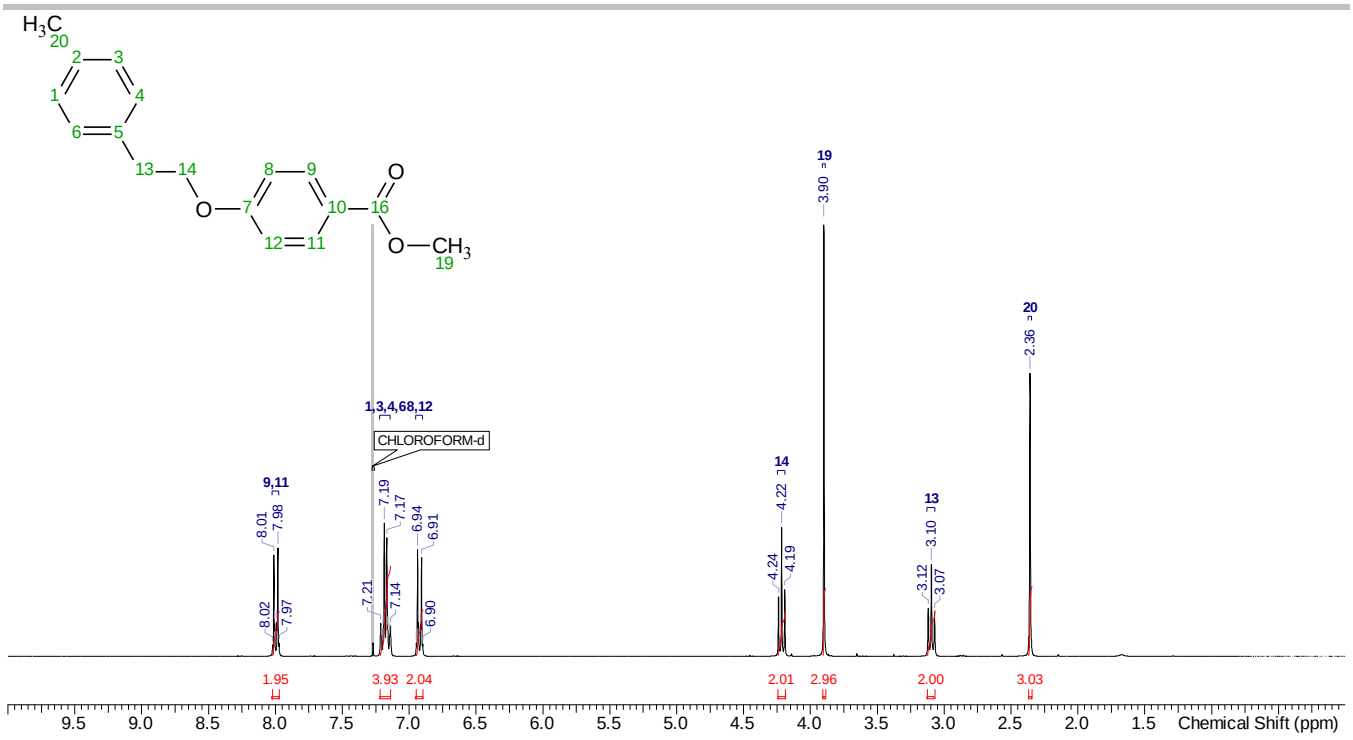


Figure S76: ^{1}H NMR spectrum of **1aa**.

