"Supporting Information"

Nanostructured BiSI-Catalyzed One-Pot Photoredox Amidation, Thioesterification and Thiol-Ene/Yne Click Reactions via Radical Mechanism Under Visible Light

Haider Ali, Sana Samreen, Bhagirath Mahto, and Sahid Hussain *

Department of Chemistry, Indian Institute of Technology Patna, Bihta, Patna 801106, Bihar, India

Email: sahid@iitp.ac.in

Experimental section

Materials & Chemicals

All the chemicals were procured from Sigma-Aldrich, Alfa-Aesar, or TCI such as bismuth nitrate $Bi(NO_3)_2.5H_2O$, thioacetamide (C_2H_5NS), acetic acid ($C_2H_4O_2$), thiobenzoic S-acid (C_7H_6OS), potassium iodide (KI), thioacetic S-acid (C_2H_4OS), aniline (C_6H_7N), 4-methyl aniline (C_7H_7N), 3-methyl aniline (C_7H_7N), 4-chloroaniline (C_6H_6ClN), 4-methoxy aniline (C_7H_9NO), deuterated chloroform ($CDCl_3$), dimethylsulphoxide (DMSO-d_6), 4-(2-aminoethyl)morpholine ($C_6H_{14}N_2O$), nitro aniline ($C_6H_6N_2O_2$), 4-isopropyl aniline ($C_9H_{13}N$), benzylamine (C_7H_9N), 2-hydroxy aniline (C_6H_7NO), 2-amino benzylalcohol (C_7H_9NO), ethoxyaniline ($C_8H_{11}NO$), triethanolamine ($C_6H_{15}NO_3$), benzyl disulfide (PhSSPh), cyclohexylamine ($C_6H_{13}N$), hexylamine ($C_6H_{15}N$), thiophenol (C_6H_6S), propylamine (C_3H_9N), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), BHT (butylated hydroxytoluene), ethyl acetate, hexane, acetonitrile, ethanol. All chemicals mentioned above were used as purchased, with no additional purification steps. Column chromatography was performed on silica gel (100–200 mesh) using a hexane/ethyl acetate solvent gradient and progress was monitored by alumina-backed TLC plates. ^1H and ^{13}C NMR data were recorded on JEOL 500 MHz instruments with $CDCl_3$ as the solvent. Chemical shifts for ^1H NMR are reported in ppm relative to the residual chloroform peak at 7.26 ppm, while ^{13}C NMR spectra are referenced to the $CDCl_3$ signal at 77.1 ppm under proton-decoupled conditions.

General Consideration

Powder X-ray diffraction (P-XRD) patterns were recorded over a 2θ range of 10–80° using a PANalytical diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å, 45 kV, 40 mA). Diffuse reflectance UV–vis spectra (DRS) were measured using a Shimadzu UV-2600 spectrophotometer, with $BaSO_4$ serving as the reference standard. Field-emission scanning electron microscopy (FE-SEM) images and corresponding energy-dispersive X-ray

spectroscopy (EDS) data were collected on a Zeiss Gemini SEM500 system. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were acquired using a JEOL JEM-200 microscope operated at 200 kV. The Brunauer–Emmett–Teller (BET) surface area and porosity were evaluated via N_2 adsorption–desorption measurements using a Quantachrome Autosorb iQ2 analyzer. Photocatalytic experiments employed an 18 W PHILIPS white LED lamp as the irradiation source. Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a JEOL 500 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference. Chemical shifts (ppm) and coupling constants (Hz) were reported using the following multiplicity abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and bs (broad singlet). Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel 60-F254 aluminum plates (100–200 mesh), using hexane as the eluent.

Note-S1 Synthetic procedure of BiSI nanomaterials

To synthesize bismuth sulfoiodide (BiSI) nanostructures, 1.46 g of bismuth nitrate pentahydrate $Bi(NO_3)_3.5H_2O$, and 0.23 g of thioacetamide (C_2H_5NS) were separately dissolved in 25 mL of acetic acid with magnetic stirring, using a previously reported method with slight modifications. Once fully dissolved, 0.75g of potassium iodide (KI) was added, and the mixture was stirred continuously for 3 h to achieve a uniform solution. The resulting mixture was then poured into a 50 mL metal autoclave and heated at 180°C for 10 h. After the reaction, the product was separated by centrifugation and thoroughly washed several times with deionized water and ethanol. Finally, the purified product was dried under vacuum at 70°C for 10 h.

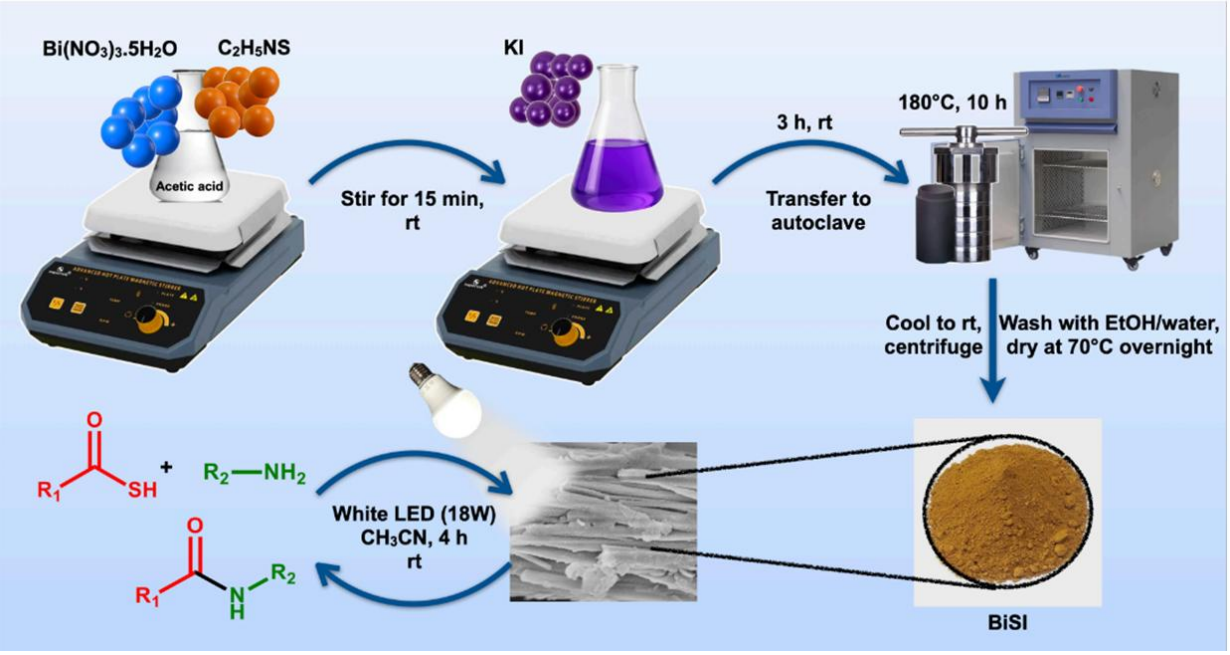


Fig. S1 Schematic diagram for the synthesis of BiSI and its use as a catalyst for visible-light-driven amide bond formation.

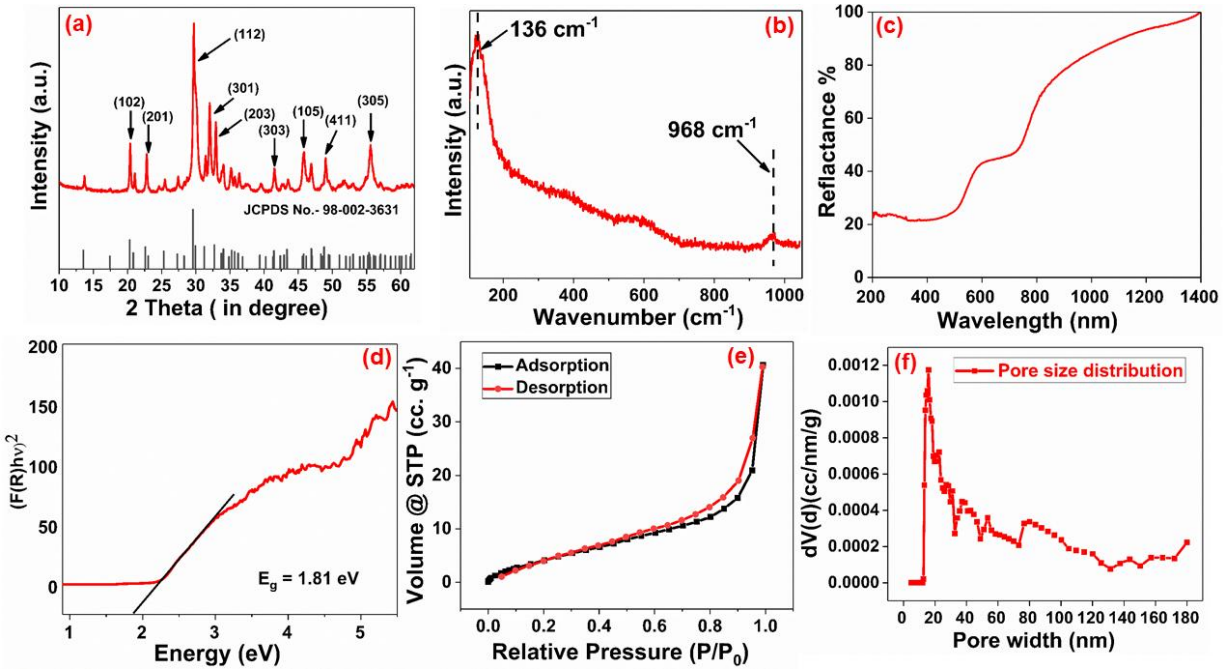


Fig. S2 (a) XRD patterns; (b) Raman spectrum; (c) DRS spectra; (d) Kubelka–Munk plot, (e) N_2 adsorption–desorption isotherms, (f) pore size distribution of BiSI nanostructures.

Note-S2

The optical band gap and light absorption characteristics of the BiSI nanostructures arrays were evaluated using UV−vis−NIR spectroscopy to determine their effectiveness as a photocatalyst. The reflectance data were further analyzed by applying the Kubelka–Munk function to derive the corresponding absorption spectra. The Kubelka–Munk equation is given by,

$$F(R) = (1-R)^2/2R \quad (1)$$

$$(h\nu F(R))^n = A(h\nu - E_g) \quad (2)$$

In this equation, A is a constant of proportionality, ν is the frequency of the incident light, E_g stands for the band gap energy, and h is Planck's constant. The exponent n defines the nature of the optical transition: n = 1/2 corresponds to an indirect allowed transition, while n = 2 indicates a direct allowed transition. The direct band gap energy (E_g) of BiSI nanostructures is calculated to be approximately 1.81 eV.[1]

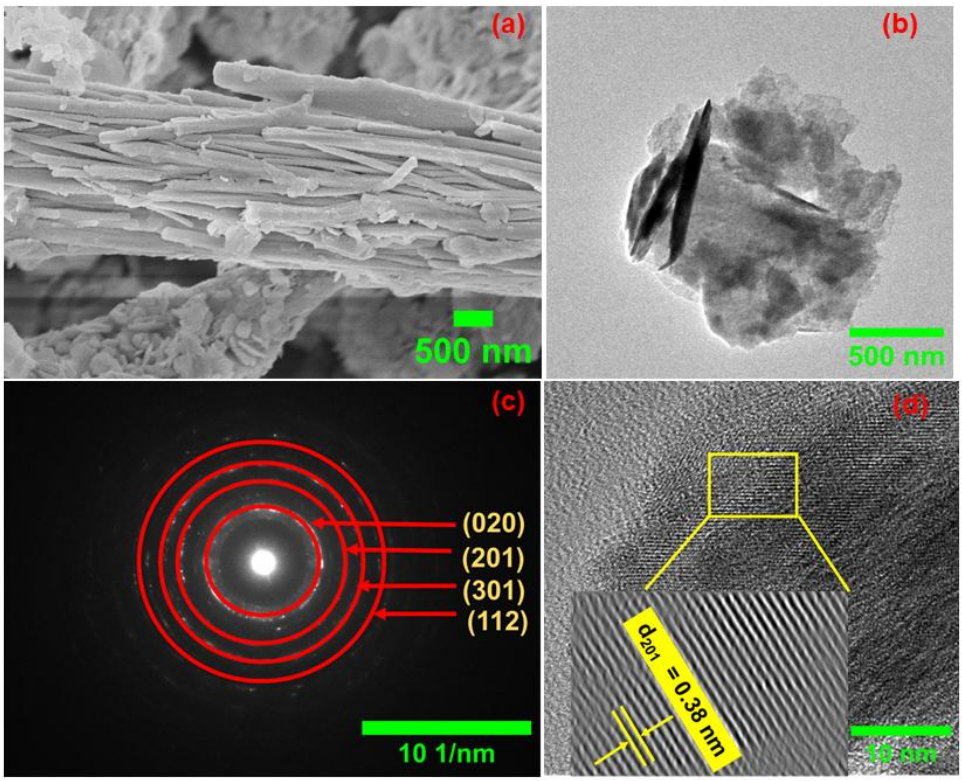
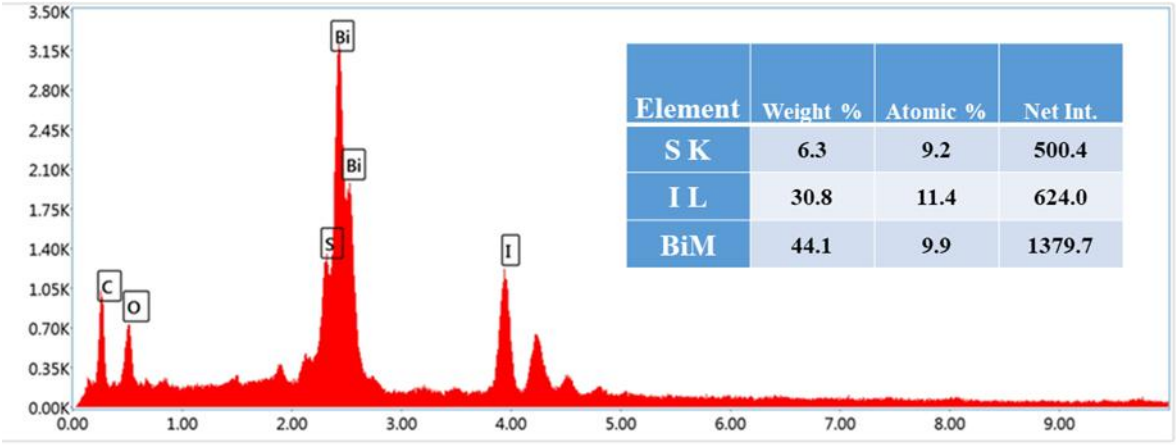


Fig. S3 (a) FE-SEM micrograph, (b) TEM micrographs, (c) SAED pattern, and (d) HRTEM of BiSI.



Element	Weight %	Atomic %	Net Int.
S K	6.3	9.2	500.4
I L	30.8	11.4	624.0
BiM	44.1	9.9	1379.7

Fig. S4 EDAX of BiSI.

Procedure for amide bond formation

Visible light-initiated amidation reactions were performed in a sealed reaction vial using a PHILIPS 18 W (wavelength 400–750 nm, 1800 Lumen) white LED as a light source. The reaction mixture consisted of 7 mg of catalyst, 1.0 mmol of thioic S-acid, 1.0 mmol of amine, and 3 mL of acetonitrile, combined in a 5 mL capped glass vial. This vial was positioned 5 cm away from the light source and stirred at room temperature for 4 h under white light irradiation. TLC monitored the reaction progress. Upon completion, the mixture was treated with acetonitrile, and the catalyst was isolated by centrifuging. The supernatant evaporated, and the product was purified through column chromatography.

Procedure for thioester formation

Visible light-initiated thioesterification reactions were performed in a sealed reaction vial using a PHILIPS 18 W (wavelength 400–750 nm, 1800 Lumen) white LED as a light source. The reaction mixture consisted of 7 mg of catalyst, 1.0 mmol of thioic S-acid, 1.0 mmol of alkynes/alkenes, and 3 mL of ethyl acetate, combined in a 5 mL capped glass vial. This vial was positioned 5 cm away from the light source and stirred at room temperature for 5 h under white light irradiation. TLC monitored the reaction progress. Upon completion, the mixture

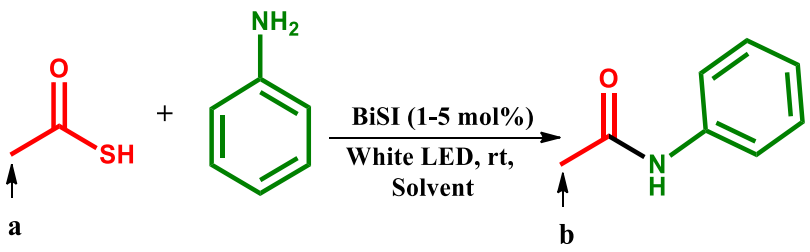
was treated with acetonitrile, and the catalyst was isolated by centrifuging. The supernatant evaporated, and the product was purified through column chromatography.

Procedure for thioether formation

Visible light-initiated thiol-ene/yne reactions were performed in a sealed reaction vial using a PHILIPS 18 W (wavelength 400–750 nm, 1800 Lumen) white LED as a light source. The reaction mixture consisted of 7 mg of catalyst, 1.0 mmol of thiol, 1.0 mmol of alkynes/alkenes, and 3 mL of acetonitrile, combined in a 5 mL capped glass vial. This vial was positioned 5 cm away from the light source and stirred at room temperature for 3 h under white light irradiation. TLC monitored the reaction progress. Upon completion, the mixture was treated with acetonitrile, and the catalyst was isolated by centrifuging. The supernatant evaporated, and the product was purified through column chromatography.

Optimisation of catalyst loading

Visible-light-driven amidation was conducted using a PHILIPS 18 W white LED (400–750 nm, 1800 lumen) to irradiate a reaction mixture composed of 1–5 mol% catalyst, 1.0 mmol thioic S-acid, 1.0 mmol amine, and 3 mL MeCN in a capped 5 mL vial. The vial was kept 5 cm from the light source and stirred at room temperature for 4 h. After separating the catalyst by centrifugation, the crude mixture was analyzed by ^{1}H NMR ($CDCl_3$) to determine amide conversion.



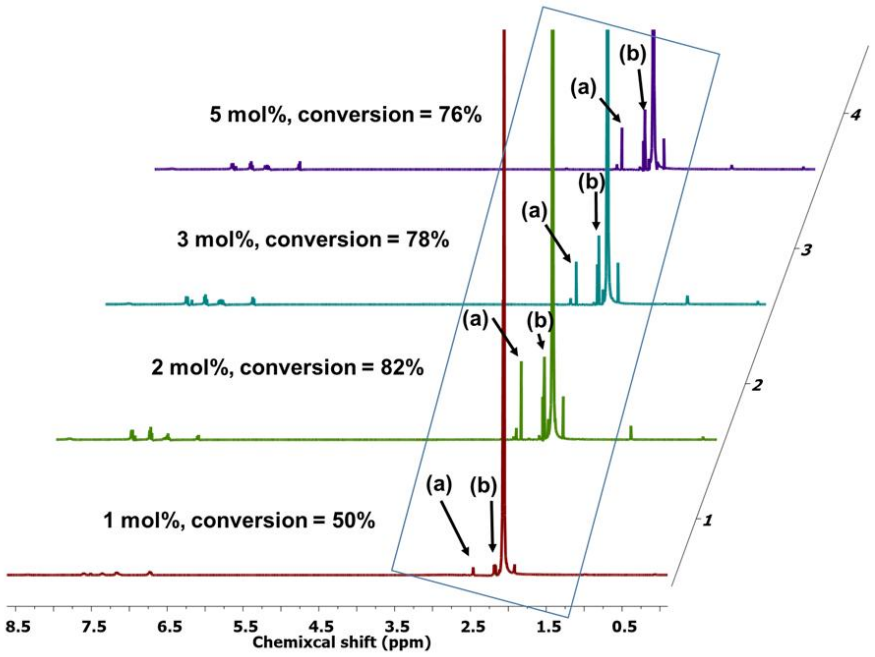
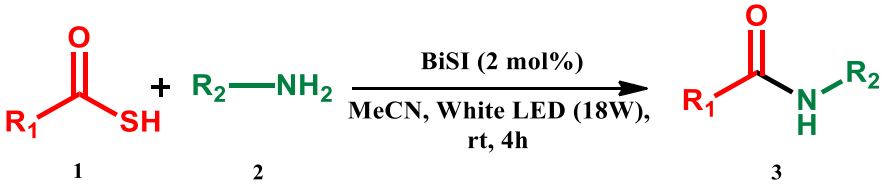


Fig. S5 Amide conversion was quantified from crude mixtures by NMR at different catalyst loadings.

Table S1 Evaluation of varying reactant (in mmol) in amidation reaction.[a]

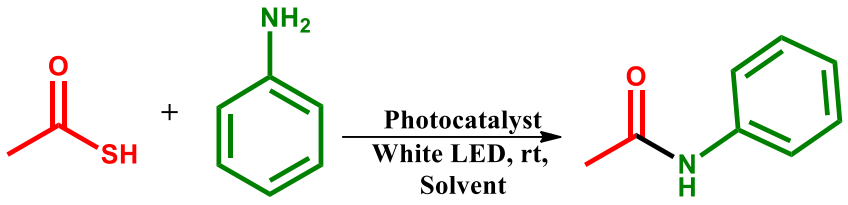


1 2 3

Entry	Thioacetic acid (mmol)	Aniline (mmols)	Yield (%)[b]
1.	0.5	1.0	53
2.	0.70	1.0	71
3.	**1.0**	**1.0**	**92**
4.	1.10	1.0	91
5.	1.0	0.5	70
6.	1.0	0.7	77
7.	1.0	1.10	90

[a]BiSI (2 mol%), Solvent (3.0 mL), 18 W white LED, 4 h, room temperature. [b]Isolated yields.

Table S2 Comparison between BiSI and other photocatalysts in amidation reaction.[a]

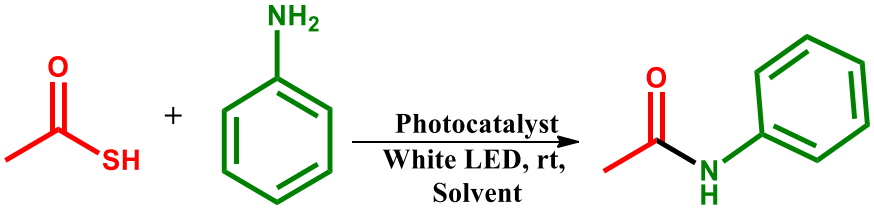


1a **2a** **3a**

Entry	Photocatalyst	Yield (%)[b]
1.	**BiSI**	**92**
2.	Rhodamine B	59
3.	Eosin Y	67
4.	Bi_2WO_6	78
5.	Orange G	33
6.	Rose Bengal	52

[a]Thioacetic S-acid (1.0 mmol), aniline (1.0 mmol), Photocatalyst (2 mol%), Acetonitrile (3 mL), 18 W white LED, 4 h, room temperature. [b]Isolated yields.

Table S3 Solvent screening for the amidation reaction.[a]



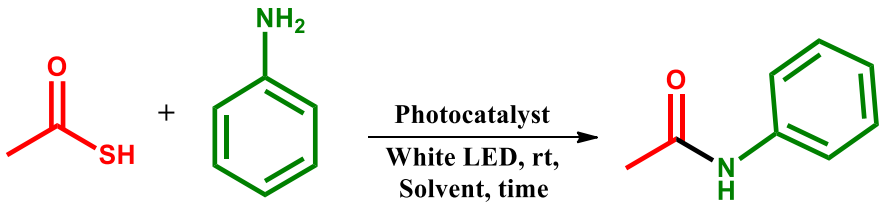
1a **2a** **3a**

Entry	Solvent	Yield (%)[b]
1.	**CH_3CN**	**92**
2.	ethyl acetate	74
3.	methanol	60
4.	ethanol	67
5.	DCM	40

6.	THF	44
7.	DMF	67
8.	acetone	59

[a]Thioacetic S-acid (1.0 mmol), aniline (1.0 mmol), BiSI (2 mol%), Solvent (3.0 mL), 18 W white LED, 4 h, room temperature. [b]Isolated yields.

Table S4 Optimization of the reaction time for the amidation[a]



1a **2a** **3a**

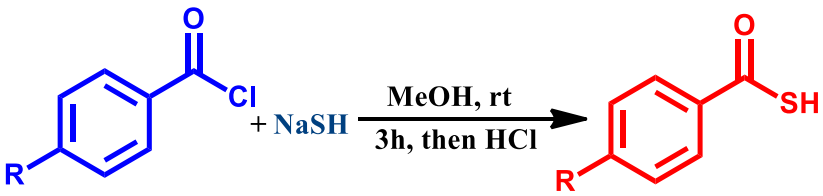
Entry	Time (h)	Yield (%)[b]
1.	**0**	**0**
2.	1.5	44
3.	2.0	51
4.	3.0	71
5.	**4.0**	**92**

[a]Thioacetic S-acid (1.0 mmol), aniline (1.0 mmol), BiSI (2 mol%), Solvent (3 mL), 18 W white LED, room temperature. [b]Isolated yields.

Note-S3 Calculation of turnover number (TON)

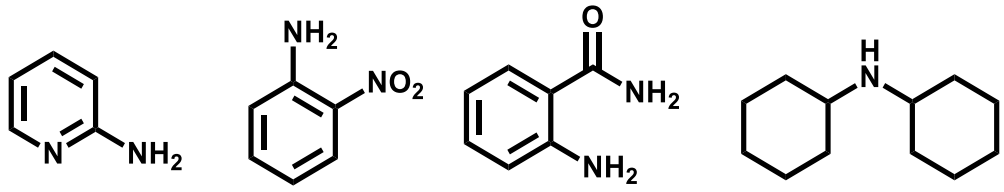
Turnover number (TON) = $No.\ of$ moles $of\ the\ products\ formed/\ No.\ of$ moles $of\ catalysed\ used.$

Synthesis of thiobenzoic S-acid



Thioacids were synthesized from the corresponding acyl chlorides and sodium hydrosulfide hydrate following literature-reported.[2] A methanolic solution of sodium hydrosulfide hydrate (2 equiv., 1 mL) was prepared, to which acyl chloride (1 equiv.) was added. The reaction mixture was stirred at 0 °C for 1 h and then allowed to proceed at room temperature for an additional 2 h. After quenching with 1 M HCl, the organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure, affording crude thiobenzoic S-acid as a pale-yellow oil, which was directly employed in subsequent reactions without further purification.

Note-S4 unsuccessful amine substrates



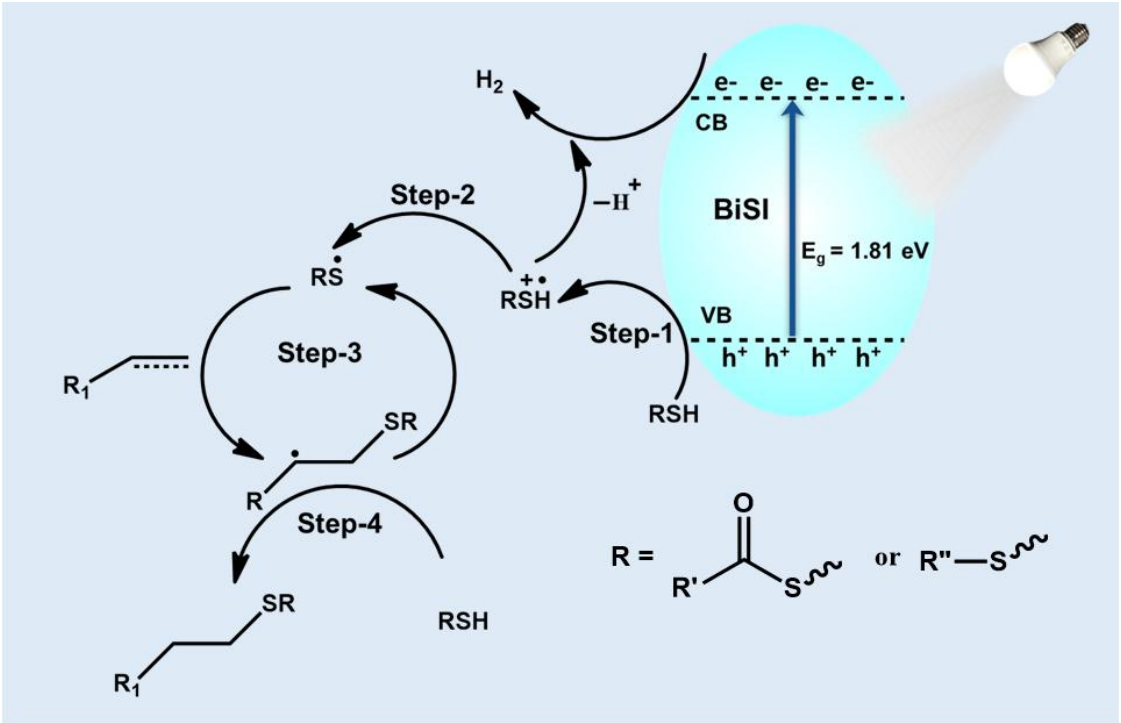


Fig. S6 Schematic illustration of the photocatalytic mechanism for thioesterification of alkenes and thiol–ene/yne click reactions.

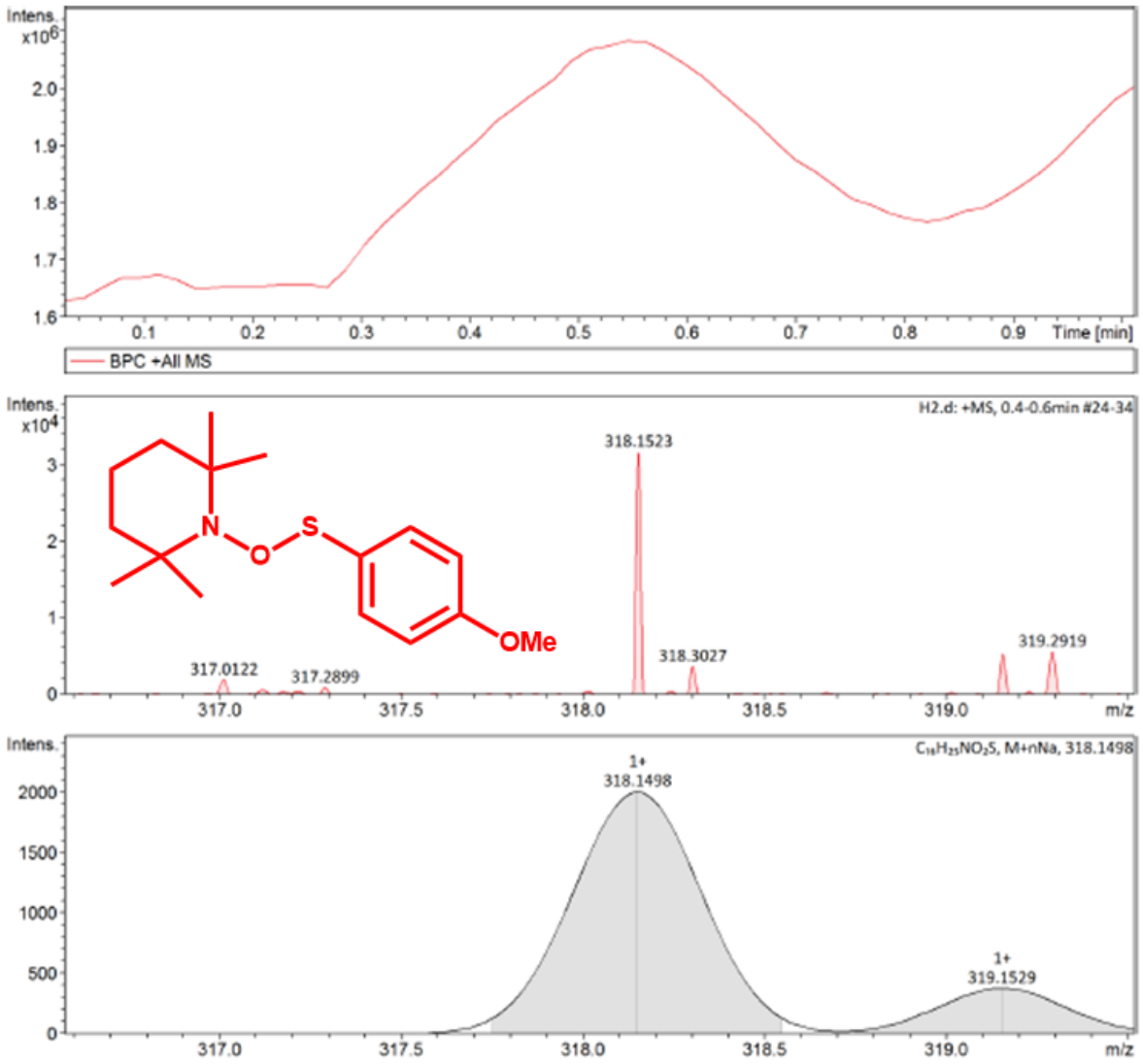


Fig. S7 ESI-MS spectrum of thiol adduct. Calculated for [M+nNa]: 318.1498; Found: 318.1523.

Note-S5 Procedure for radical trapping experiment with TEMPO and BHT

The amide synthesis from thioacetic S-acid and an amine was carried out in a sealed vial under visible-light activation using a single 18 W PHILIPS white LED source. The 5 mL reaction vial contained thioacetic S-acid (1.0 mmol), aniline (1.0 mmol), TEMPO/BHT (2.0 mmol), BiSI catalyst (7.0 mg), and acetonitrile (3.0 mL). After 4 h of irradiation, the mixture was diluted with additional acetonitrile and the BiSI photocatalyst was separated by centrifugation. The supernatant was concentrated by rotary evaporation, and the crude reaction mixture was analyzed via ^{1}H NMR to confirm the formation of the TEMPO adduct with thioacetic S-acid.

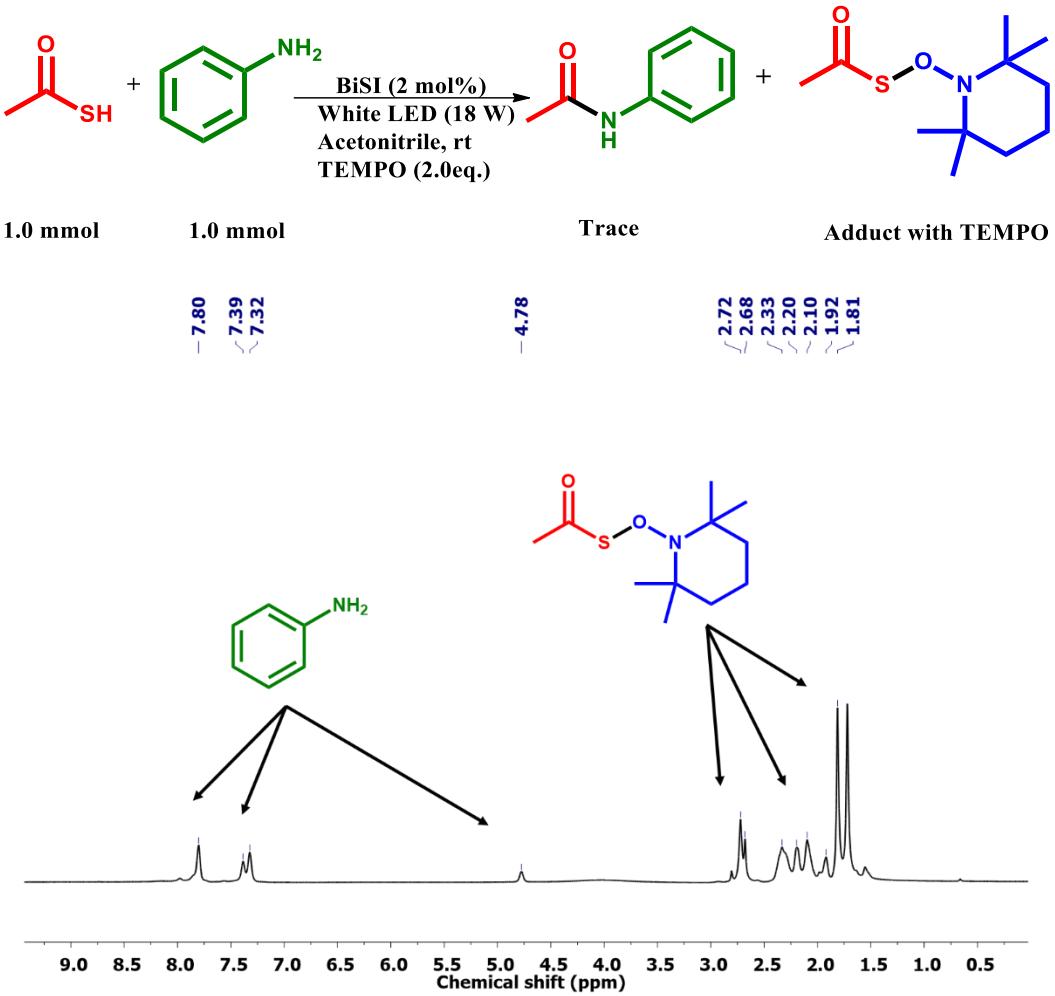


Fig. S8 Reaction scheme for amidation of thioacetic S-acid in the presence of TEMPO, and ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the crude product derived from BiSI photocatalyzed amidation in the presence of TEMPO.

Note-S6 Scaled-up experiments

A scaled-up reaction was performed using 92.0 mg of BiSI catalyst, 13.13 mmol of aniline, and 13.13 mmol of thiobenzoic S-acid in 10 mL of acetonitrile, according to the abovementioned procedure.

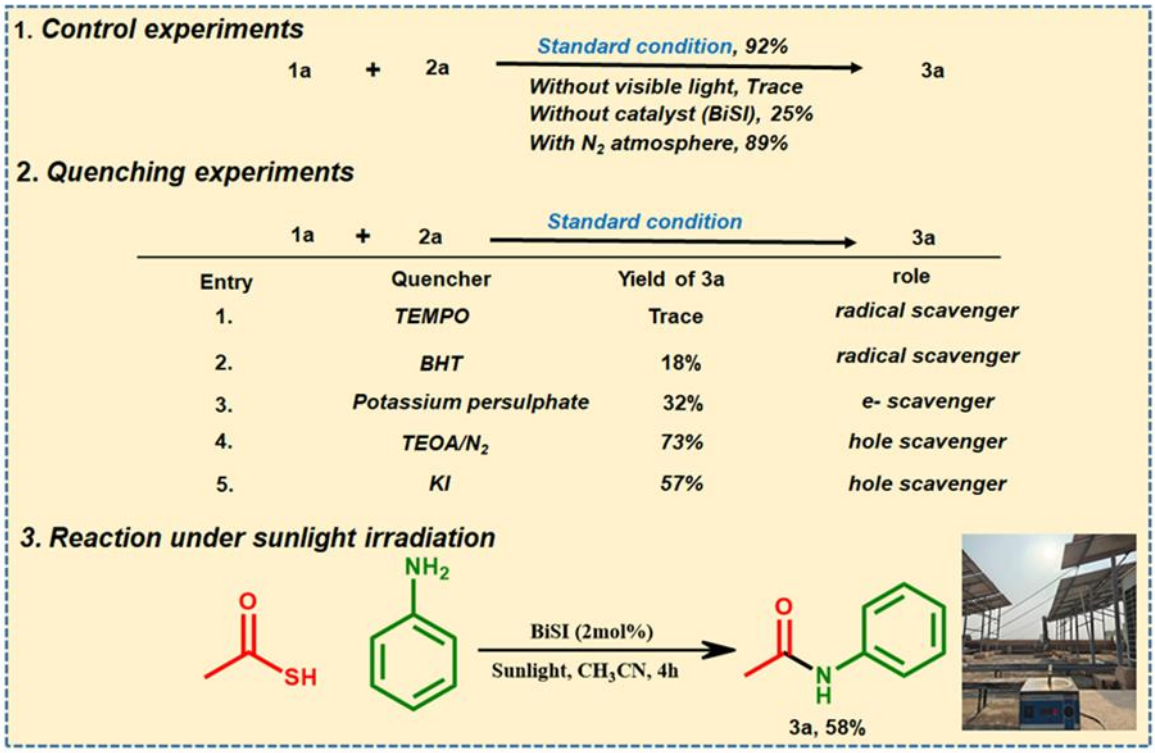


Fig. S9 Mechanistic studies, (1) Control experiments, (2) Quenching experiments, and (3) Reaction under sunlight irradiation.

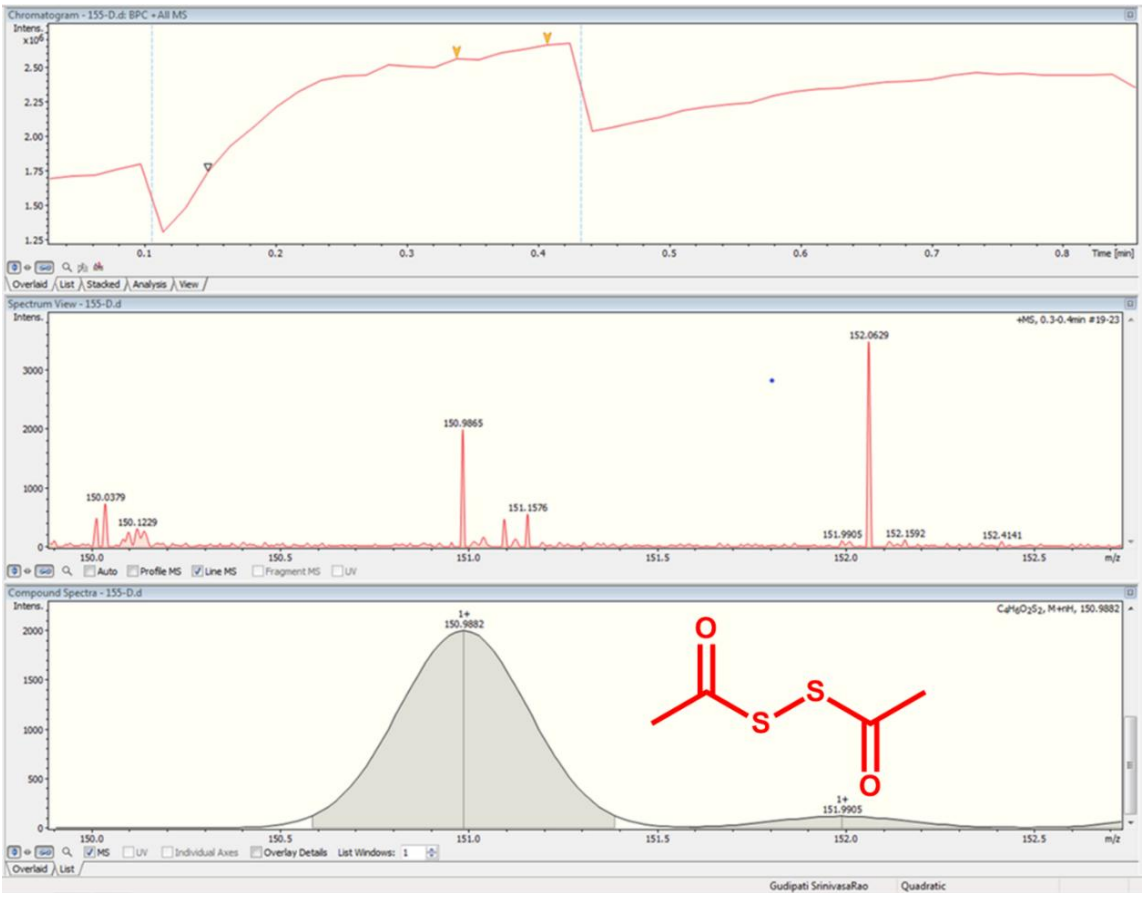


Fig. S10 ESI-MS of acetyldisulphide ($C_4H_6O_2S_2$). Calculated for $[M+H]^+$: 150.9882; Found: 150.9865.