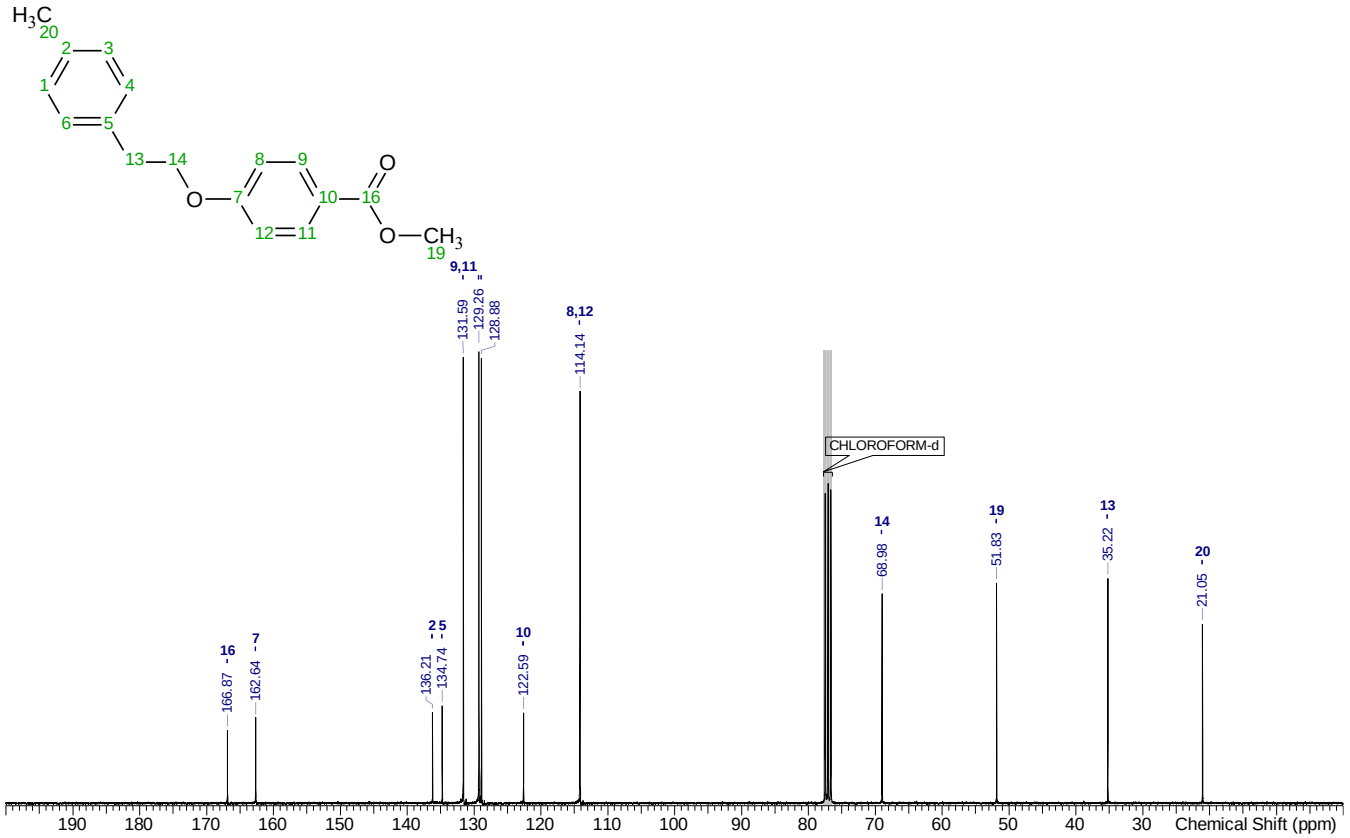


Figure S77: ^{13}C NMR spectrum of **1aa.**

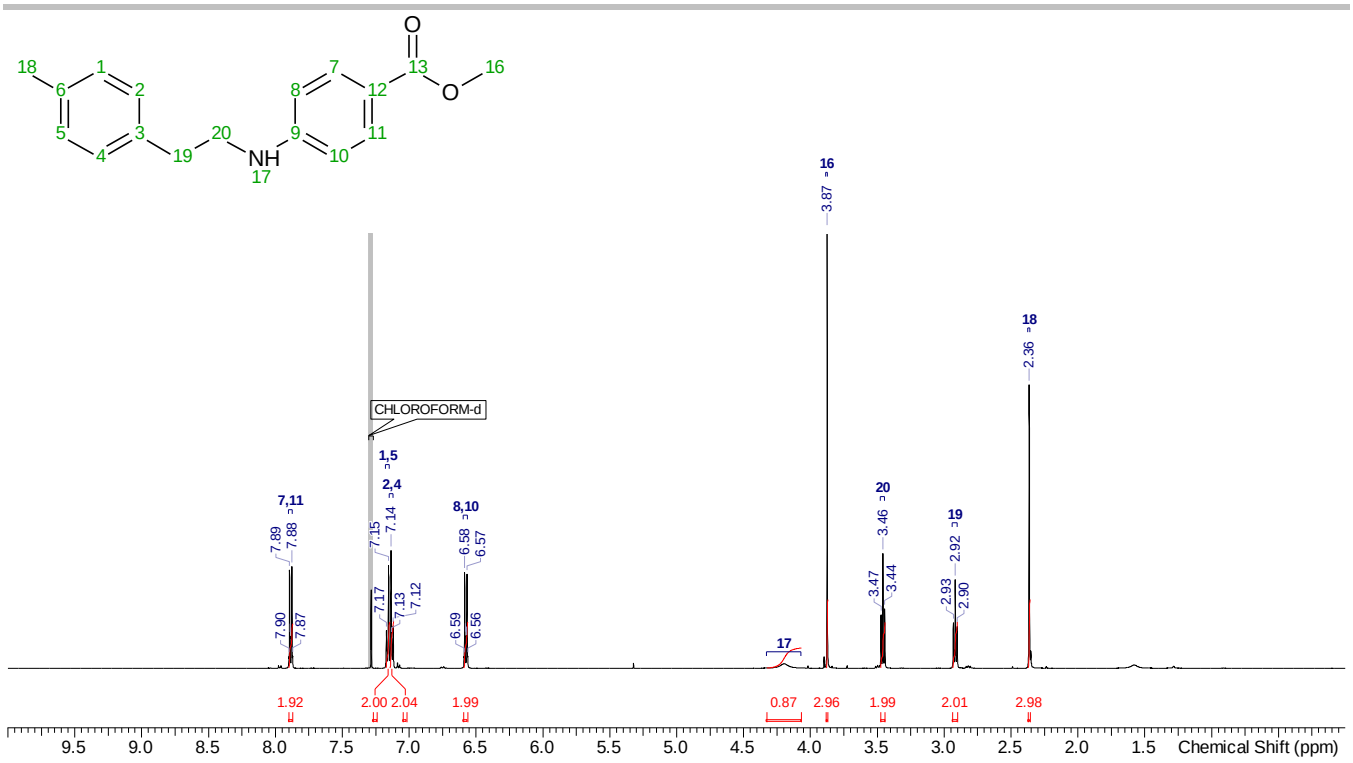


Figure S78: ^{1}H NMR spectrum of **1ab**.

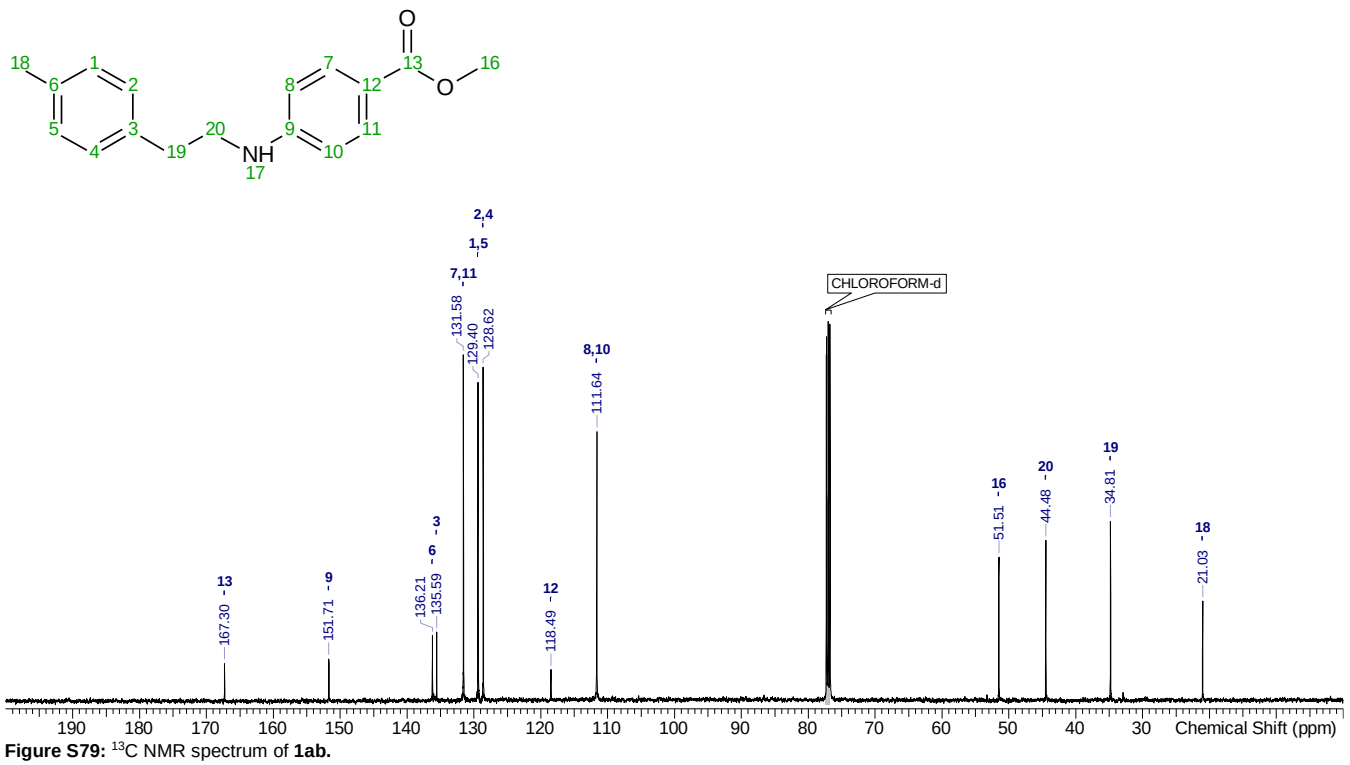


Figure S79: ^{13}C NMR spectrum of **1ab.**

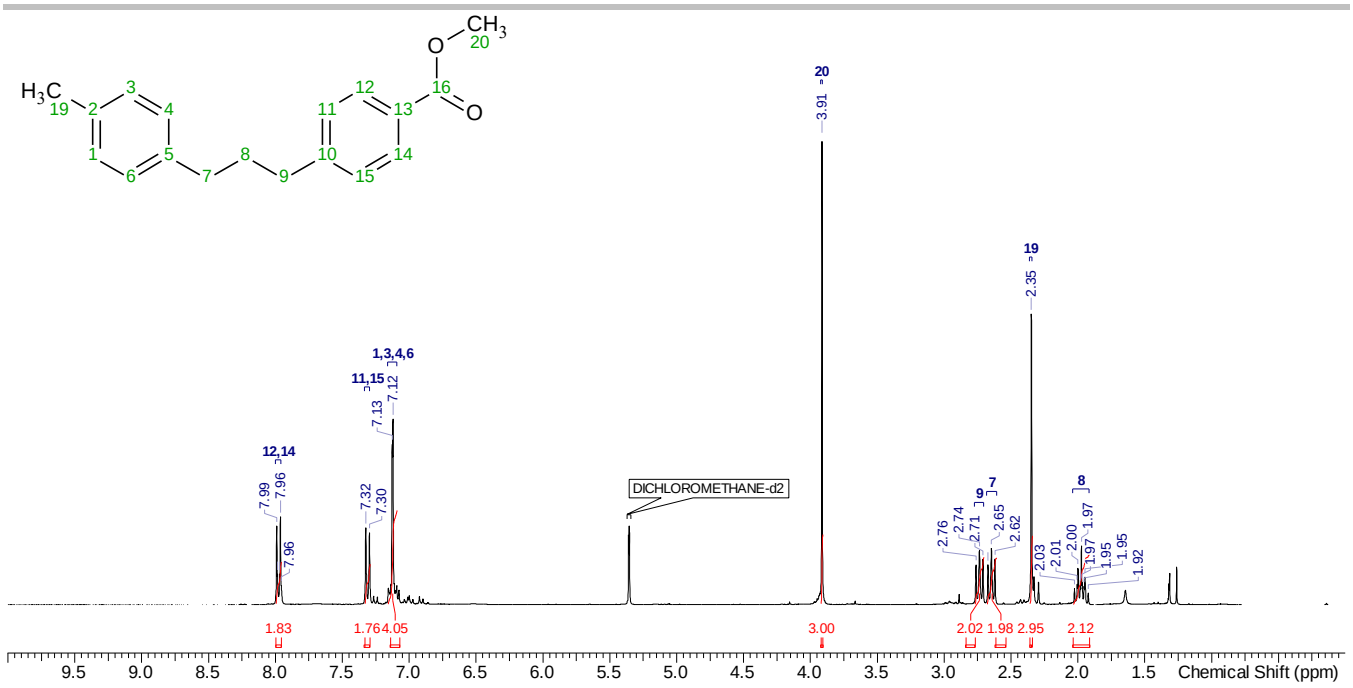


Figure S80: ^{1}H NMR spectrum of **1ac**.