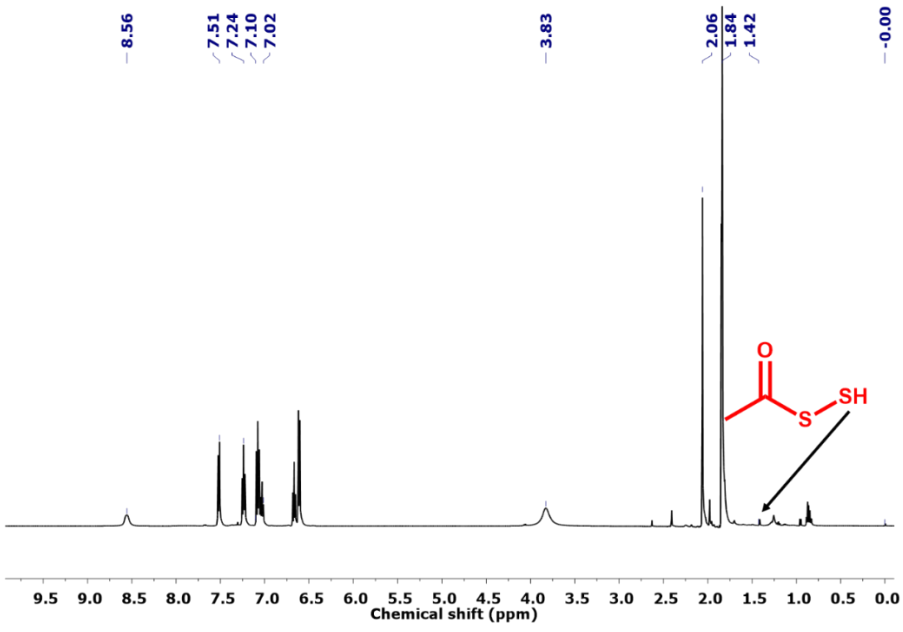
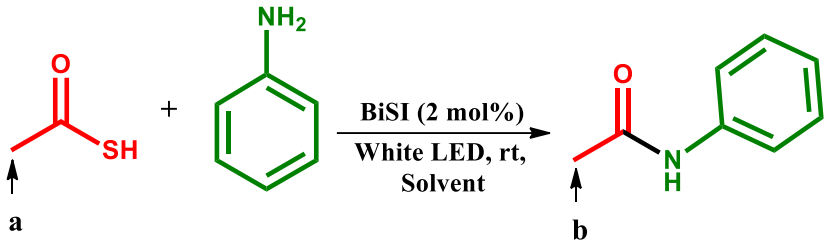


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the crude product derived from BiSI photocatalyzed amide formation.

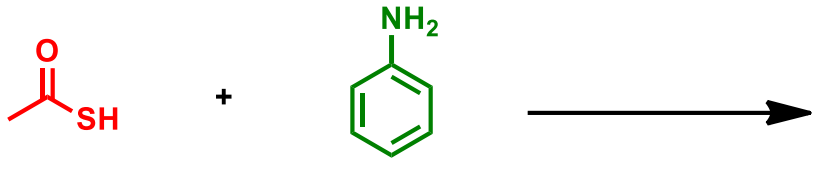
Note-S7 Evaluation of the photocatalytic activity of BiSI for amide formation

Visible light-initiated amidation reactions were performed in a sealed reaction vial using a PHILIPS 18 W (wavelength 400–750 nm, 1800 Lumen) white LED as a light source. The reaction mixture consisted of 7 mg of catalyst, 1.0 mmol of thioic S-acid, 1.0 mmol of amine, and 3 mL of acetonitrile, combined in a 5 mL capped glass vial. This vial was positioned 5 cm away from the light source and stirred at room temperature for 4 h under white light irradiation. Upon completion, centrifugation was used to separate the catalyst; the conversion of amide was analysed by ^{1}H NMR using $CDCl_3$ as the solvent.[3]



$$\textbf{Conversion (\%)} = \frac{b}{a+b} \times 100\ \%$$

Table S5. Evaluation of green chemistry metrics for gram-scale synthesis



Chemical Formula : C_2H_4OS
Formula Mass : 76.1176

Chemical Formula : C_6H_7N
Formula Mass : 93.1265

Chemical Formula : C_8H_9ON
Formula Mass : 135.1632
Yield = 81%

Total= 76.1176 + 93.1265 = 169.2441

Total =135.1632

	Chemicals	Wt. (g)	Formula Wt.
Reactant A	Thioacetic S-acid	1	76.1176
Reactant B	Aniline	1.22	93.1265
Solvent	CH_3CN	7.86	41.05
Recycle Solvent	-	6.13	41.05
Product	*N*-phenylacetamide	1.43	135.1632

Atom economy (%) $= \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants}} \times 100 = \frac{135.1632}{(76.1176+93.1265)} \times 100 = \mathbf{80\%}$

Atom efficiency (%) = (%yield of products × % atom economy) × 100 = (81% × 80%) = **65%**

Carbon efficiency (%) $= \frac{(\text{moles of product} \times \text{no.of carbon in products})}{(\text{moles of thiobenoic S-acid} \times \text{no.of carbon}) + (\text{moles of styrene} \times \text{no.of carbon in styrene})} \times 100 = \frac{(10.57 \times 8)}{(13.13 \times 2 + 13.13 \times 6)} = \mathbf{80\%}$

Product mass Intensity (PMI) $= \frac{mass\ of\ all\ reactant + solvent}{mass\ of\ product} = \frac{1.0+1.22+7.86}{1.43} = \mathbf{7.04}$

Reaction mass efficiency (%) or

Curzons RME % $= \frac{\text{Mass of isolated product}}{\text{Mass of all reactant}} \times 100 = \frac{1.43}{(1+1.22)} \times 100 = \mathbf{65\%}$

Optimum efficiency (OE) $= \frac{RME}{AE} \times 100 = \frac{0.65}{0.80} \times 100 = \mathbf{82\%}$

E factor $= \frac{\textbf{Total waste in (g)}}{\textbf{Total product (g)}} = \frac{(1+1.22+7.86)-(1.43+6.13)}{1.43} = \mathbf{1.76}$

Note-S8 Calculation of green chemistry metrics

We calculated the green chemistry metrics for our optimized reaction using the following parameters.

(1) Atom economy (AE) (%) = $\frac{molecular\ mass\ of\ desired\ product}{molecular\ mass\ of\ all\ reactant} \times 100$

(2) Reaction mass efficiency (RME) (%) = $\frac{mass\ of\ desired\ product}{mass\ of\ all\ reactant} \times 100$

(3) Carbon efficiency (CE) (%) = $\frac{amount\ of\ carbon\ in\ desired\ product}{total\ amount\ of\ carbon\ presented\ in\ all\ reactants} \times 100$

(4) Atom efficiency (AE_f) (%) = (%yield of product × %atom economy) × 100

(5) Environmental factor (E-factor) = $\frac{Amount\ of\ waste}{amount\ of\ product} \times 100$

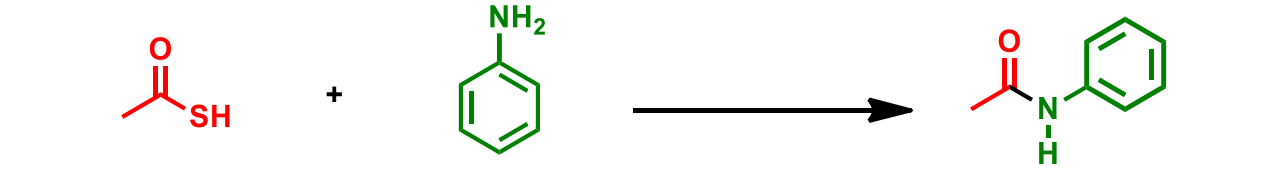
(6) Optimum efficiency (OE) = $\frac{RME}{AE} \times 100$

(7) Product mass intensity (PMI) = $\frac{mass\ of\ all\ reactant + solvent}{mass\ of\ product}$

Evaluation of green chemistry metrics for the synthesis of amide

---

(Song & Li's Work)



Chemical Formula : C_2H_4OS
Formula Mass : 76.1176

Chemical Formula : C_6H_7N
Formula Mass : 93.1265

Chemical Formula : C_8H_9ON
Formula Mass : 135.1632
Yield = 95%

Total= 76.1176 + 93.1265 = 169.2441

Total =135.1632

0.40 mmol	**0.20 mmol**	**0.19 mmol**
30.0 mg	**19.0 mg**	**26.0 mg**
C_2H_4OS	**C_6H_7N**	**C_8H_9ON**
FW = 76.1176	**FW = 93.1265**	**FW = 135.1632**
Solvent	**CH_3CN (2.0 mL)**	**FW = 41.05**

Product **3a** *N*-phenylacetamide

Yield of product 3a = **95 %**

(1) AE = $\frac{135.1632}{76.1176+93.1265} \times 100 = \mathbf{80}\%$

(2) RME = $\frac{26.0}{30.0+19.0} \times 100 = \mathbf{53}\ \%$

(3) CE (%) = $\frac{0.95 \times 8}{2+6} \times 100 = \mathbf{95}\ \%$

(4) $AE_f = 0.95 \times 0.80 = \mathbf{76}\ \%$

(5) OE = $\frac{70}{86} \times 100 = \mathbf{70}\ \%$

(6) PMI = $\frac{30.0 + 19.0 + 1564}{26.0} = \mathbf{62.0}$

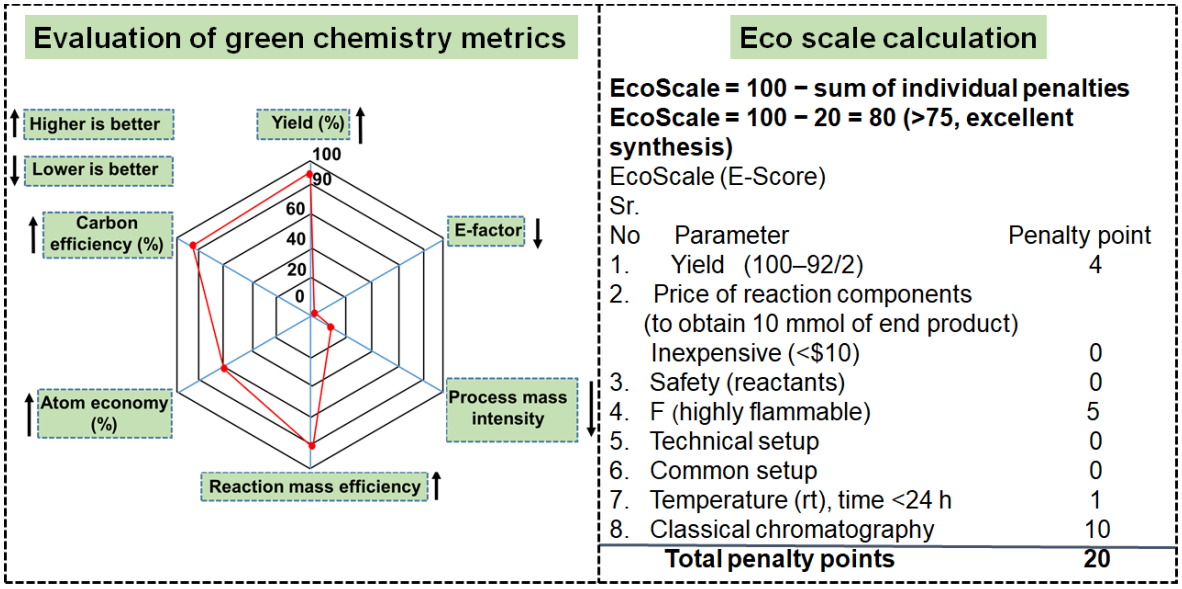


Fig. S12 Evaluation of green chemistry metrics and eco-scale calculation for amide.

Table S6 penalty points to calculate the Eco-Scale[4]

EcoScale = 100 − sum of individual penalties

EcoScale = 100 − 20 = **80** (>75, excellent synthesis)

Sr. no.	**Parameter**	**Value**	**Penalty point**
1	Yield	100–92/2	4
2	Price of reaction components (to obtain 10 mmol of end product)	Inexpensive (<$10)	0
3	Safety (reactants)	F (flammable)	5
4	Technical setup	Common setup	0
5	Temperature, time	>1 h	1
6	Purification	Classical chromatography	10
Total penalty points			**20**

Note-S9 Apparent quantum efficiency (AQE) determination,

Calculations,

The apparent quantum efficiency (AQE) for amide synthesis was evaluated under blue LED irradiation (λ = 420 nm). Using the amount of product obtained after 4 h of photocatalysis, the AQE was determined following the standard calculation formula;

$$\eta(AQE) = (2 \times M \times N_A \times h \times c)/(S \times P \times T \times \lambda)$$

$$= 0.94\%$$

M = yield of product (mol); $N_A = 6.02 \times 10^{23}$ mol^{-1}; $h = 6.626 \times 10^{-34}$ J s; $c = 3 \times 10^8$ m s^{-1}; S = irradiation area (cm^2); P is the intensity of irradiation light (W/cm^2); T is the photoreaction time (s); λ is the wavelength of the monochromatic light (m).

M = 0.00072 (72%); $N_A = 6.02 \times 10^{23}$ mol^{-1}; $h = 6.626 \times 10^{-34}$ J s; $c = 3 \times 10^8$ m s^{-1}; S = 3.5×1.2 (cm^2); P = 0.72 (W/cm^2); T is the photoreaction time (14,400 s); λ is the wavelength of the monochromatic light (420 nm).

Note-S10 Stern-Volmer fluorescence quenching experiments

Stern–Volmer quenching studies were carried out for each component of the reaction system by measuring the emission response of BiSI (0.2 mM) with increasing concentrations of the quencher in acetonitrile. Fluorescence data were recorded at 440 nm (λ_{exc} = 302 nm) using an 2550 spectrophotometer (Shimadzu). Emission data for the samples were collected and analyzed using the Stern–Volmer plot based on the equation $I_0/I = 1 + K_q t_0[Q]$.

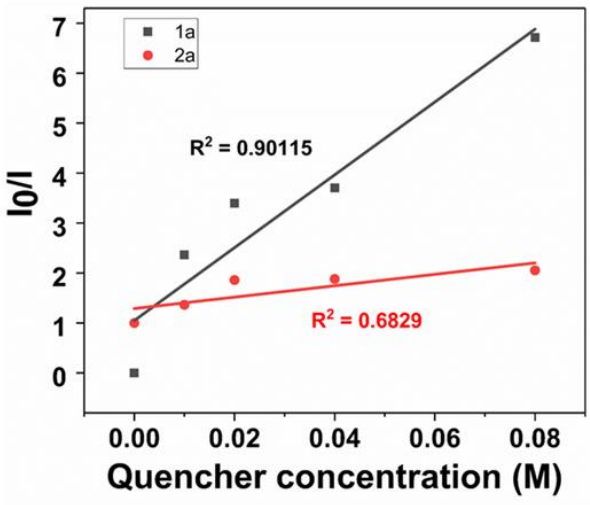


Fig. S13 Stern−Volmer plots of **1a** and **2a** of amidation reaction.

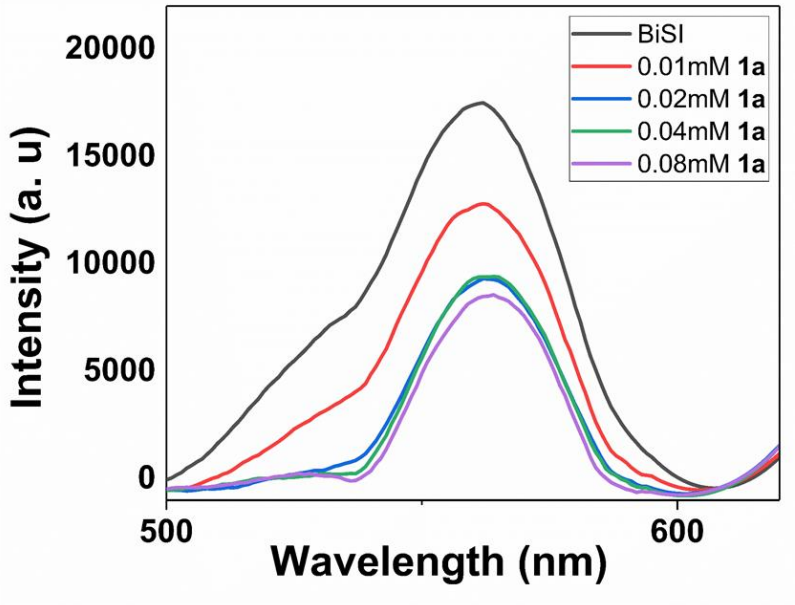


Fig. S14 Fluorescence quenching experiment of BiSI by **1a** of the amidation reaction.

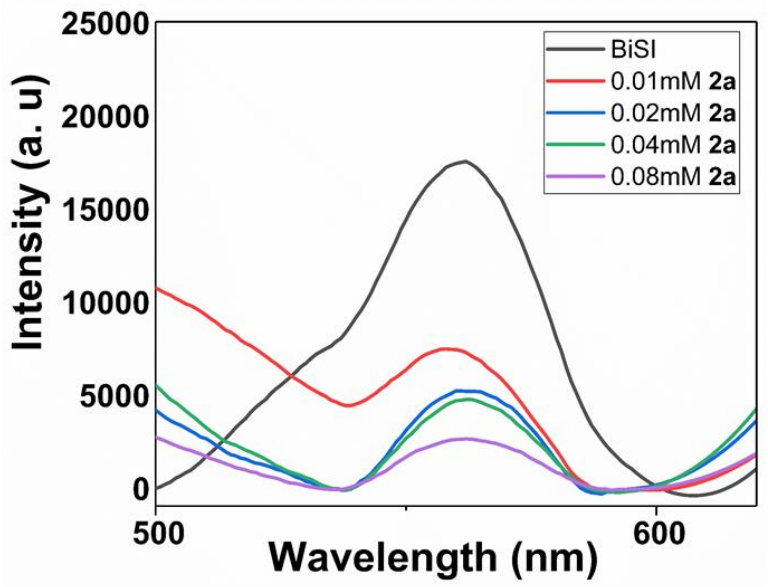


Fig. S15 Fluorescence quenching experiment of BiSI by **2a** of the amidation reaction.

Note-S11 Light-on/off experiment

Six identical reaction mixtures were prepared in 5.0 mL vials, each containing thioacetic S-acid 1a (1.0 mmol) and aniline 2a (1.0 mmol) in 3.0 mL of acetonitrile. The vials were stirred at room temperature and irradiated with an 18 W white LED. After 1.5 h of irradiation, the light was switched off, and one vial was sampled for analysis. The remaining mixtures were kept stirring in the dark for another 1.5 h, after which a second vial was taken for analysis, and

the light was turned on again. This light/dark cycle was repeated two more times, with one vial removed after each 1.5 h interval of irradiation or darkness. In **Fig. S14a**, the blue plot shows how the reaction yield changed in response to the alternating periods of light exposure and darkness.

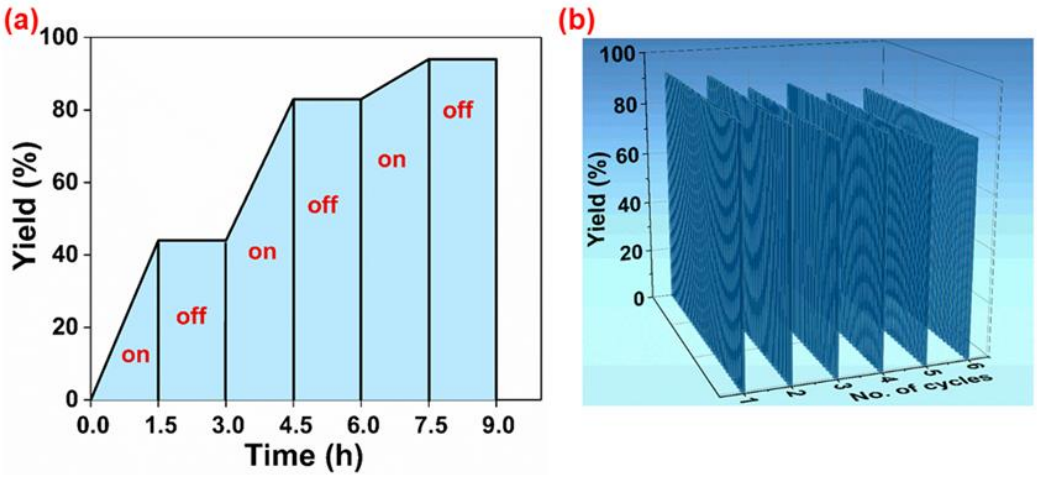


Fig. S16 (a) Light on–off experiments, (b) Recyclability plot of catalyst BiSI.

Note-S12 Procedure for photocatalyst recycling

Amide synthesis from thioacetic S-acid and aniline was carried out under visible-light irradiation in a sealed 5 mL reaction vial using a PHILIPS 18 W white LED source. The reaction mixture contained thioacetic S-acid (1.0 mmol), aniline (1.0 mmol), 7.0 mg of the catalyst, and acetonitrile (3.0 mL). After completion of each experiment, the catalyst was collected by centrifugation, and the recovered catalyst was employed directly in the next reaction cycle without any additional purification or activation.

No. of cycles	**Cycle-1**	**Cycle-2**	**Cycle-3**	**Cycle-4**	**Cycle-5**	**Cycle-6**
Yield (%)	92	90	84	85	80	81

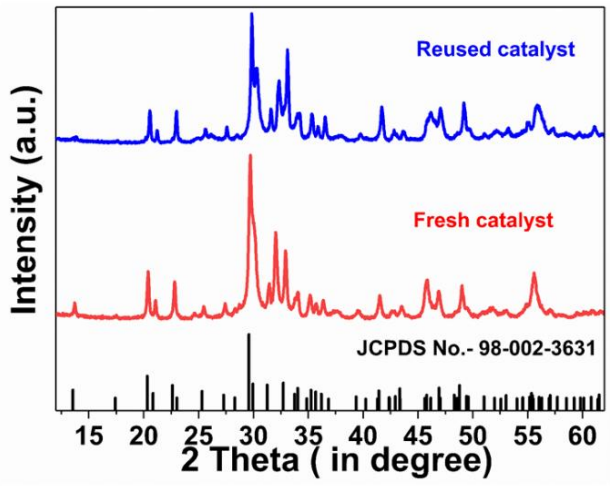
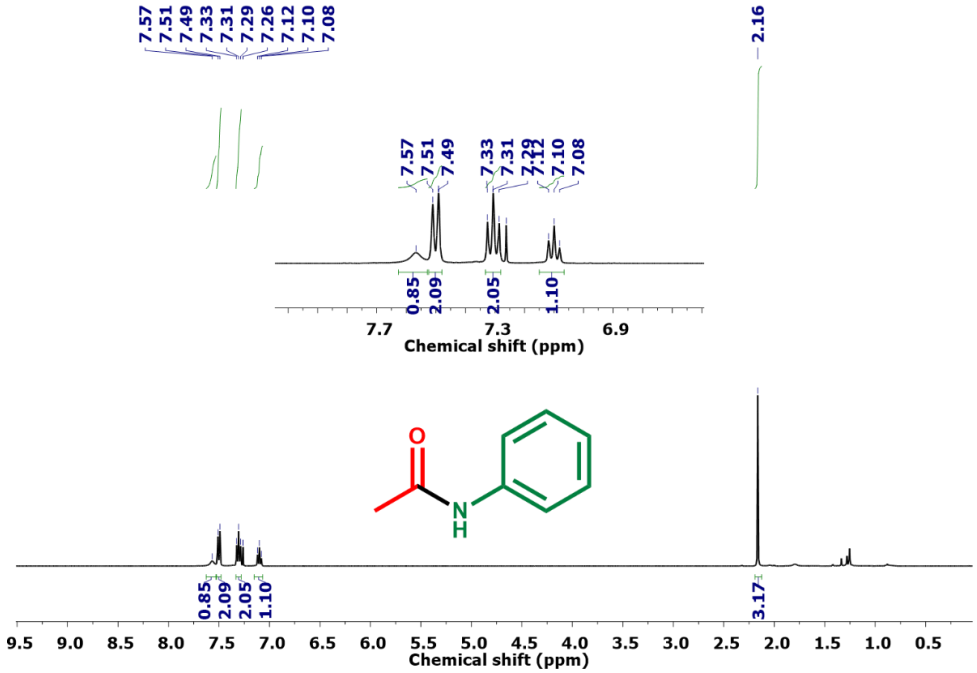


Fig. S17 PXRD pattern of recycled catalyst BiSI.

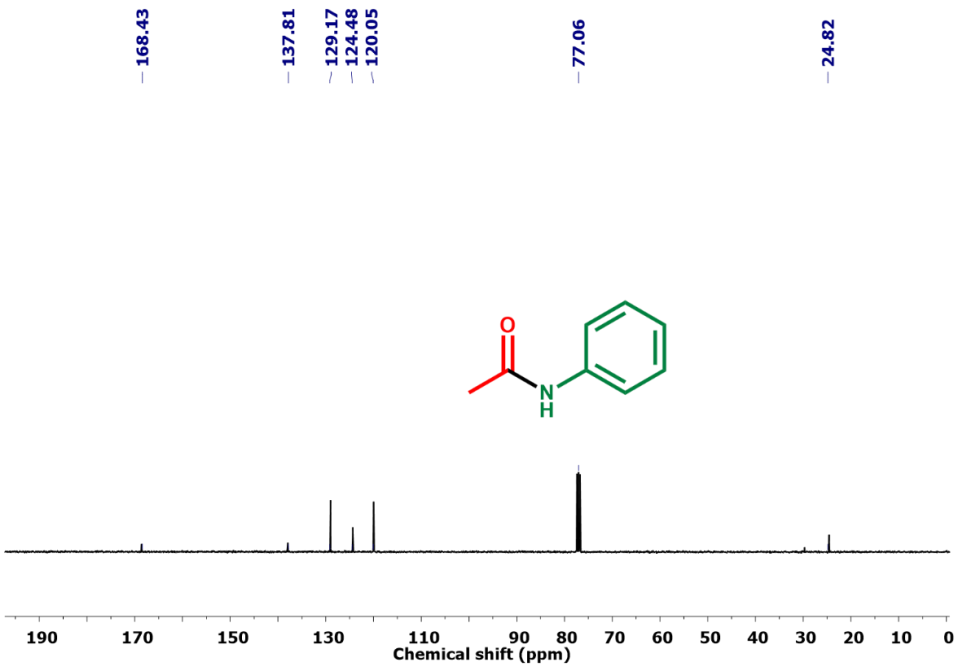
Table S7. Comparison of various photocatalysts for amide bond formation.

S No.	Catalyst	Light source	Yield(%)	References
1.	Mes-Acr-$MeBF_4$	Blue LED	95	[5]
2.	$Ru(bpy)_3Cl_2$	Visible light	87	[6]
3.	*fac*-$[Ir(ppy)_3]$	Visible light	70	[7]
4.	RFTA	Blue LED	90	[8]
5.	RFTA/$TBAF_4$	Blue LED	70	[9]
6.	*fac*-$[Ir(ppy)_3]/(Boc)_2$	Blue LED	75	[10]
7.	Eosin Y	Blue LED	89	[11]
8.	CBr_4/Collidine	UVA light	98	[12]
9.	Rhodamine B	Blue LED	83	[13]
10.	BiOBr nanosheets	Xe lamp	75	[14]
11.	Rose Bengal	Visible light	81	[15]
12.	$Ru(bpy)_3Cl_2$	Blue LED	98	[16]
13.	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	Blue LED	74	[17]
14.	4CzIPN	CFL lamp	67	[18]
15.	$[Ir(dFppy)_2(dtbbpy)]PF_6$	Blue LED	76	[19]
16.	**BiSI**	**Visible light**	**92**	**This work**

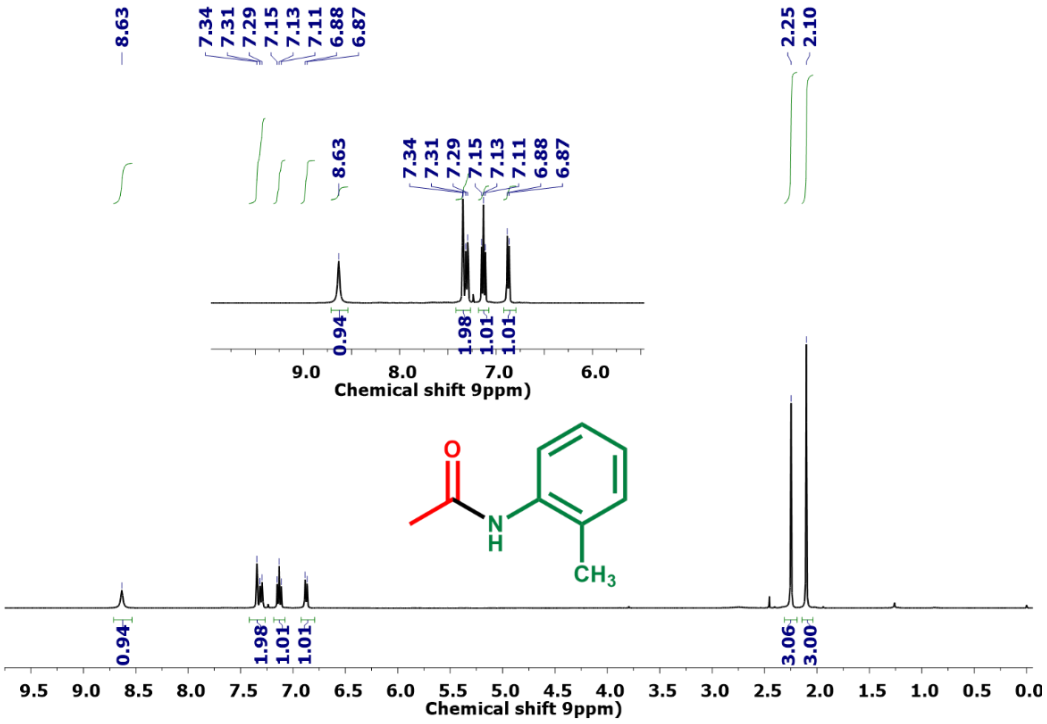
Data of compounds and copies of all NMR spectra



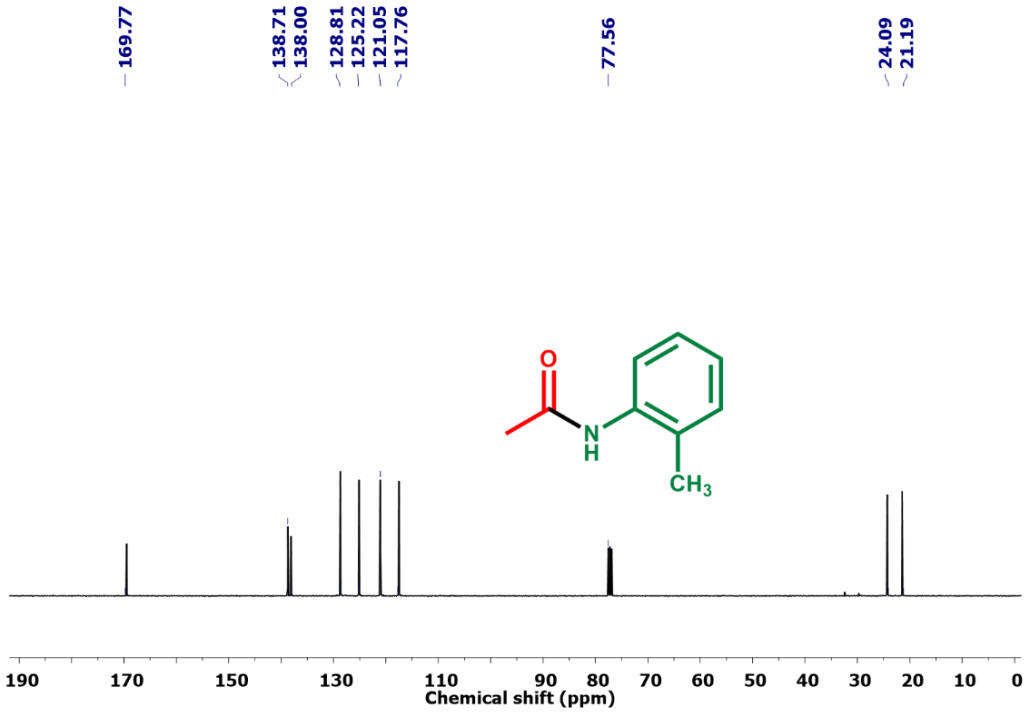
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **3a.**



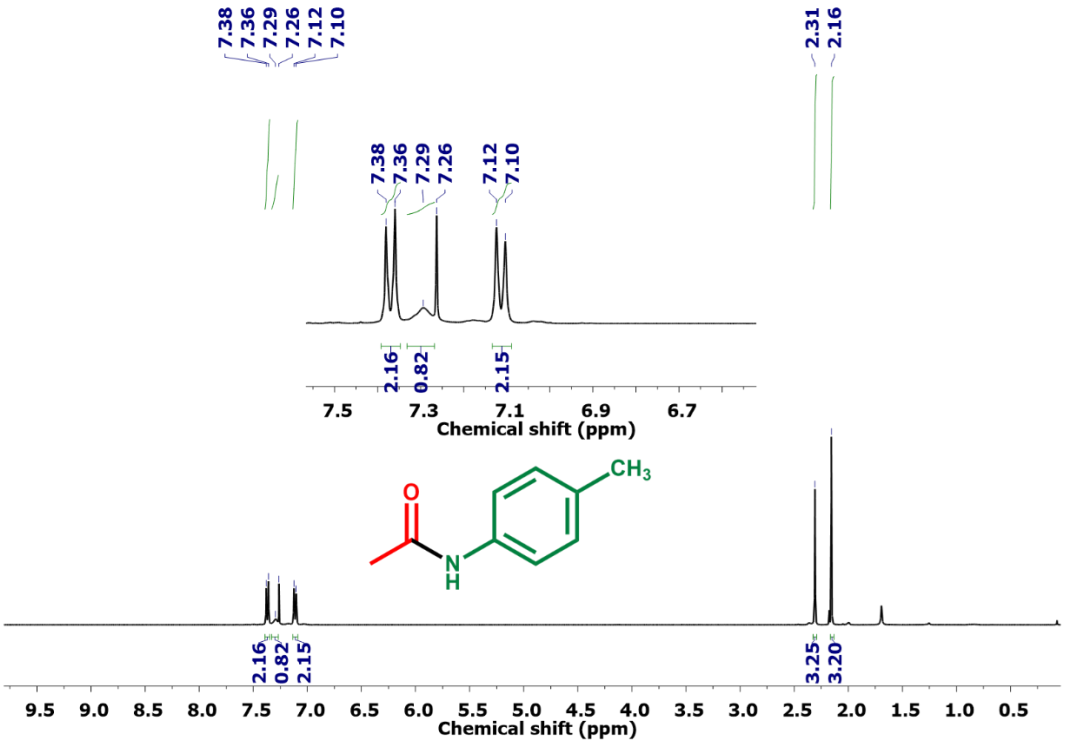
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **3a.**



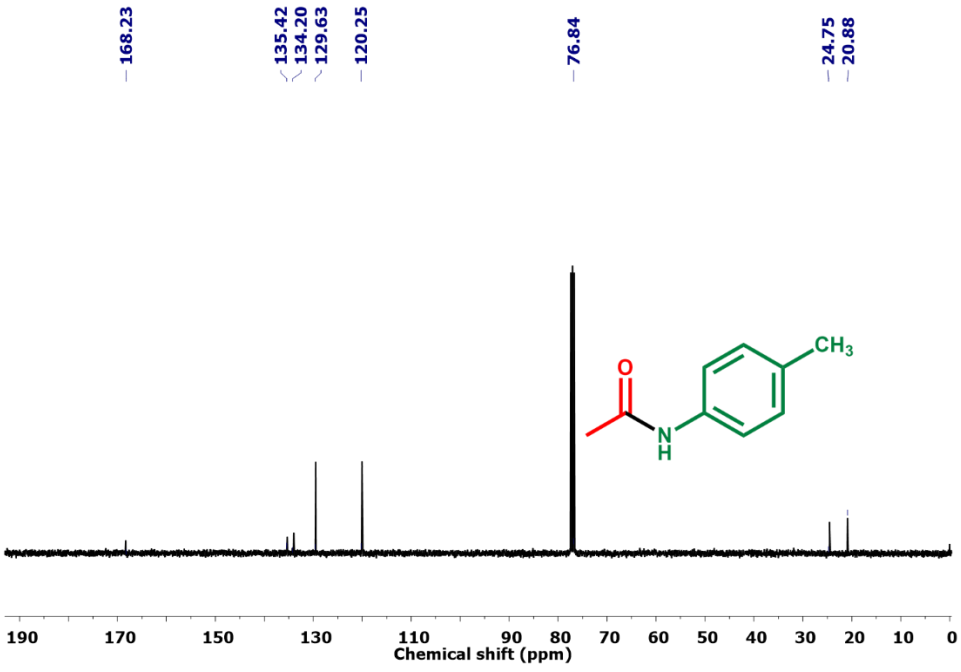
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **4a.**



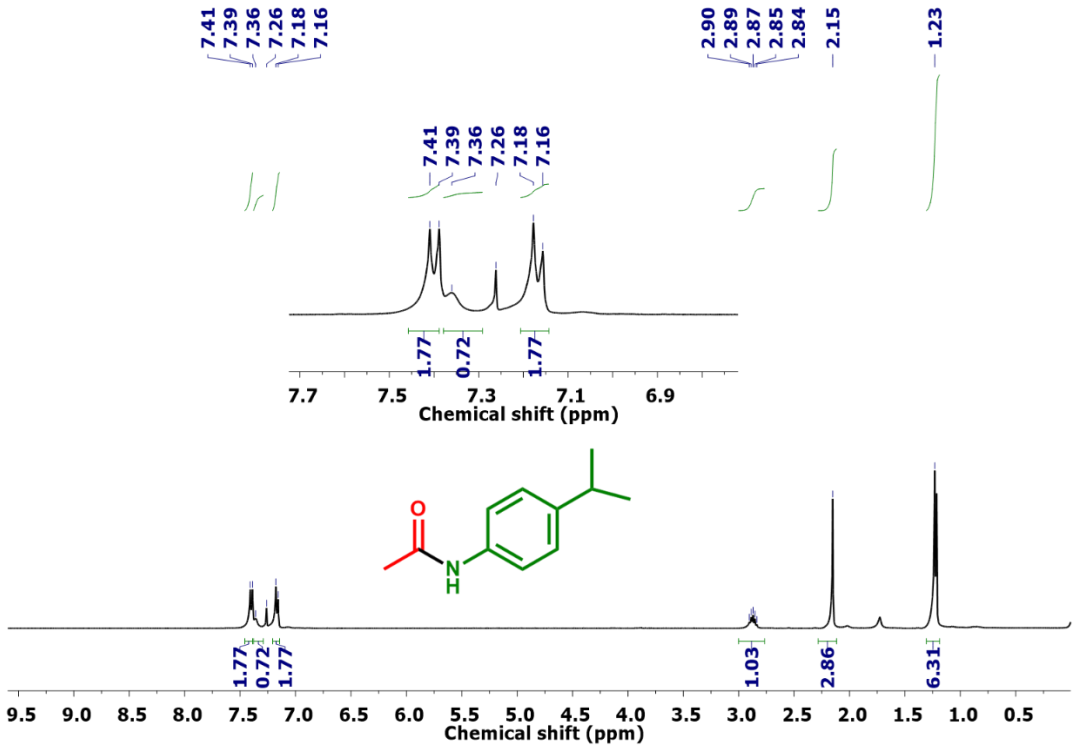
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **4a.**



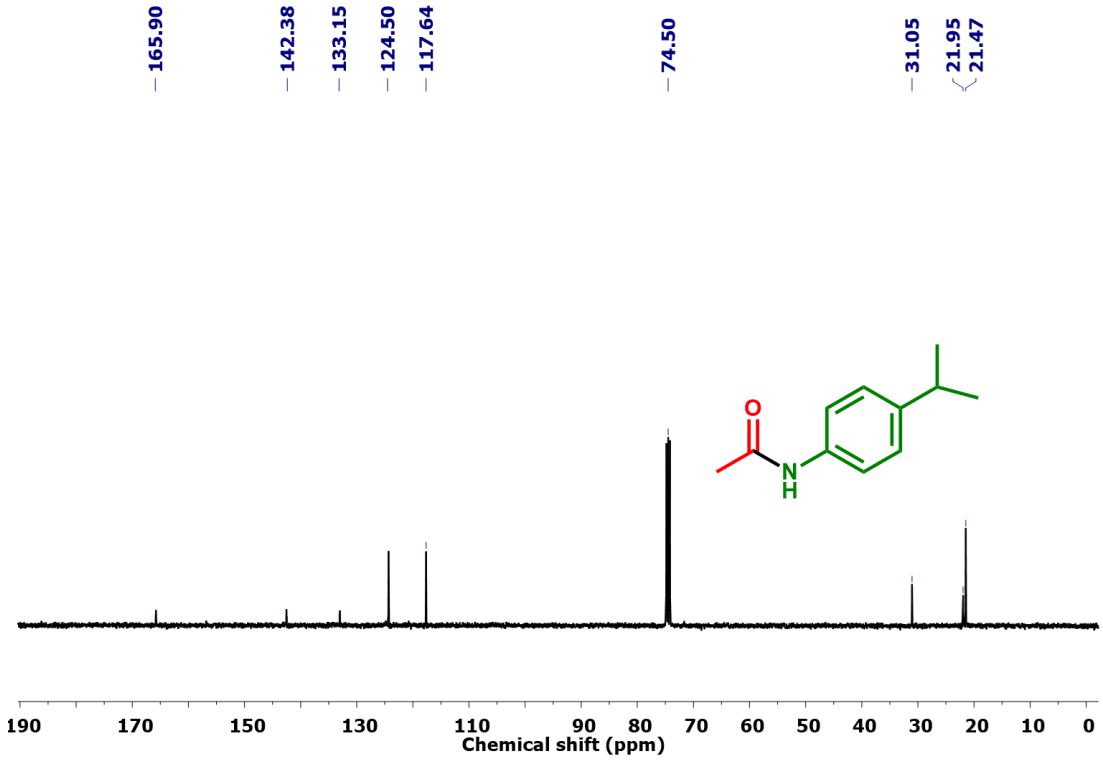
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **5a.**



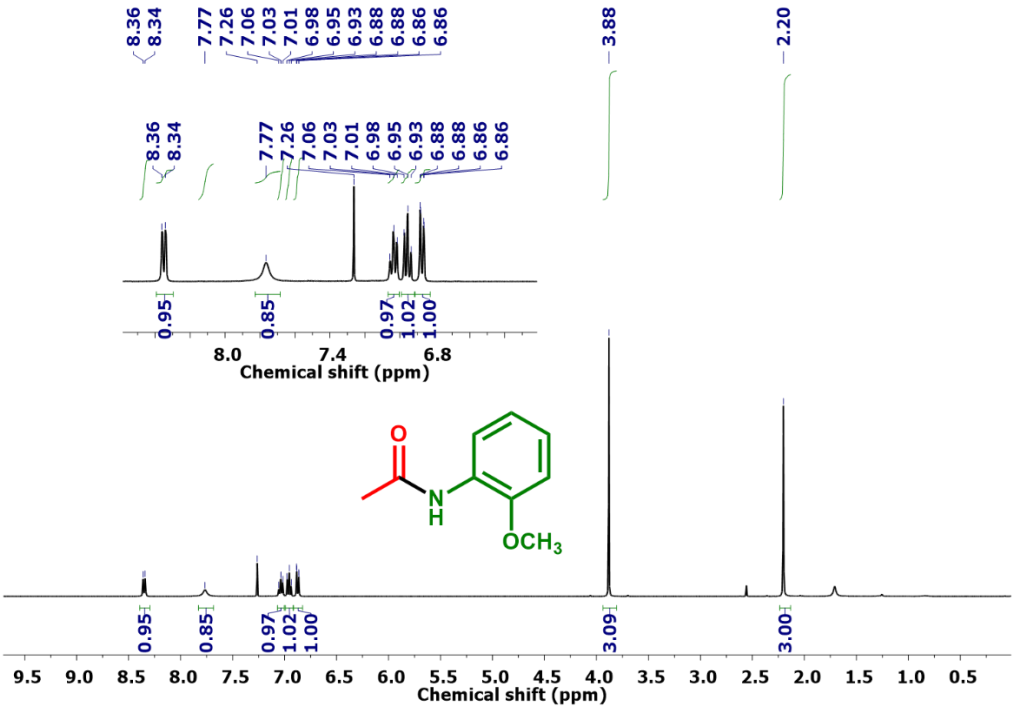
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **5a.**



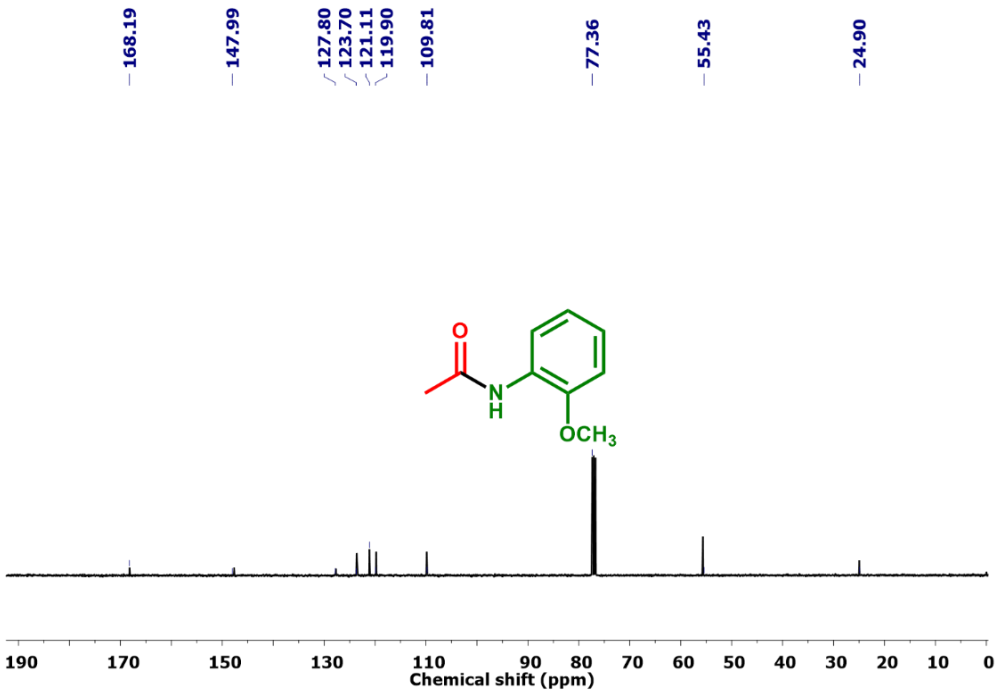
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **6a.**



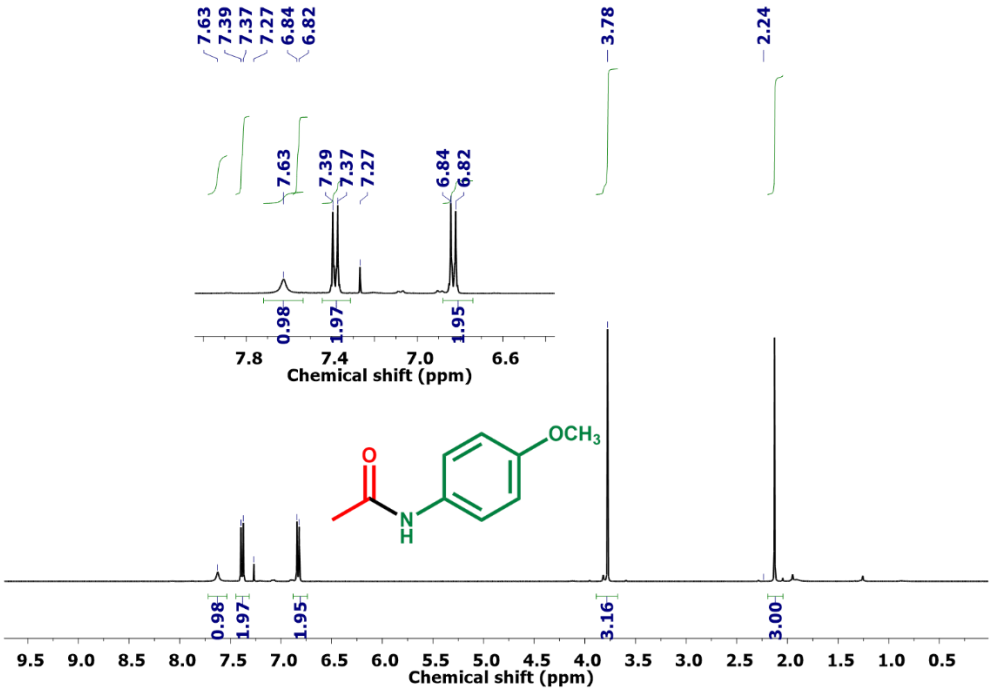
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **6a.**



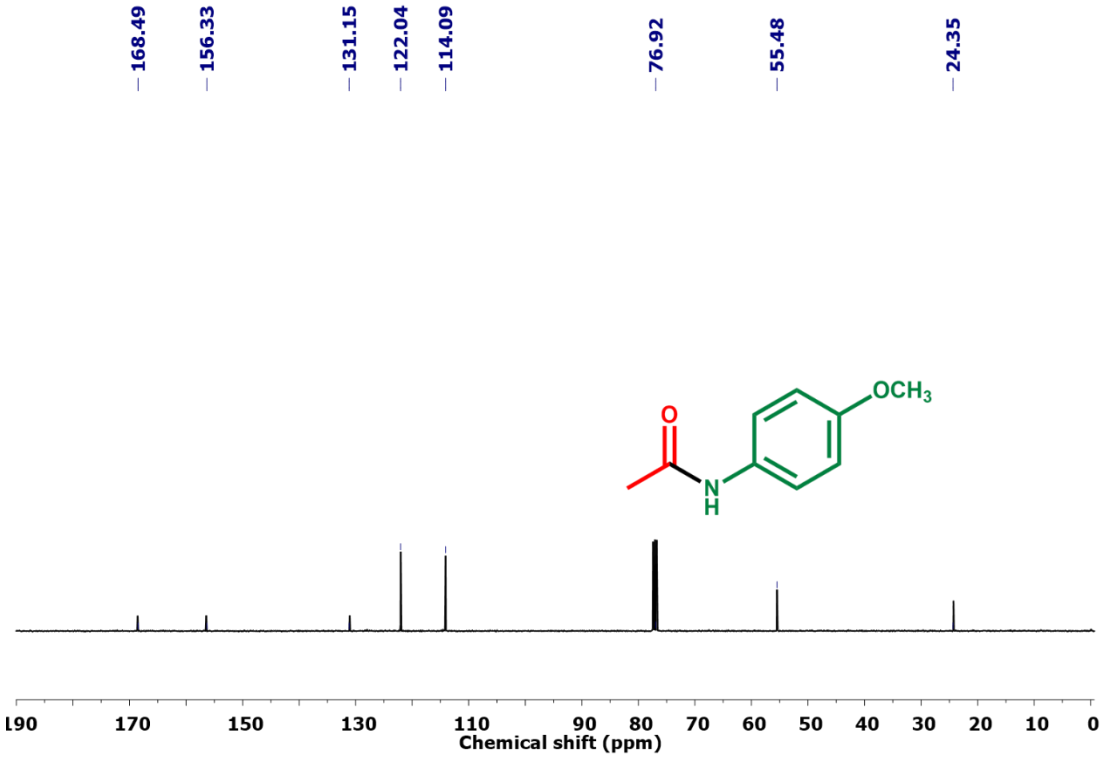
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **7a**.