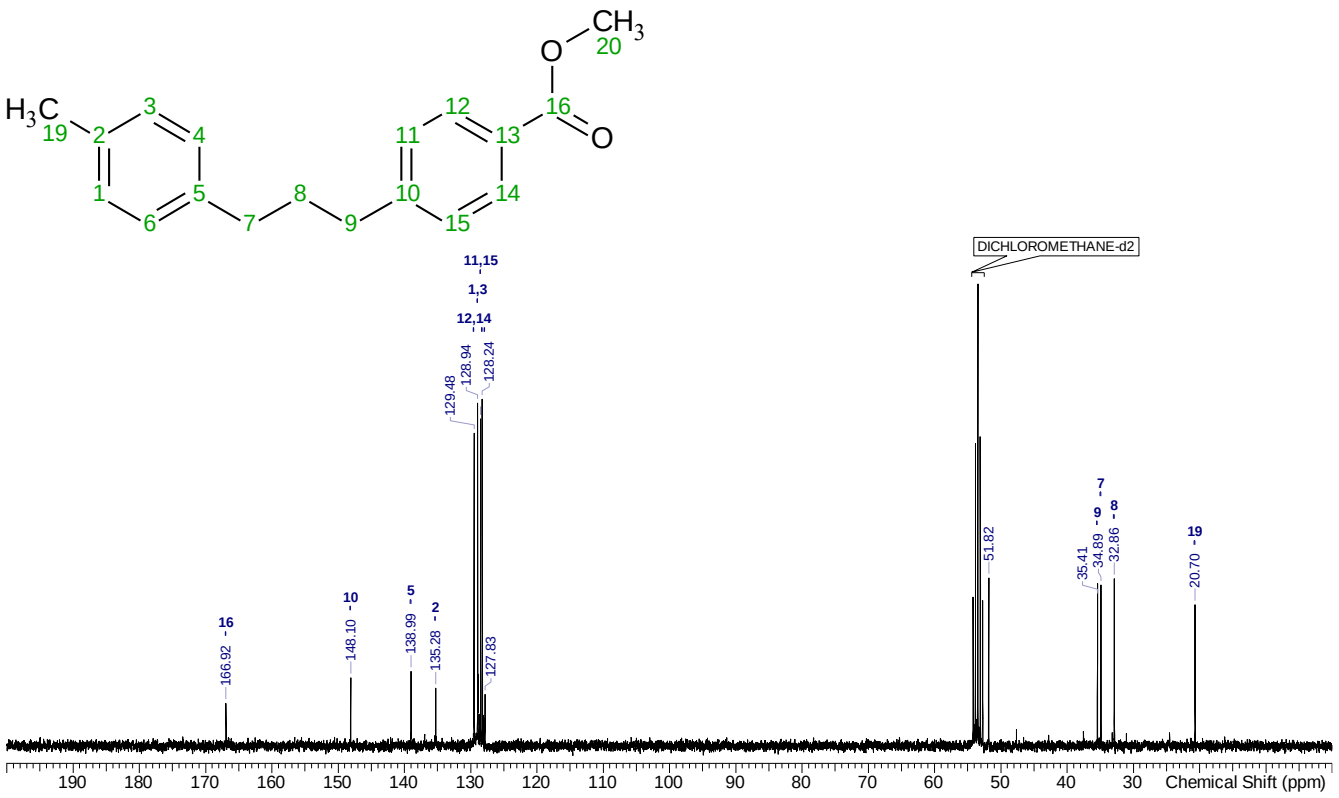


Figure S81: ^{13}C NMR spectrum of **1ac.**

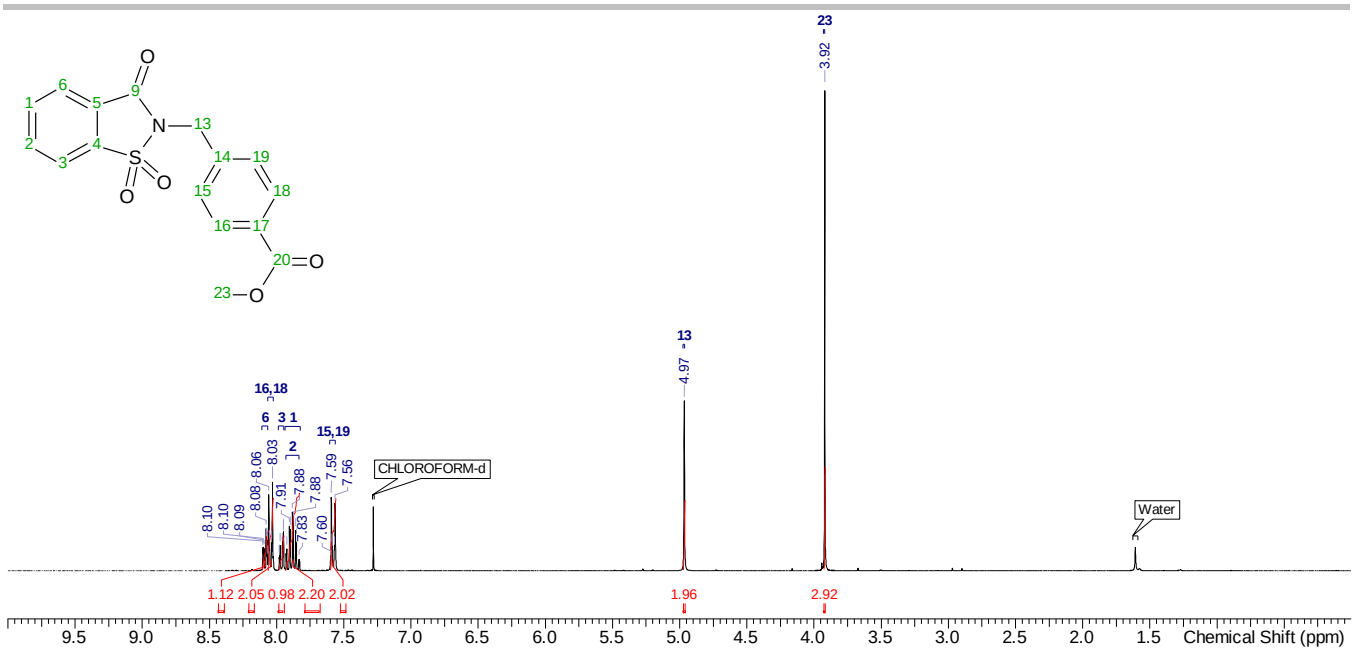


Figure S82: ^{1}H NMR spectrum of **1ad**.