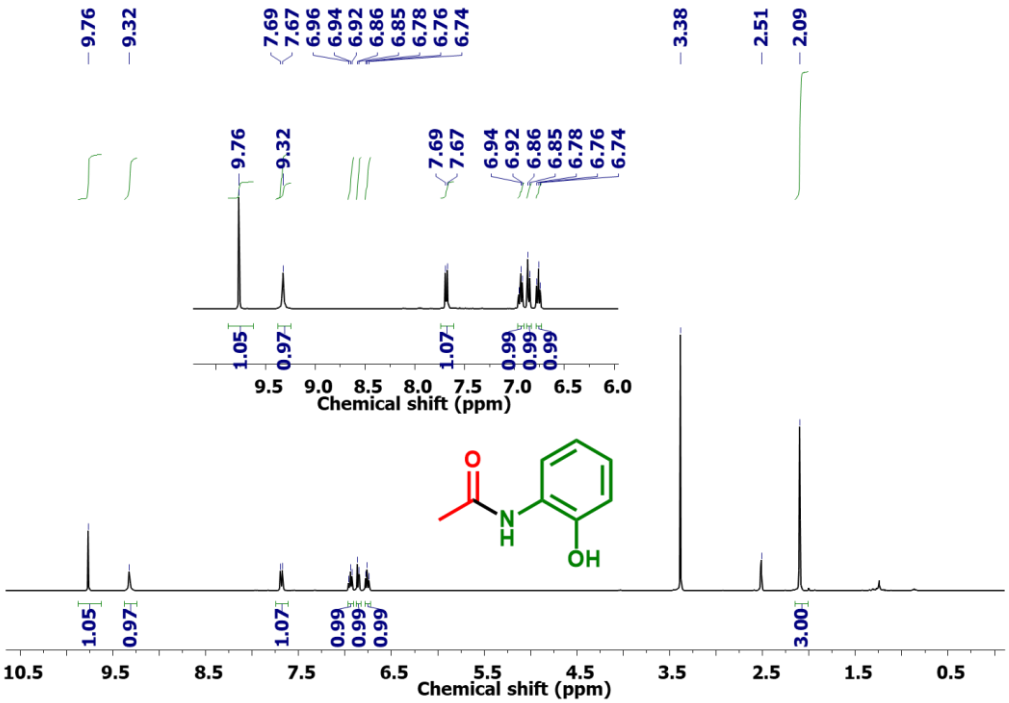
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **7a.**



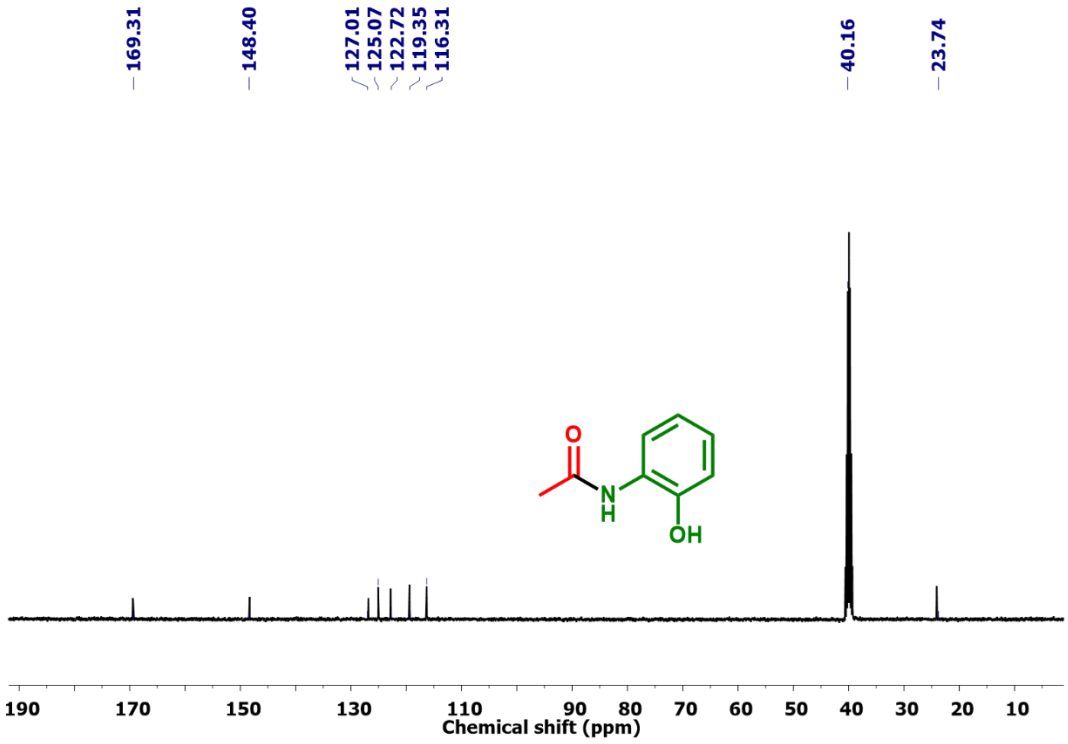
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **8a.**



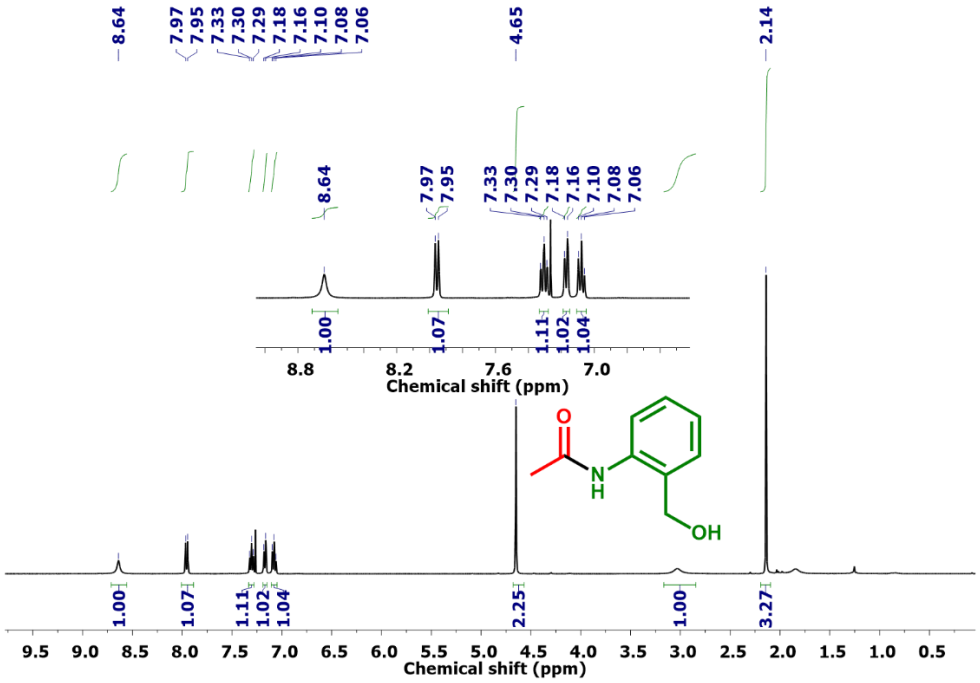
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **8a.**



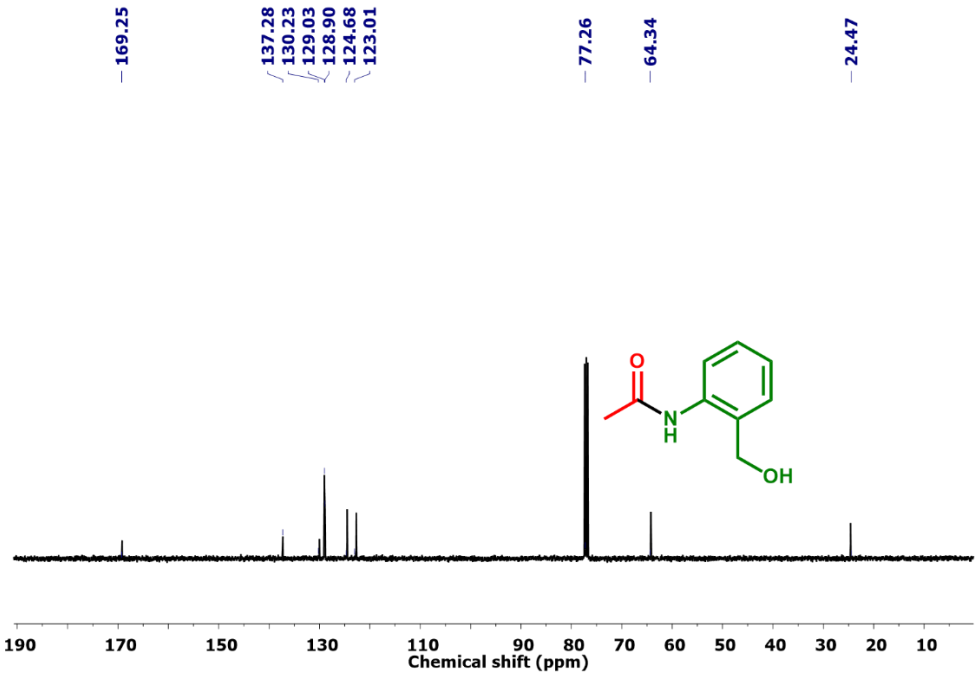
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **9a.**



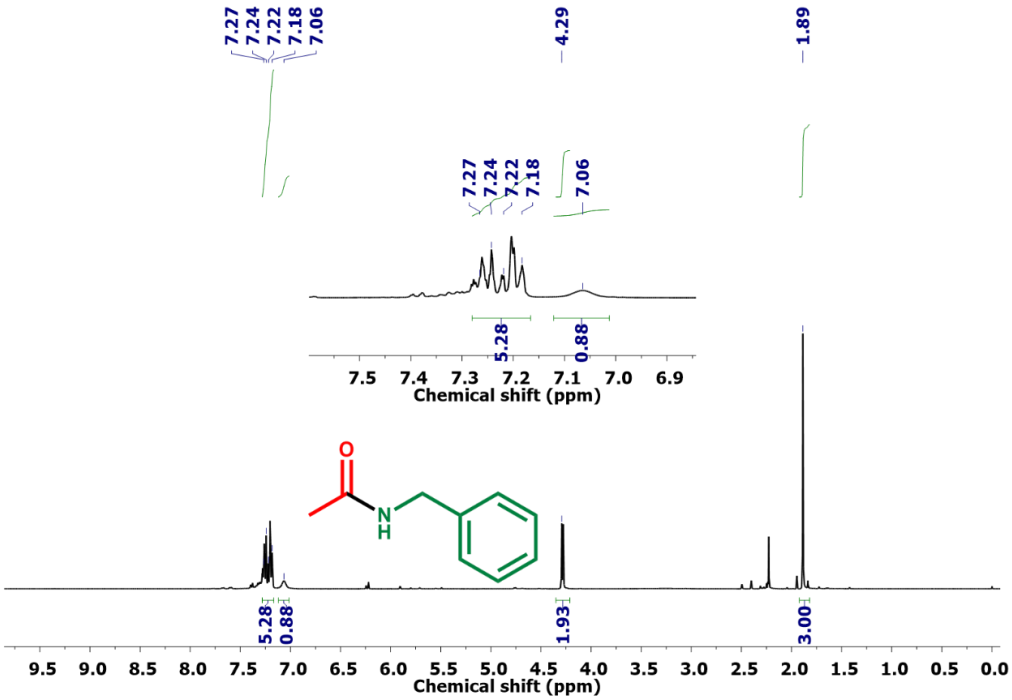
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **9a.**



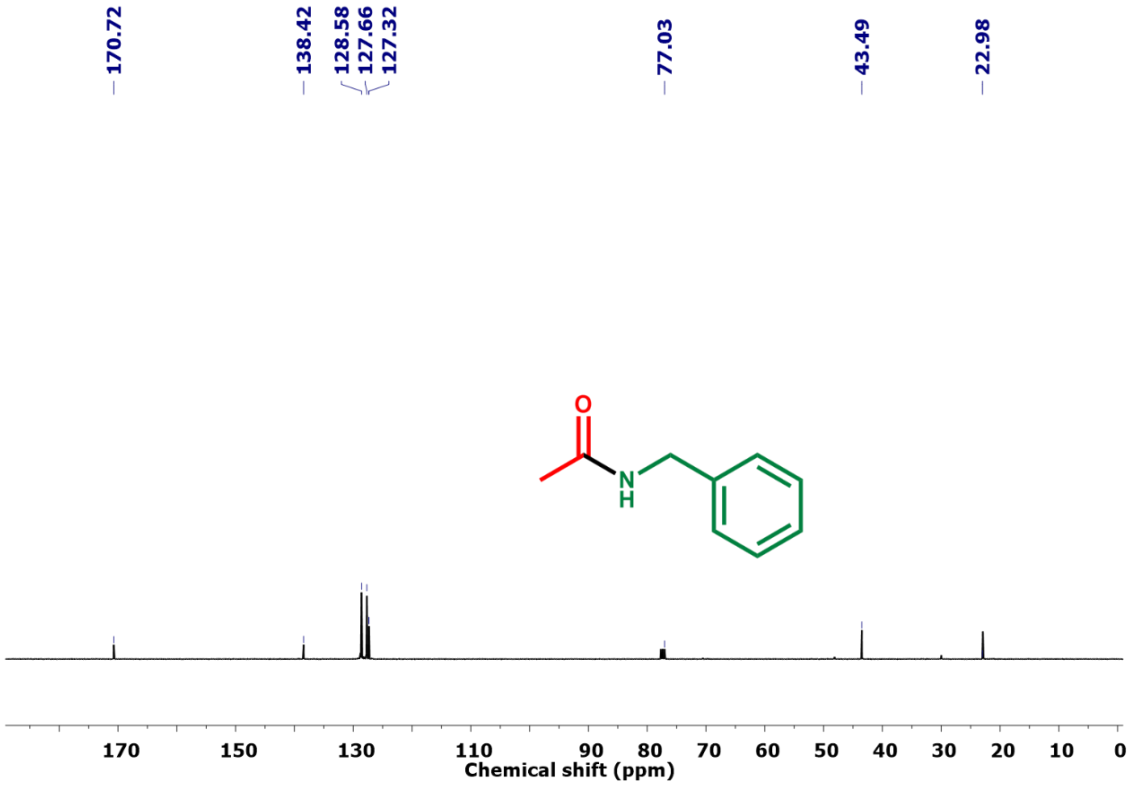
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **10a.**



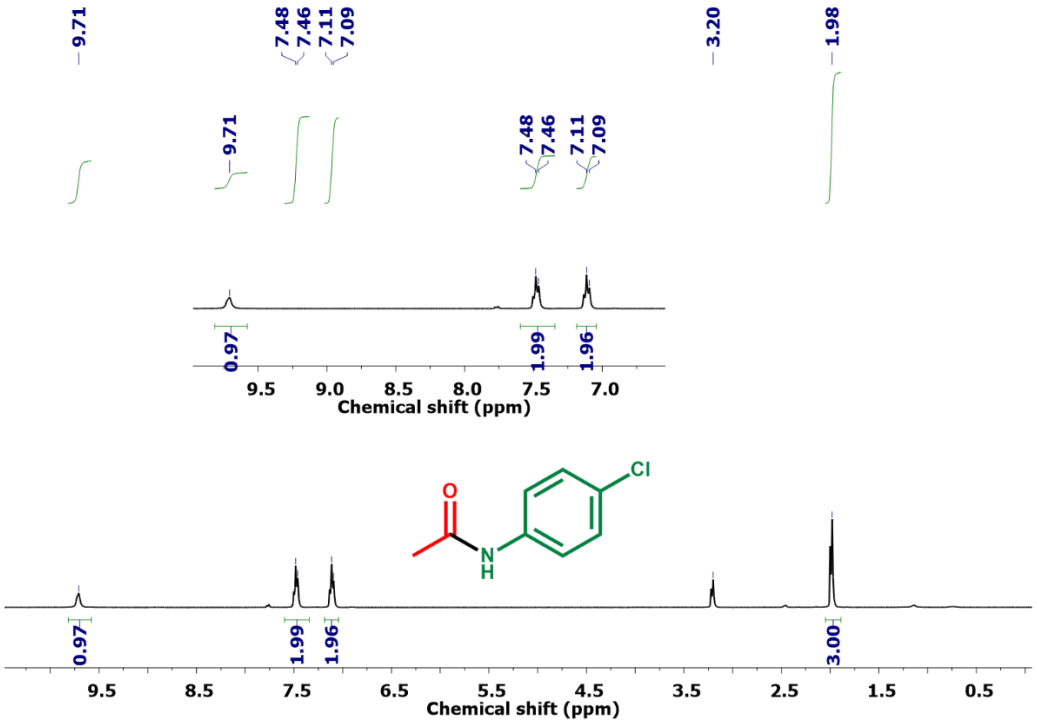
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **10a.**



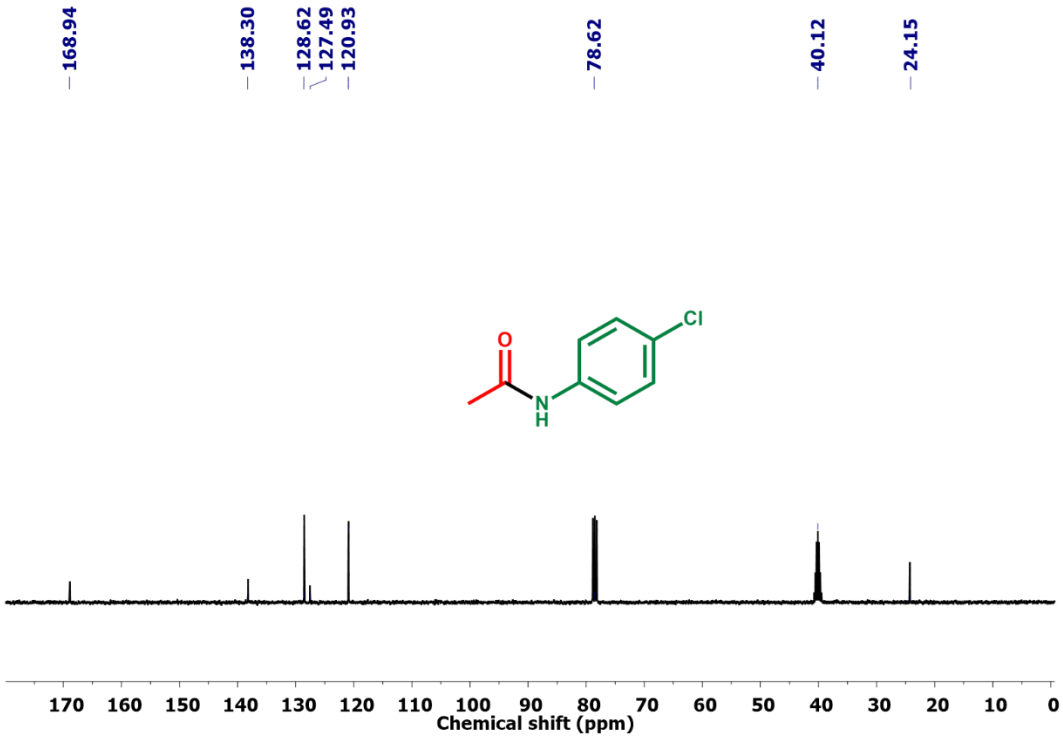
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **11a.**



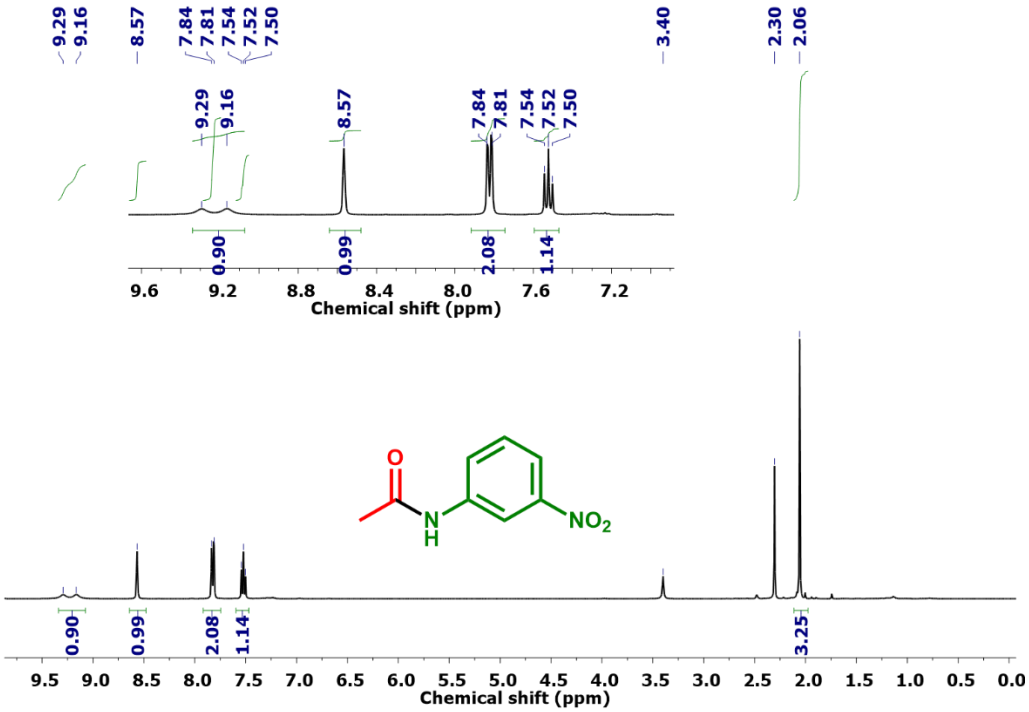
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **11a.**



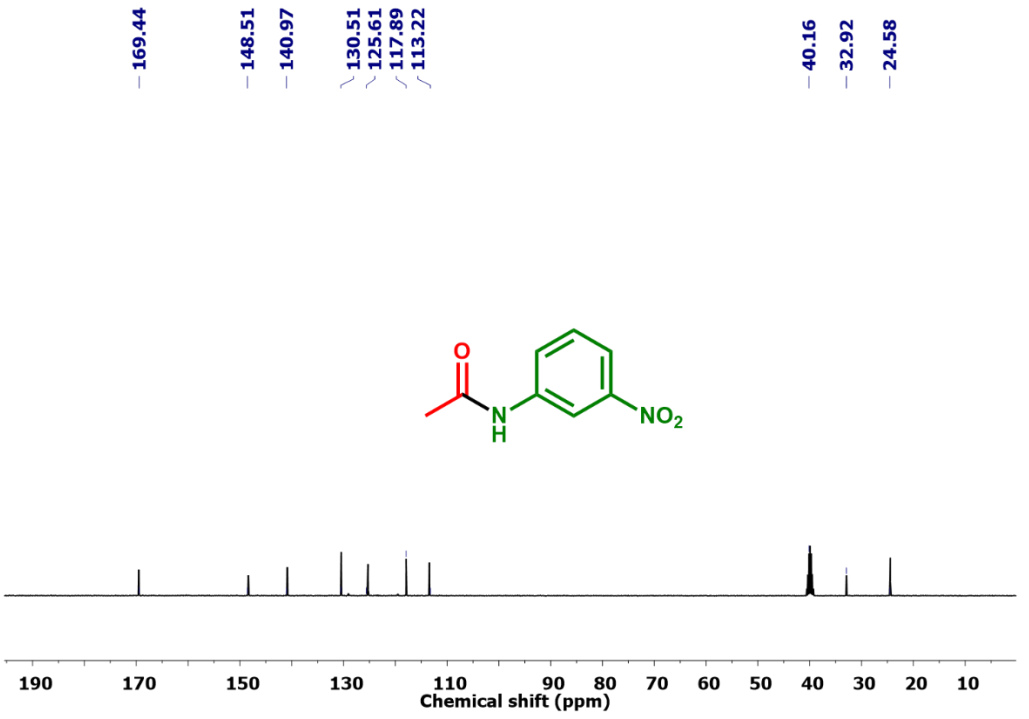
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **12a.**



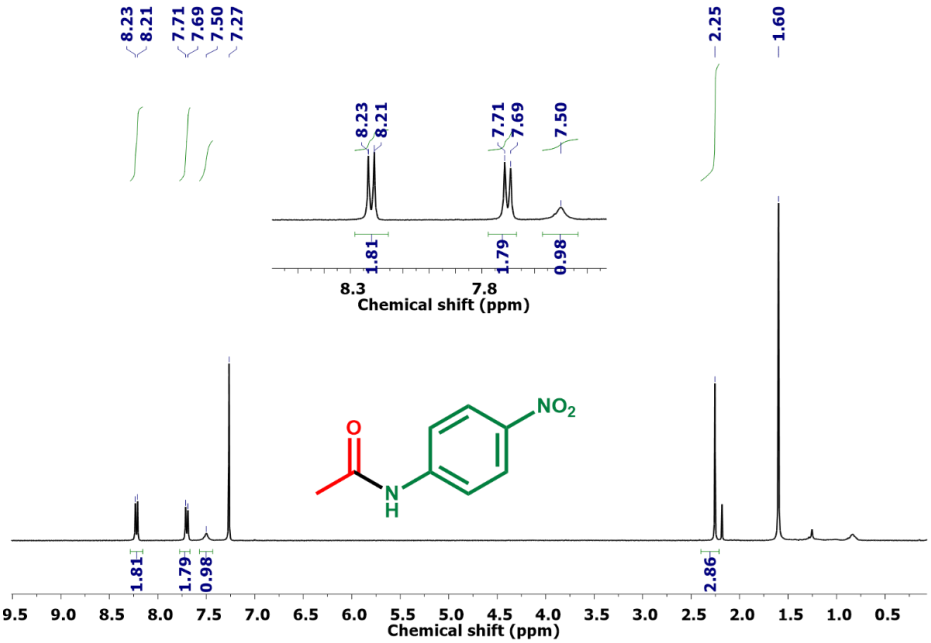
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **12a.**



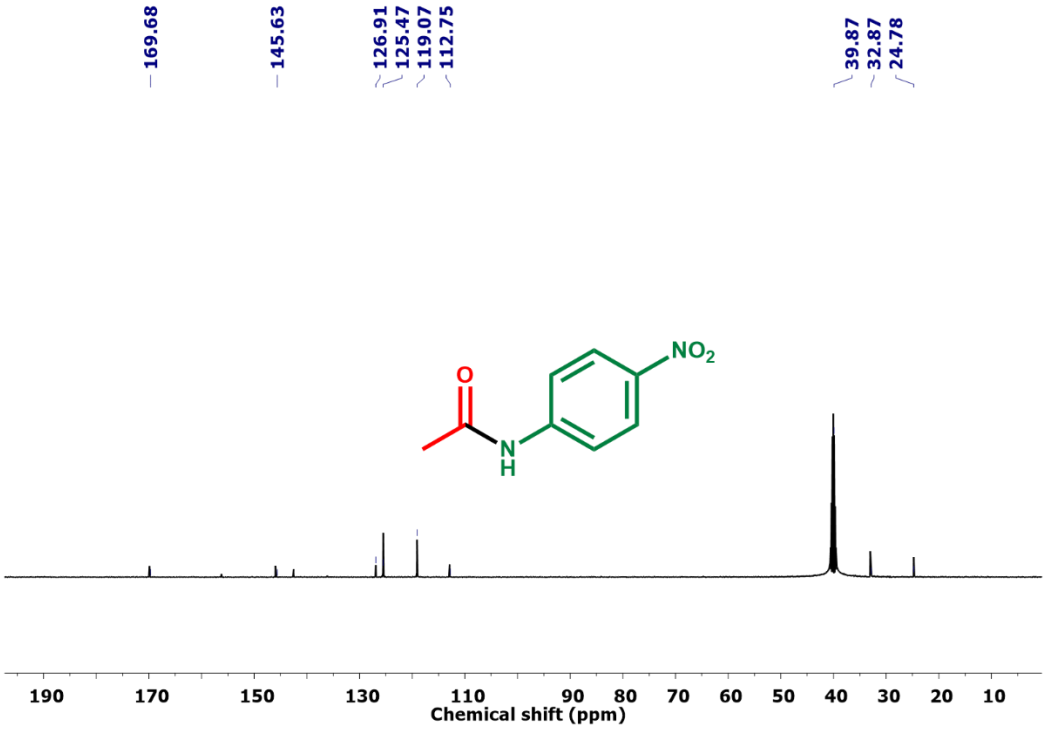
^{1}H NMR (DMSO-d_6, 500 MHz) of Compound **13a.**



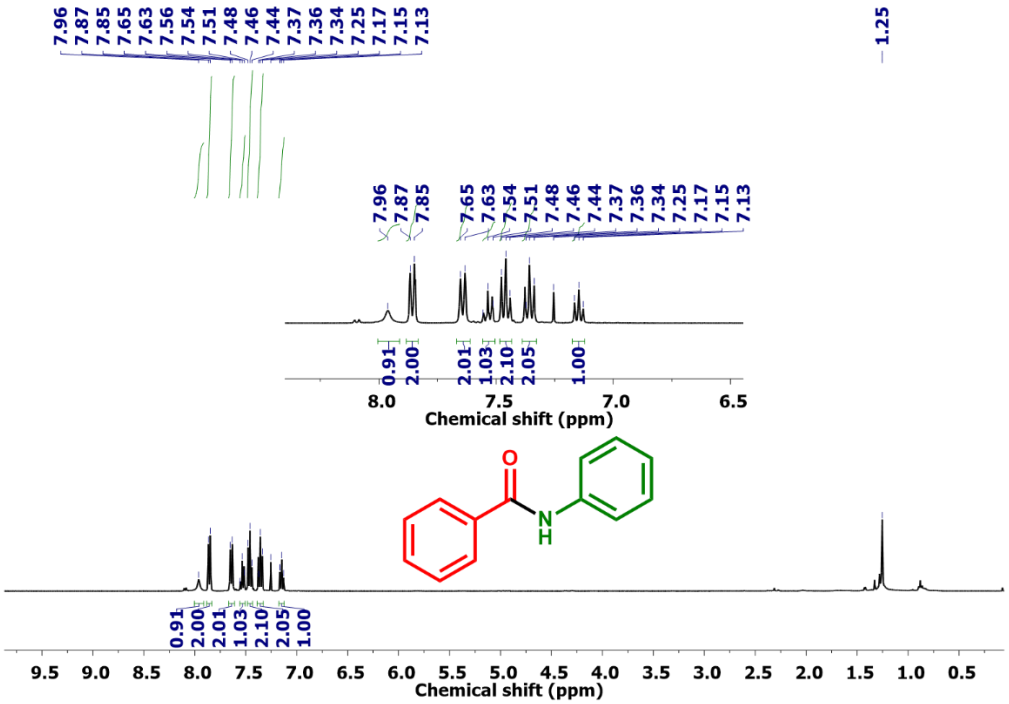
^{13}C NMR (DMSO-d_6, 125 MHz) of Compound **13a.**



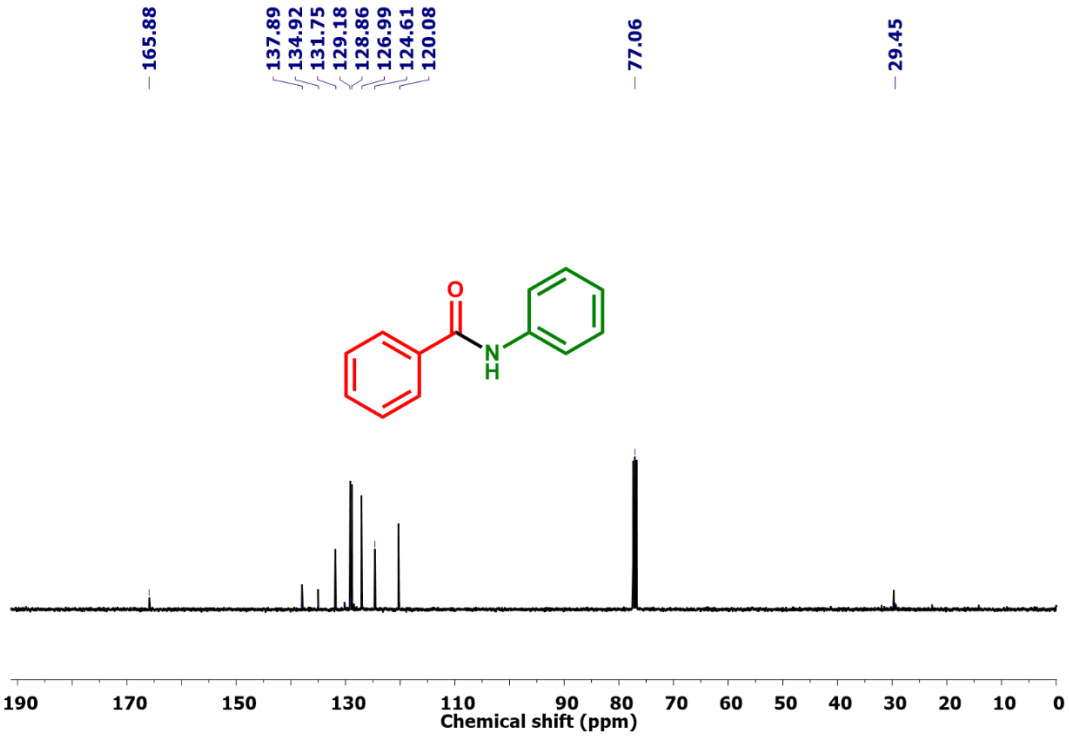
^{1}H NMR (DMSO-d_6, 500 MHz) of Compound **14a.**



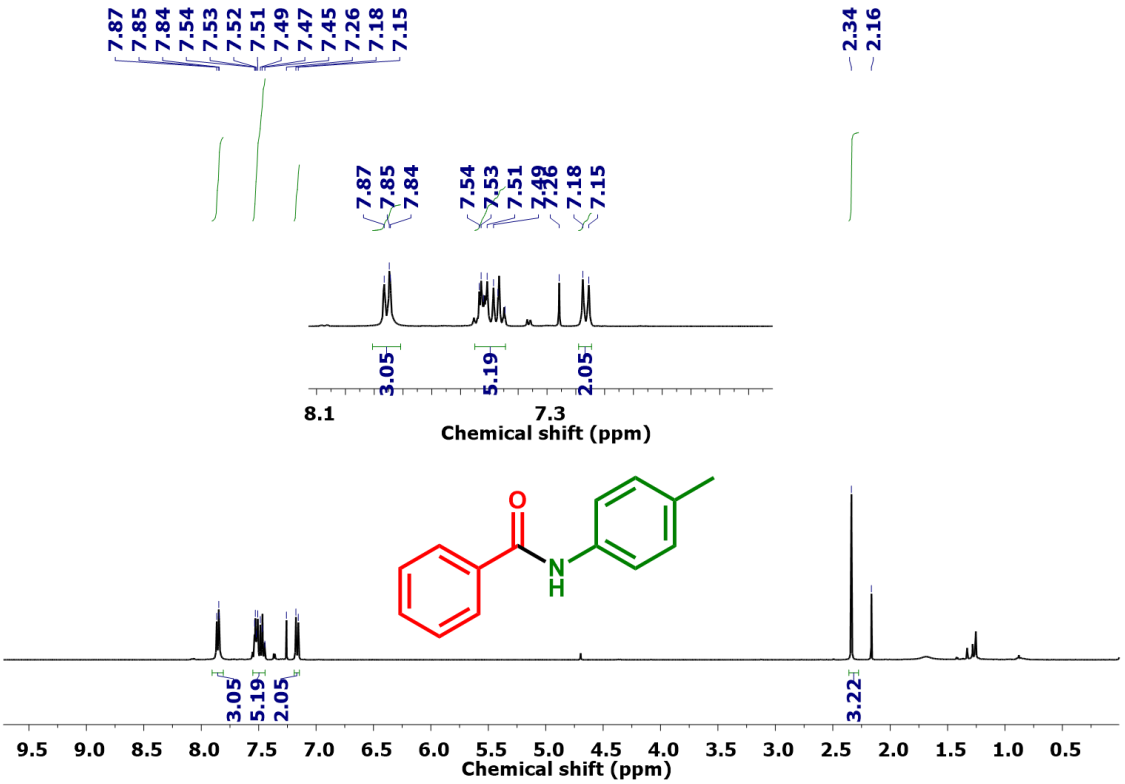
^{13}C NMR (DMSO-d_6, 125 MHz) of Compound **14a.**



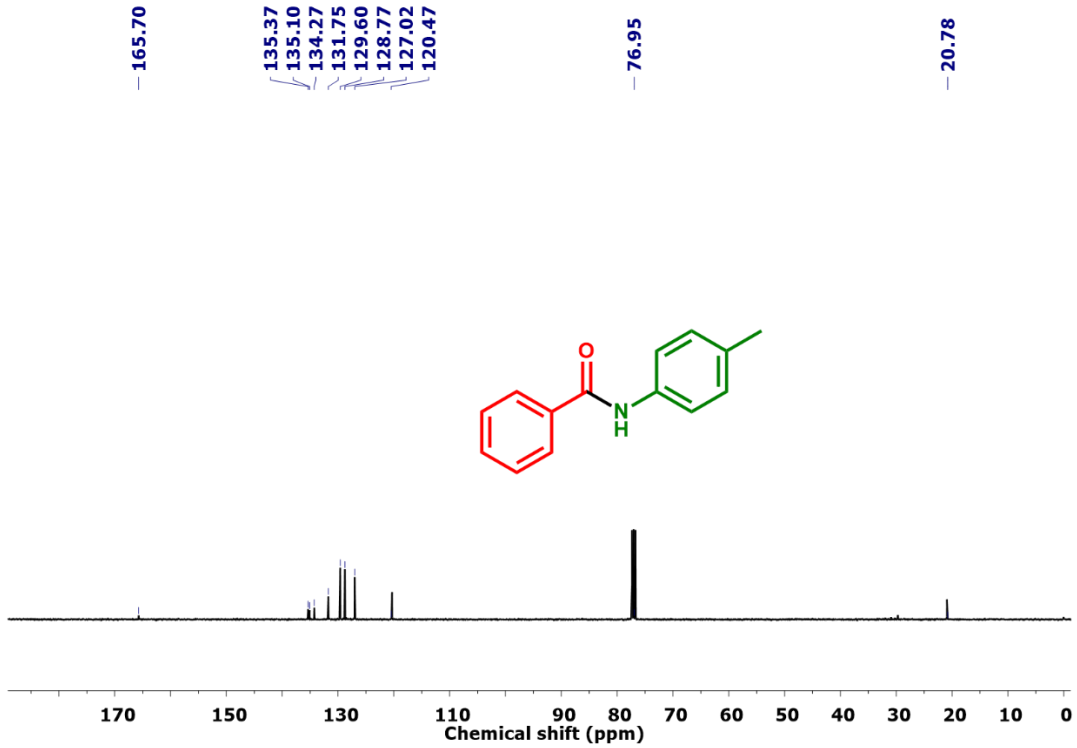
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **15a.**



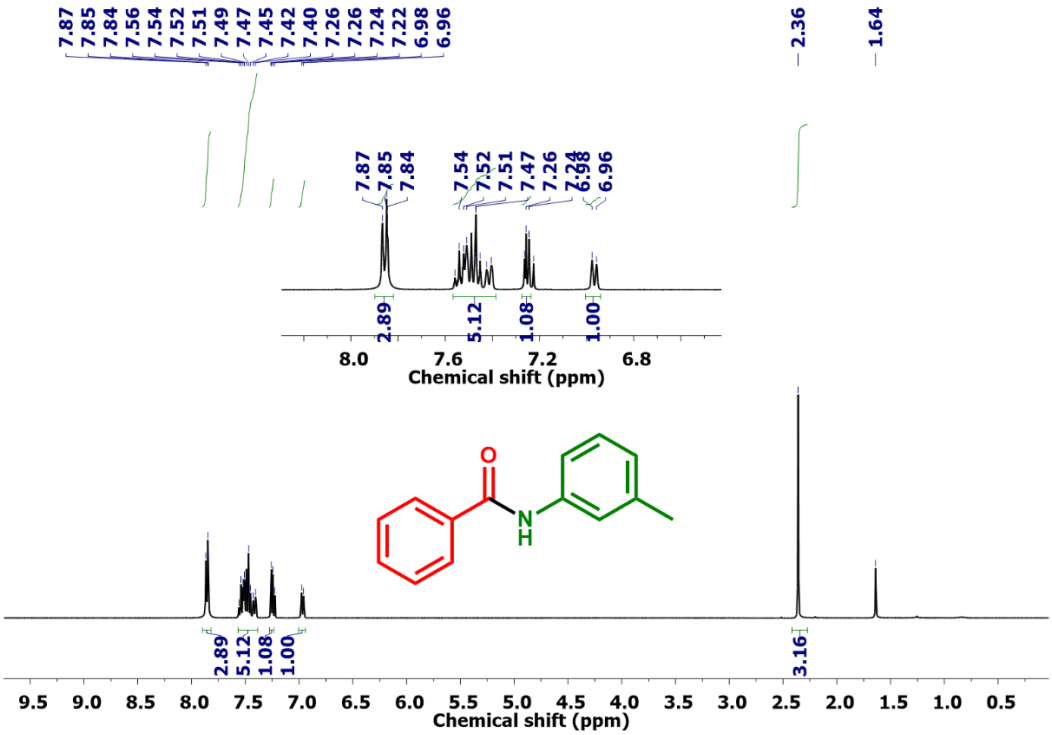
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **15a.**



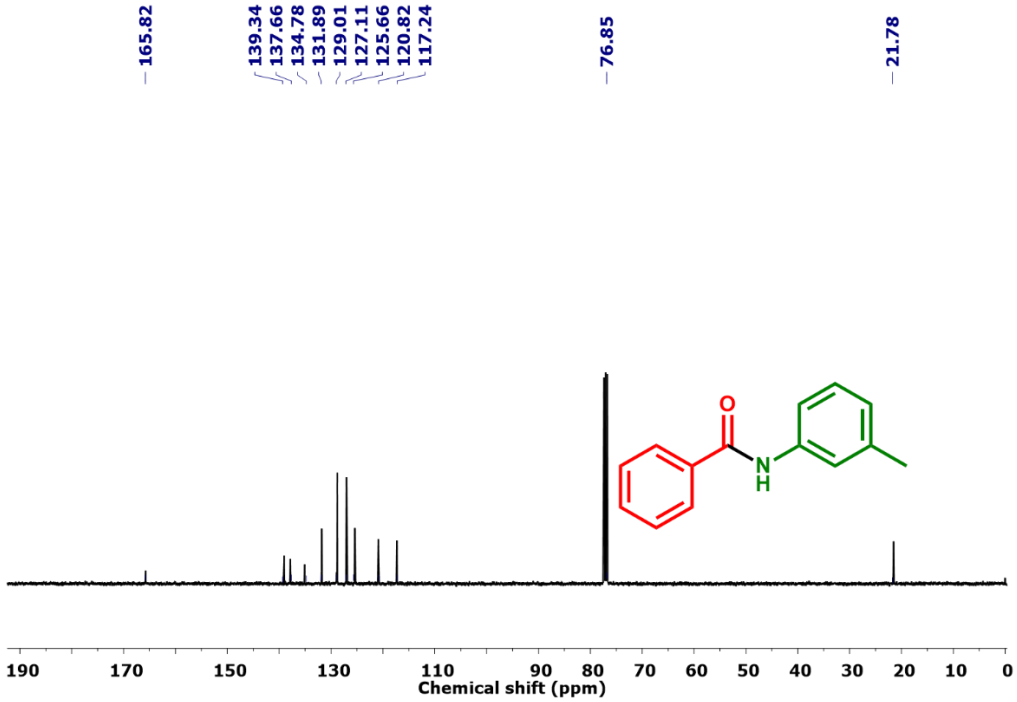
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **16a.**



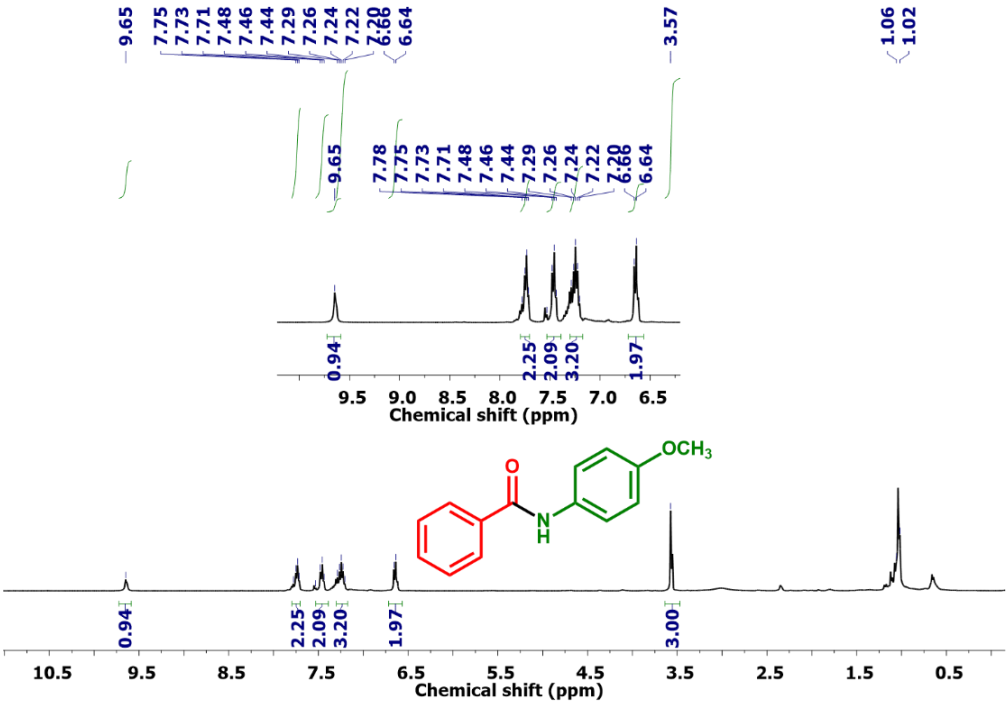
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **16a.**



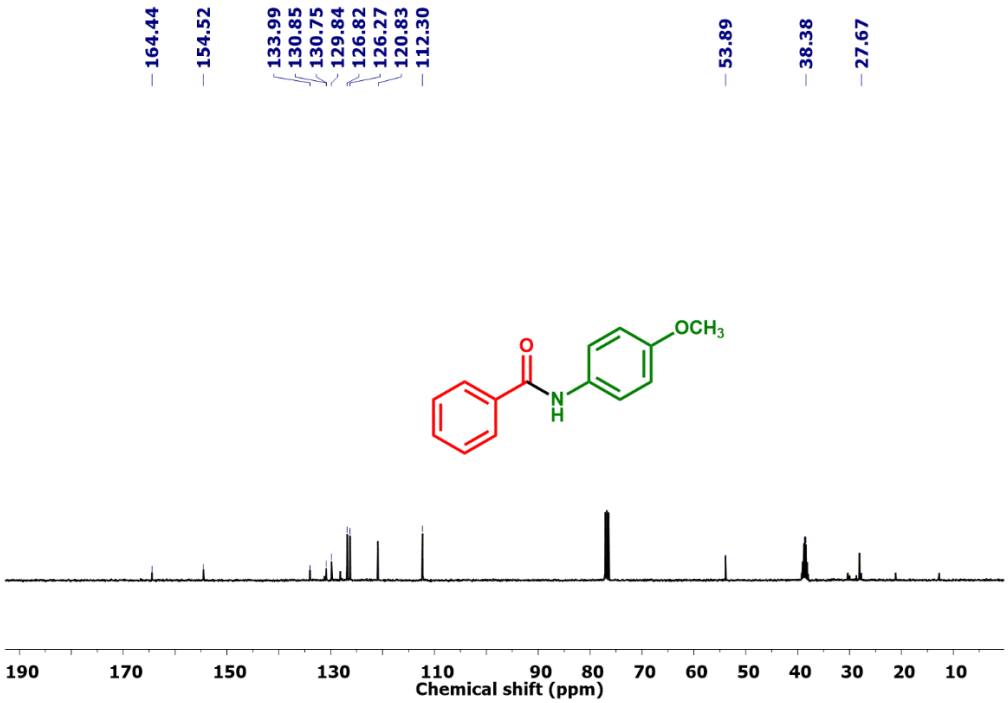
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **17a.**



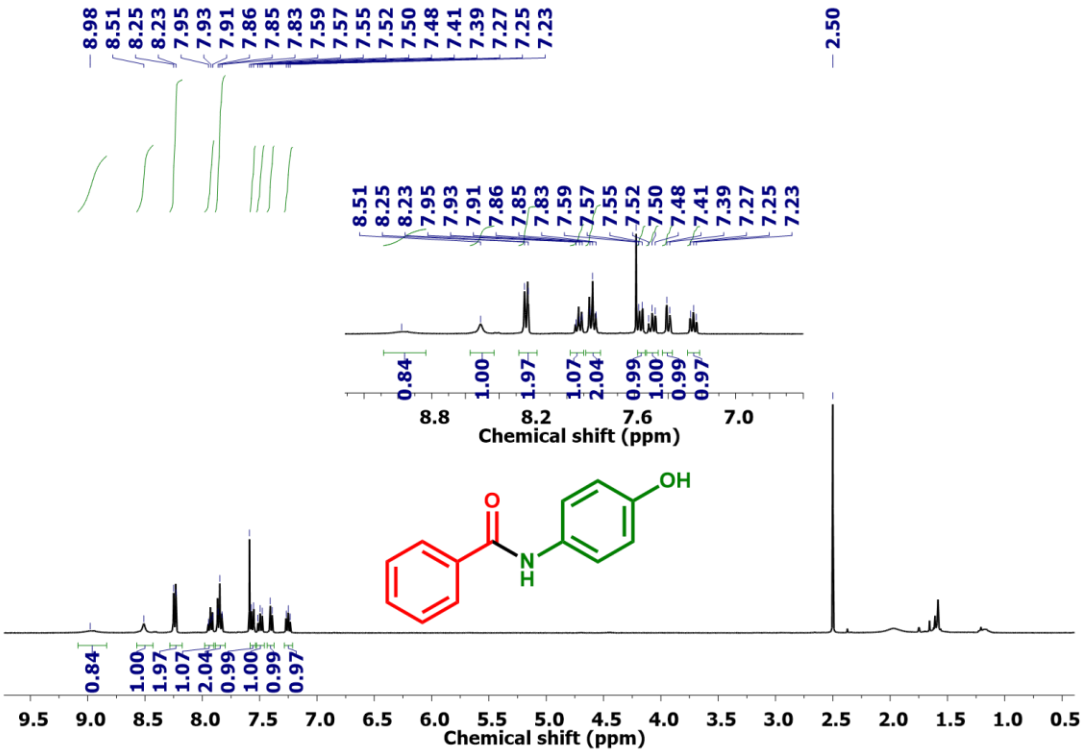
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **17a.**



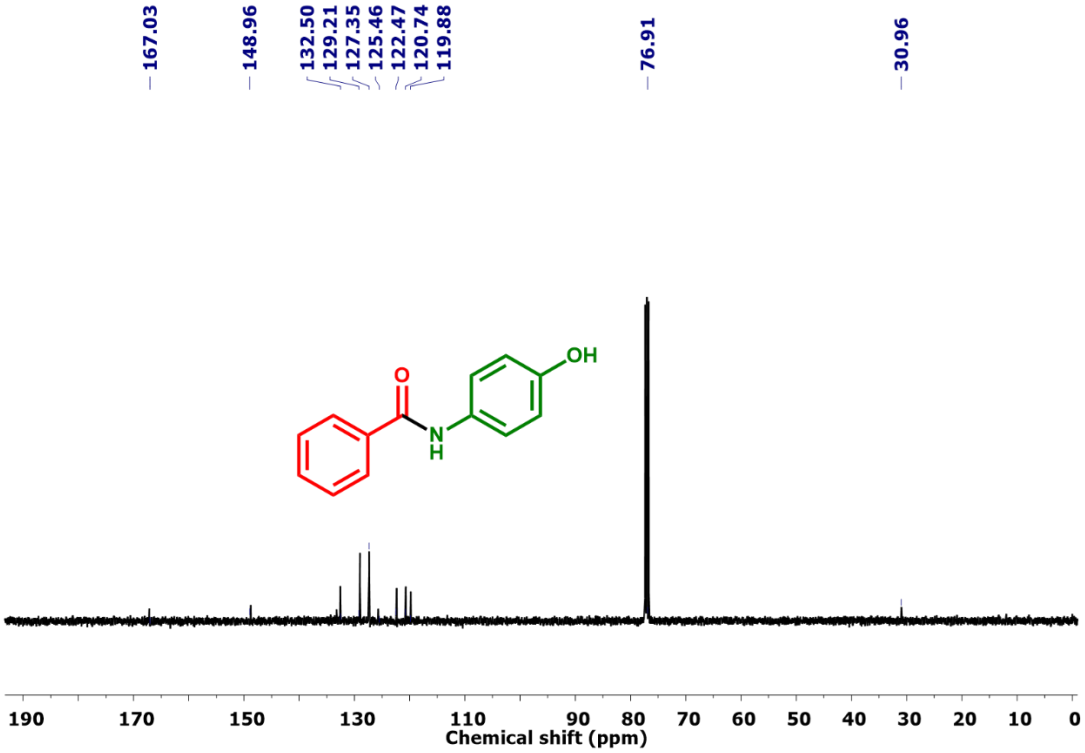
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **18a.**



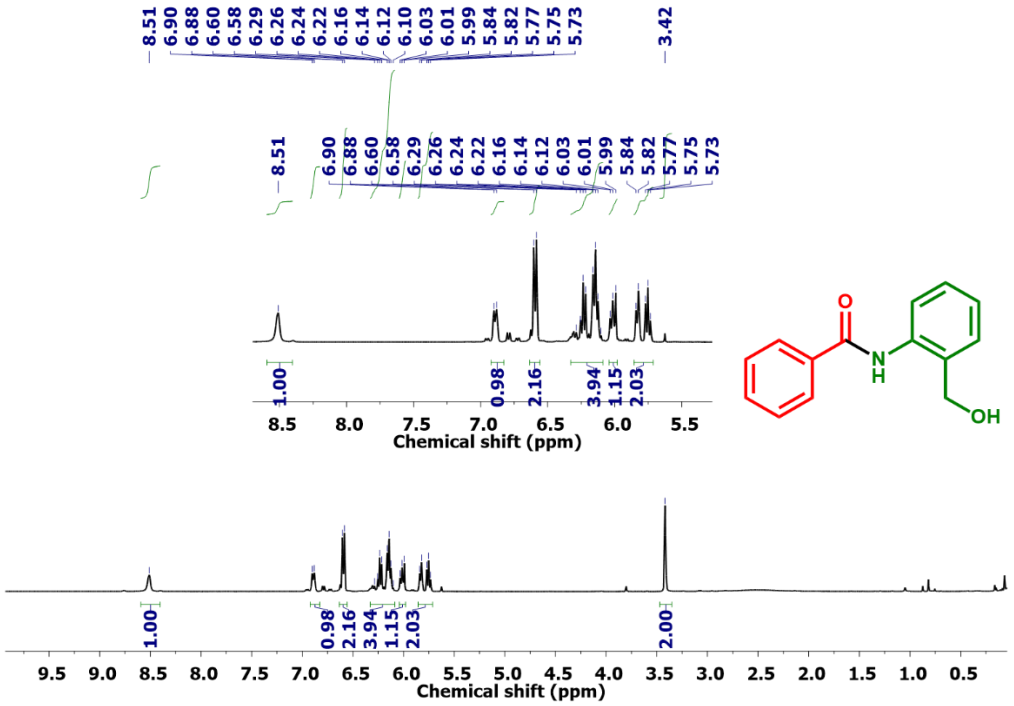
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **18a.**



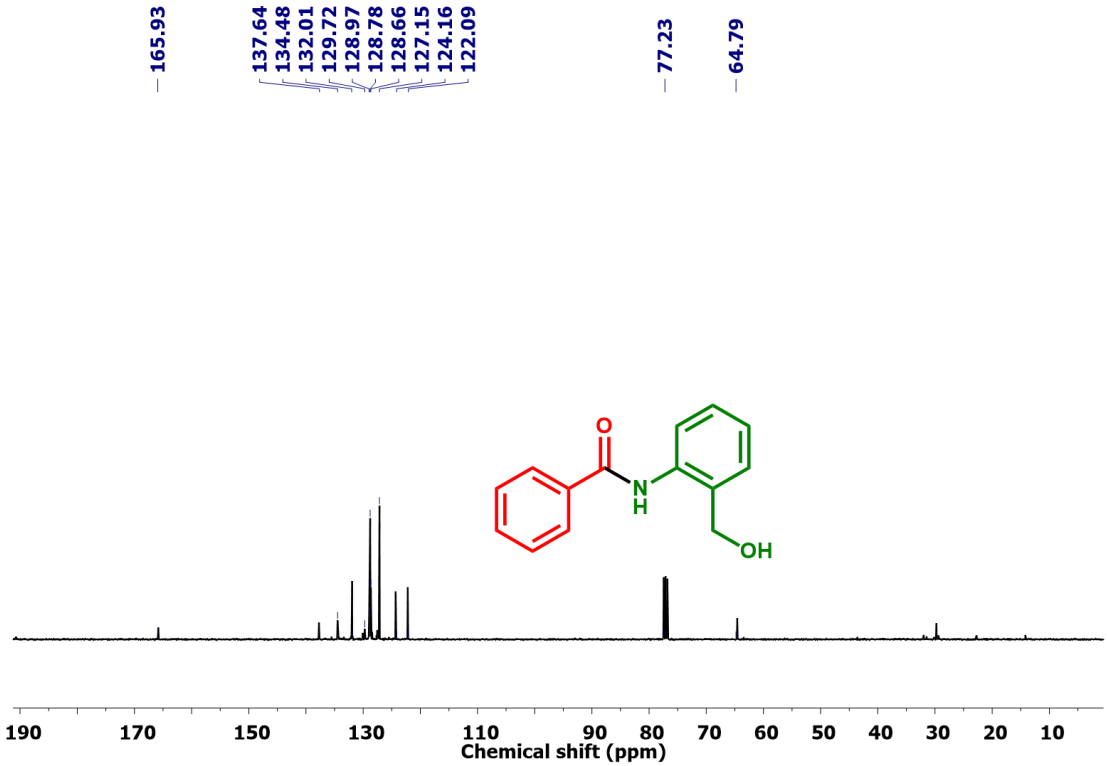
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **19a.**



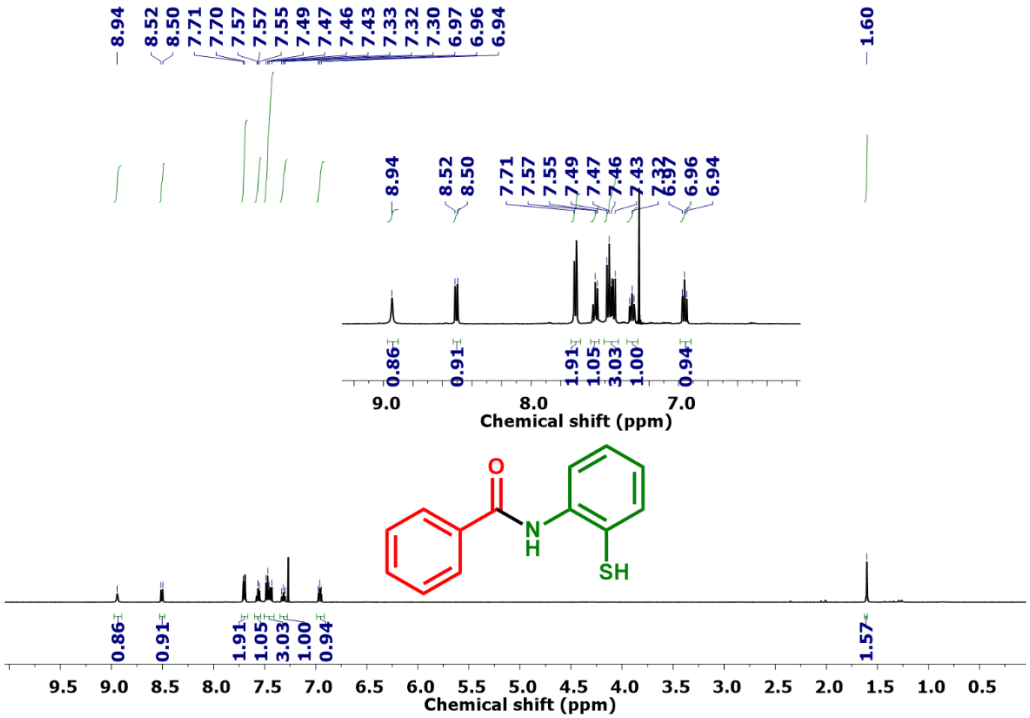
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **19a.**



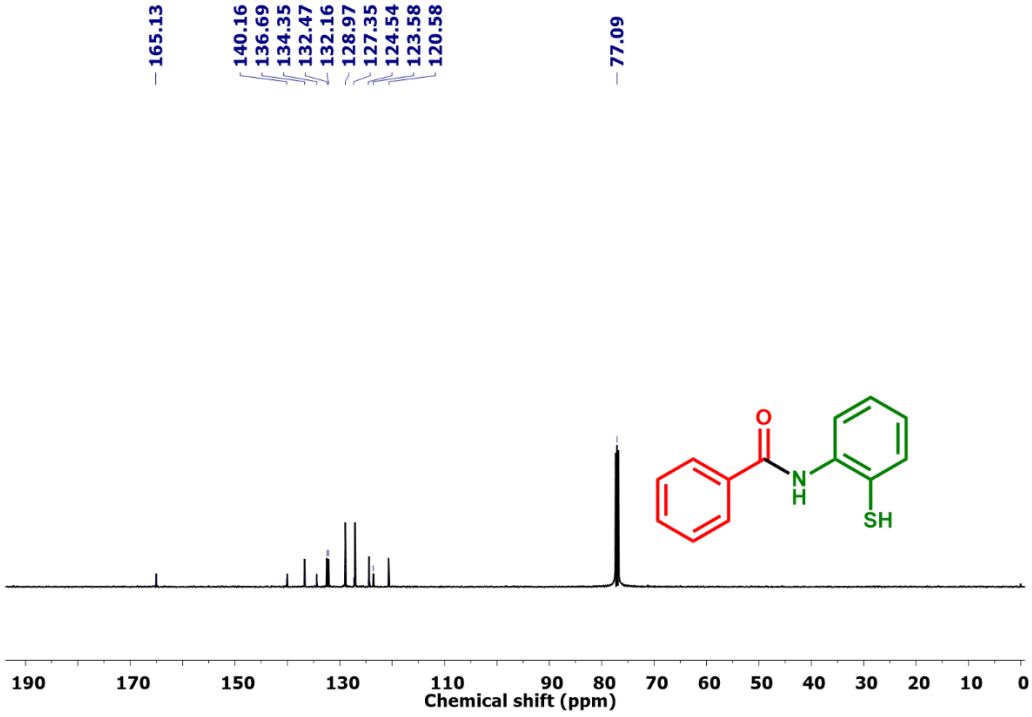
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **20a.**



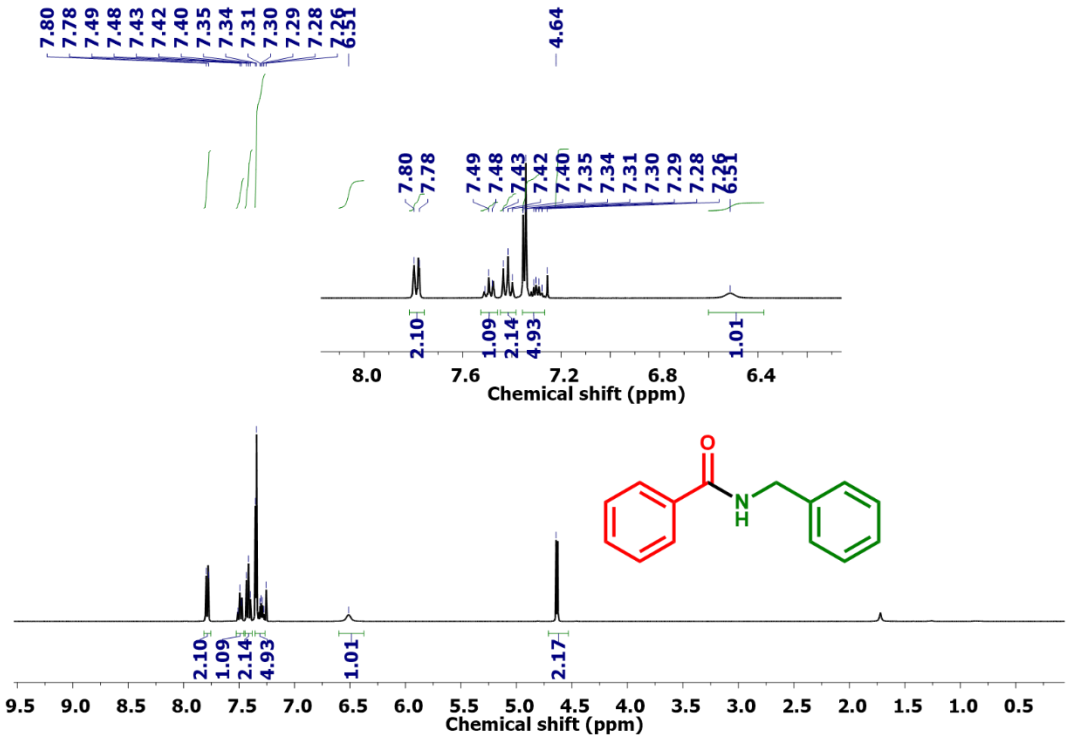
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **20a.**



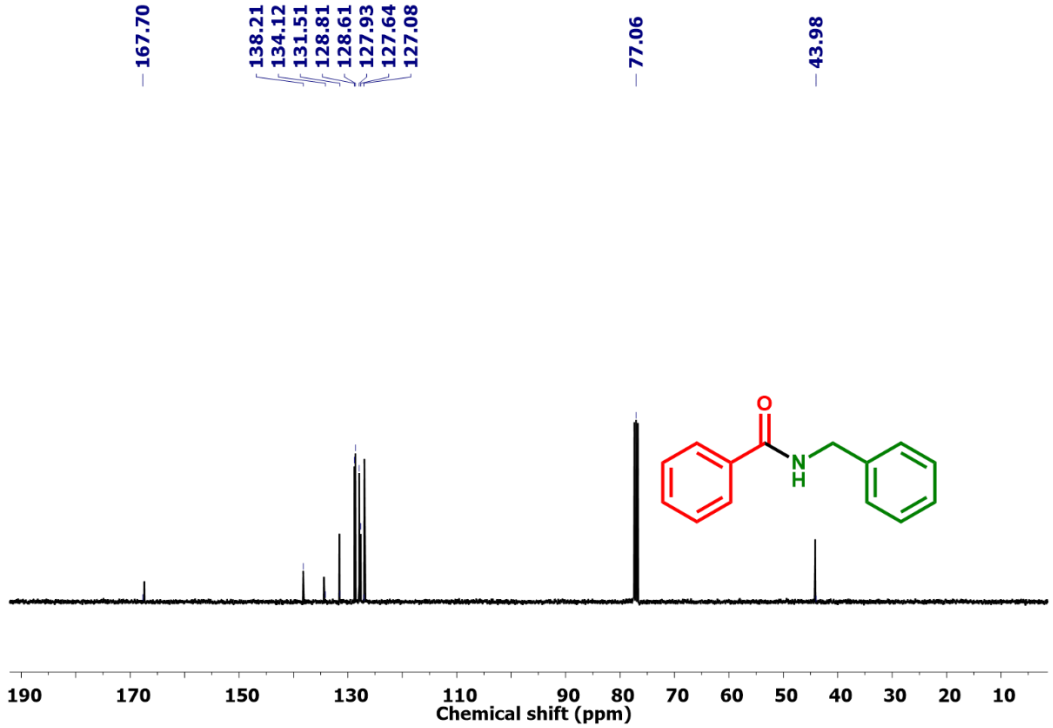
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **21a.**



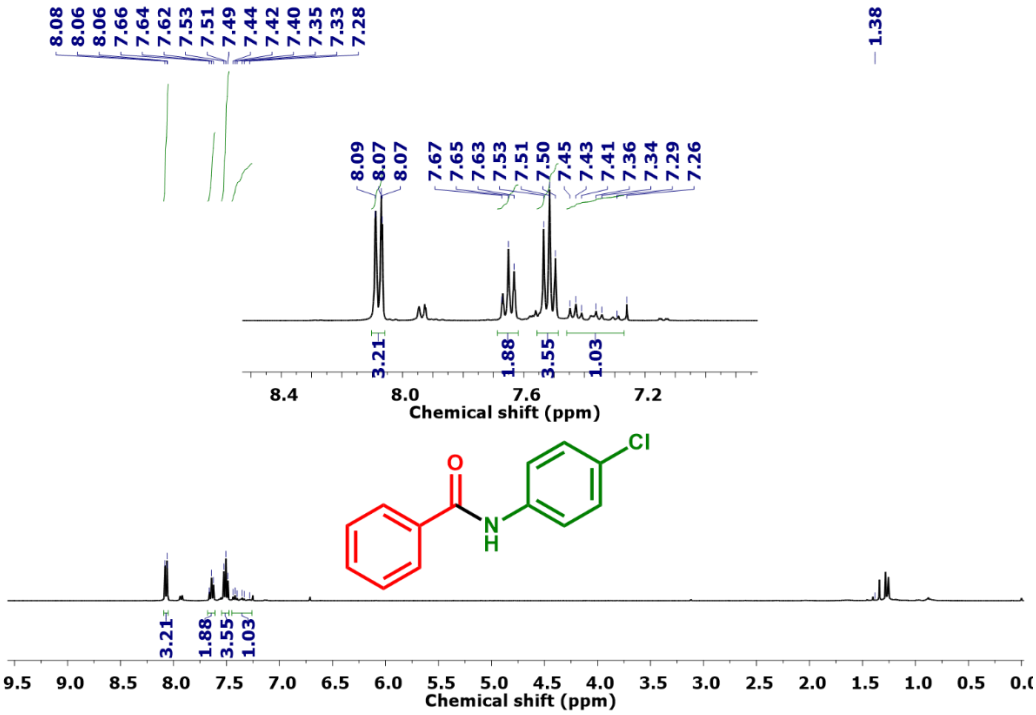
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **21a.**



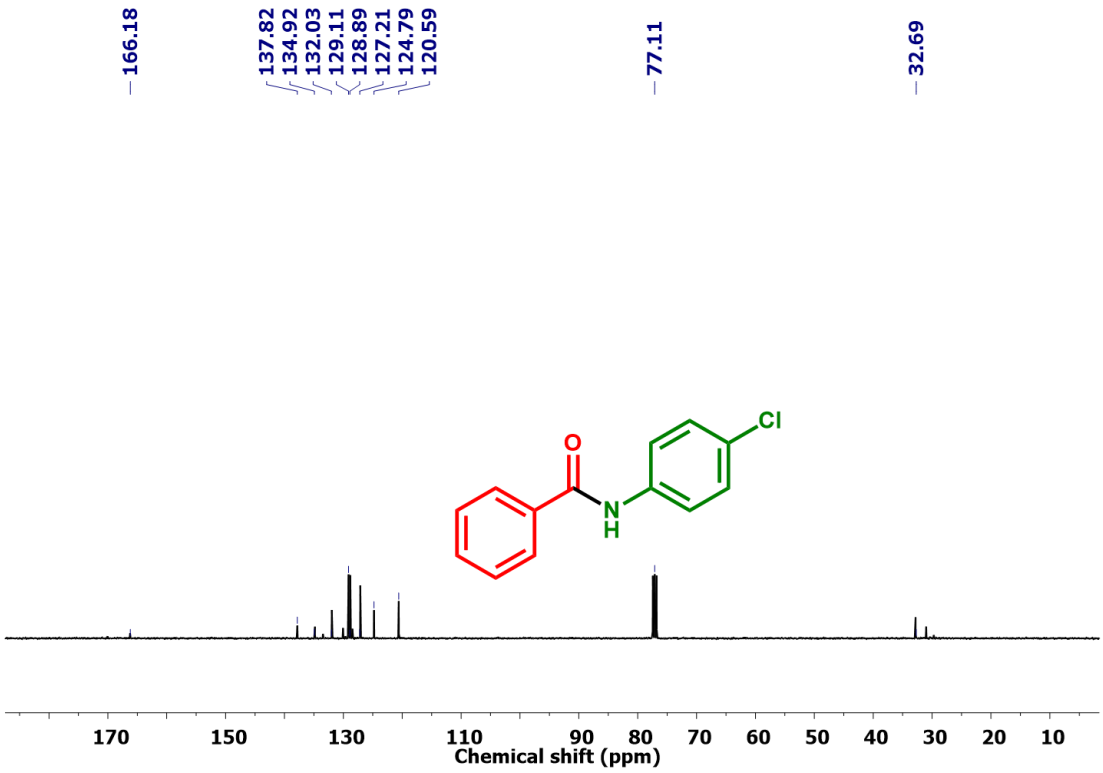
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **22a.**



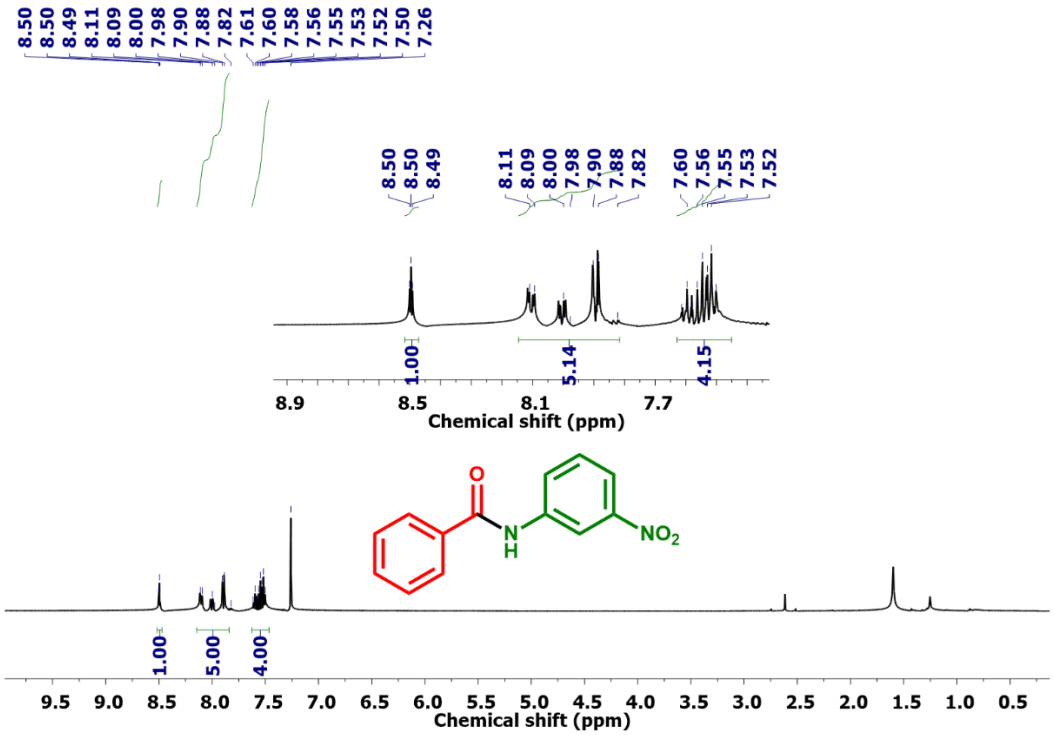
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **22a.**



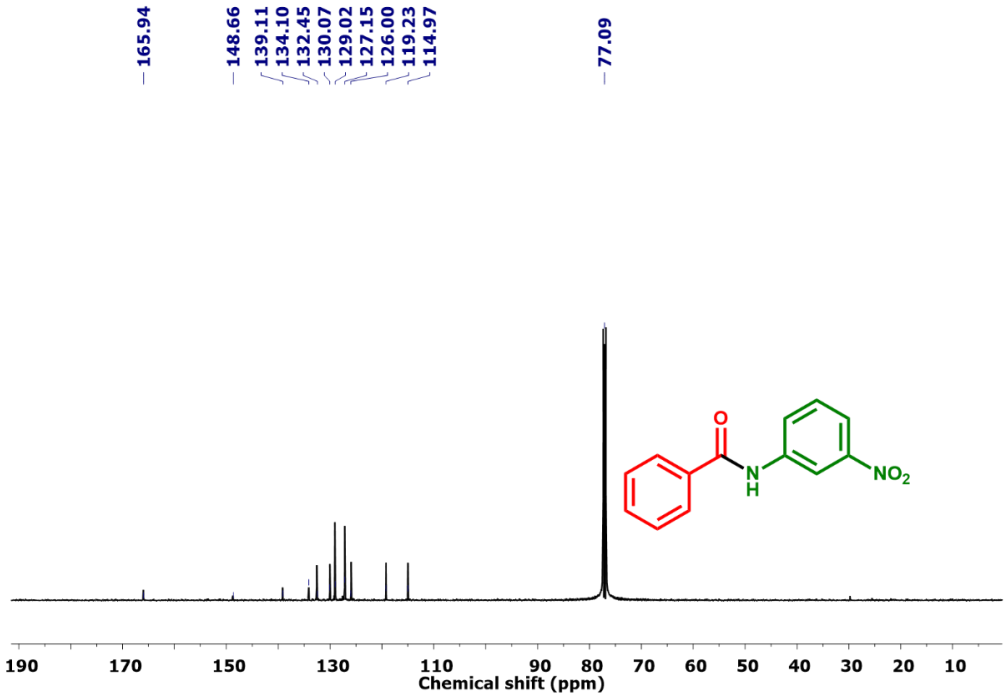
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **23a.**



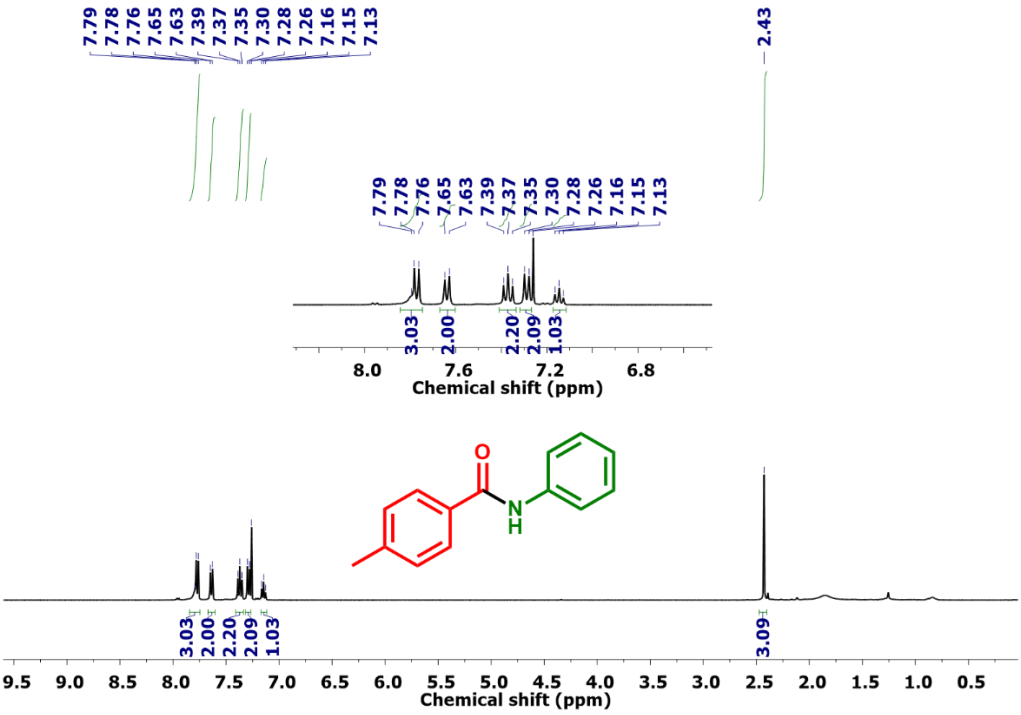
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **23a.**



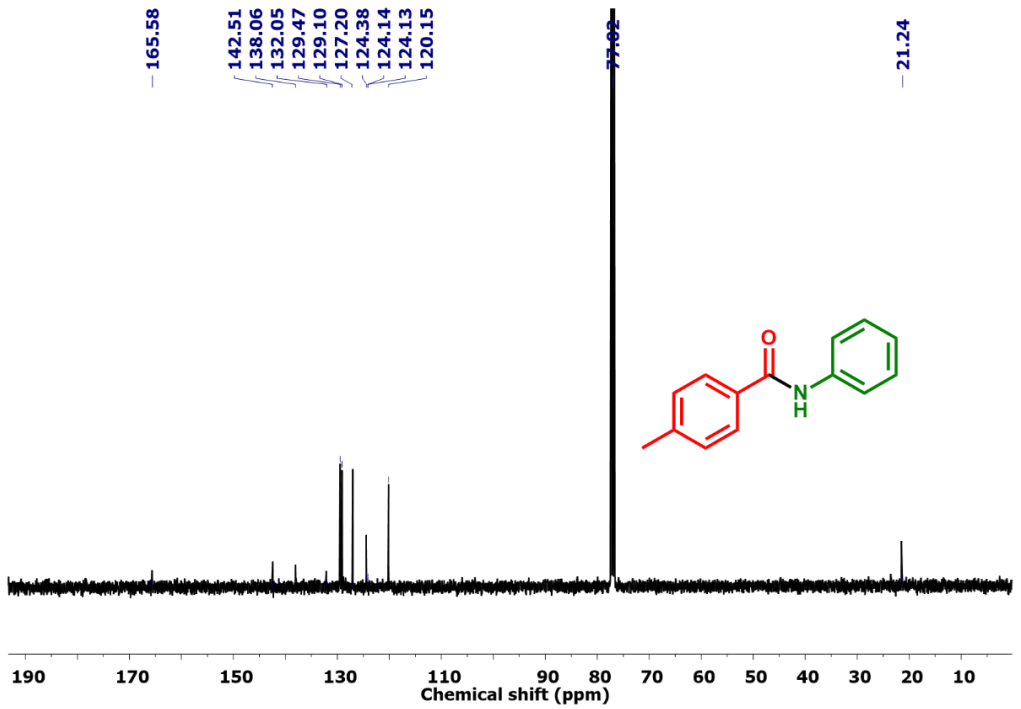
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **24a.**



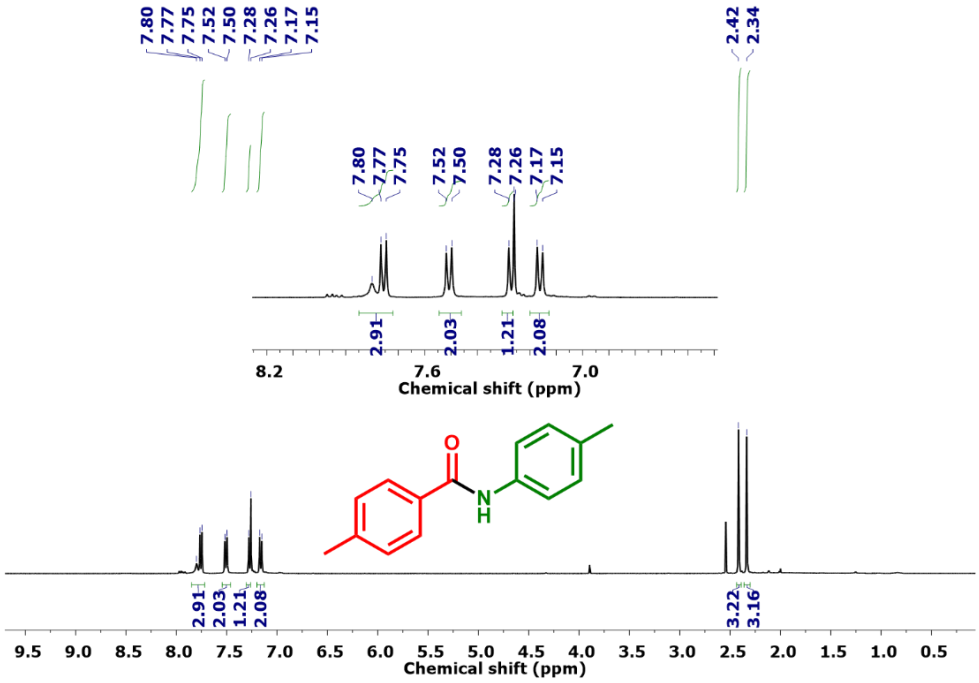
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **24a.**