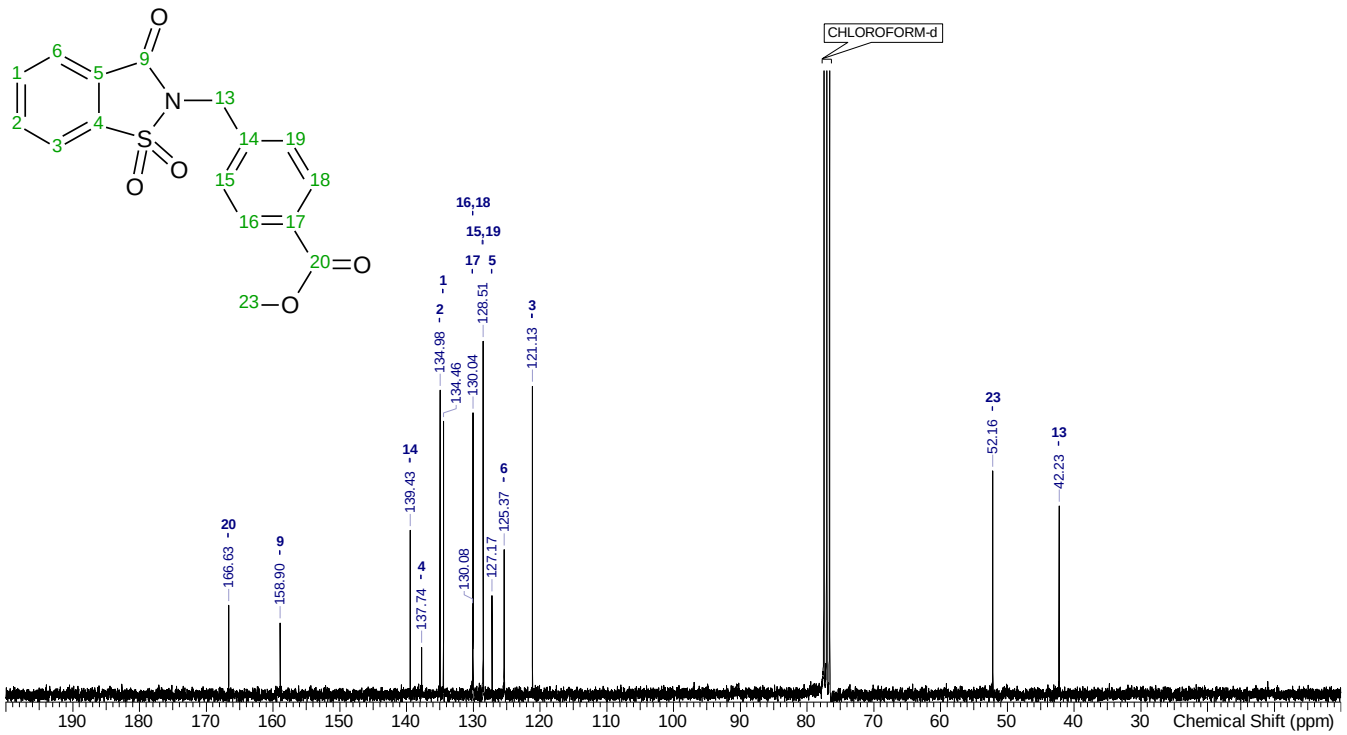


Figure S83: ^{13}C NMR spectrum of **1ad.**

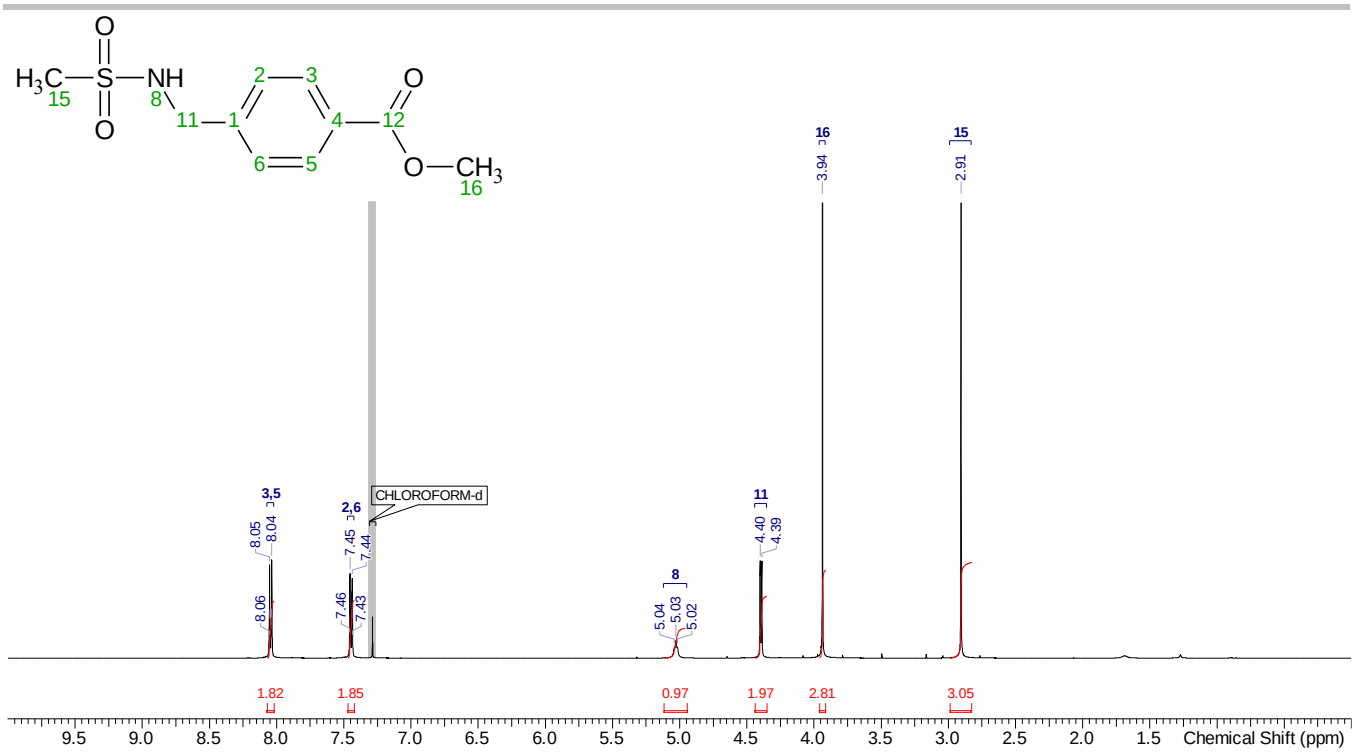


Figure S84: ^{1}H NMR spectrum of **1ae.**

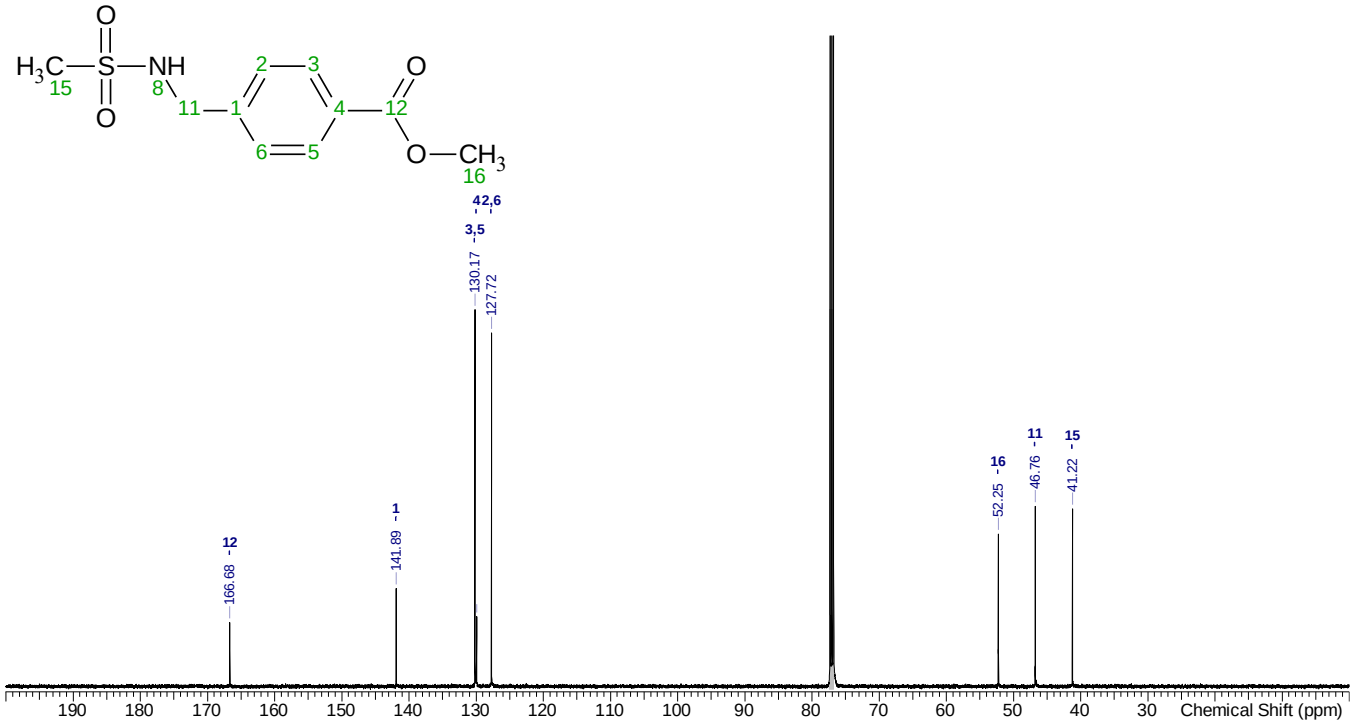


Figure S85: ^{13}C NMR spectrum of **1ae.**

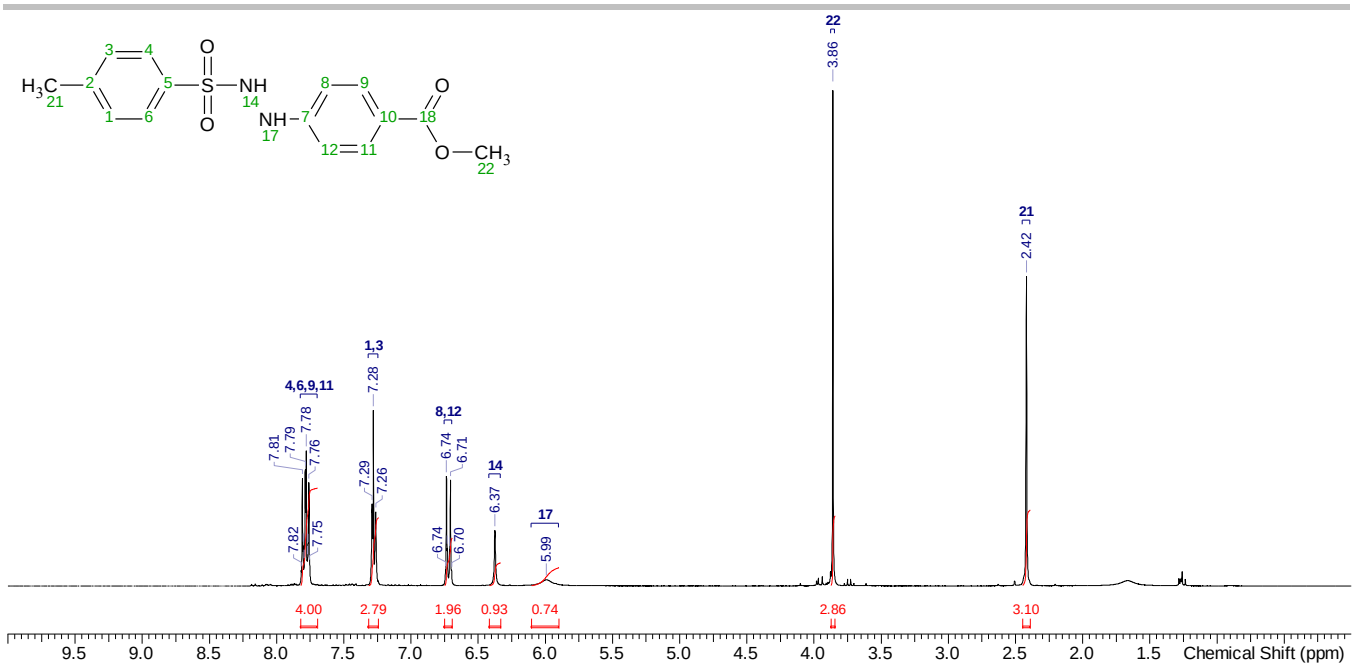


Figure S86: ^{1}H NMR spectrum of **1af**.