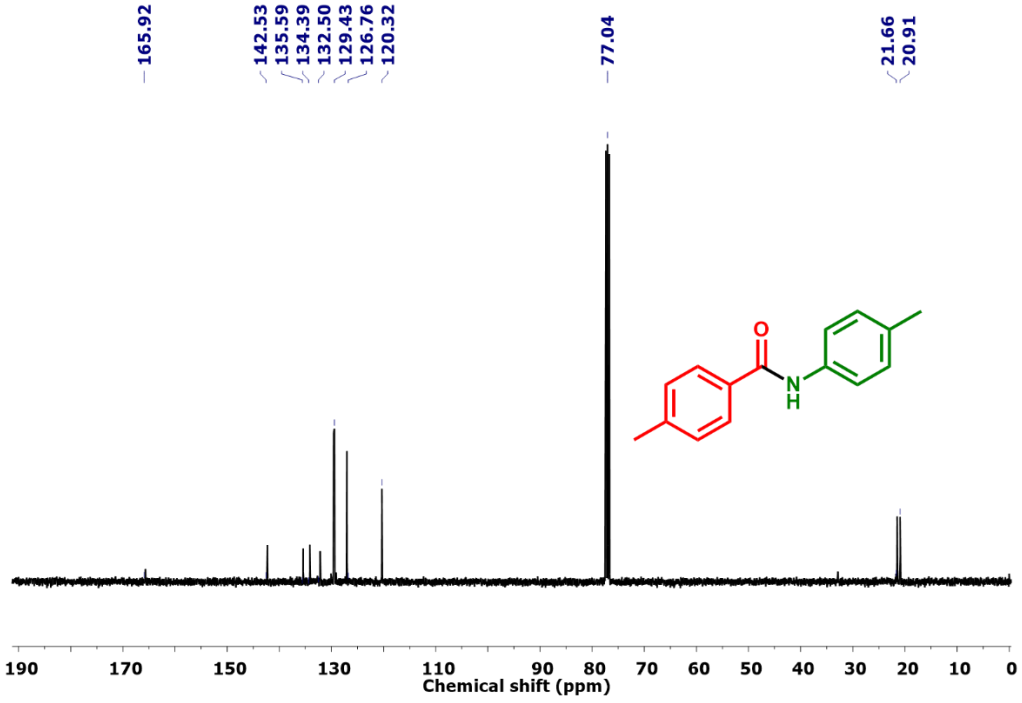
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **25a.**



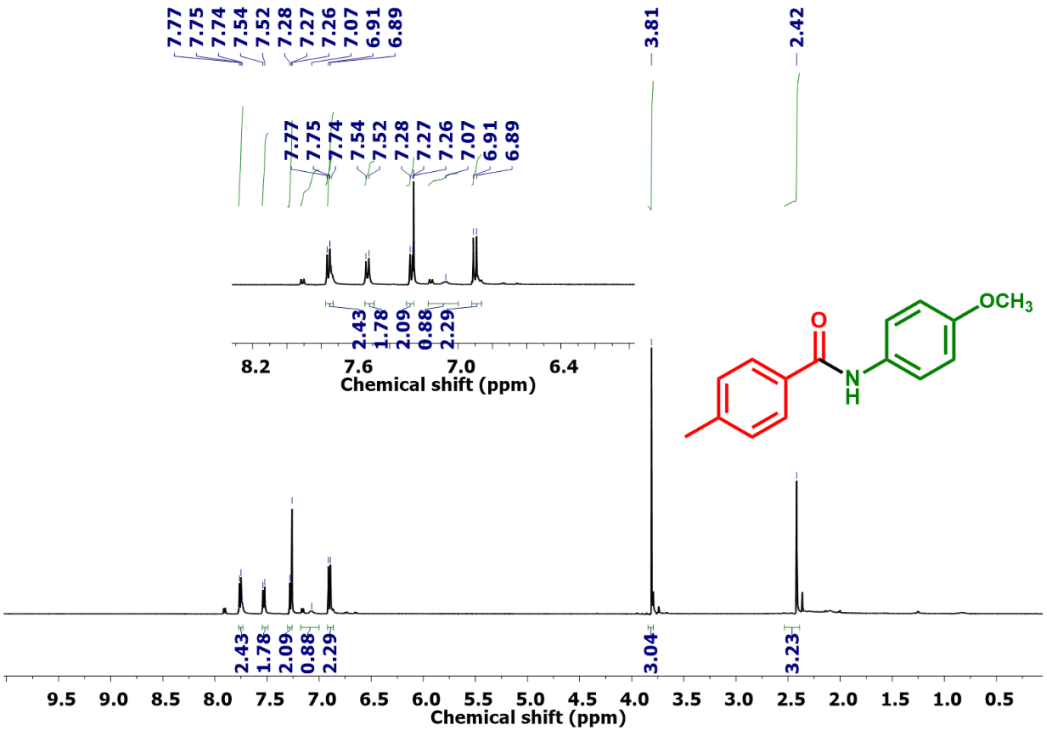
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **25a.**



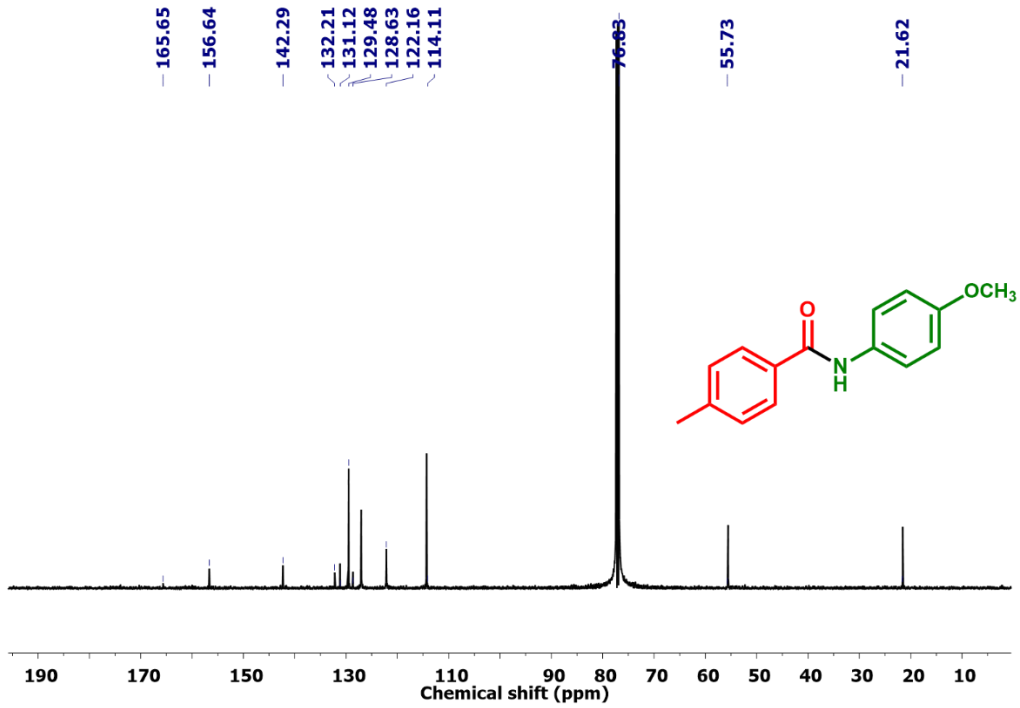
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **26a.**



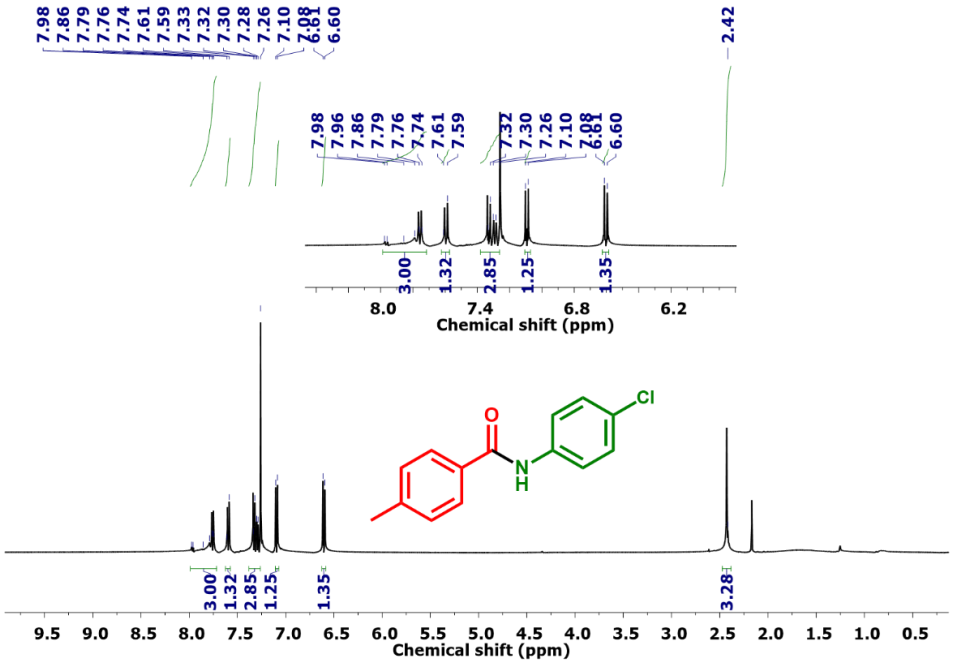
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **26a.**



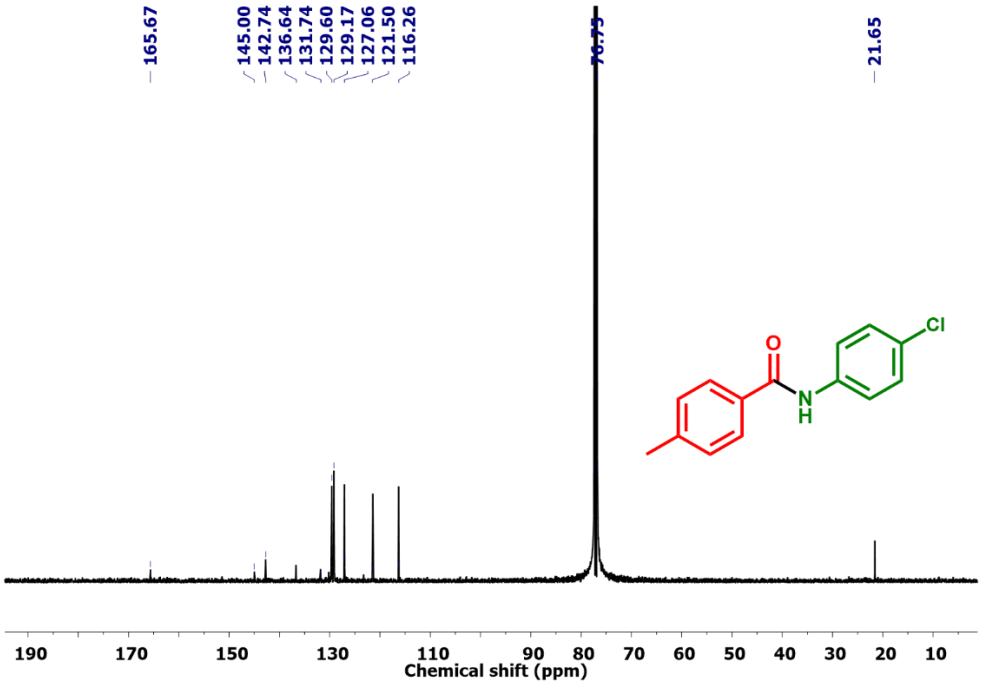
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **27a.**



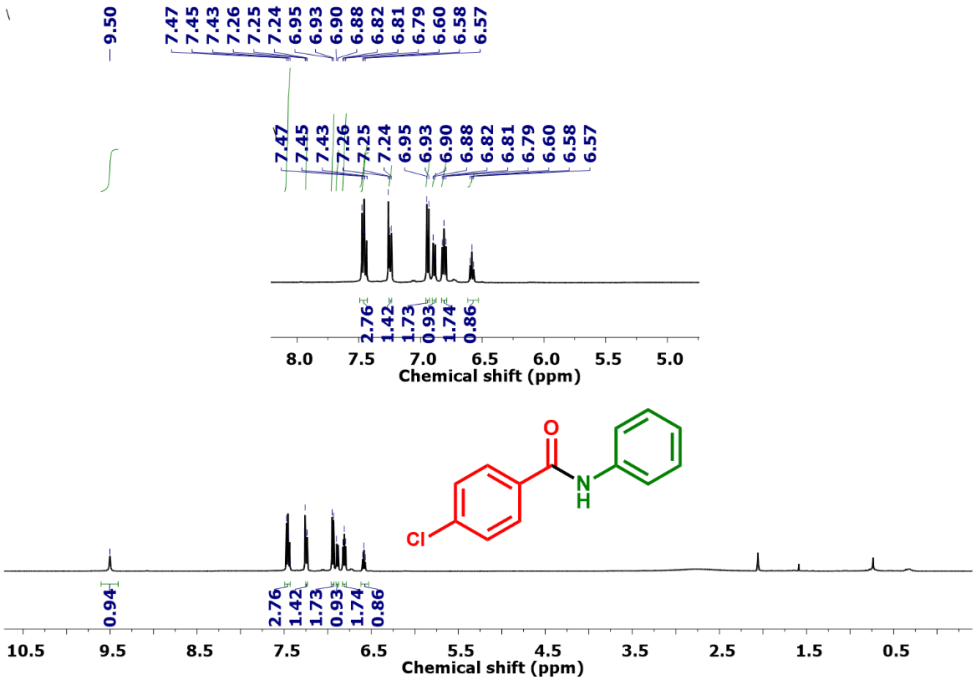
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **27a.**



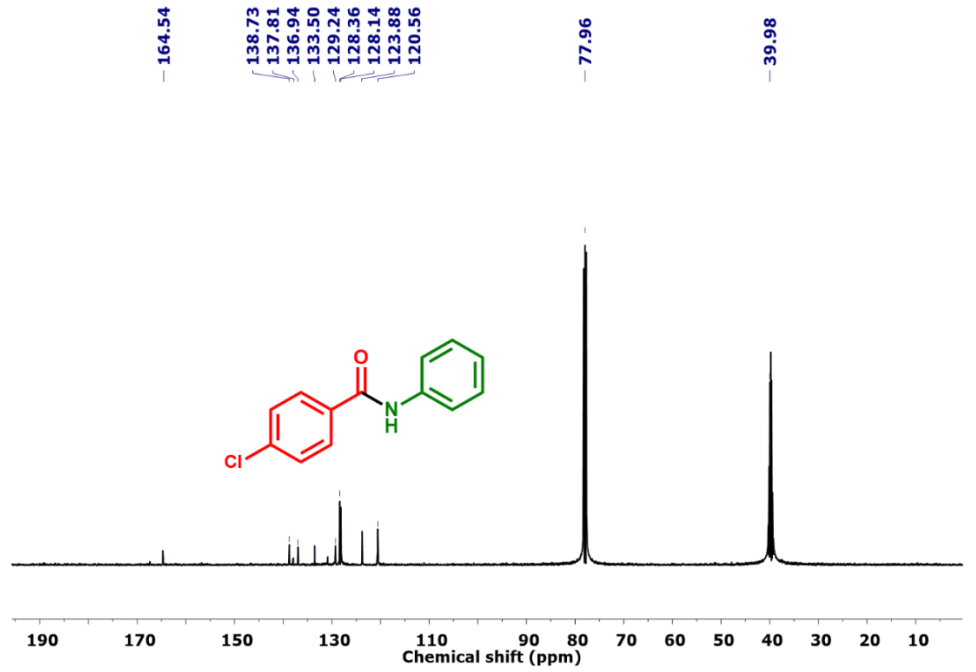
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **28a.**



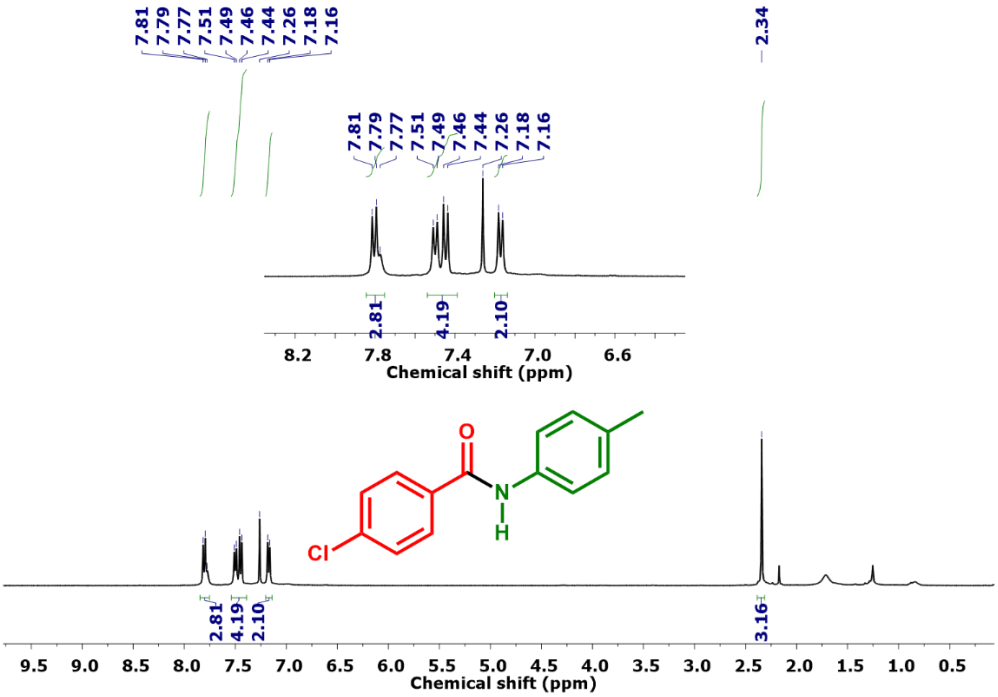
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **28a.**



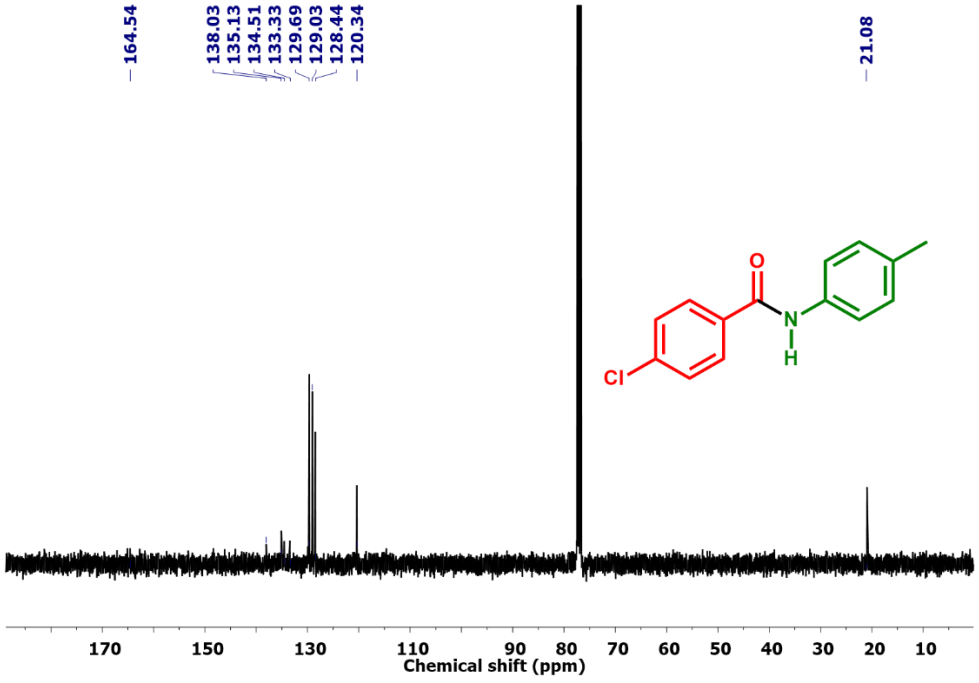
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **29a.**



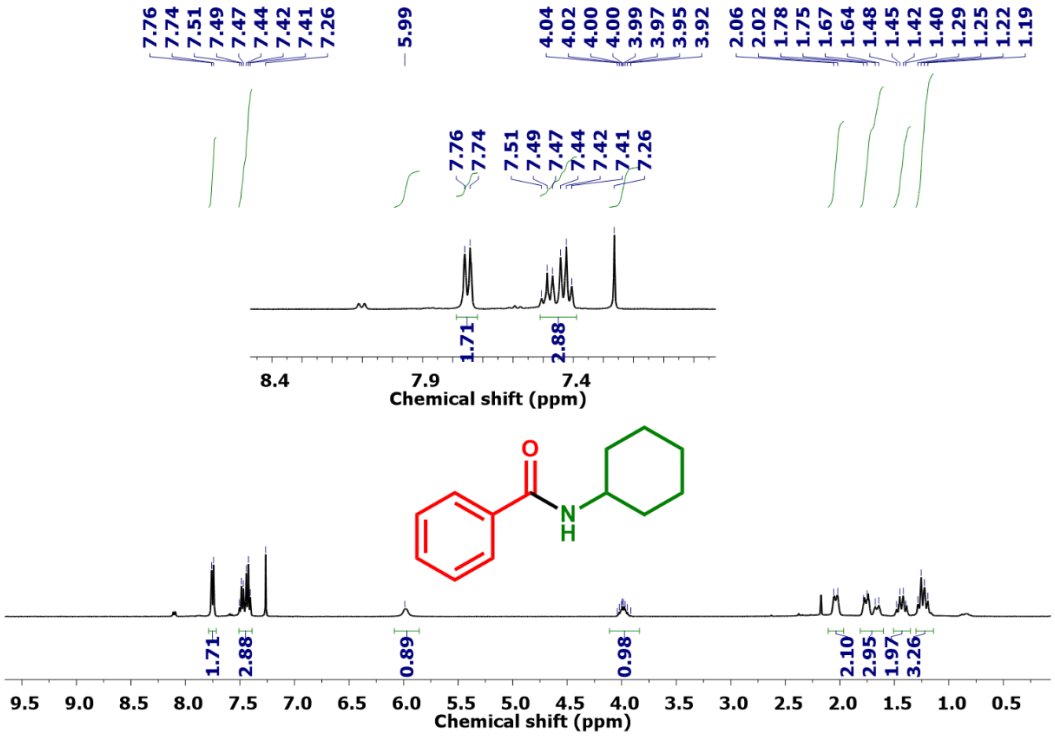
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **29a.**



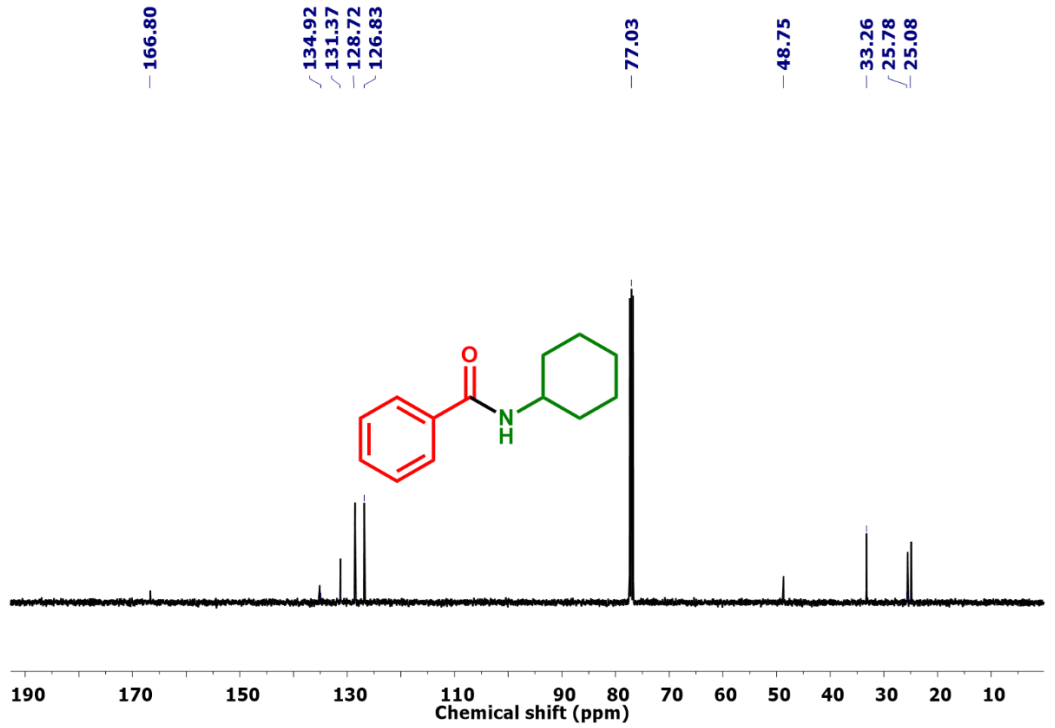
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **30a.**



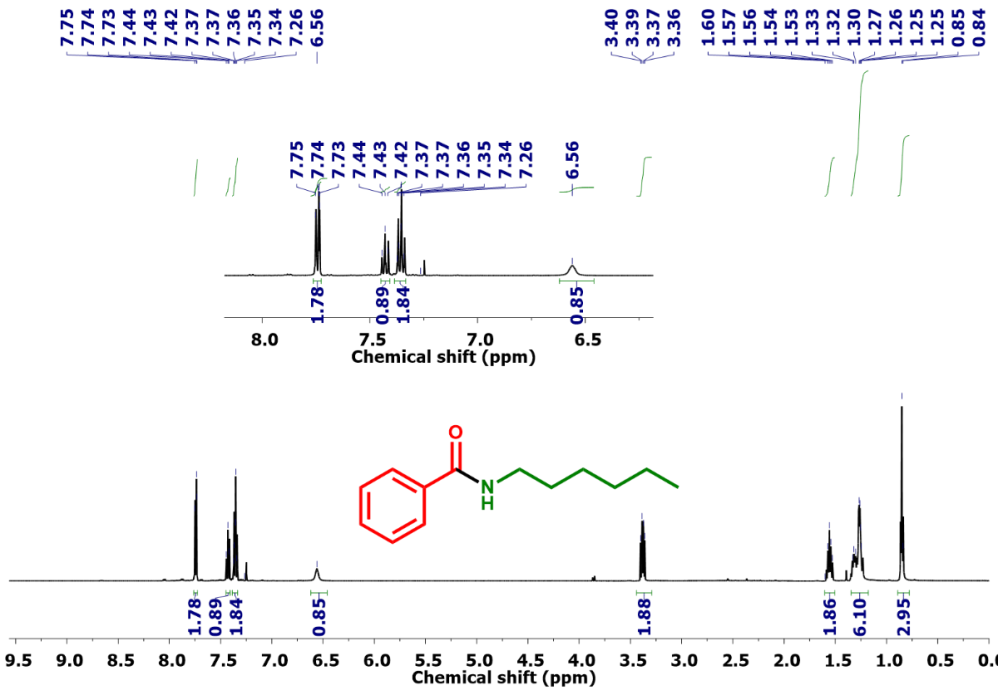
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **30a.**



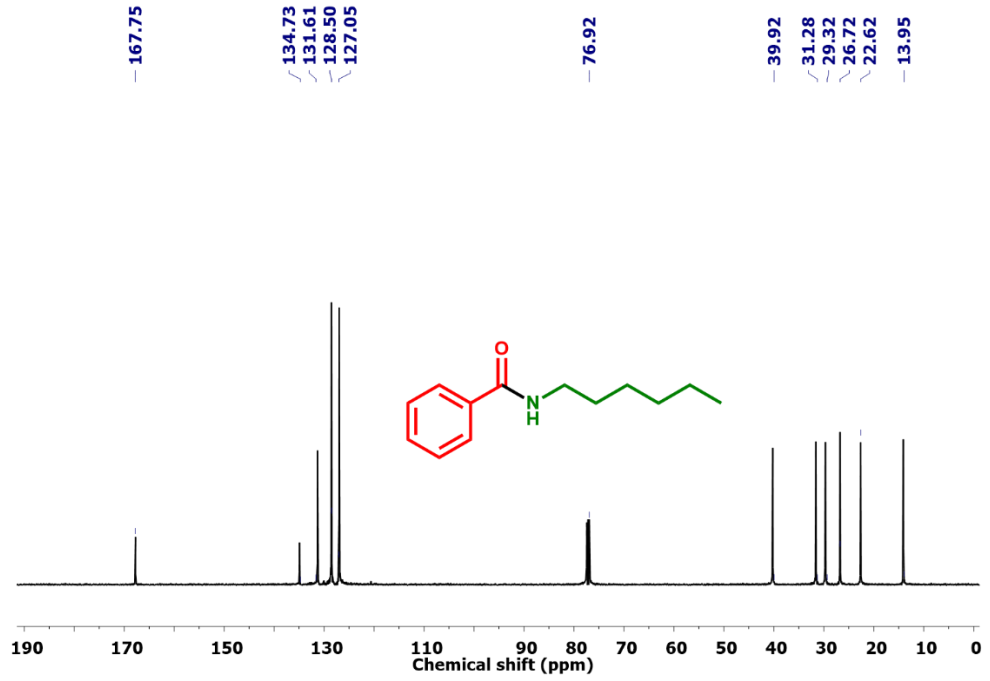
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **31a.**



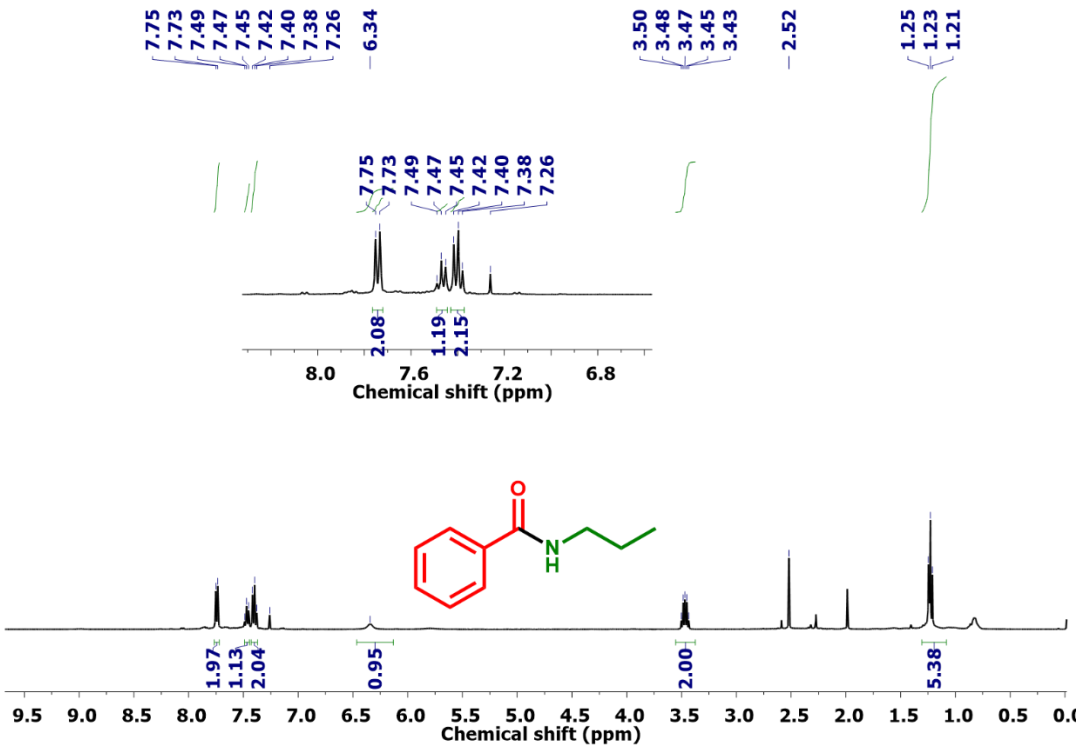
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **31a.**



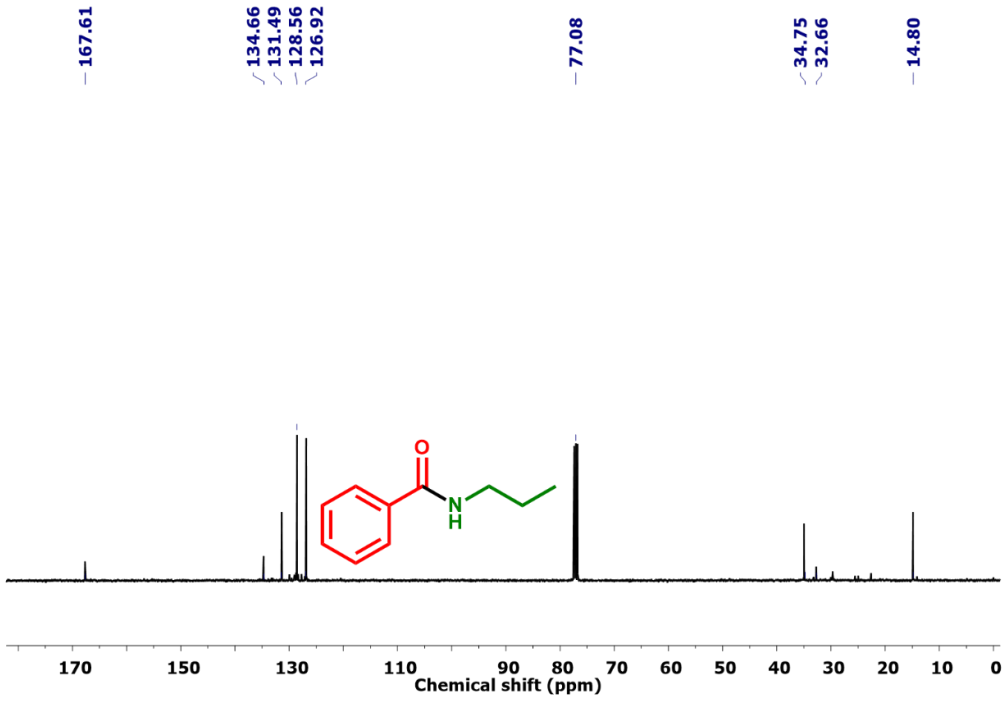
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **32a.**



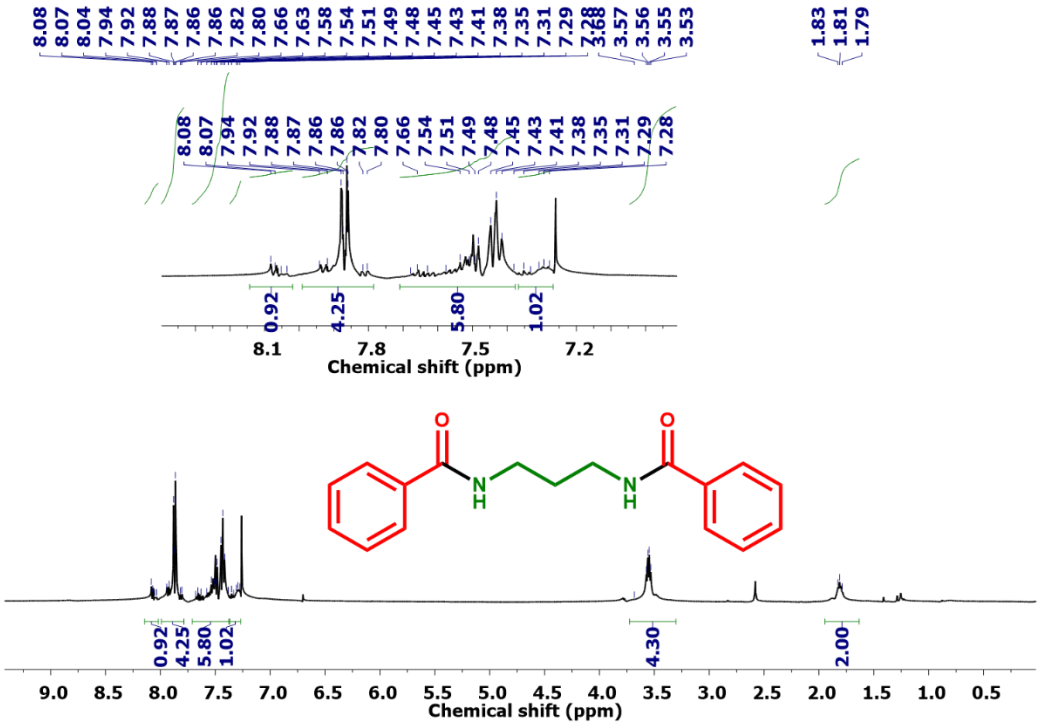
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **32a.**



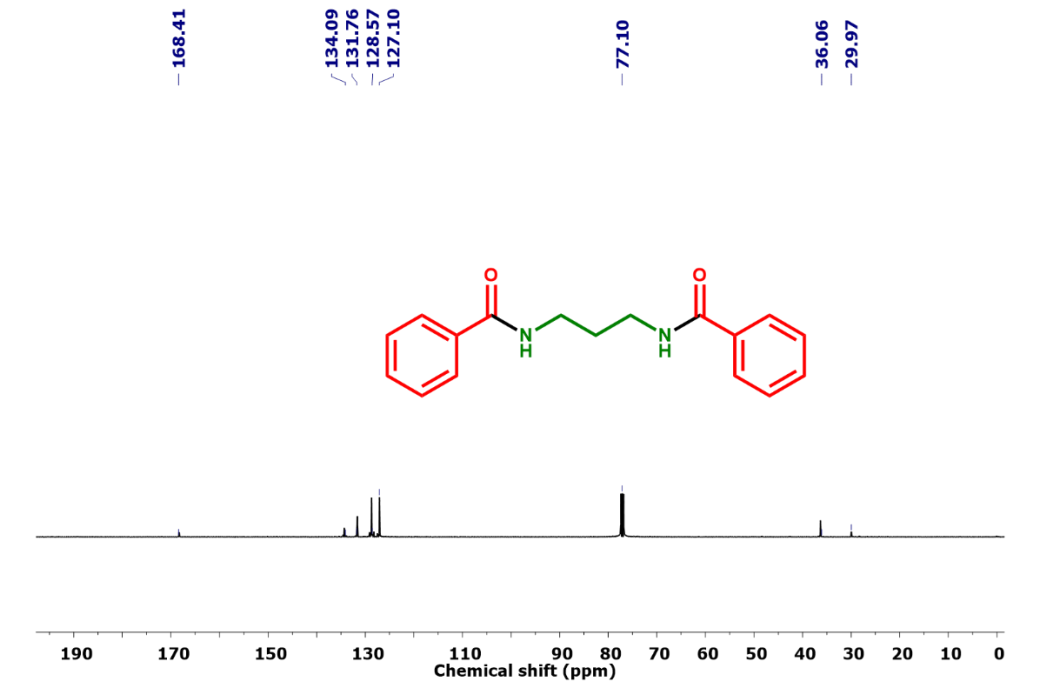
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **33a.**



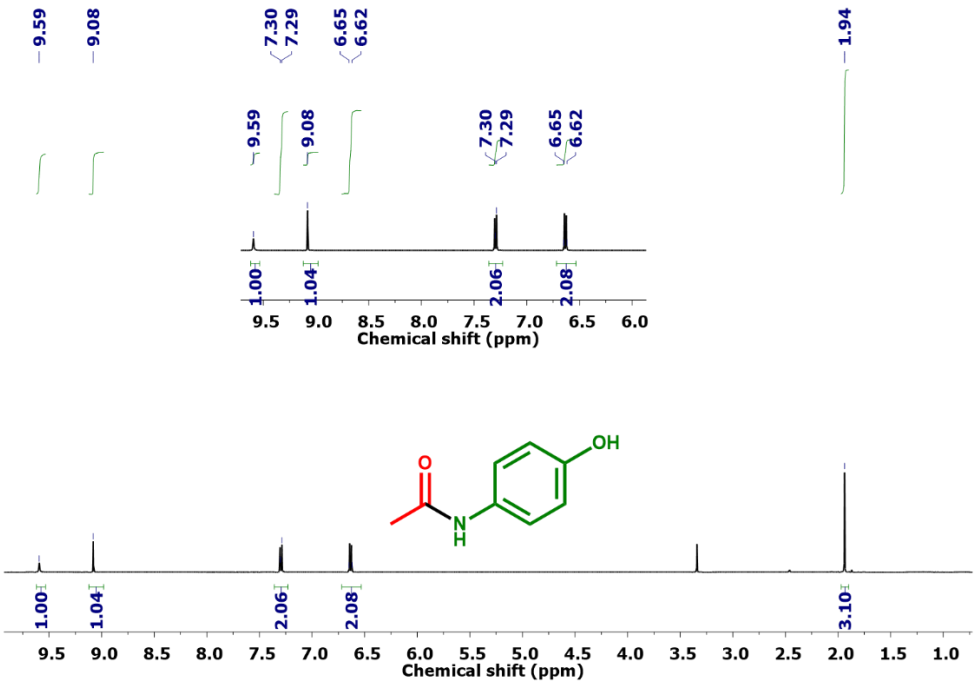
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **33a.**



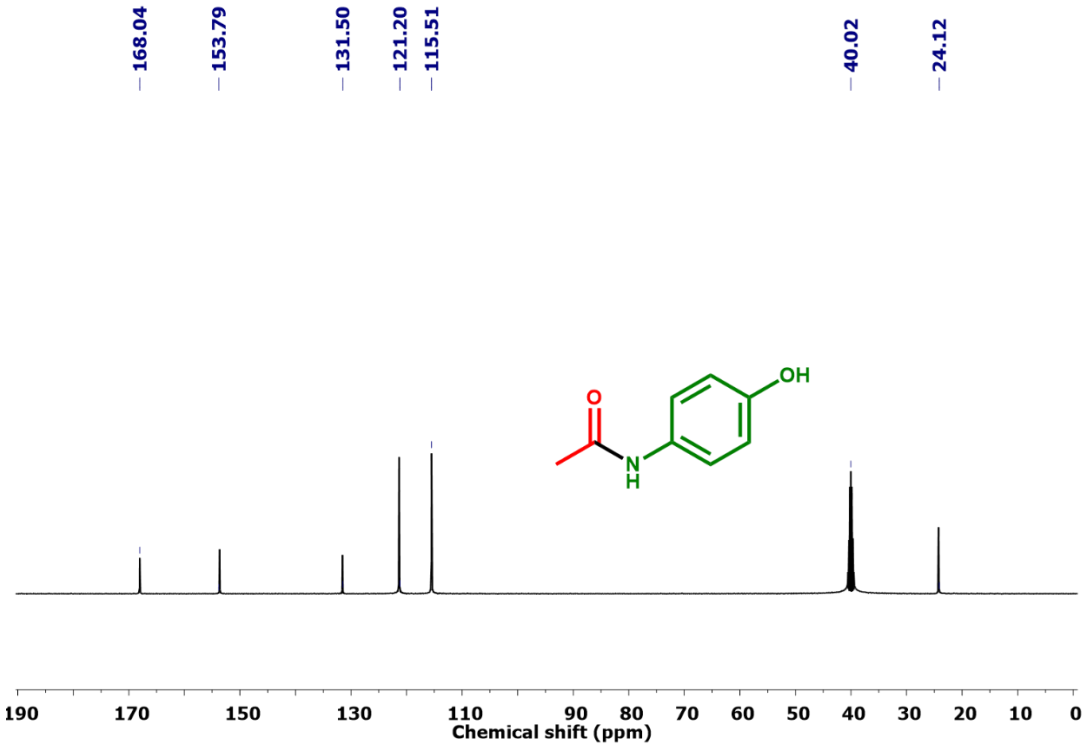
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **34a.**



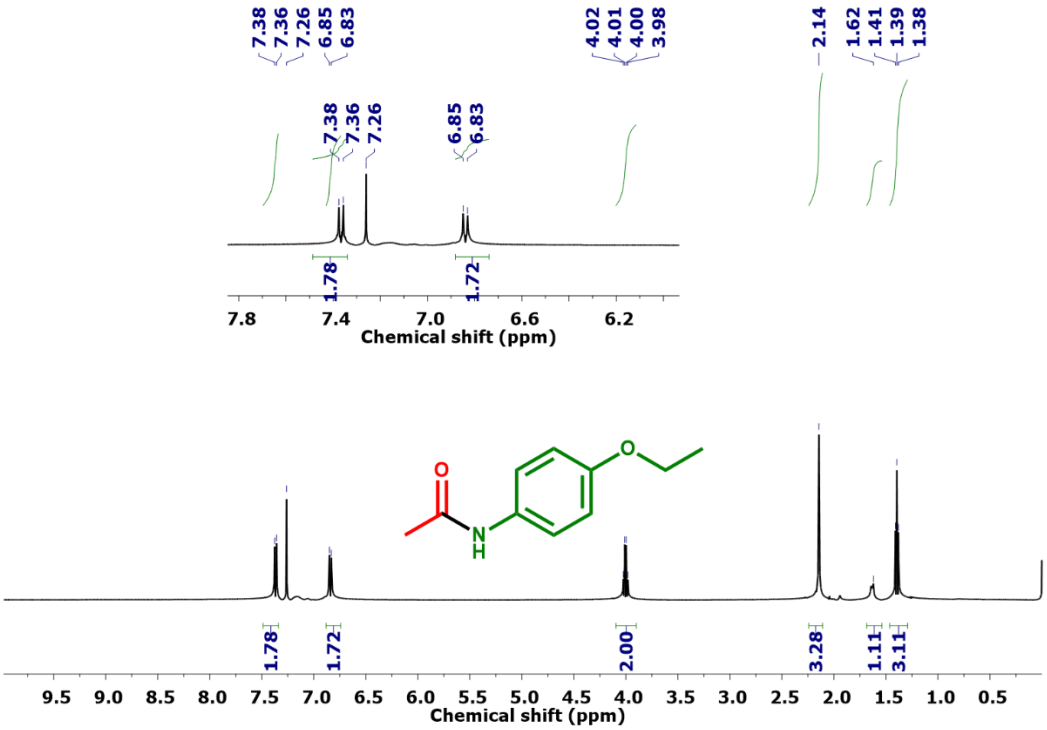
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **34a.**



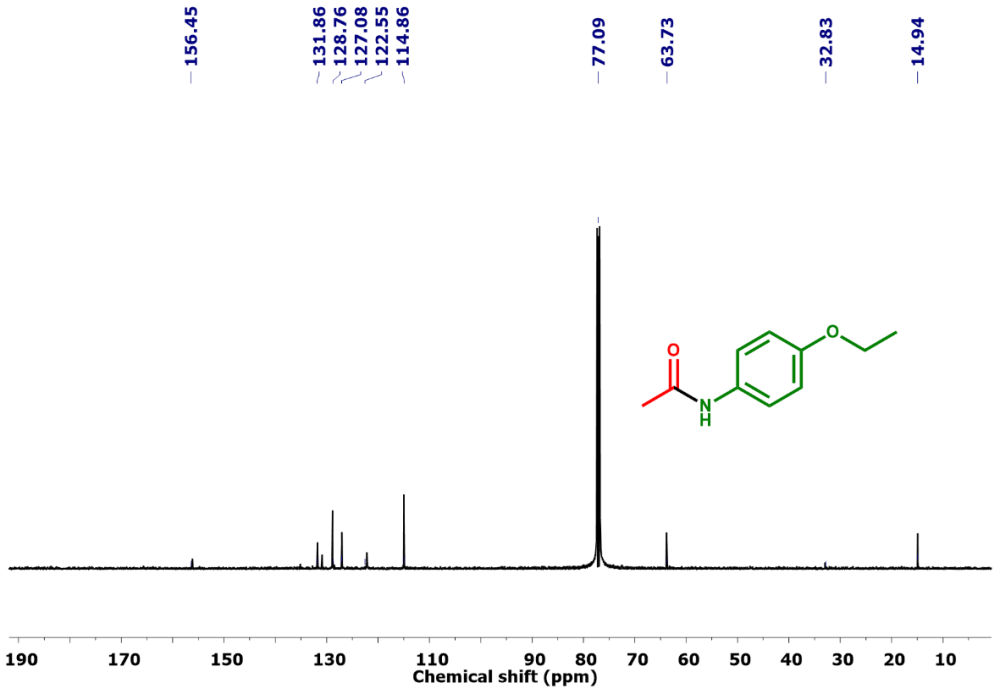
^{1}H NMR (DMSO-d_6, 500 MHz) of Compound **3x.**



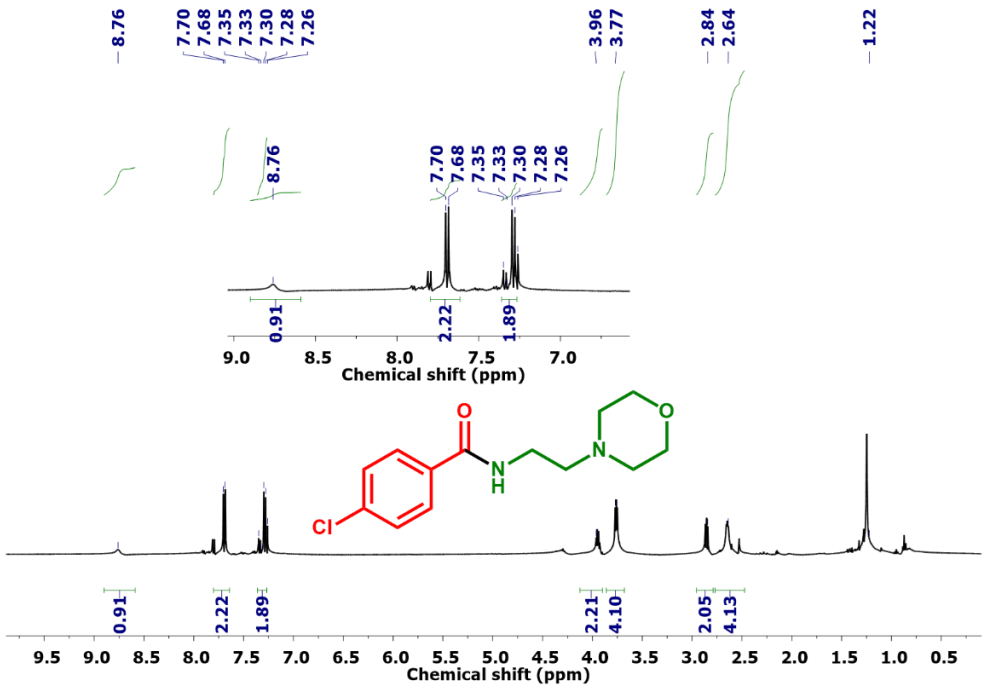
^{13}C NMR (DMSO-d_6, 125 MHz) of Compound **3x.**



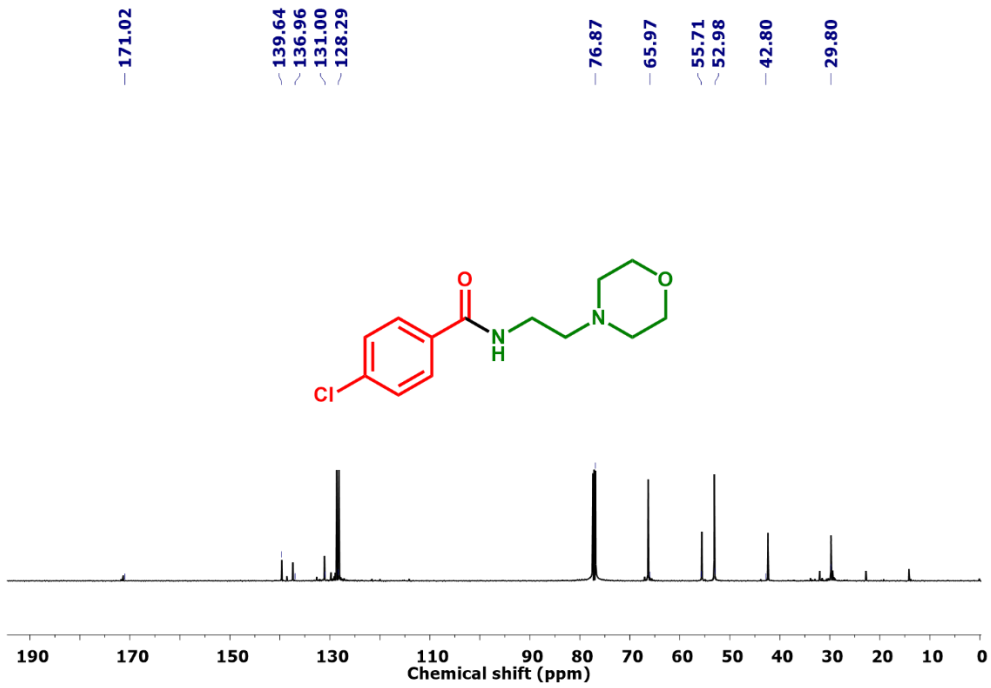
^{1}H NMR (DMSO-d_6, 500 MHz) of Compound **3y.**



^{13}C NMR (DMSO-d_6, 125 MHz) of Compound **3y.**



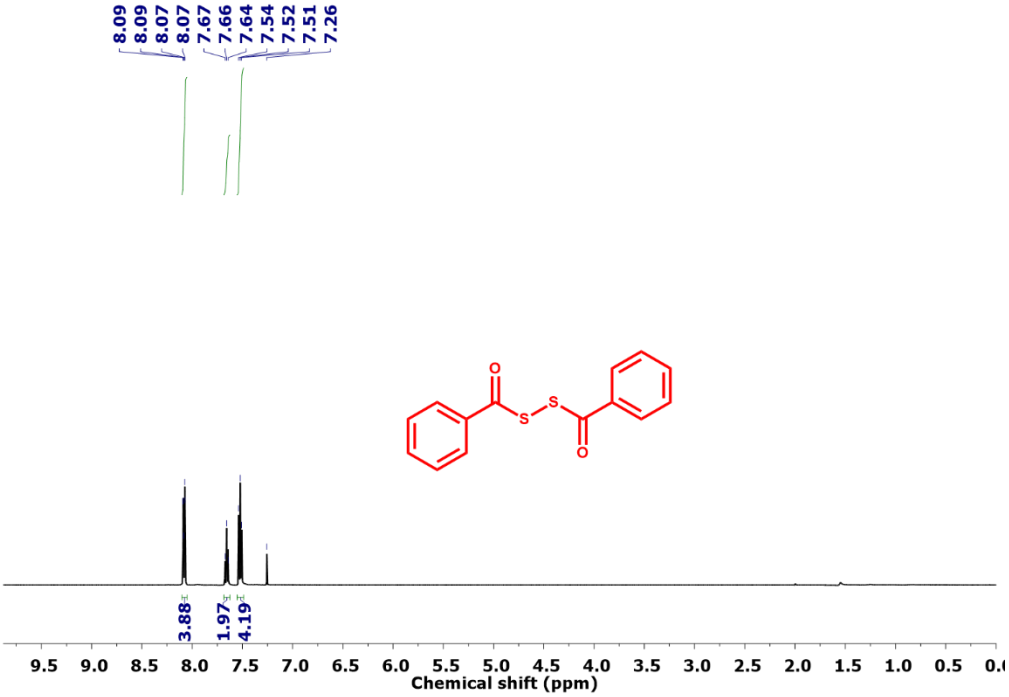
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **3z.**



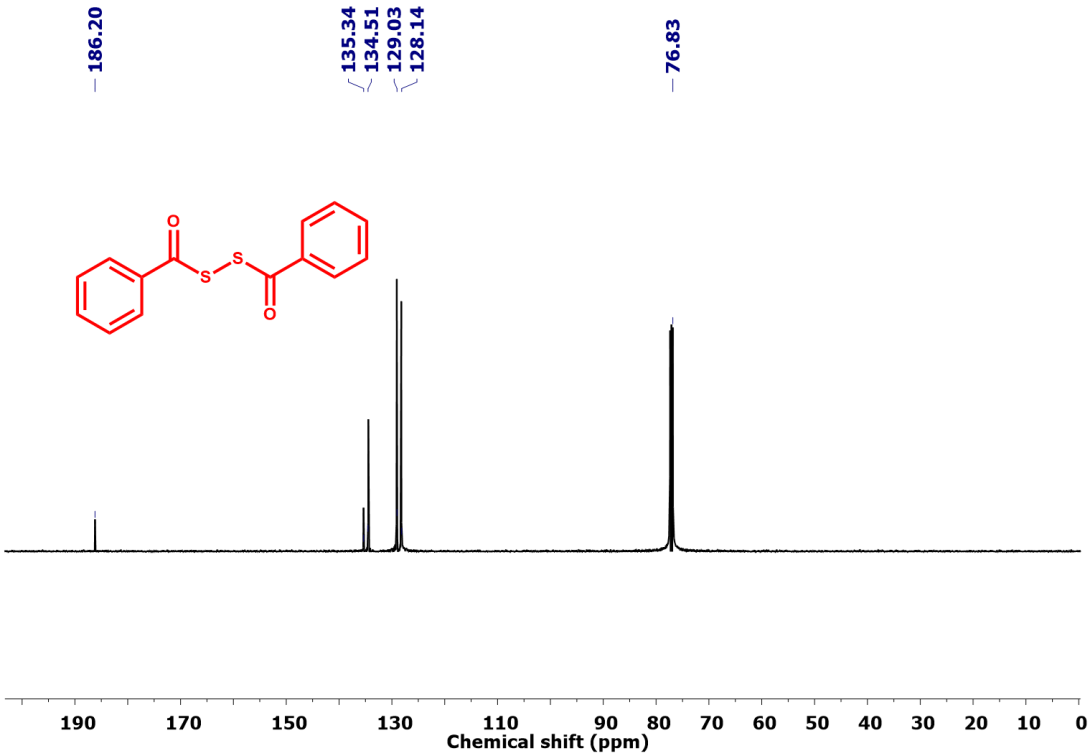
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **3z.**

Benzoic Dithioperoxyanhydride (4b)

Purified by column chromatography (hexane), yielding a white solid (81mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, 4H), 7.67–7.64 (m, 2H), 7.52 (t, 4H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 186.2, 135.3, 134.5, 129.0, 128.1. Compound **4b** is consistent with literature reports.[2]



^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **4b**.

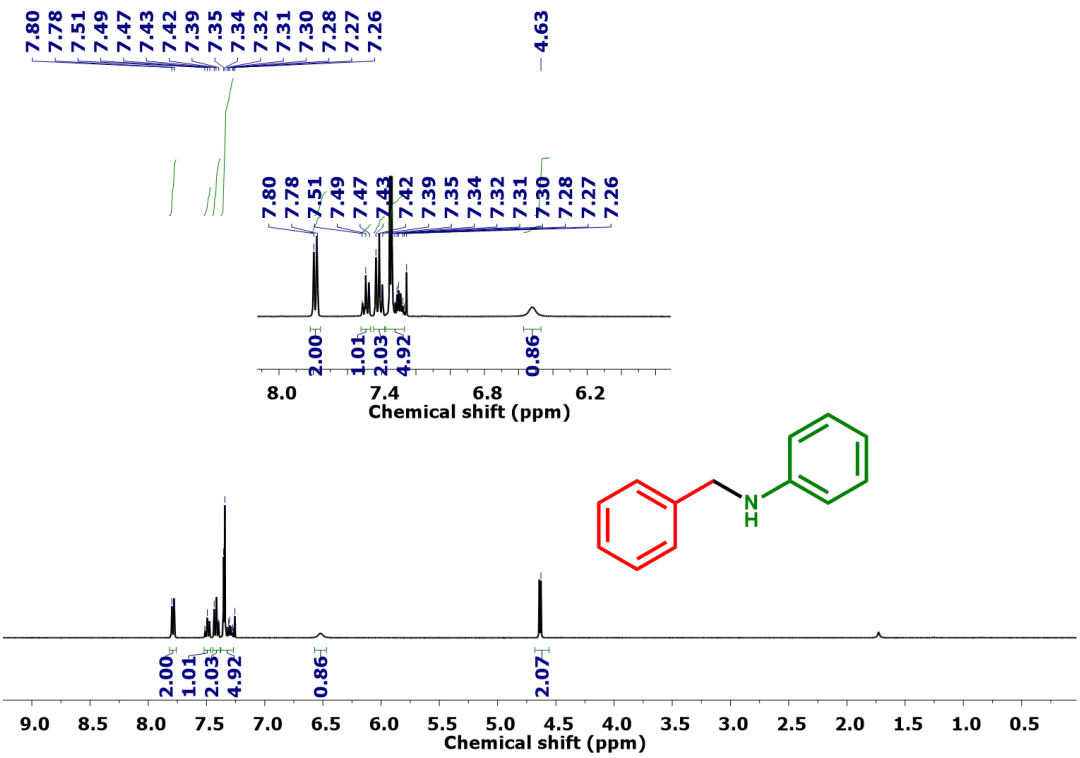


^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **4b.**

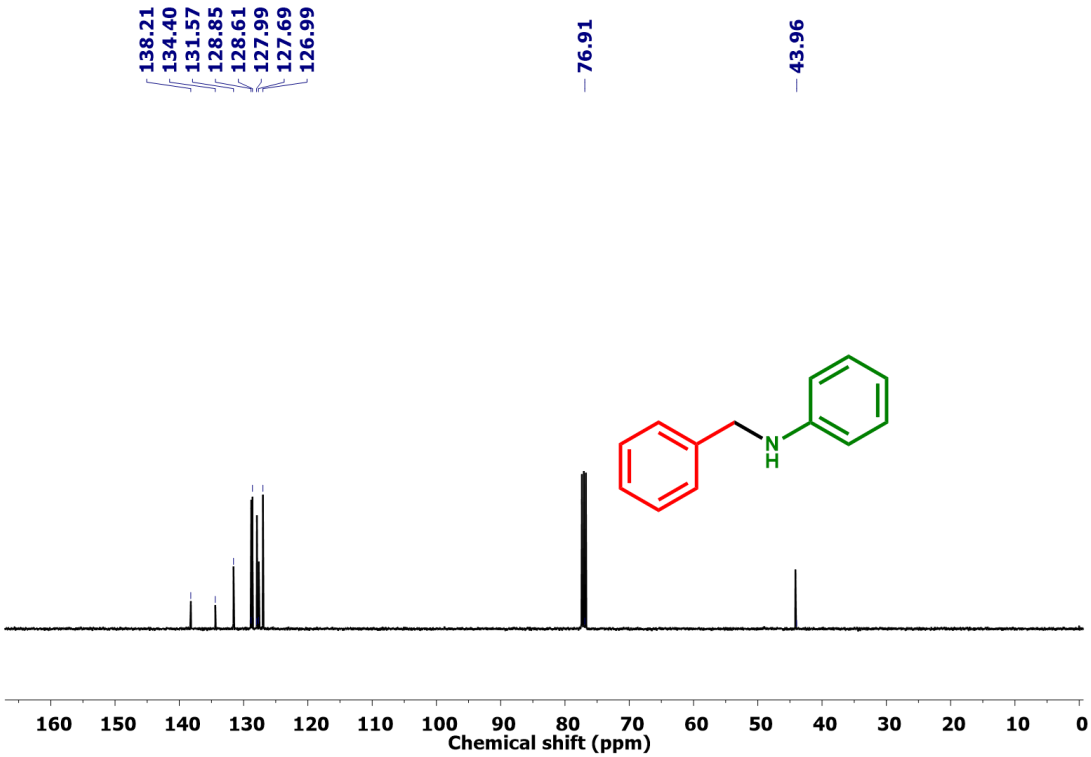
_N_-Benzylaniline (15b)

_N_-Phenylbenzamide (98.50 mg, 0.5 mmol) was dissolved in 2.00 mL of THF, followed by the addition of $LiAlH_4$ (2.5 mmol). The reaction was stirred at 0 °C for 1 h, followed by heating at 80 °C for an additional 2 h. After cooling to room temperature, the reaction was quenched with water (2 mL) and 6 N NaOH (1 mL). The resulting mixture was extracted with ethyl acetate, and the combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to yield compound **15b** (50.30 mg, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41-8.38 (m, 2H), 7.93 (d, 2H), 7.59-7.56 (m, 1H), 7.53-7.51 (m, 2H), 7.41 (d, 1H), 7.18 (d, 1H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.3, 135.4, 134.8, 133.3, 132.5, 132.1, 129.2, 128.9, 127.0, 121.7, 113.6, 20.8. Compound **15b** is consistent with literature reports.[20]



^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **15b.**

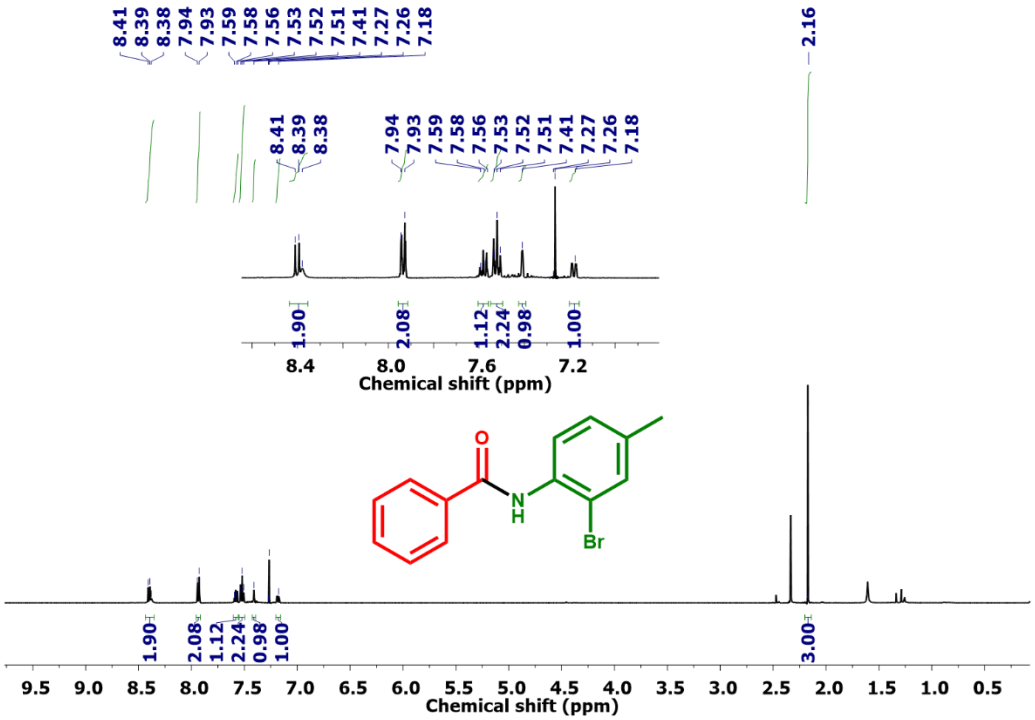


^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **15b.**

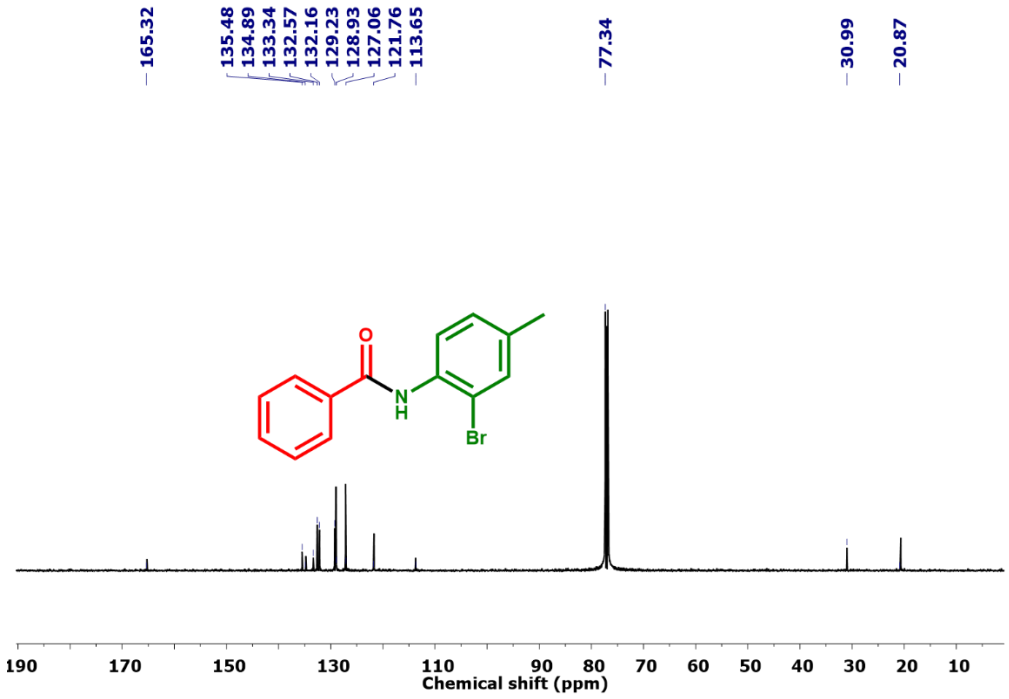
***N*-(2-Bromo 4-Methylphenyl)benzamide (16b)**

N-(4-Methylphenyl)benzamide (105.63 mg, 0.5 mmol) was dissolved in 2.00 mL of acetonitrile, followed by the addition of PhSSPh (1.5 mmol) and NBS (1.5 mmol). The reaction mixture was stirred at room temperature for 6 h. After the reaction was complete, a saturated (1:1) aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$ was added. The mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1) as the eluent to yield **compound 16b** (99.10 mg, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41-8.38 (m, 2H), 7.93 (d, 2H), 7.59-7.56 (m, 1H), 7.53-7.51 (m, 2H), 7.41 (d, 1H), 7.18 (d, 1H), 2.16 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.3, 135.4, 134.8, 133.3, 132.5, 132.1, 129.2, 128.9, 127.0, 121.7, 113.6, 20.8. Compound **16b** is consistent with literature reports.[20]



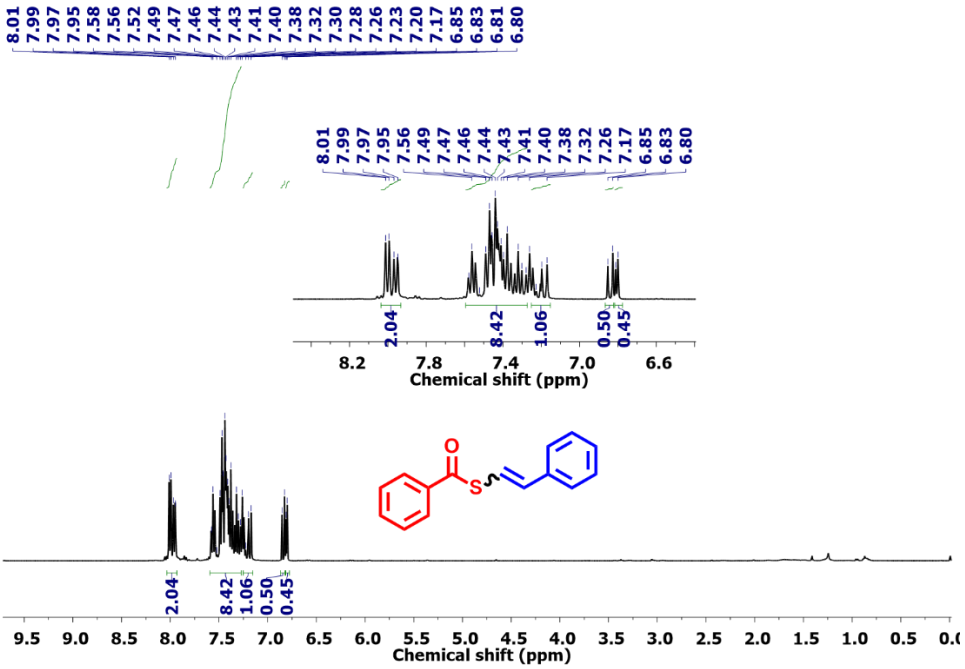
^{1}H NMR ($CDCl_3$, 500 MHz) of Compound **16b.**



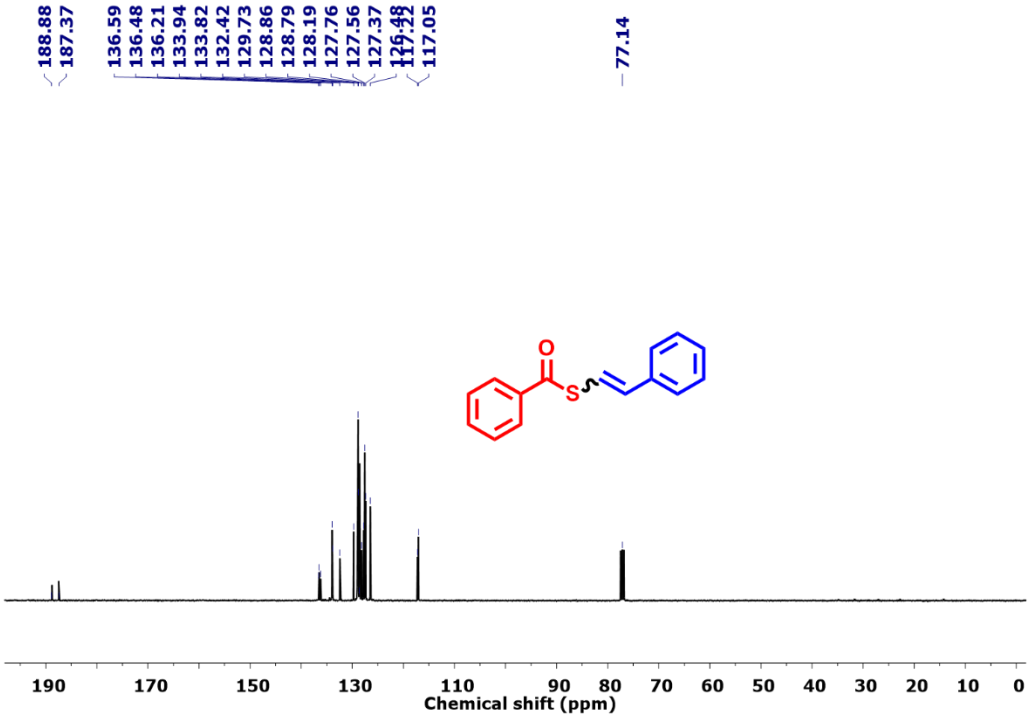
^{13}C NMR ($CDCl_3$, 125 MHz) of Compound **16b.**

S-styrylbenzothioate (2c)

Purified by column chromatography (hexane), yielding a white solid (163 mg, 68%, E : Z = 50 : 50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.95 (m, 2H), 7.56-7.43 (m, 8H), 7.41-7.32 (m, 1H), 6.84 (d, *J* = 8.0Hz, 0.5H), 6.80 (d, 0.5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.8, 187.3, 136.5, 136.4, 136.2, 133.9, 132.4, 129.7, 128.8, 128.7, 128.1, 127.7, 127.5, 127.3, 126.4, 117.2, 117.0.



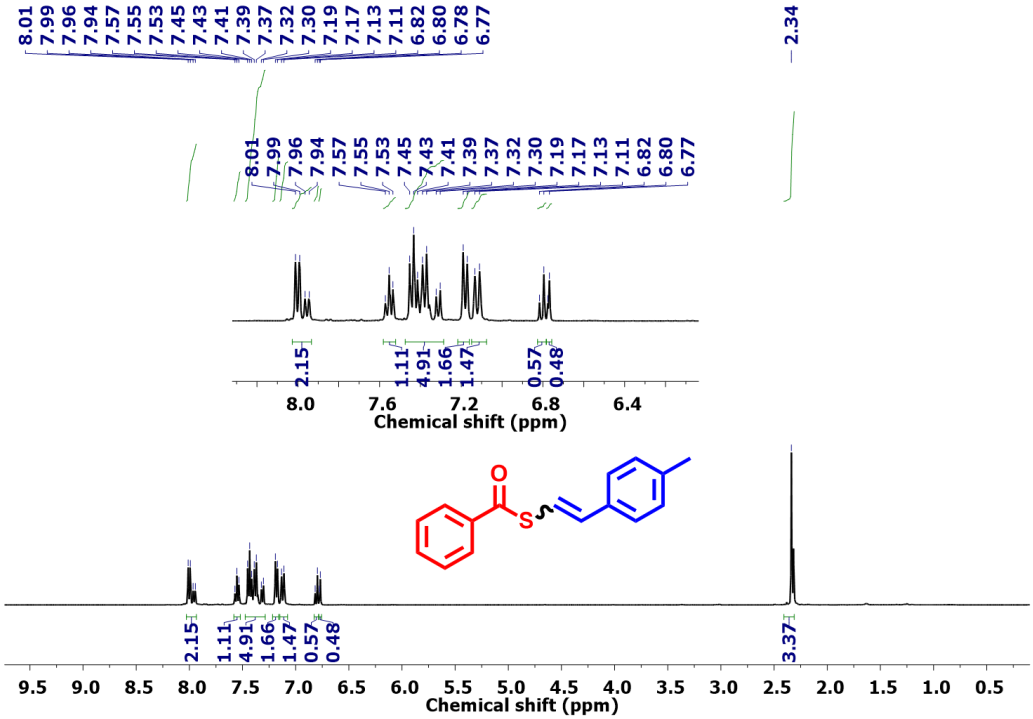
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **2c.**



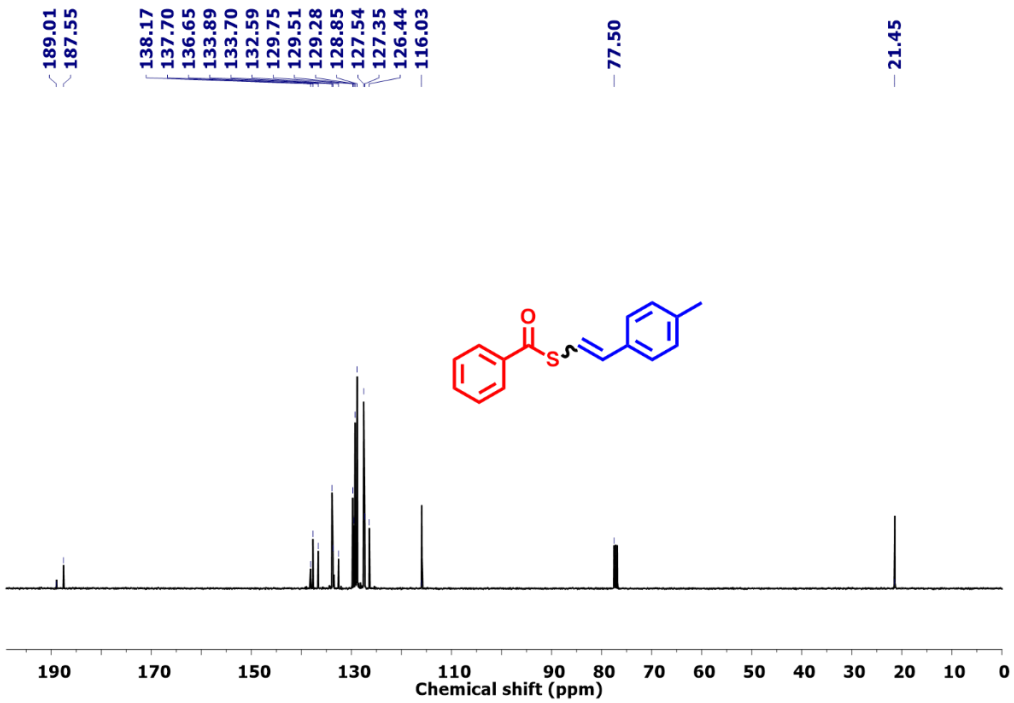
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **2c.**

S-4-methylstyrylbenzothioate (3c)

Purified by column chromatography (hexane), yielding a white solid (198 mg, 78%, E : Z = 50 : 50). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.94 (m, 2H), 7.57-7.53 (m, 1H), 7.45-7.30 (m, 5H), 7.18 (d, 1.5H), 7.12 (d, 1.5H), 6.8I (d, *J* = 8.0 Hz, 0.5H), 6.77 (d, 0.5H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.0, 187.5, 138.1, 137.7, 136.6, 133.8, 132.5, 129.7, 129.5, 129.7, 128.8, 127.5, 127.3, 126.4, 116.0, 21.4.



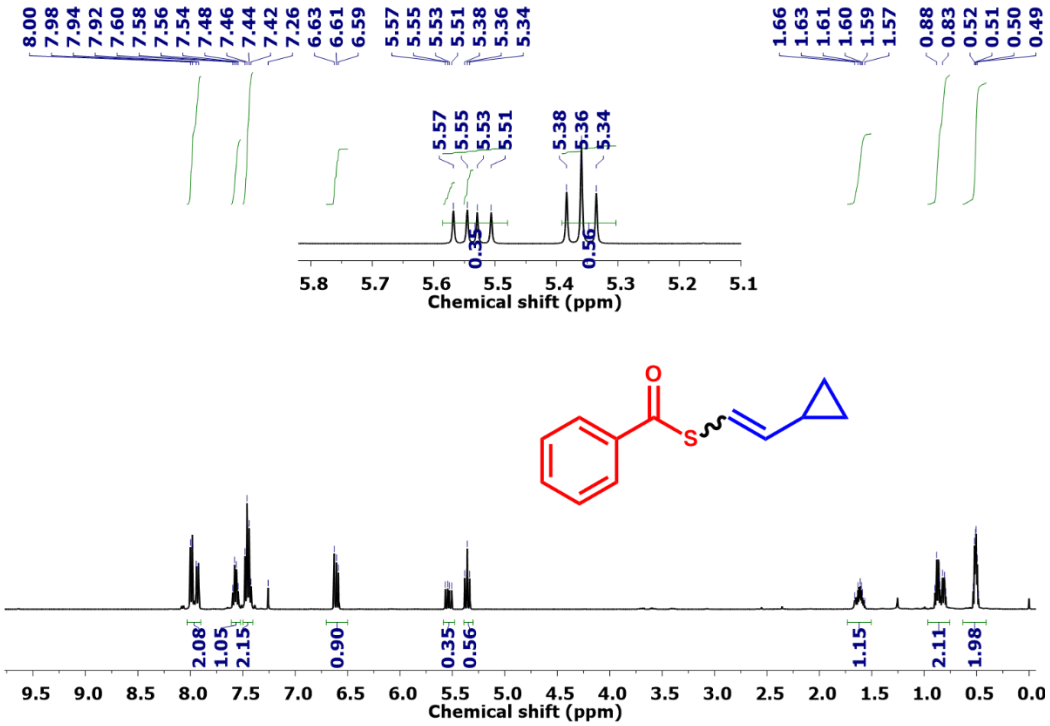
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **3c.**



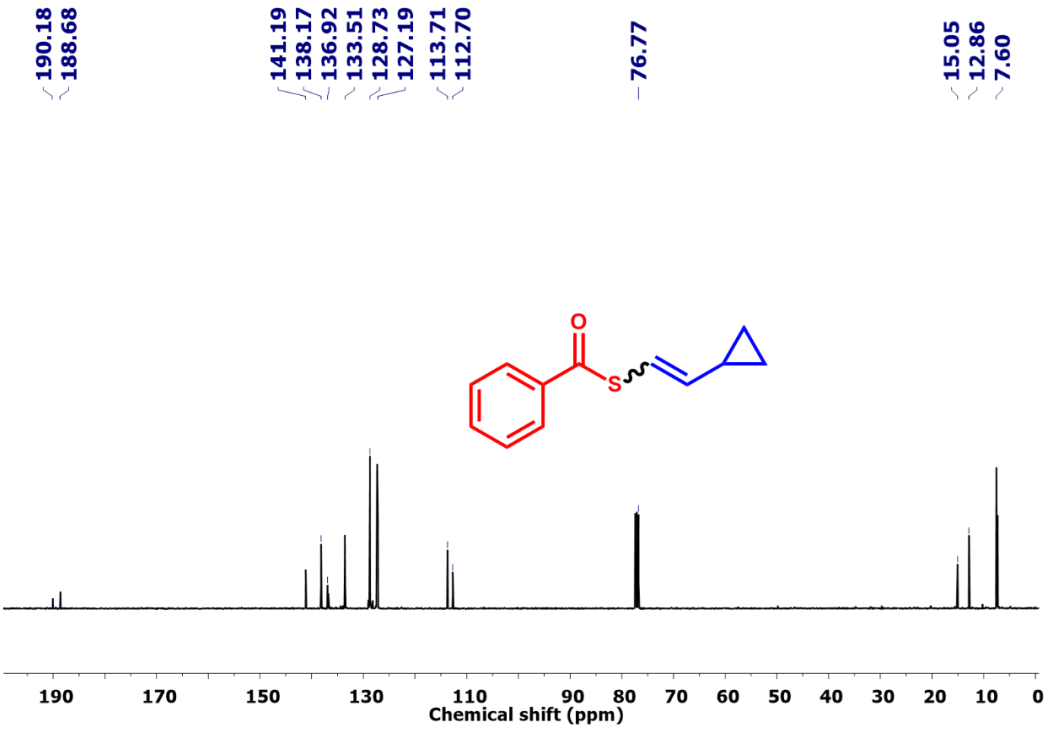
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **3c.**

S-(2-cyclopropylvinyl)benzothioate (4c)

Purified by column chromatography (hexane), yielding a white solid (115 mg, 55%, E : Z = 35 : 65). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.92 (m, 2H), 7.60-7.54 (m, 1H), 7.48-7.42 (m, 2H), 6.63-6.59 (m, 1H), 5.55 (dd, J = 16.0Hz, 0.35H), 5.58-5.34 (m, 0.65H), 1.66-1.57(m, 1H), 0.90-0.79 (m, 2H), 0.52-0.48 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.1, 188.6, 141.1, 138.1, 136.9, 133.5, 128.7, 127.1, 113.7, 112.7, 15.0, 12.8, 7.6.



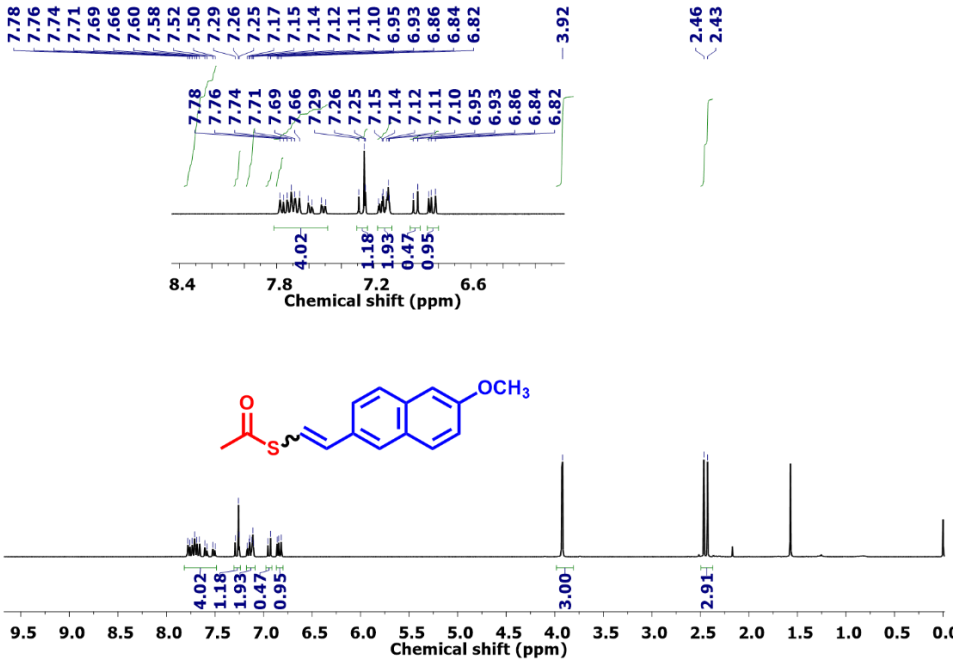
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **4c.**



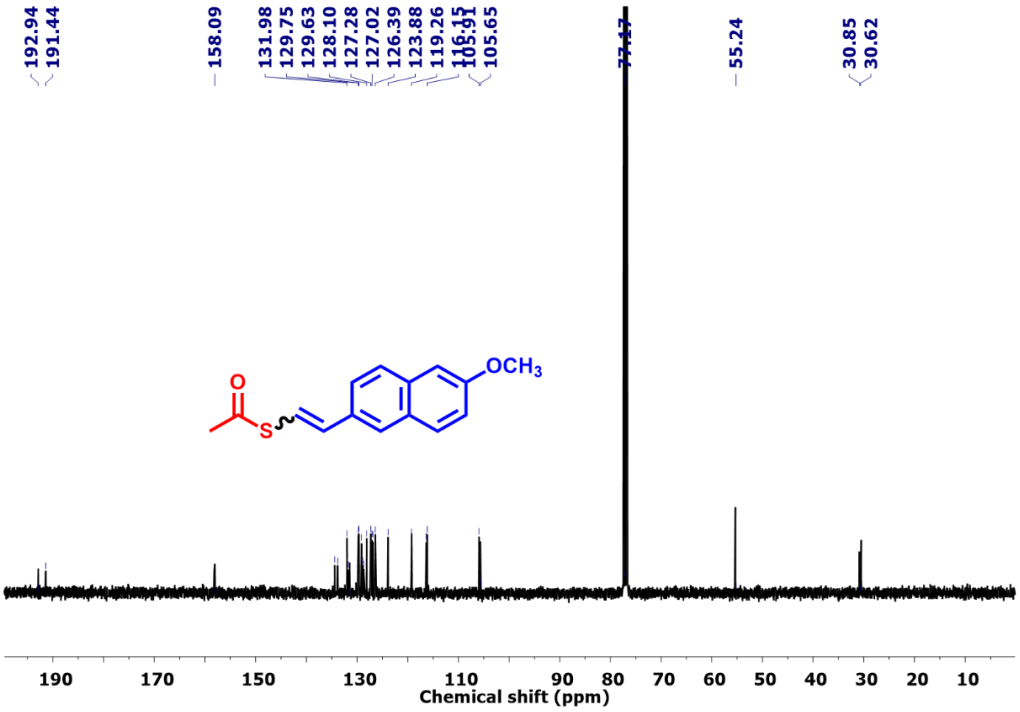
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **4c.**

S-(2-methyl 6-methoxynaphthalene 2-yl)ethanethioate (5c)

Purified by column chromatography (hexane), yielding a white solid (186 mg, 72%, E : Z = 67 : 33). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.50 (m, 4H), 7.29-7.25 (m, 1H), 7.17-7.10 (m, 2H), 6.94 (d, *J* = 8.0Hz, 0.5H), 6.86-6.82 (d, 1H), 3.92 (s, 3H), 2.46 (d, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.9, 191.4, 158.0, 131.9, 129.7, 129.6, 128.1, 127.2, 127.0, 126.3, 123.8, 119.2, 116.1, 105.6, 55.2, 30.8, 30.6.