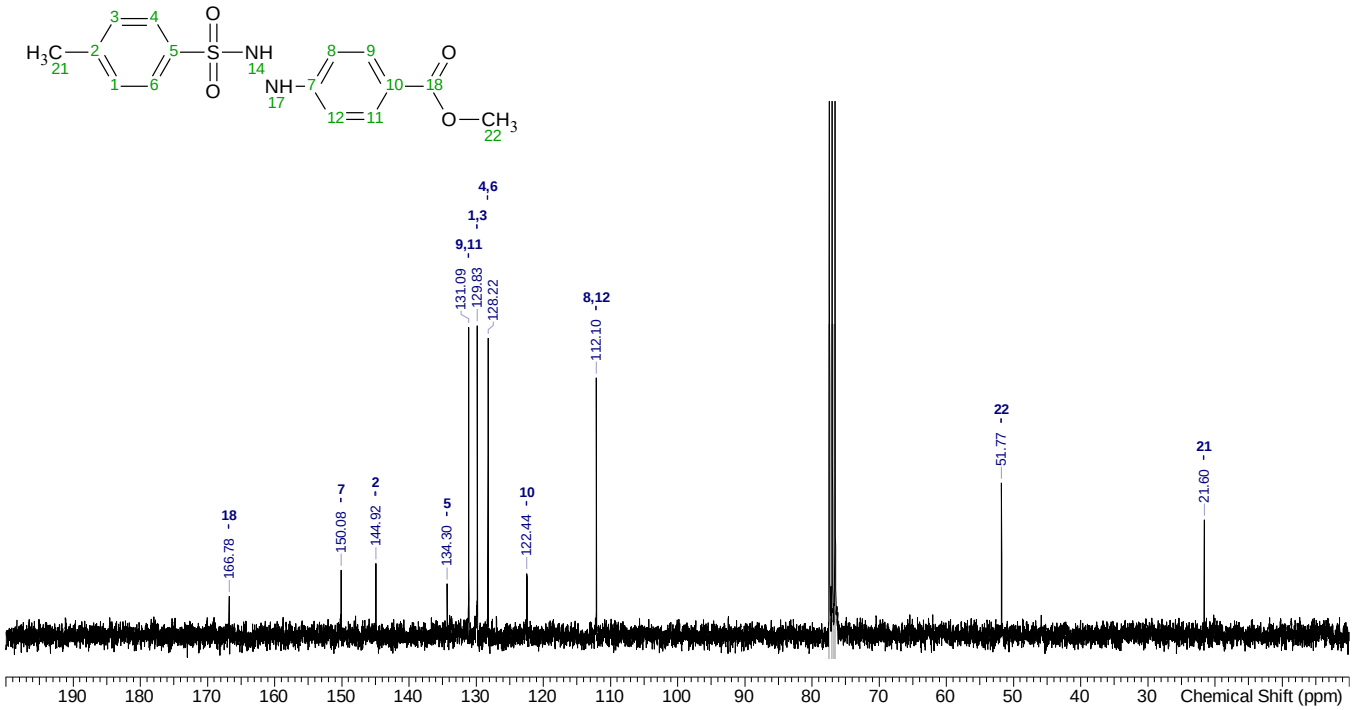


Figure S87: ^{13}C NMR spectrum of **1af.**

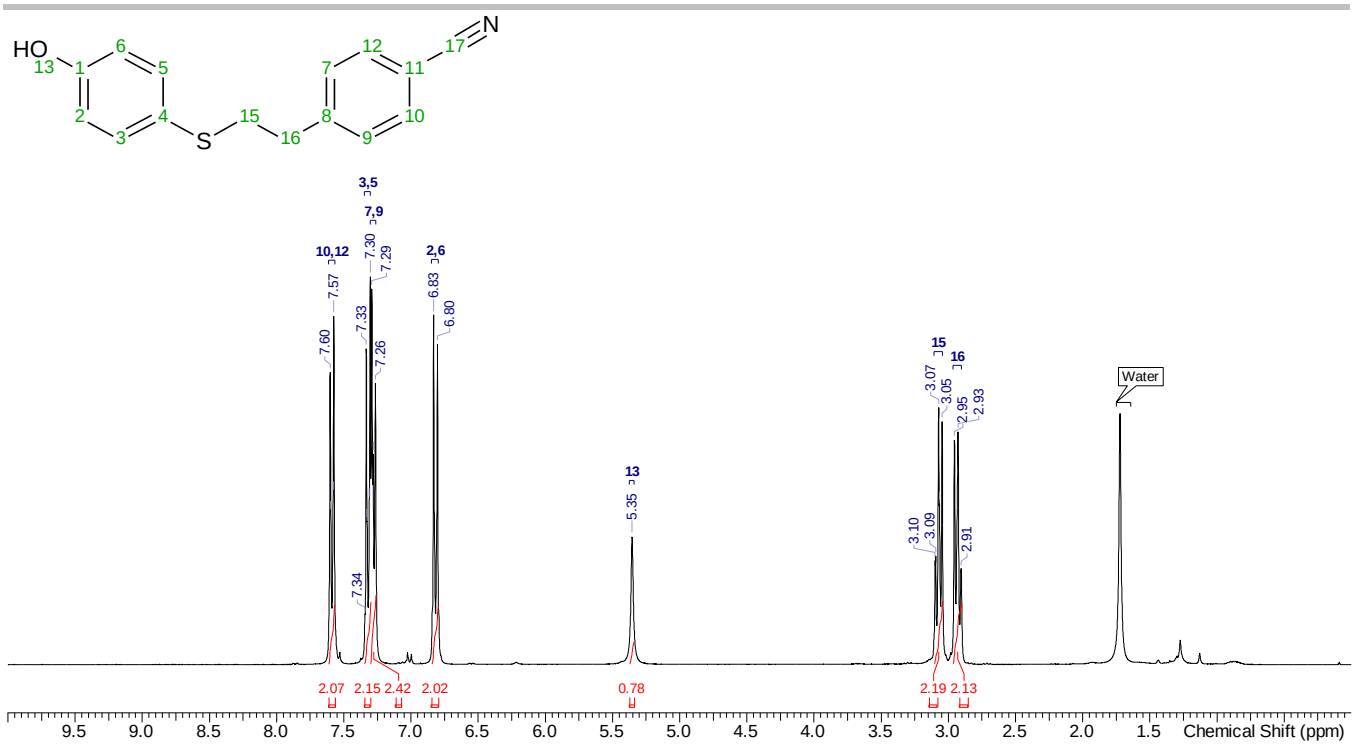


Figure S88: ^{1}H NMR spectrum of **1ag.**

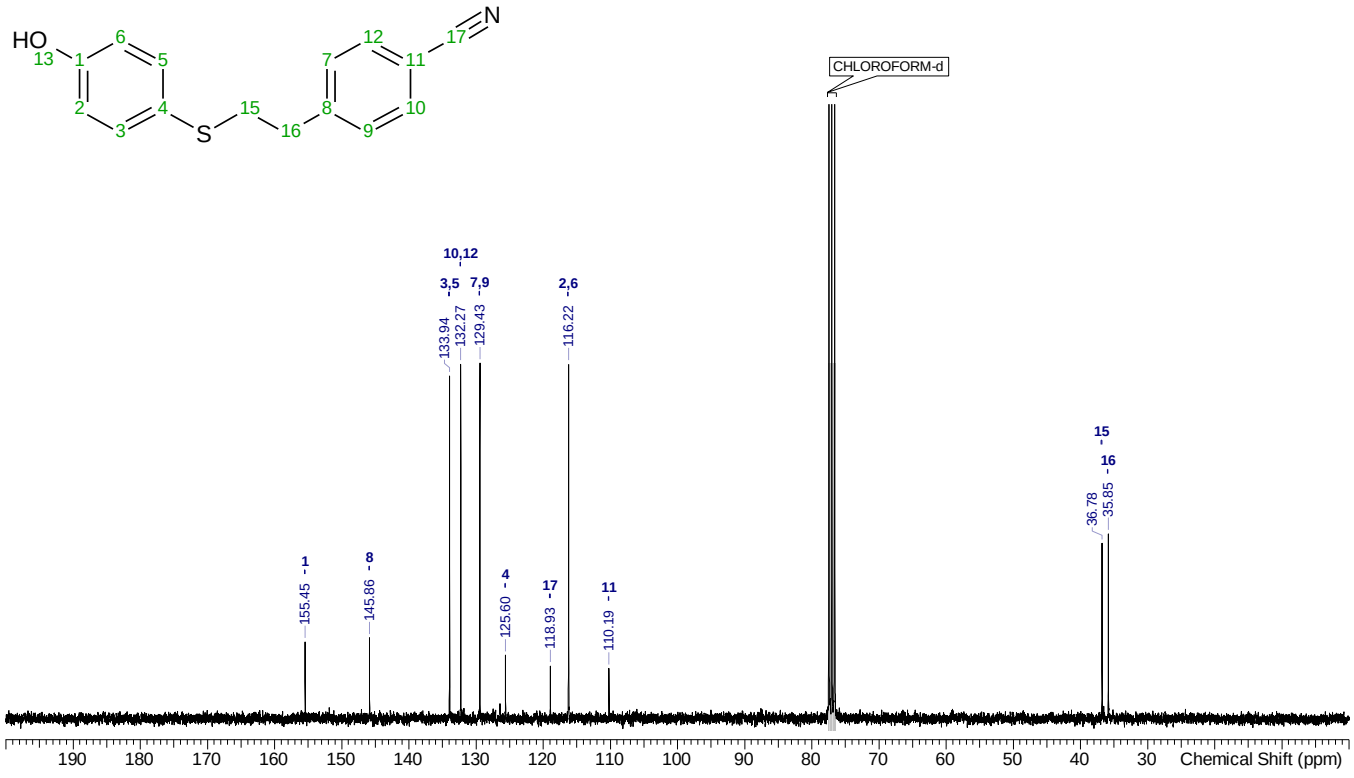


Figure S89: ^{13}C NMR spectrum of **1ag.**