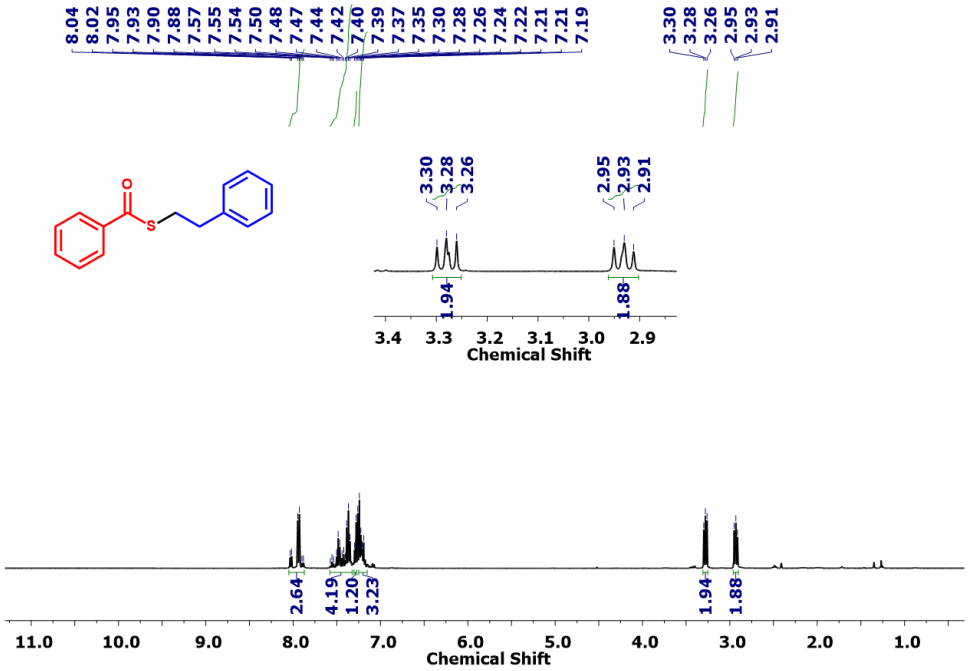
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **5c.**



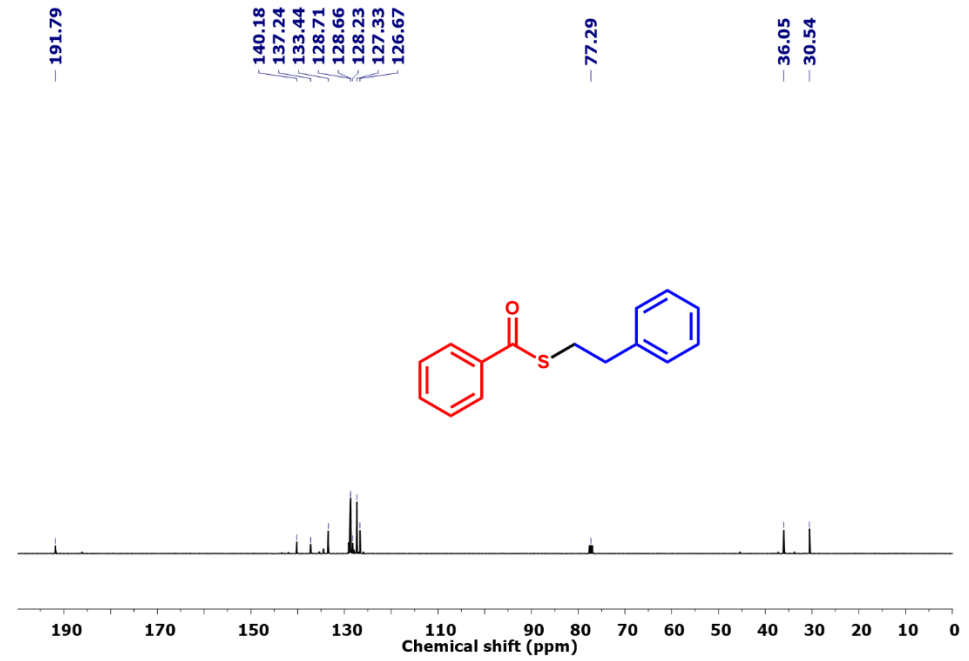
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **5c.**

S-(2-Phenylethyl) benzenecarbothioate (6c)

Purified by column chromatography (hexane), yielding a light yellow oil (236 mg, 94%). ^{1}H NMR (400 MHz, chloroform-d): δ 8.04-7.88 (m, 2H), 7.57-7.35 (m, 4H), 7.30-7.19 (m, 4H), 3.28 (t, 2H), 2.93 (t, 2H). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d): δ 191.8, 140.1, 137.2, 133.4, 129.1, 128.8, 128.7, 128.6, 128.2, 127.9, 127.3, 126.6, 36.0, 30.5. Compound **6c** is consistent with literature reports.[21]



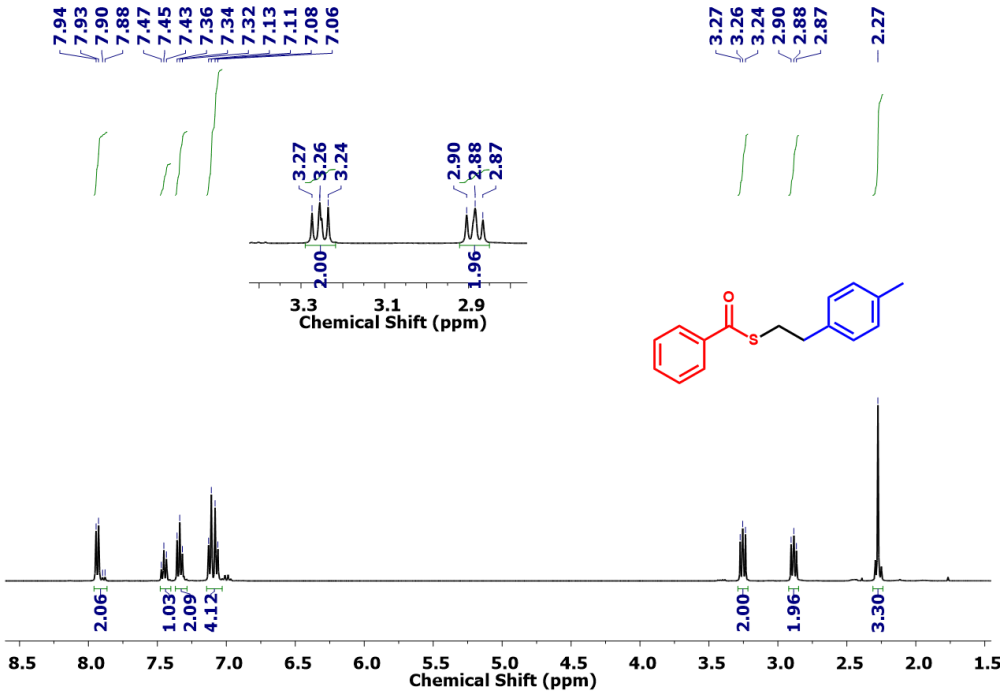
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **6c.**



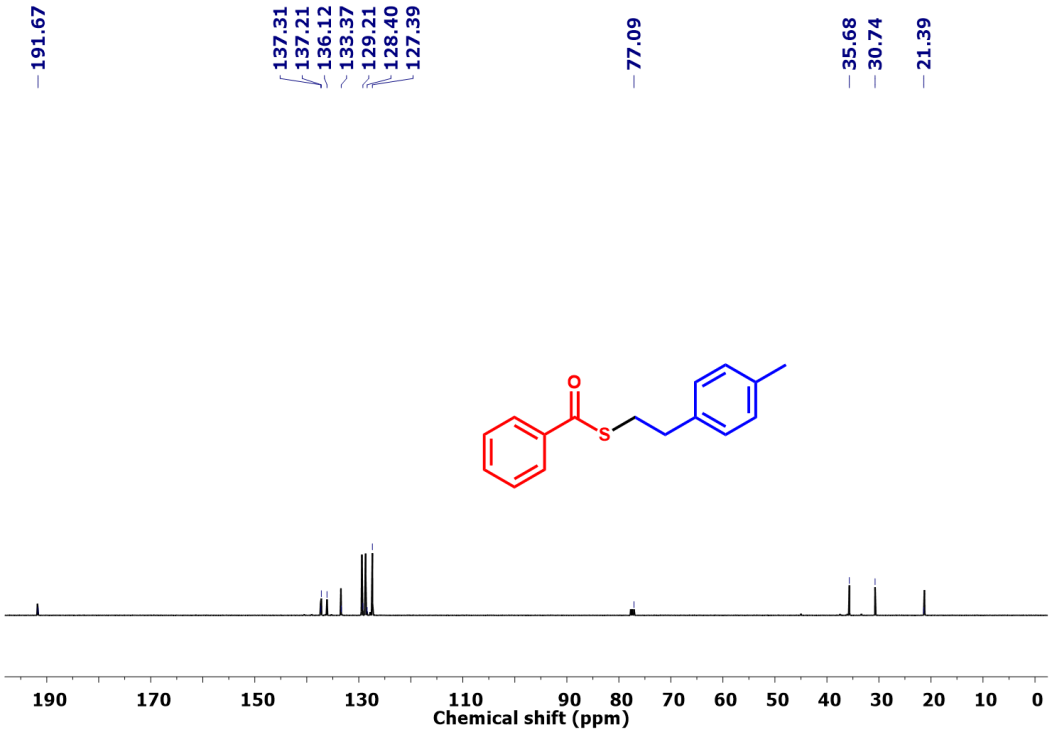
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **6c.**

S-(2-phenylethyl) 4-methylbenzenecarbothioate (7c)

Purified by column chromatography (hexane), yielding a light yellow oil (248 mg, 97%). ^{1}H NMR (400 MHz, chloroform-d): δ 7.93 (d, 2H), 7.47 (t, 1H), 7.34 (t, 2H), 7.13-7.06 (m, 4H), 3.26 (t, 2H), 2.88 (t, 2H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d): δ 191.7, 137.3, 137.2, 136.1, 133.4, 129.4, 128.7, 128.6, 127.3, 35.7, 30.7, 21.3. Compound **7c** is consistent with literature reports.[21]



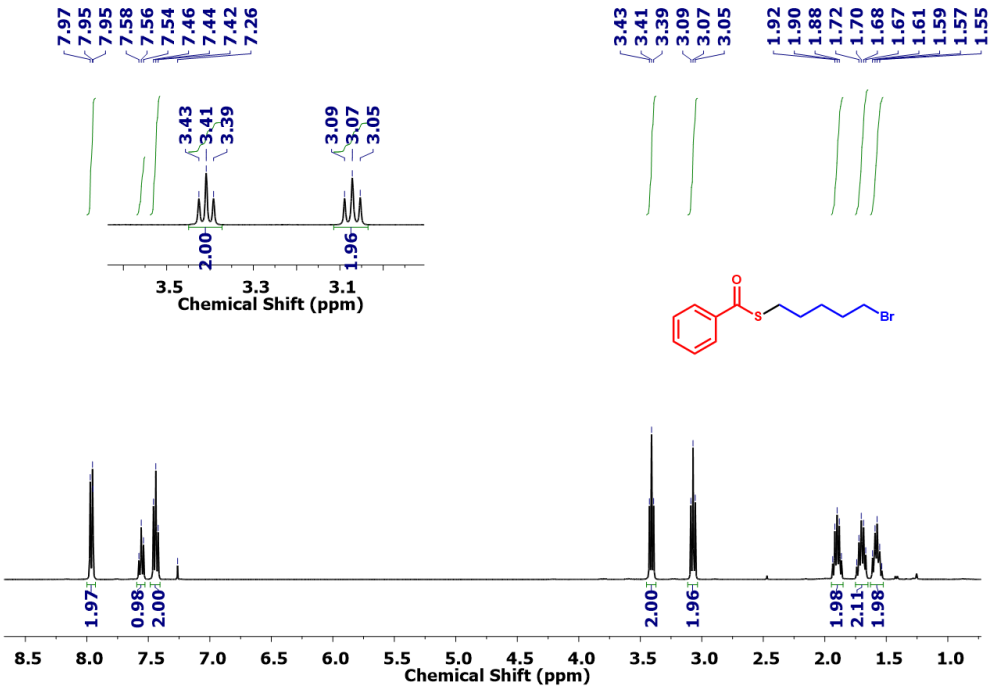
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **7c.**



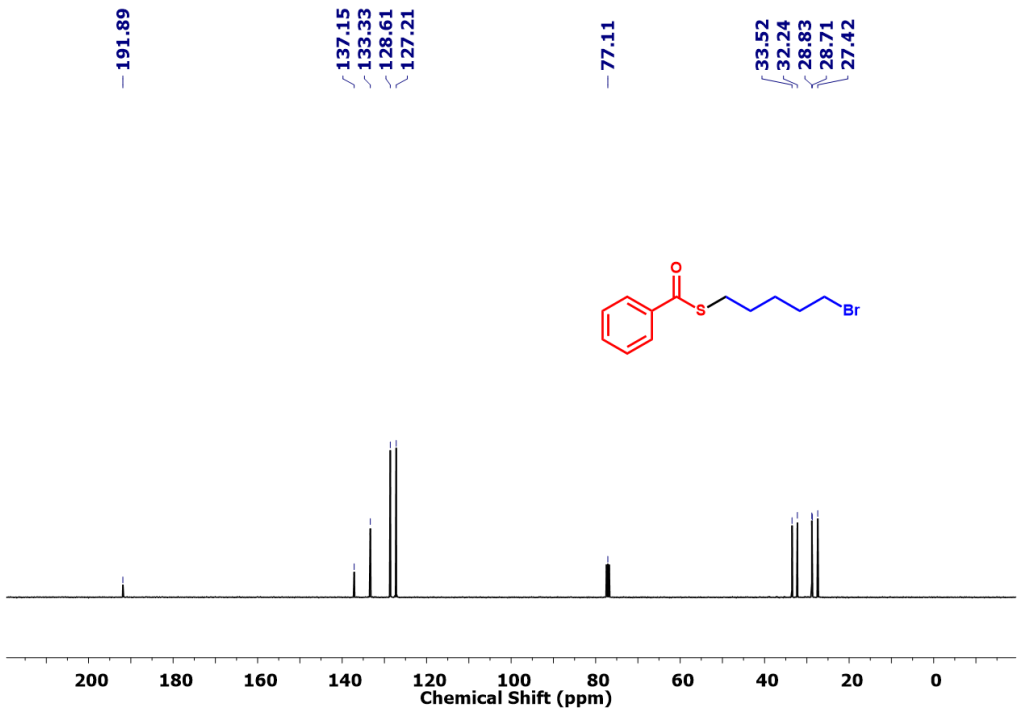
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **7c.**

S-(5-Bromopentyl) benzenecarbothioate (8c)

Purified by column chromatography (hexane), yielding a light yellow oil (115 mg, 47%). ^{1}H NMR (400 MHz, chloroform-d): δ 7.96(d, 2H), 7.56 (t, 1H), 7.44(t, 2H), 3.41 (t, 2H), 3.07 (t, 2H), 1.93-1.86 (m, 2H), 1.74-1.66 (m, 2H), 1.61-1.54 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d): δ 191.8, 137.1, 133.3, 128.6, 127.2, 33.5, 32.2, 28.8, 28.7, 27.4. Compound **8c** is consistent with literature reports.[21]



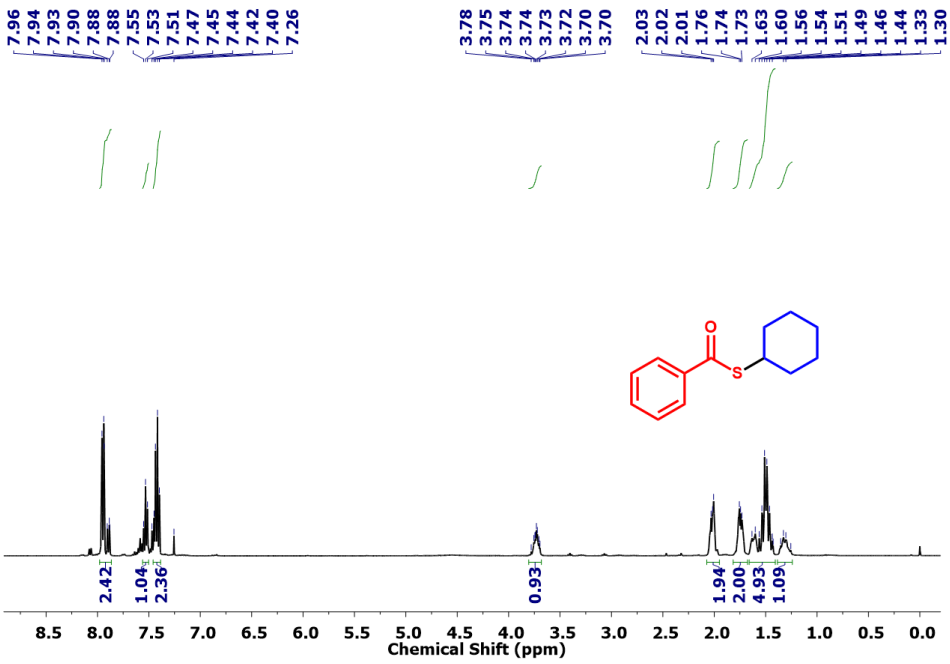
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **8c.**



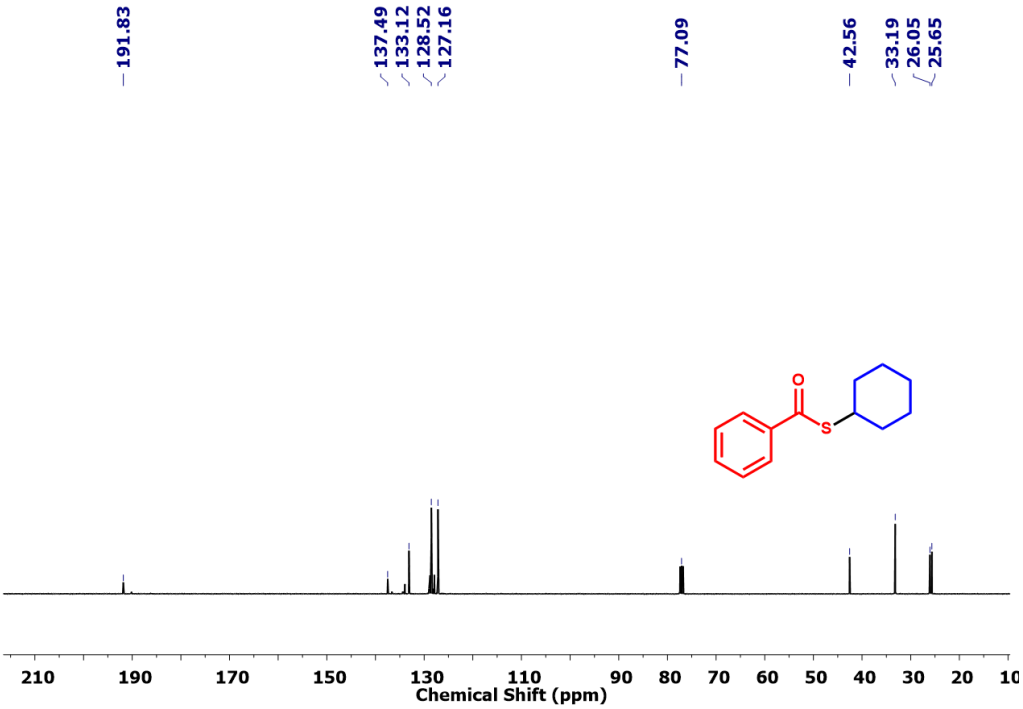
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **8c.**

S-Cyclohexyl benzenecarbothioate (9c)

Purified by column chromatography (hexane), yielding a light yellow oil (132 mg, 60%). ^{1}H NMR (400 MHz, chloroform-d): δ 7.96-7.88 (m, 2H), 7.53 (t, 1H), 7.47-7.40(m, 2H), 3.78-3.70 (m, 2H), 2.03-2.01 (m, 1H), 1.76-1.73 (m, 2H), 1.63-1.43 (m, 5H), 1.35-1.25 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d): δ 191.8, 137.4, 133.1, 128.5, 127.1, 42.5, 32.8, 26.0, 25.6. Compound **9c** is consistent with literature reports.[21]



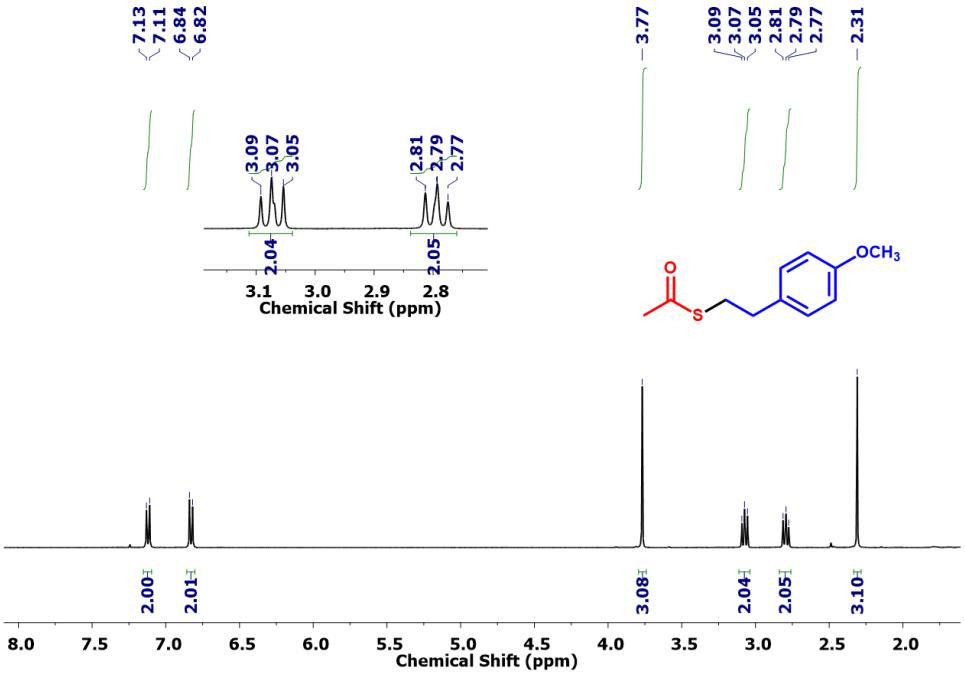
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **9c.**



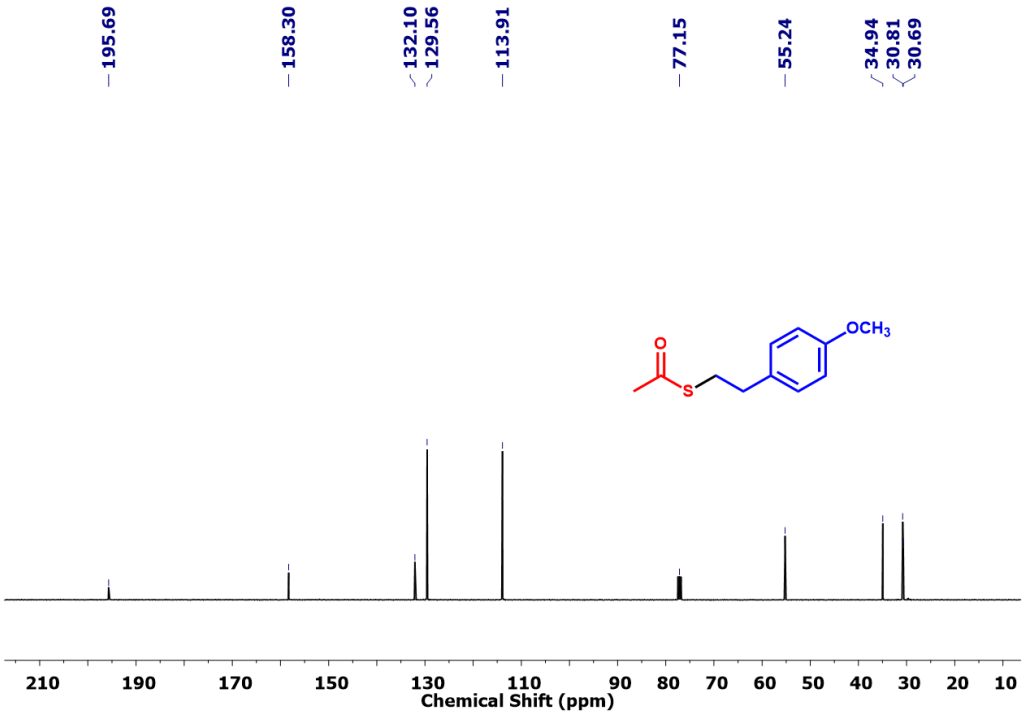
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **9c.**

S-[2-[4-(Methoxy)phenyl]ethyl] benzenecarbothioate (10c)

Purified by column chromatography (hexane), yielding a light yellow oil (138 mg, 67%). ^{1}H NMR (400 MHz, chloroform-d): δ 7.12(d, 2H), 6.83(d, 2H), 3.77 (s, 3H), 3.07 (t, 2H), 2.79 (t, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, chloroform-d): δ 195.6, 158.3, 132.1, 129.5, 113.9, 55.2, 34.9, 30.8, 30.6. Compound **10c** is consistent with literature reports.[21]



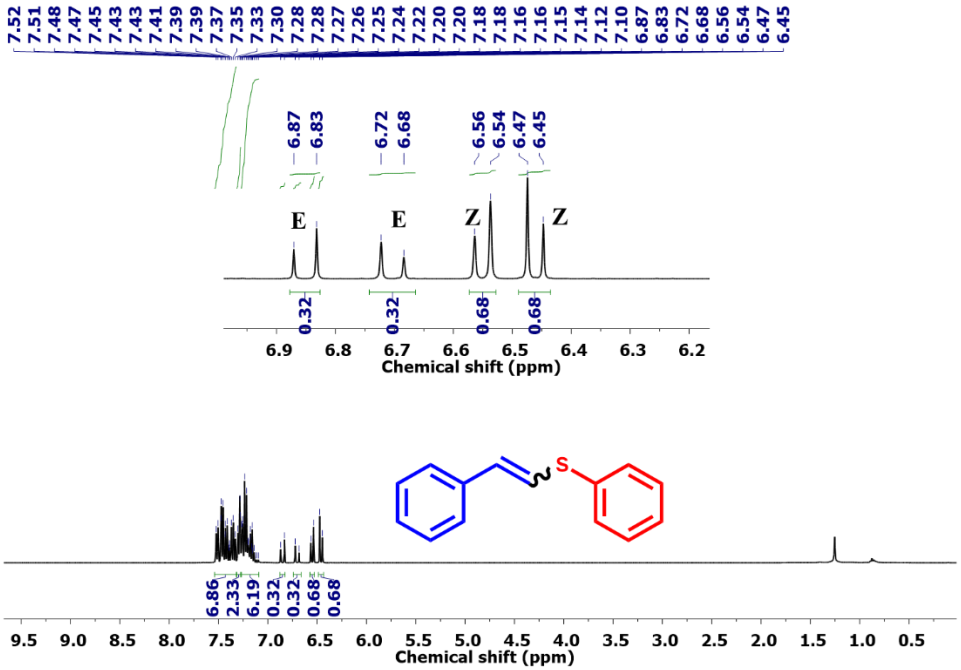
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **10c.**



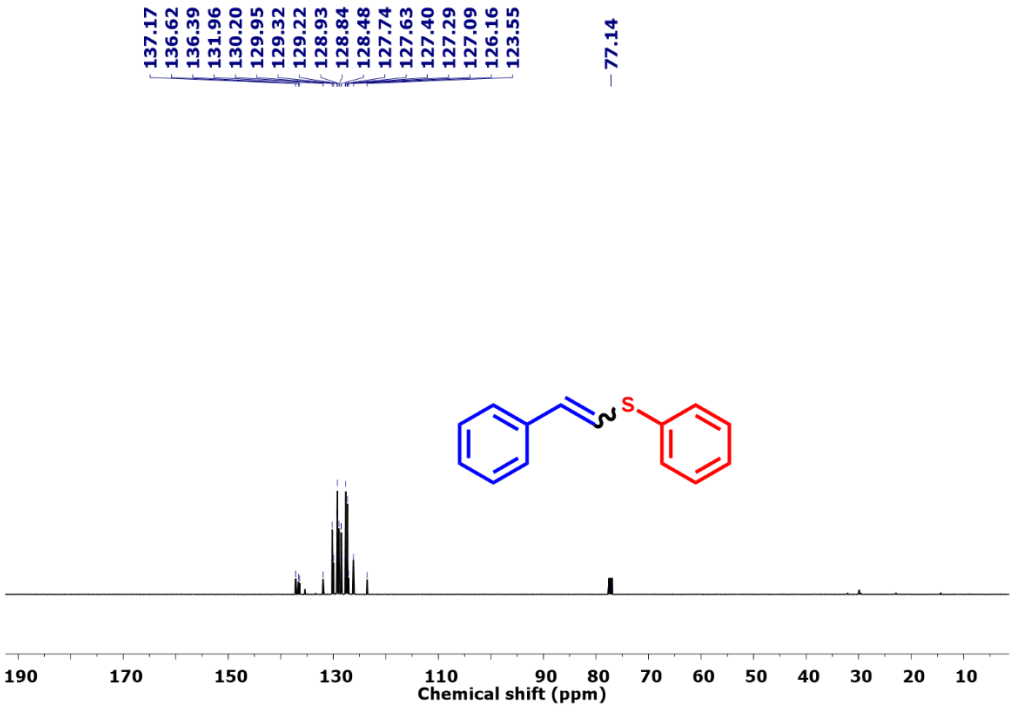
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **10c.**

Phenyl(styryl)sulfane (11c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (179 mg, 85%, E: Z ratio: 32:68). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.33 (m, 7 H), 7.30 – 7.27 (m, 2H), 7.25 – 7.10 (m, 6H), 6.85 (d, 0.32 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.70 (d, 0.32 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.55 (d, 0.68 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz), 6.46 (d, 0.30 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.1, 136.6, 136.3, 131.9, 130.2, 129.9, 129.3, 129.2, 128.9, 128.8, 128.4, 127.6, 127.4, 127.2, 126.1, 123.4. Compound **11c** is consistent with literature reports.[22]



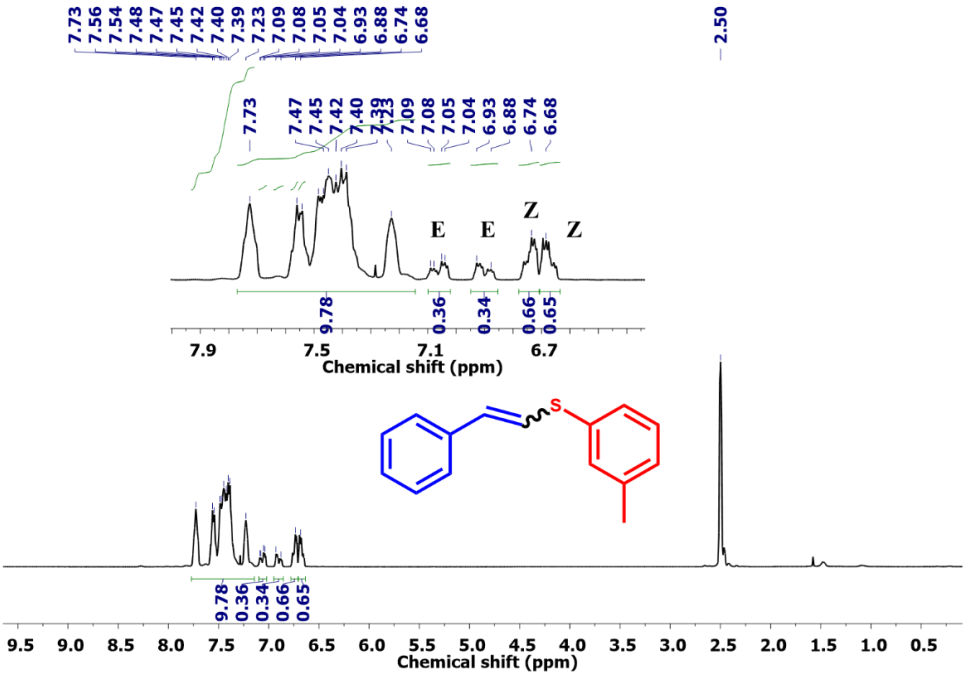
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **11c**.



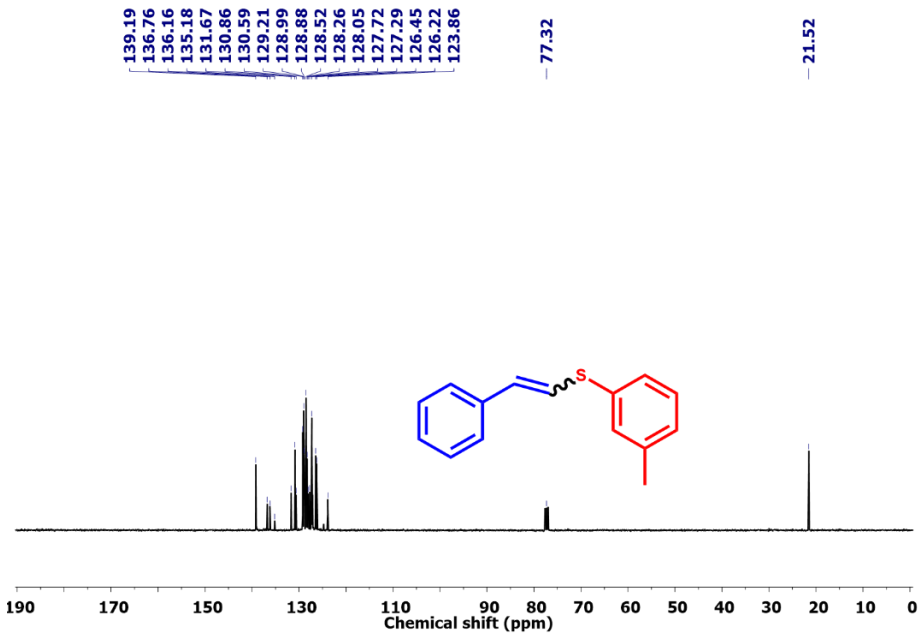
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **11c.**

3-Methylphenyl(styryl)sulfane (12c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (183 mg, 81%, E: Z ratio: 35:65). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.23 (m, 10H), 7.06 (d, 0.35 × 1H, $^{3}J_{H-H}$ = 16.00 Hz), 6.90 (d, 0.35 × 1H, $^{3}J_{H-H}$ = 16.00 Hz), 6.74 (d, 0.65 × 1H, $^{3}J_{H-H}$ = 8.00 Hz), 6.68 (d, 0.65× 1H, $^{3}J_{H-H}$ = 8.00 Hz), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.1, 136.7, 136.1, 135.1, 131.6, 130.8, 130.5, 129.2, 128.9, 128.8, 128.5, 128.2, 128.0, 127.7, 127.2, 126.4, 126.2, 123.8, 21.5. Compound **12c** is consistent with literature reports.[22]



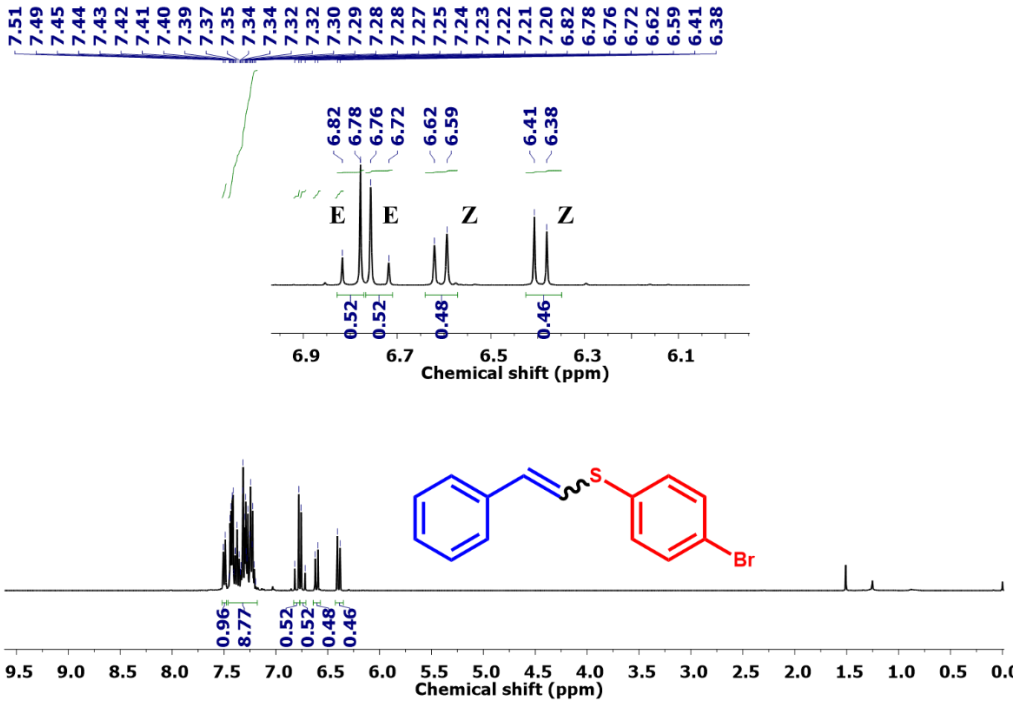
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **12c**.



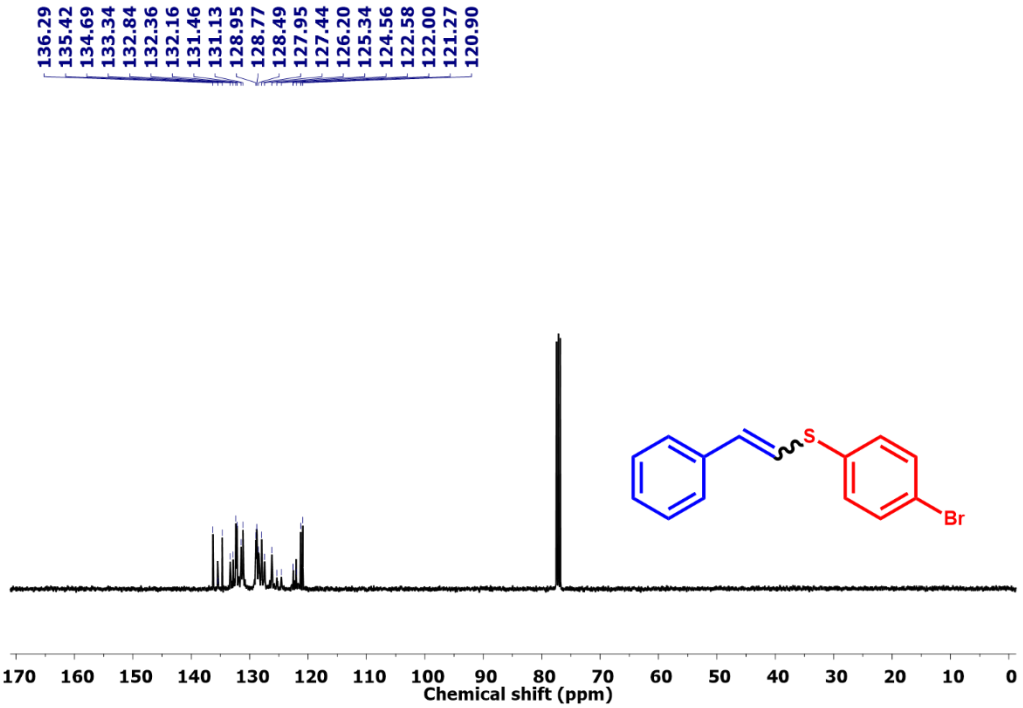
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **12c**.

4-Bromophenyl(styryl)sulfane (13c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (114 mg, 40%, E: Z ratio: 52:48). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 2H), 7.45 – 7.20 (m, 9H), 6.80 (d, 0.52 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.74 (d, 0.52 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.60 (d, 0.48 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.40 (d, 0.48 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.2, 135.4, 134.6, 133.3, 132.8, 132.3, 132.1, 131.4, 131.1, 128.9, 128.7, 128.4, 127.9, 127.4, 126.2, 125.3, 124.5, 122.5, 122.0, 121.2, 120.9. Compound **13c** is consistent with literature reports.[22]



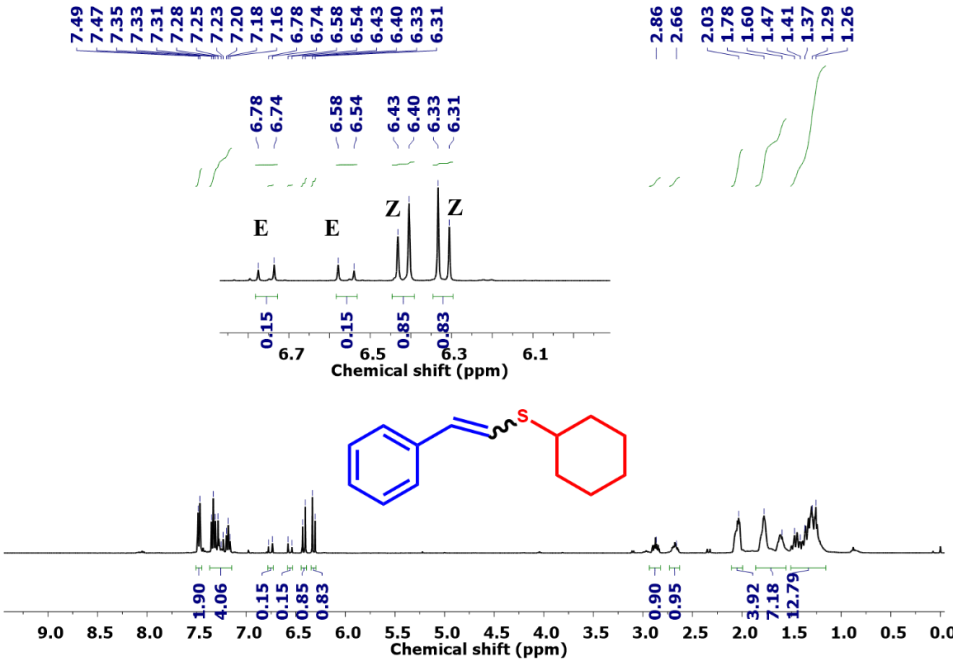
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **13c**.



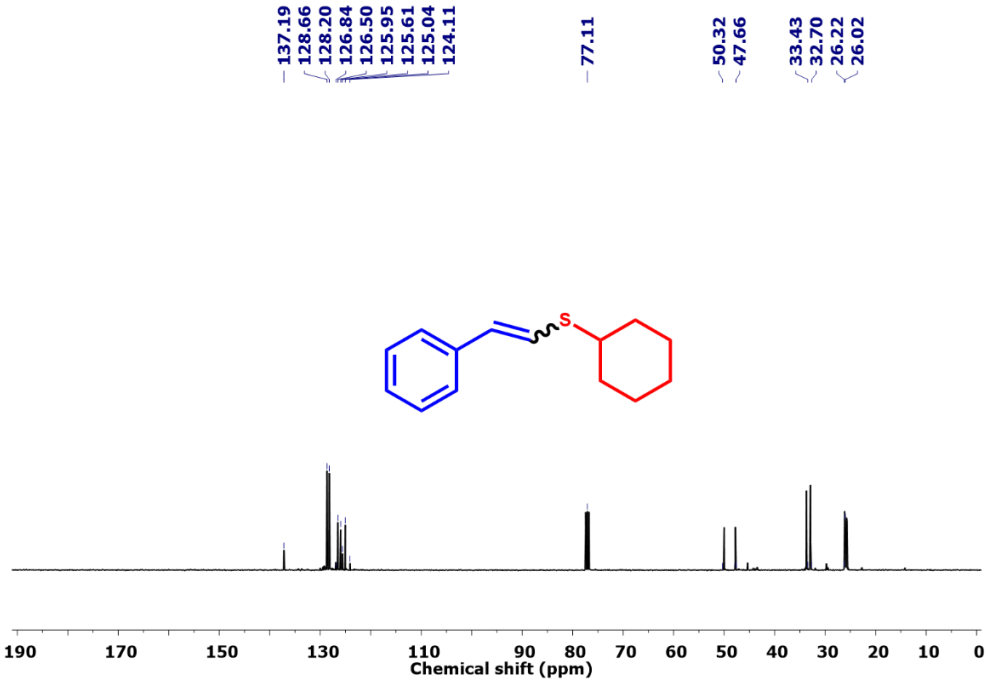
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **13c**.