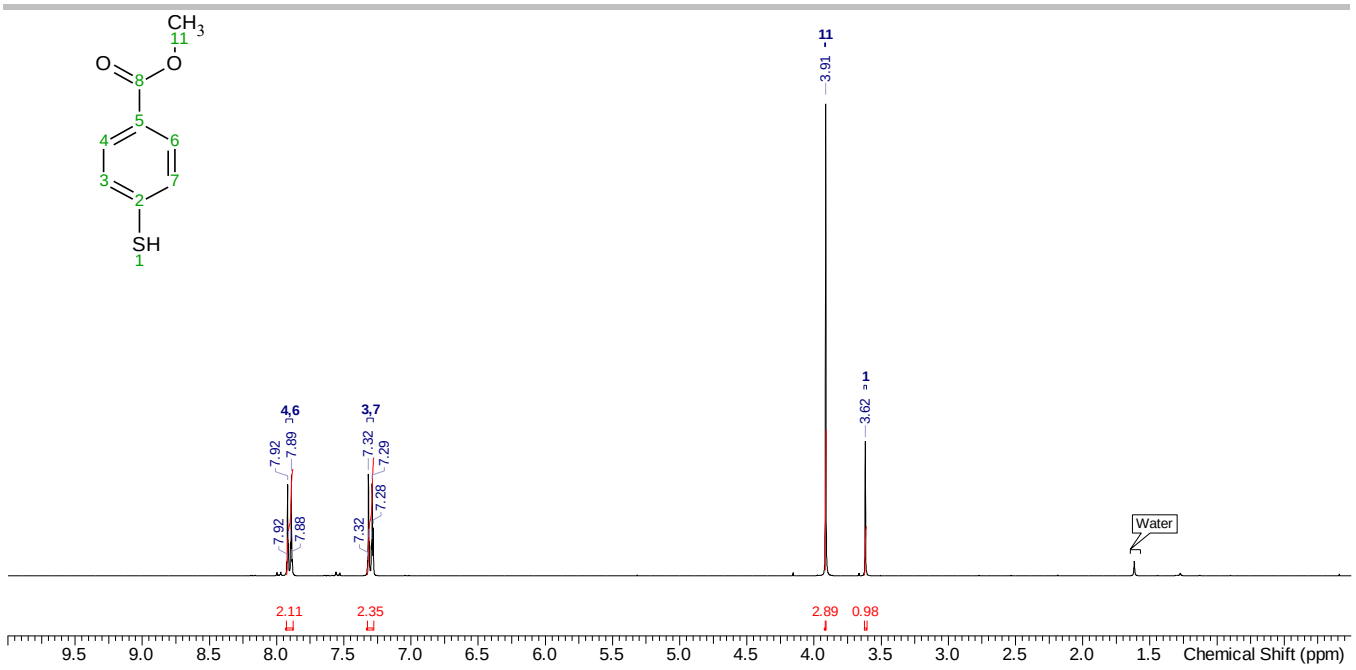


Figure S90: ^{1}H NMR spectrum of **1ah**.

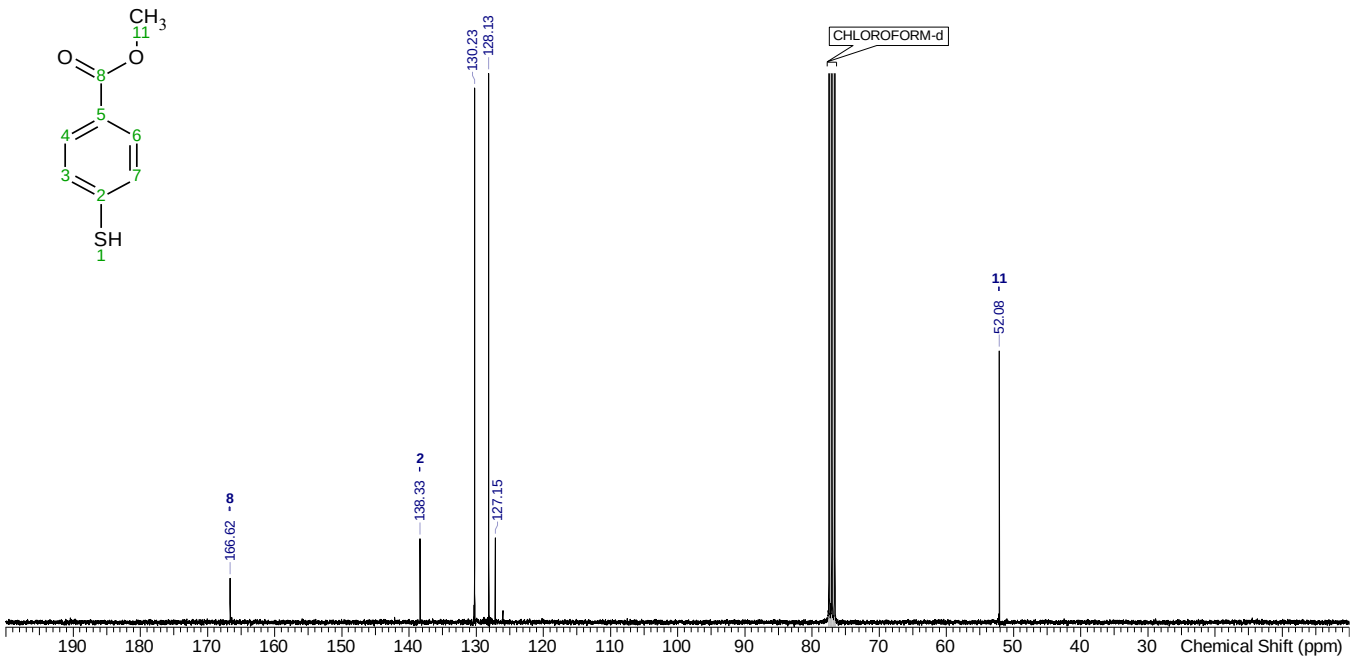


Figure S91: ^{13}C NMR spectrum of **1ah.**

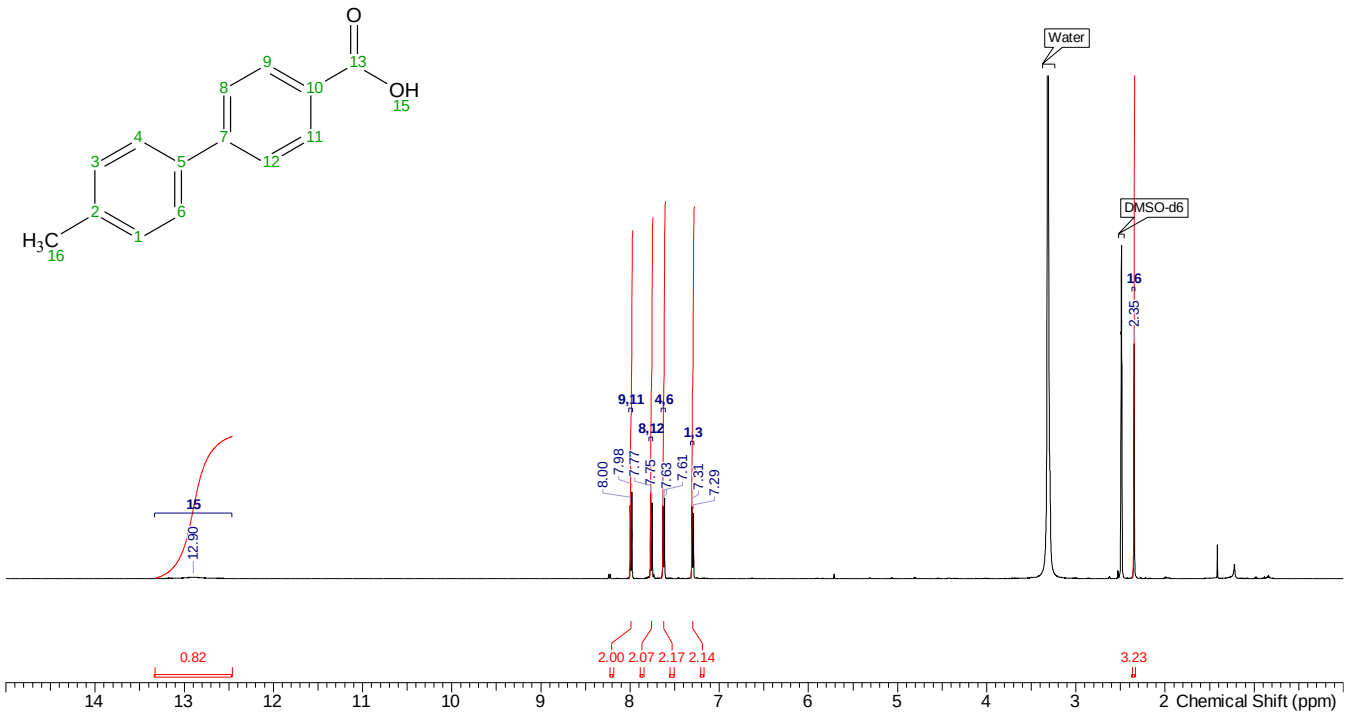


Figure S92: ^{1}H NMR spectrum of **2c**.

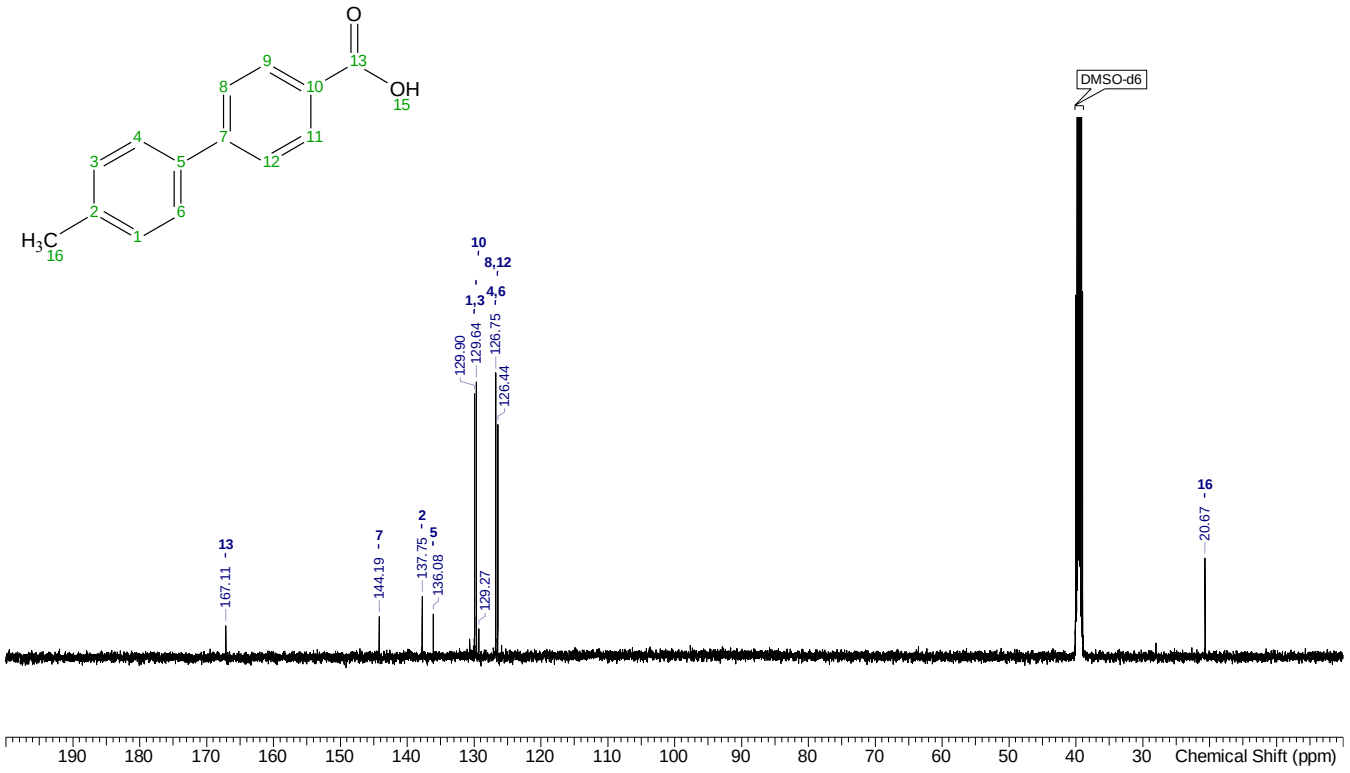


Figure S93: ^{13}C NMR spectrum of **2c.**

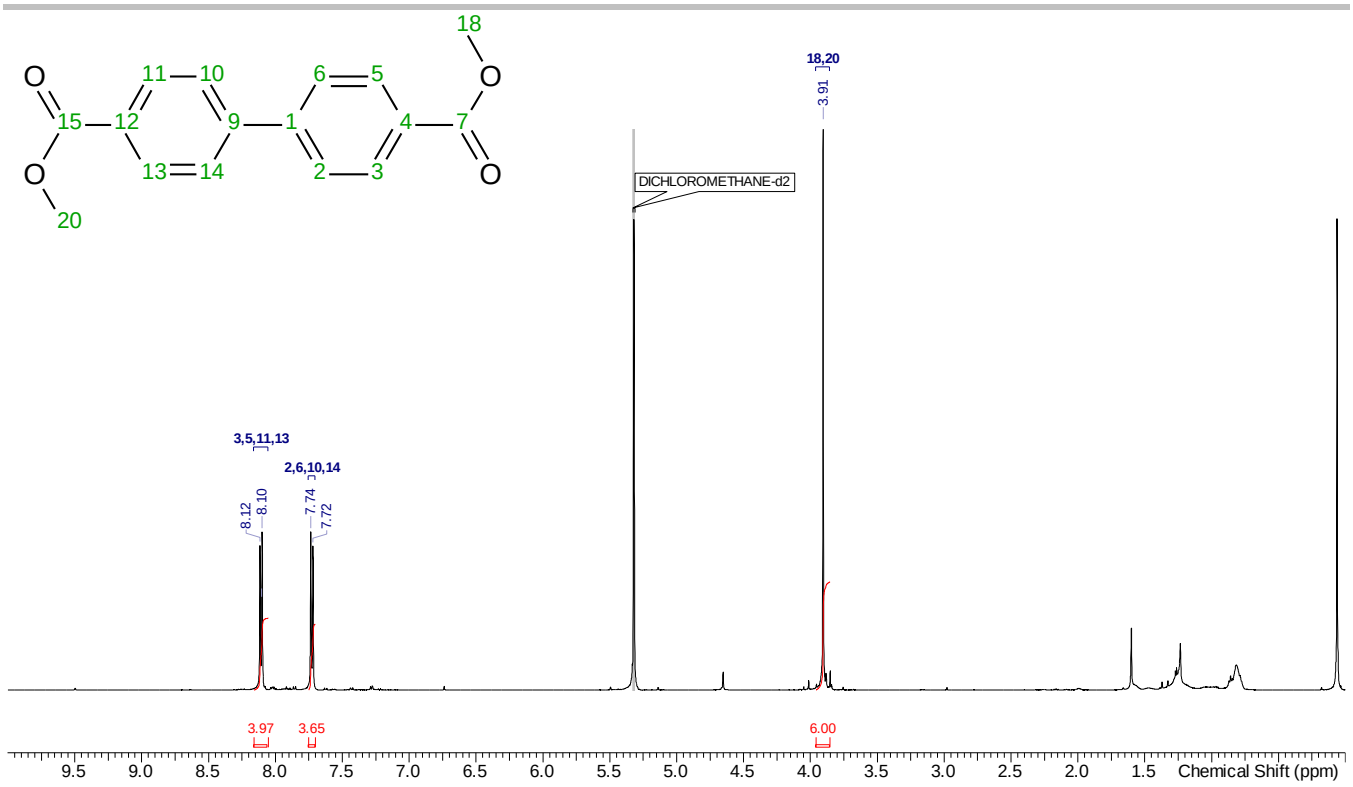


Figure S94: ^{1}H NMR spectrum of **2d**.

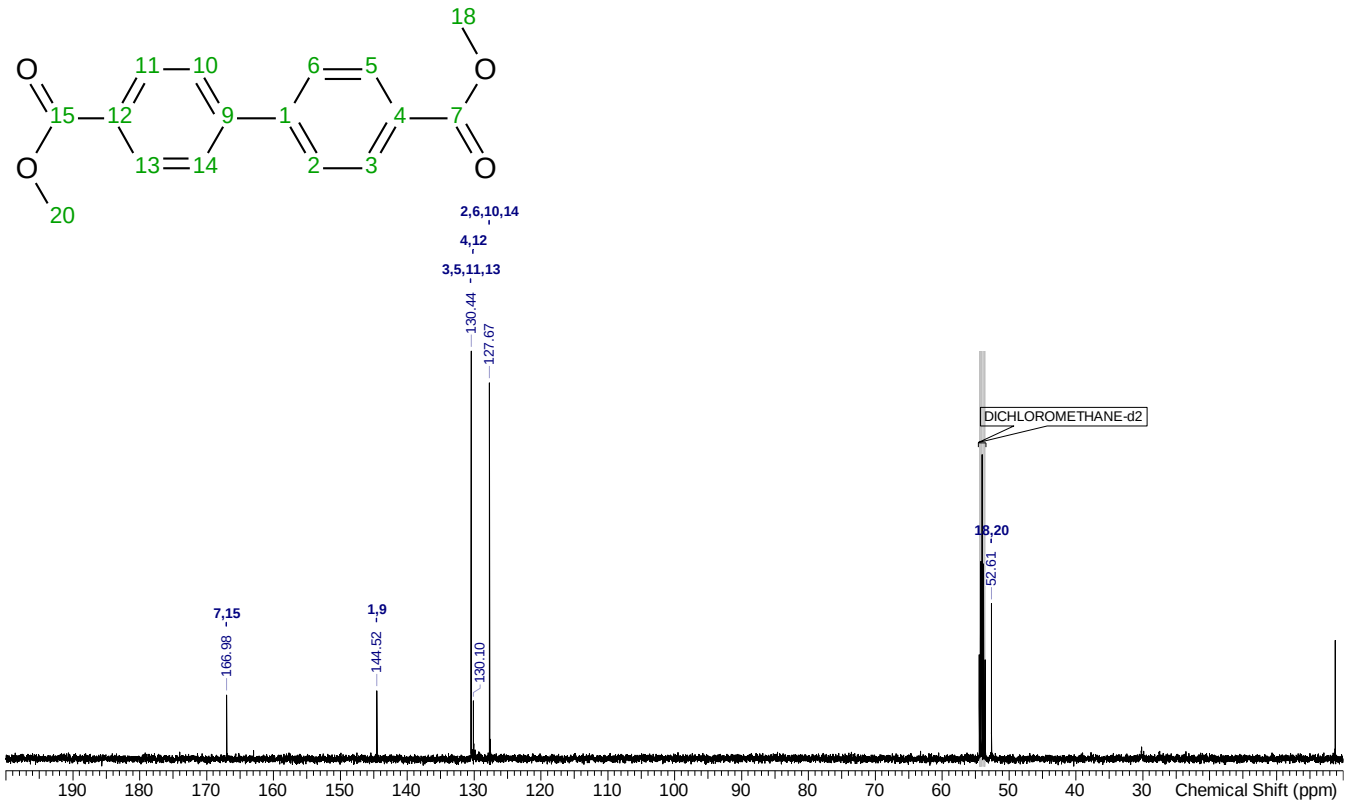


Figure S95: ^{13}C NMR spectrum of **2d.**

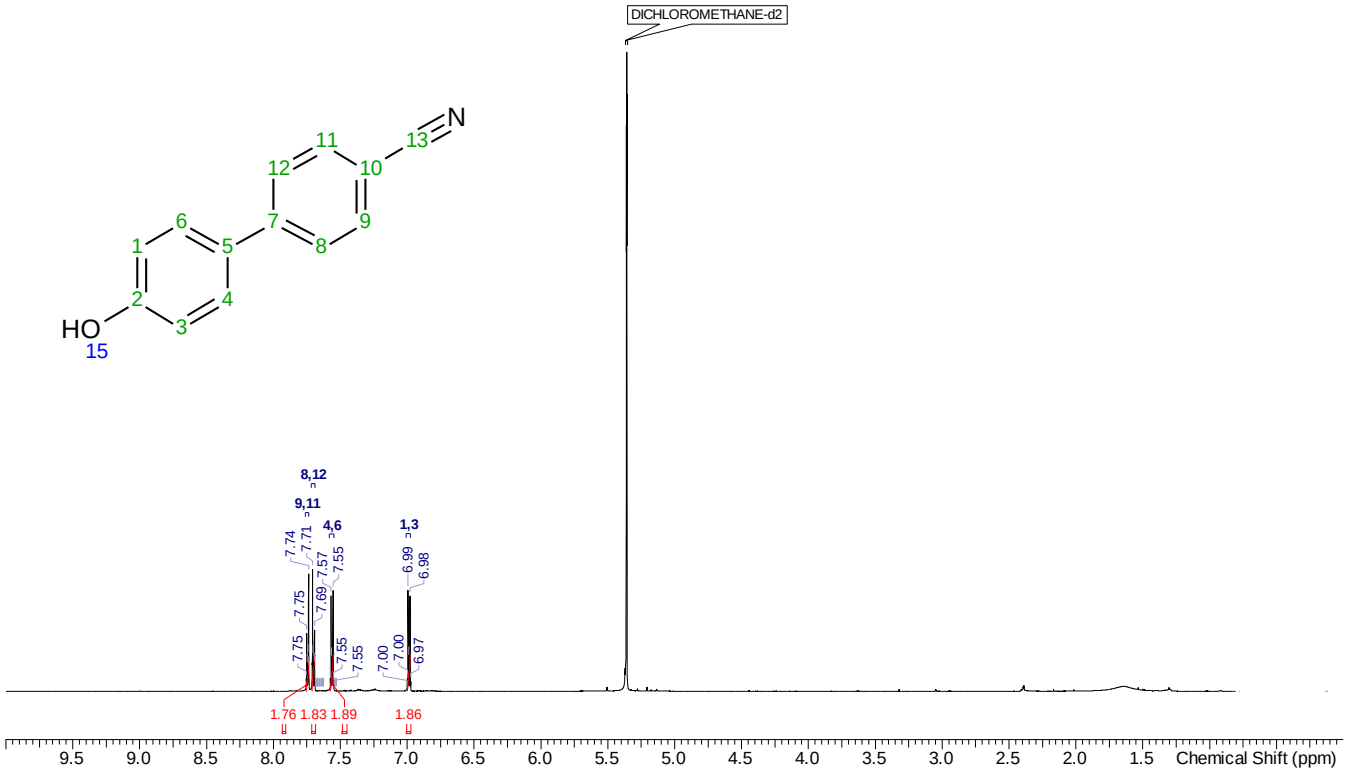


Figure S96: ^{1}H NMR spectrum of **2e**.

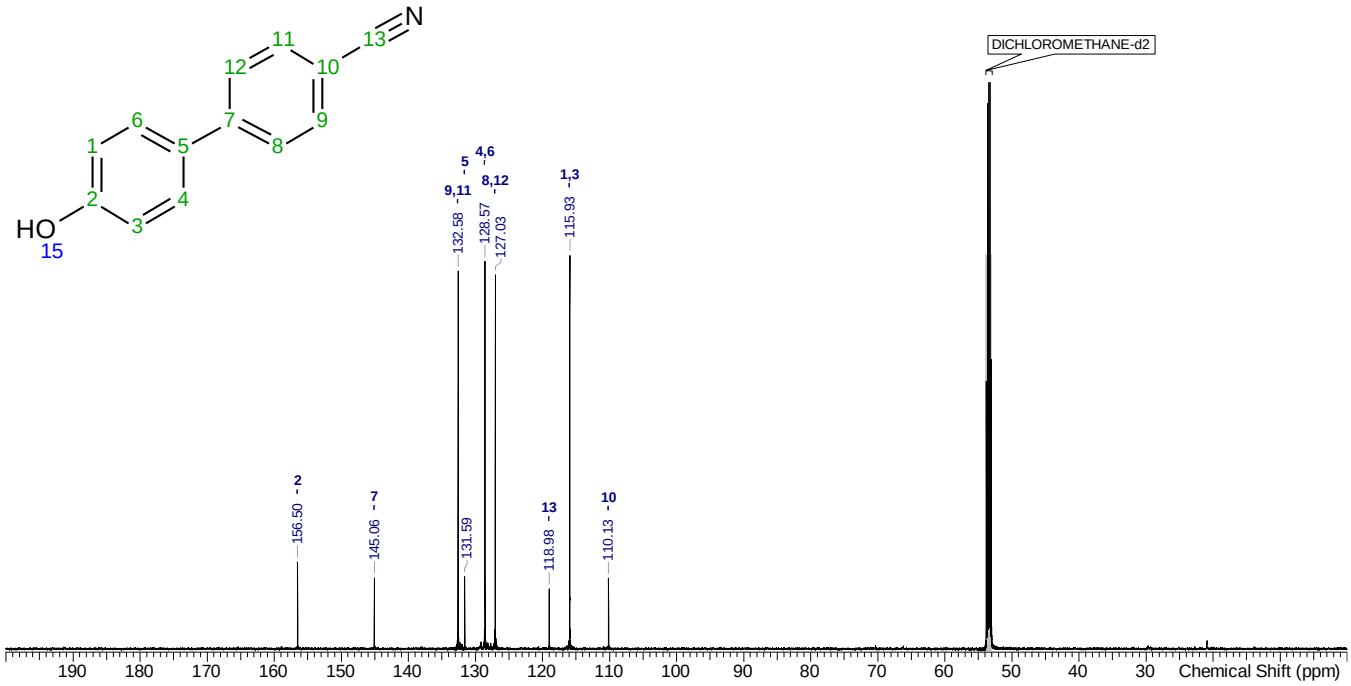


Figure S97: ^{13}C NMR spectrum of **2e.**