2-(Cyclohexylthio)ethenylbenzene (14c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (174 mg, 79%, E: Z ratio: 15:85). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H), 7.35-7.16 (m, 4H), 6.76 (d, 0.15 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.56 (d, 0.15 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.42 (d, 0.85 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz), 6.32 (d, 0.85× 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz), 2.90-2.85 (m, 1H), 2.70-2.65 (m, 1H), 2.06-2.03 (m, 3H), 1.78-1.60 (m, 7H), 1.47-1.26 (m, 13H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.1, 128.6, 128.2, 126.5, 125.9, 125.6, 125.0, 124.1, 50.3, 47.6, 33.4, 32.7, 26.2, 26.0. Compound **14c** is consistent with literature reports.[22]



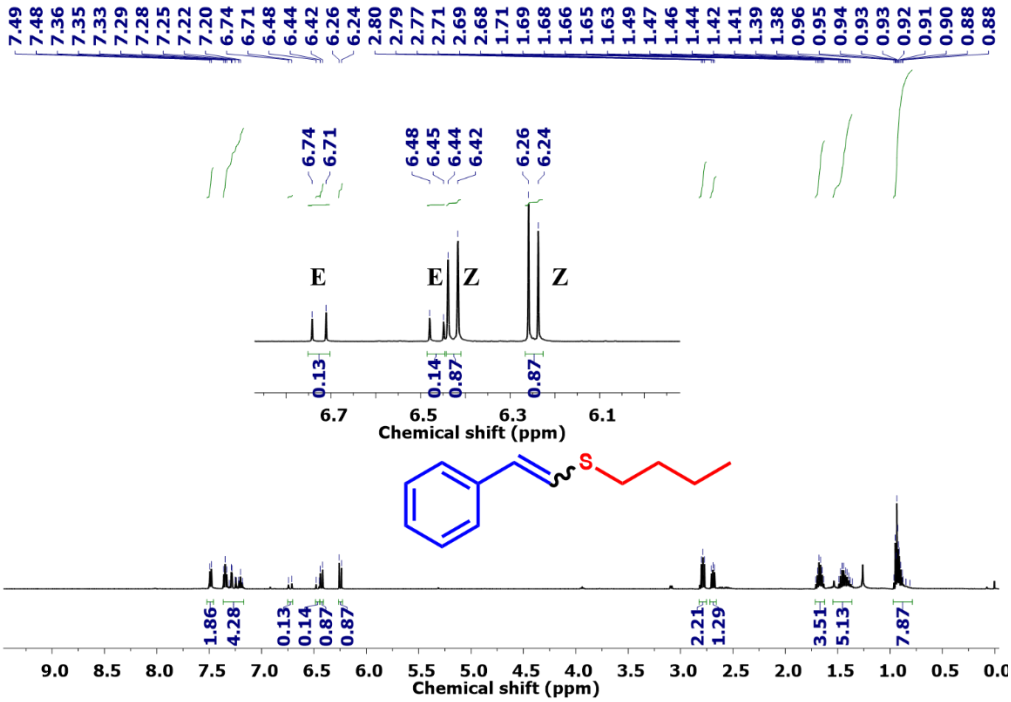
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **14c**.



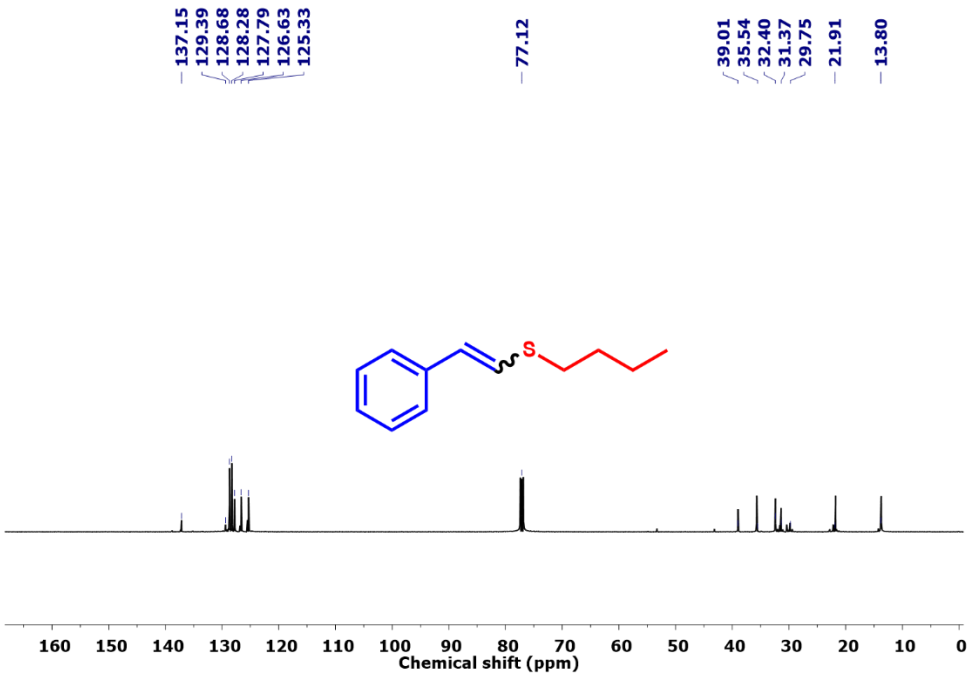
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **14c**.

Butyl(styryl)sulfane (15c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (123 mg, 64%, E: Z ratio: 13:87). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H), 7.35-7.18 (m. 4H), (d, 0.13 × 1H, $^{3}J_{H-H}$ = 12.00 Hz), 6.47 (d, 0.13 × 1H, $^{3}J_{H-H}$ = 12.00 Hz), 6.43 (d, 0.87 × 1H, $^{3}J_{H-H}$ = 8.00 Hz), 6.25 (d, 0.87 × 1H, $^{3}J_{H-H}$ = 8.00 Hz), 2.79 (t, 2H), 2.69 (t, 1H), 1.71-1.63 (m, 3H), 1.49-1.36 (m, 5H), 0.96-0.81 (m, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.1, 129.3, 128.6, 128.2, 127.7, 126.6, 125.3, 39.0, 35.5, 32.4, 31.3, 29.7, 21.9, 13.8. Compound **15c** is consistent with literature reports.[22]



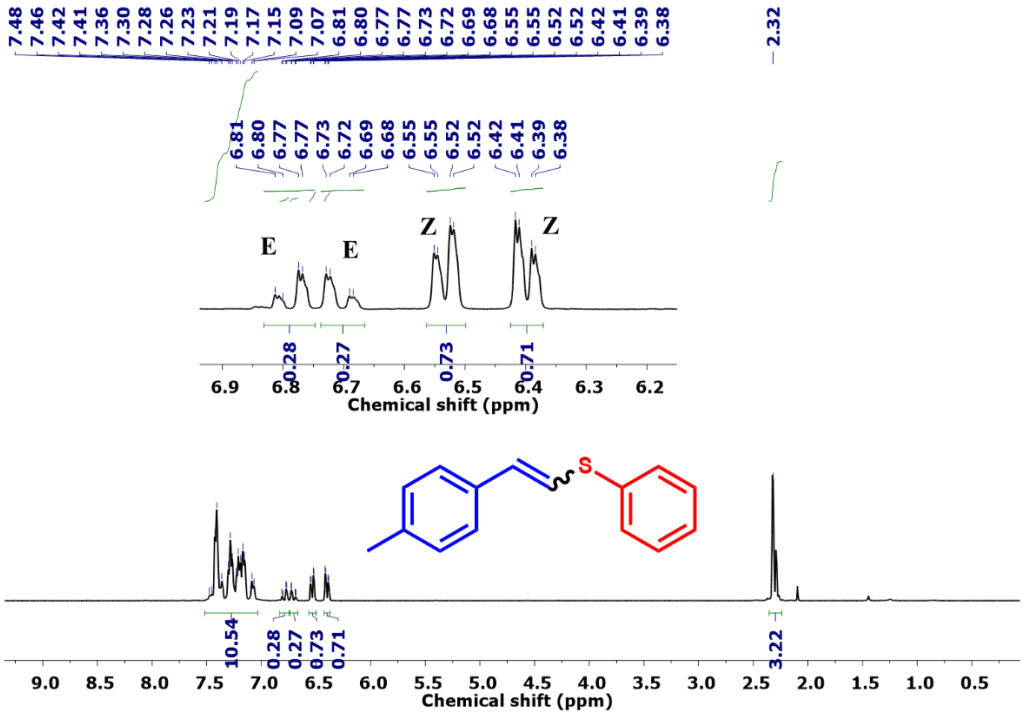
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **15c**.



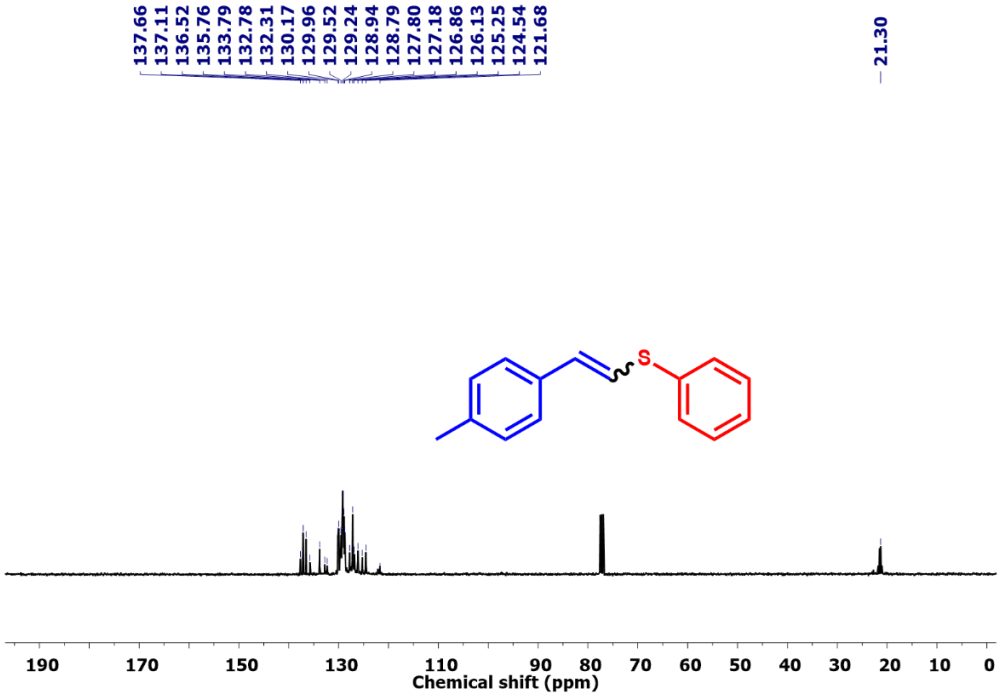
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **15c**.

(4-Methylstyryl) (phenyl)sulfane (16c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (198 mg, 88%, E: Z ratio: 28:72). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.07 (m, 10H), 6.79 (d, 0.28 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.72 (d, 0.28 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.55 (d, 0.72 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.40 (d, 0.72 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.1, 136.5, 135.7, 133.7, 132.7, 132.3, 130.1, 129.9, 129.5, 129.2, 128.9, 127.8, 127.1, 126.8, 126.1, 125.2, 124.5, 121.6, 21.3. Compound **16c** is consistent with literature reports.[22]



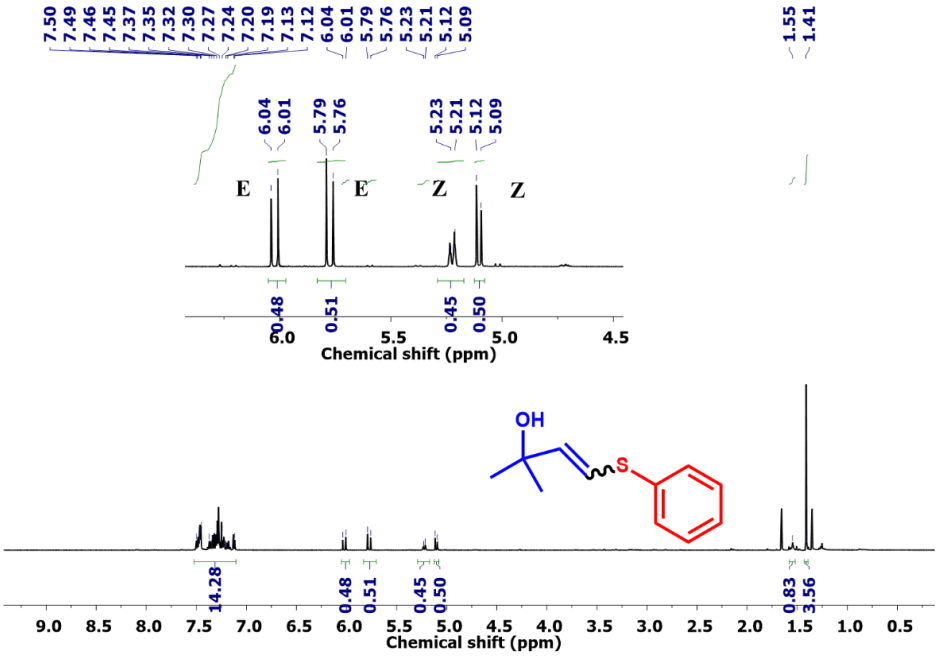
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **16c**.



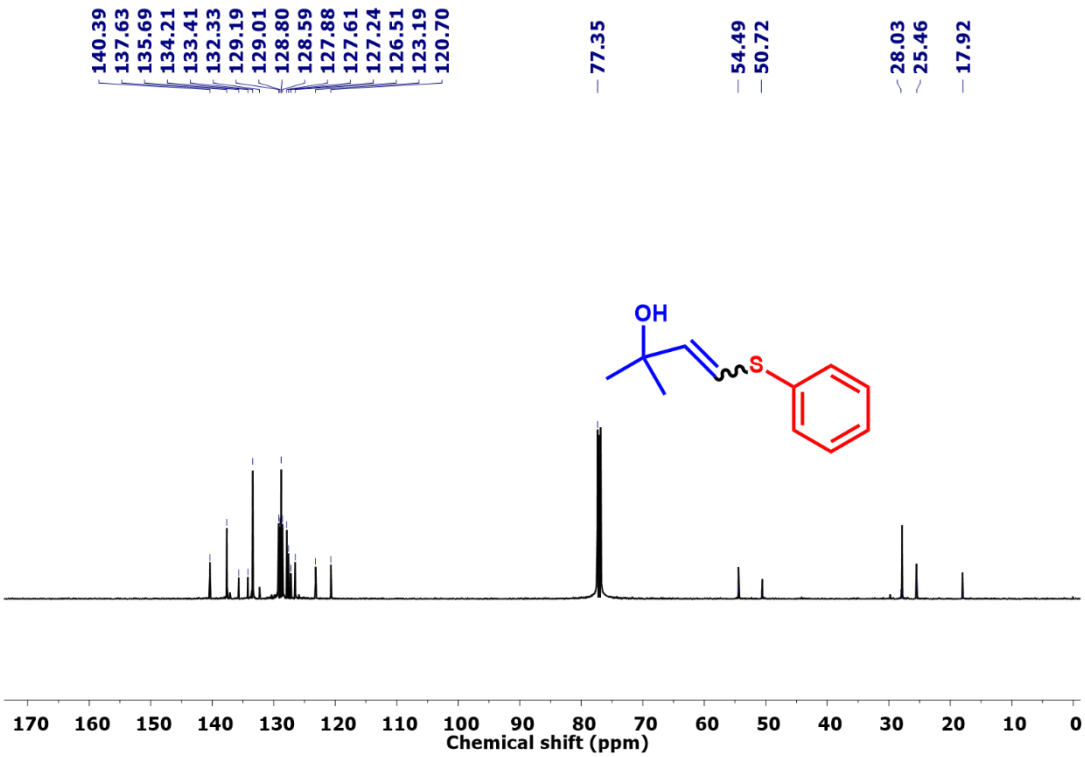
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **16c**.

2-Methyl-4-(phenylthio)-3-buten-2-ol (17c)

Purified by column chromatography (hexane), yielding a White solid (114 mg, 59%, E: Z ratio: 48:52). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.12 (m, 14H), 6.03 (d, 0.48 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 5.77 (d, 0.48 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 5.22 (d, 0.52 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 5.10 (d, 0.52 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz), 6.40 (d, 0.52 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 1.55 (bs, 1H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 137.6, 135.6, 134.2, 133.4, 132.3, 129.1, 129.0, 128.8, 128.5, 127.8, 127.6, 127.2, 126.5, 123.1, 120.7, 54.4, 50.7, 28.0, 25.4, 17.9. Compound **17c** is consistent with literature reports.[23]



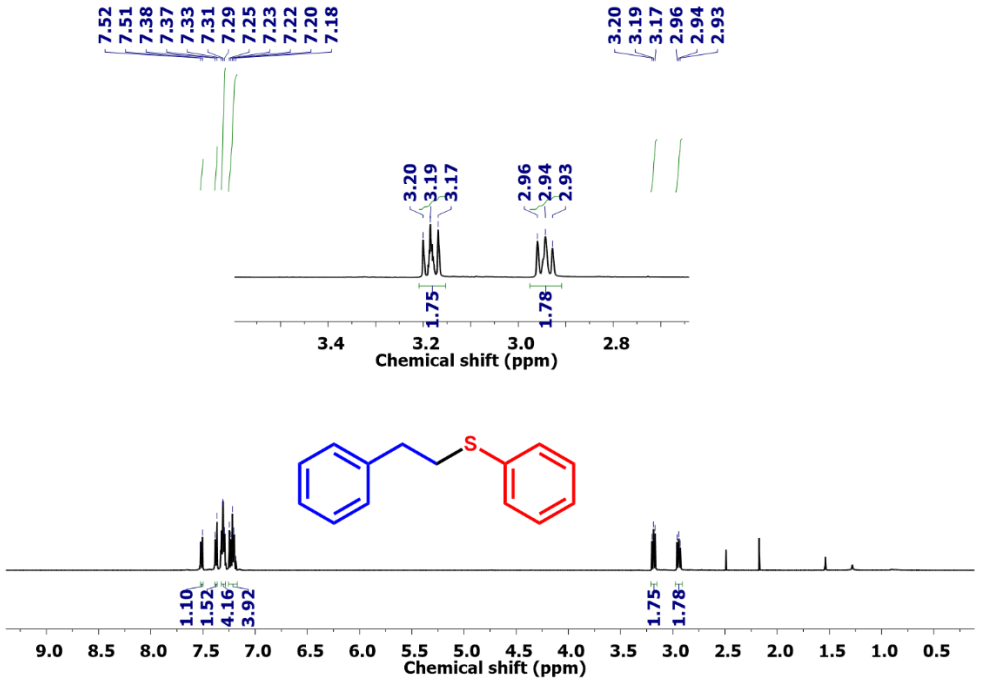
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **17c**.



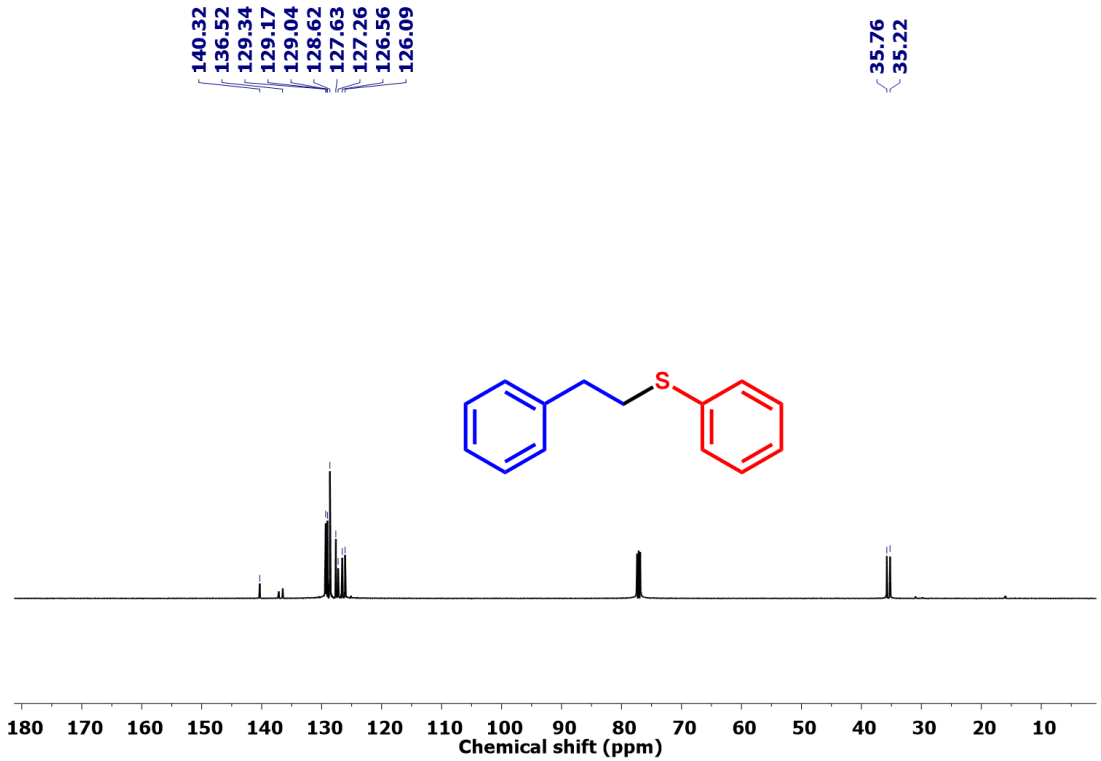
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **17c**.

Phenethyl(phenyl)sulfane (18c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (163 mg, 77%), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 1H), 7.38 (m, 1H), 7.33-7.29 (m, 4H), 7.25-7.18 (m, 4H), 3.19 (t, 2H), 2.94 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 136.5, 129.3, 129.1, 129.0, 128.6, 127.6, 126.0, 35.7, 35.2. Compound **18c** is consistent with literature reports.[22]



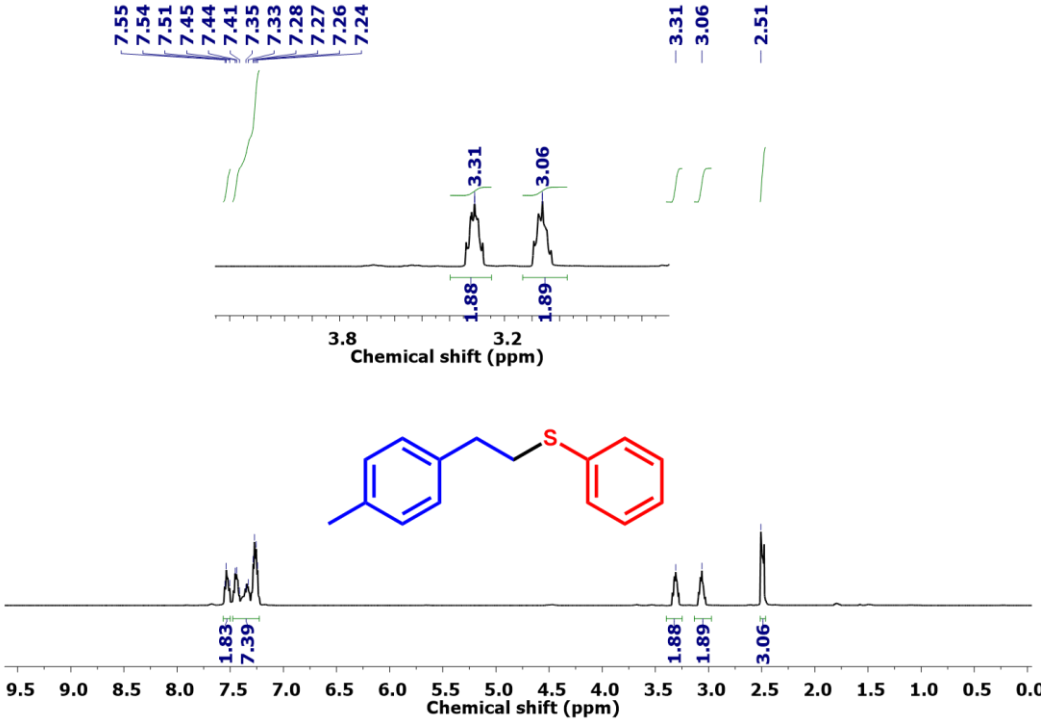
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **18c**.



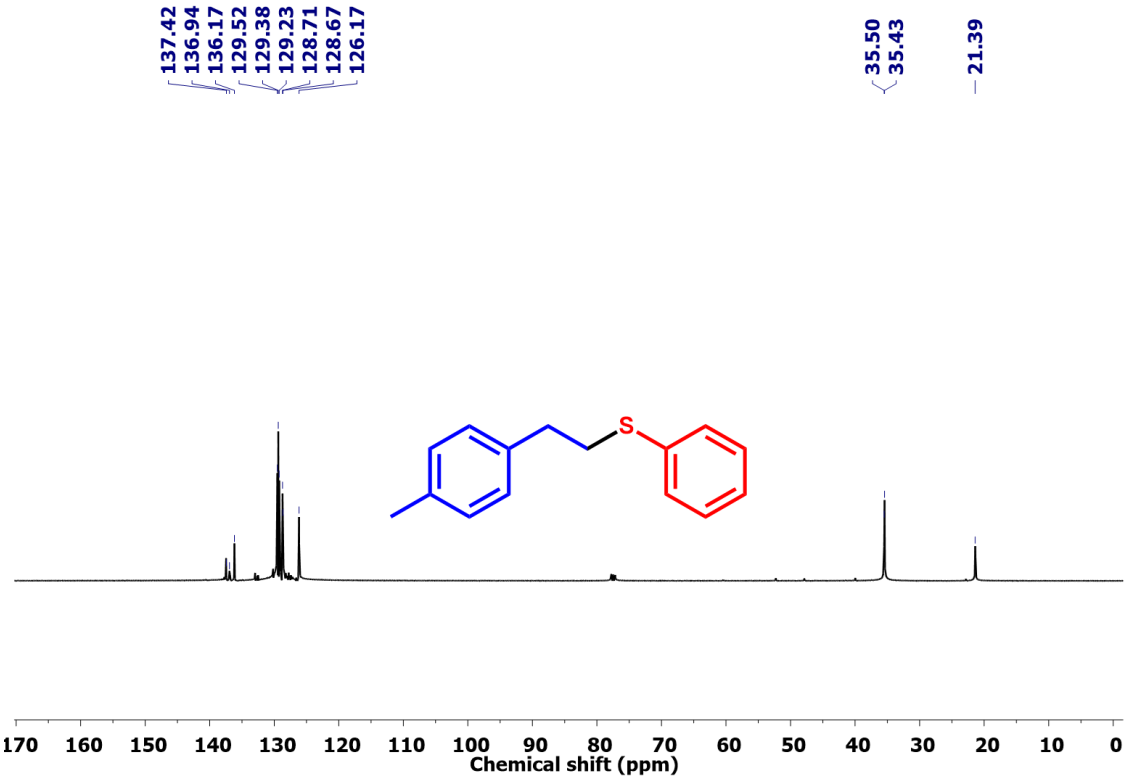
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **18c**.

1-Methylphenethyl(phenyl)sulfane (19c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (209 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 1H), 7.38 (m, 1H), 7.33-7.29 (m, 4H), 7.25-7.18 (m, 4H), 3.19 (t, 2H), 2.94 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.9, 136.1, 129.5, 129.3, 128.7, 128.6, 126.1, 35.5, 35.4, 21.3. Compound **19c** is consistent with literature reports.[22]



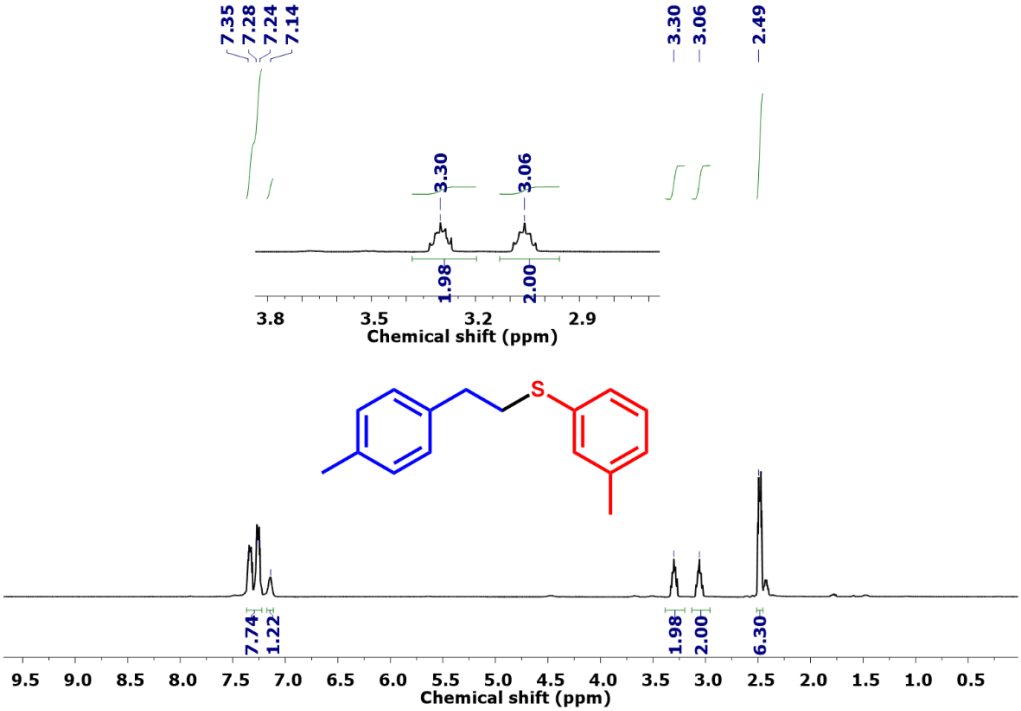
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **19c**.



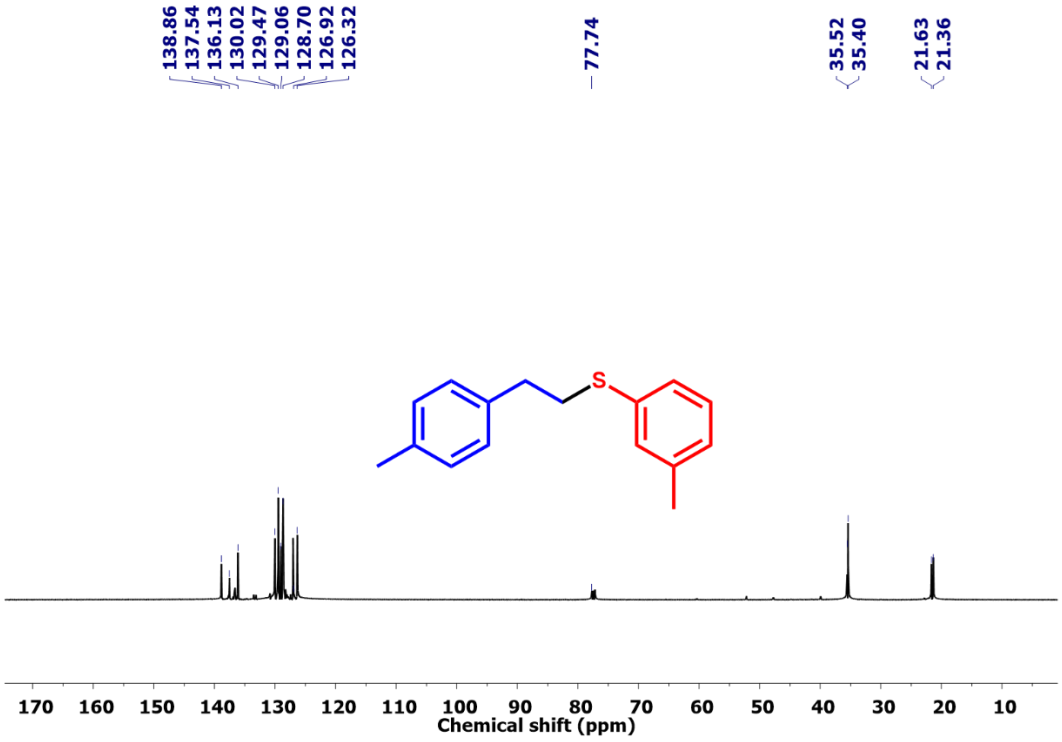
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **19c**.

4-Methylphenethyl(m-tolyl)sulfane (20c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (187 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 1H), 7.38 (m, 1H), 7.35-7.24 (m, 8H), 7.14 (s, 1H), 3.30 (d, 2H), 3.06 (t, 1H), 2.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 137.5, 136.1, 130.0, 129.4, 129.0, 128.7, 126.9, 126.3, 35.5, 35.4, 21.6, 21.3. Compound **20c** is consistent with literature reports.[22]



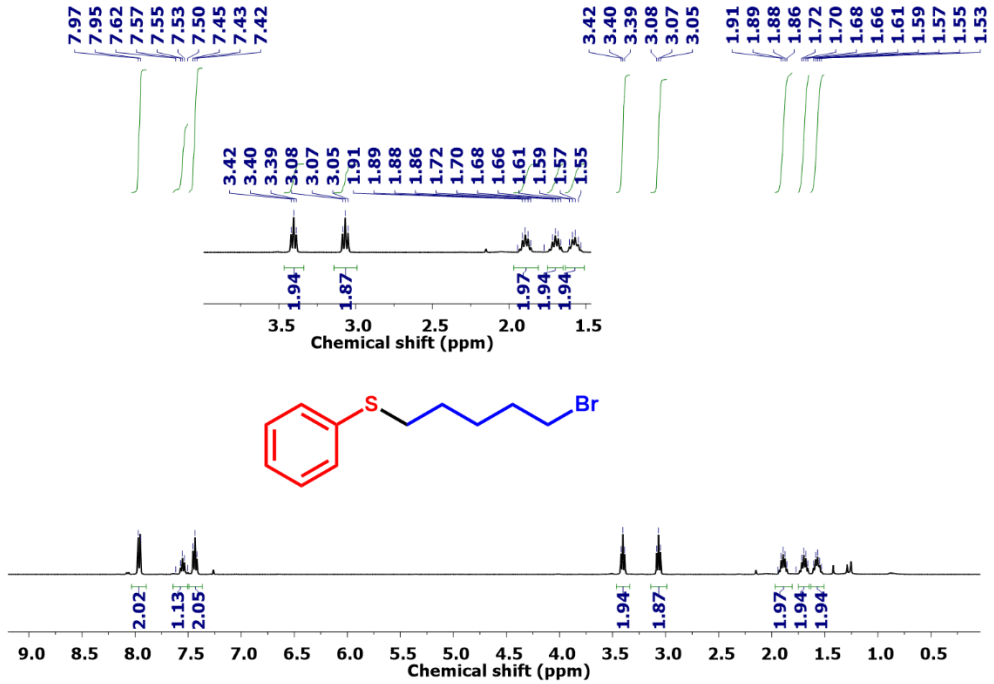
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **20c**.



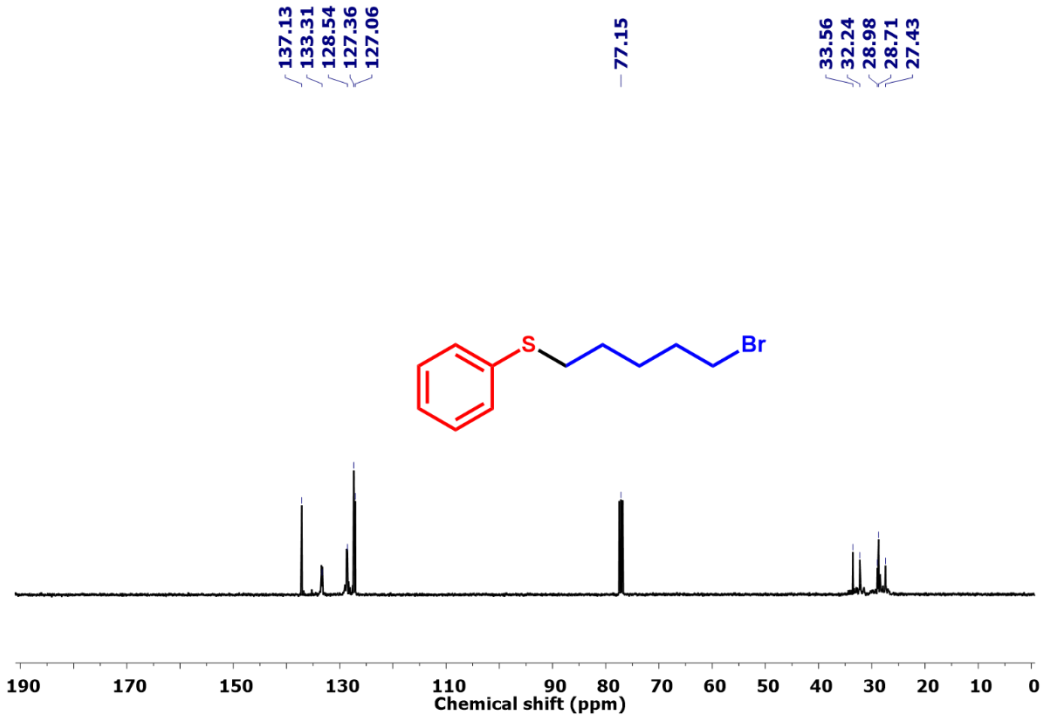
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **20c**.

(5-Bromopentyl)thiobenzene (21c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (146 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 2H), 7.62-7.53 (m, 1H), 7.45-7.42 (t, 2H), 3.40 (t, 2H), 3.07 (t, 2H), 1.94-1.86 (m, 2H), 1.77-1.66 (m, 2H), 1.61-1.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 133.3, 128.5, 127.3, 127.0, 33.5, 32.2, 28.9, 28.7, 27.4. Compound **21c** is consistent with literature reports.[24]



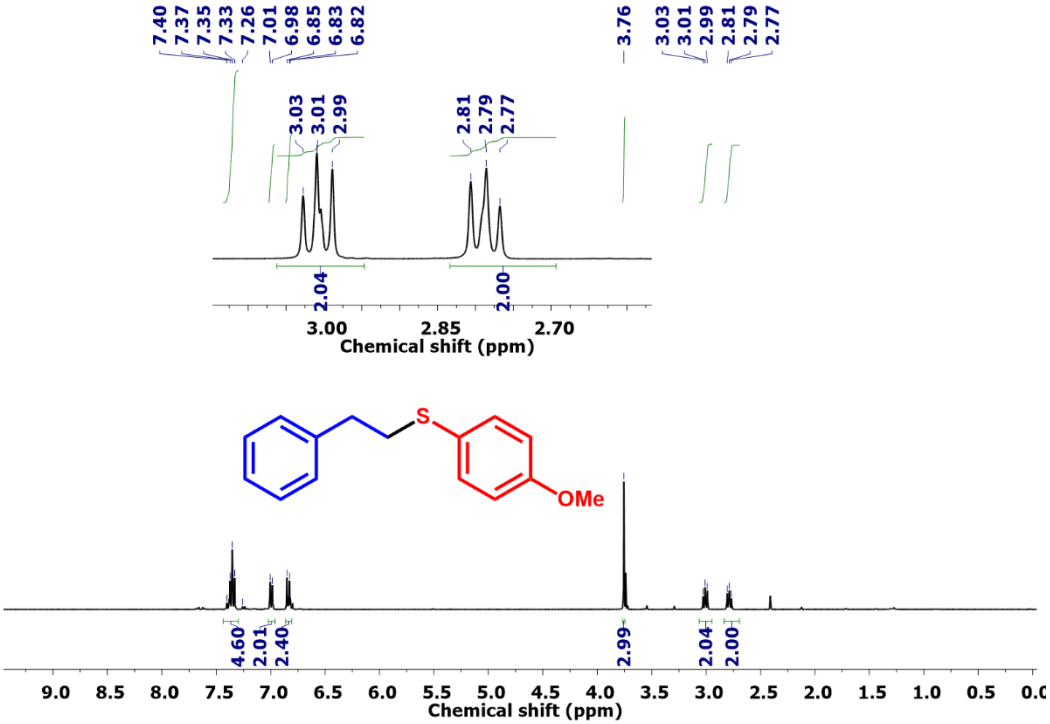
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **21c**.



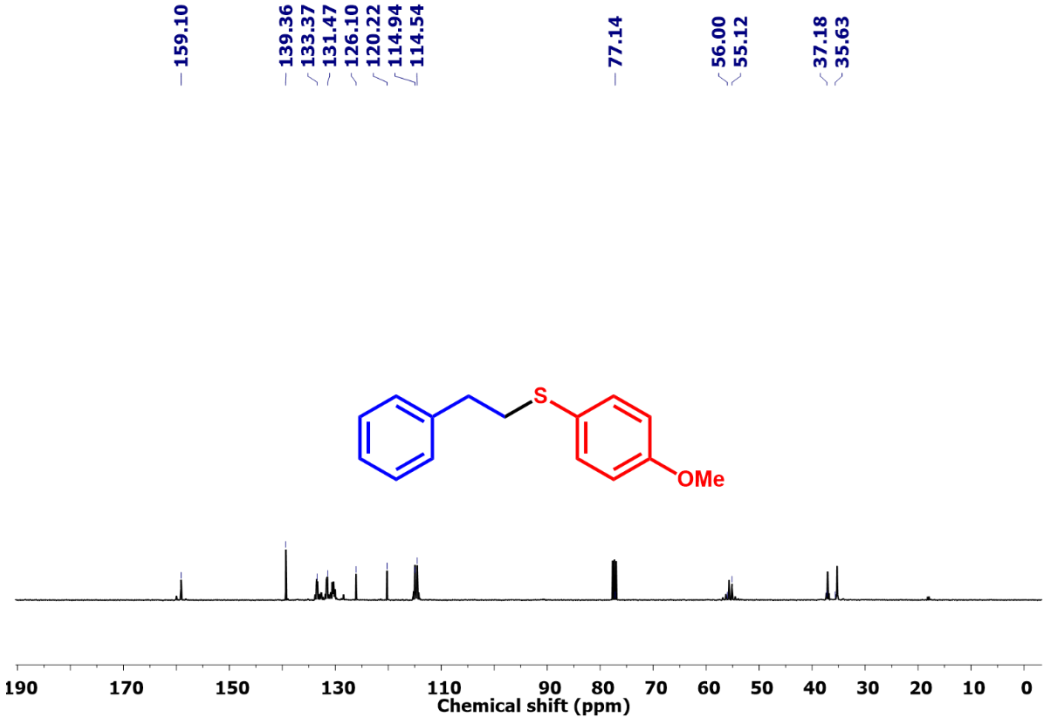
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **21c**.

1-Methoxy-4-[(2-phenylethyl)thio]benzene (22c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (171 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.33 (m, 4H), 7.00 (d, 2H), 6.85-6.82 (m, 3H), 3.76 (s, 3H), 3.01 (t, 2H), 2.79 (t, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.1, 139.3, 133.3, 131.4, 126.1 120.2, 114.9, 114.5, 56.0, 55.1, 37.1, 35.6. Compound **22c** is consistent with literature reports.[21]



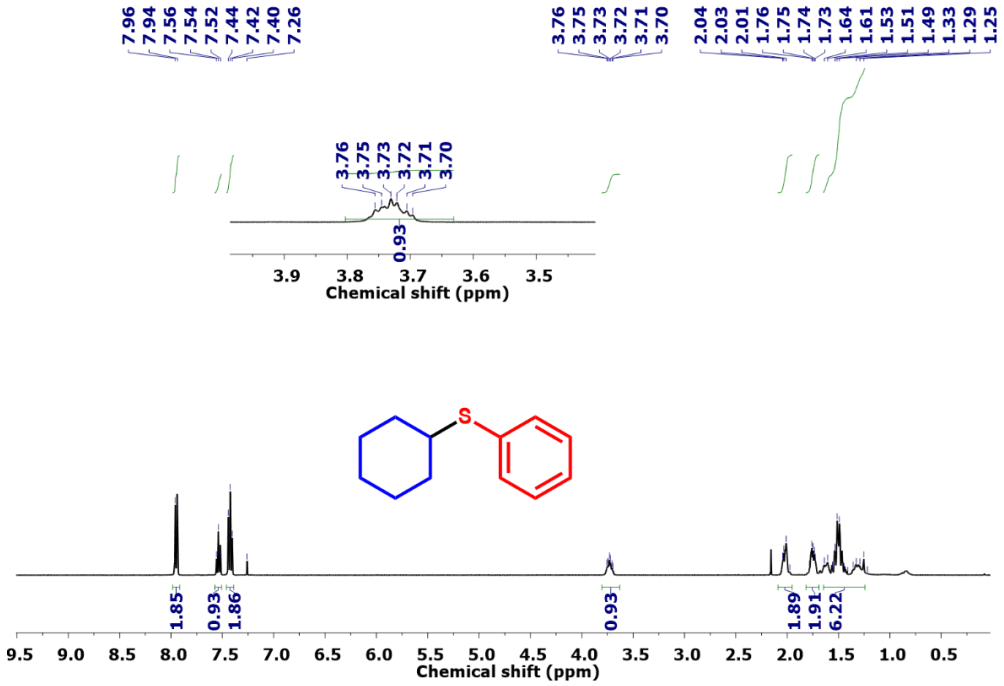
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **22c**.



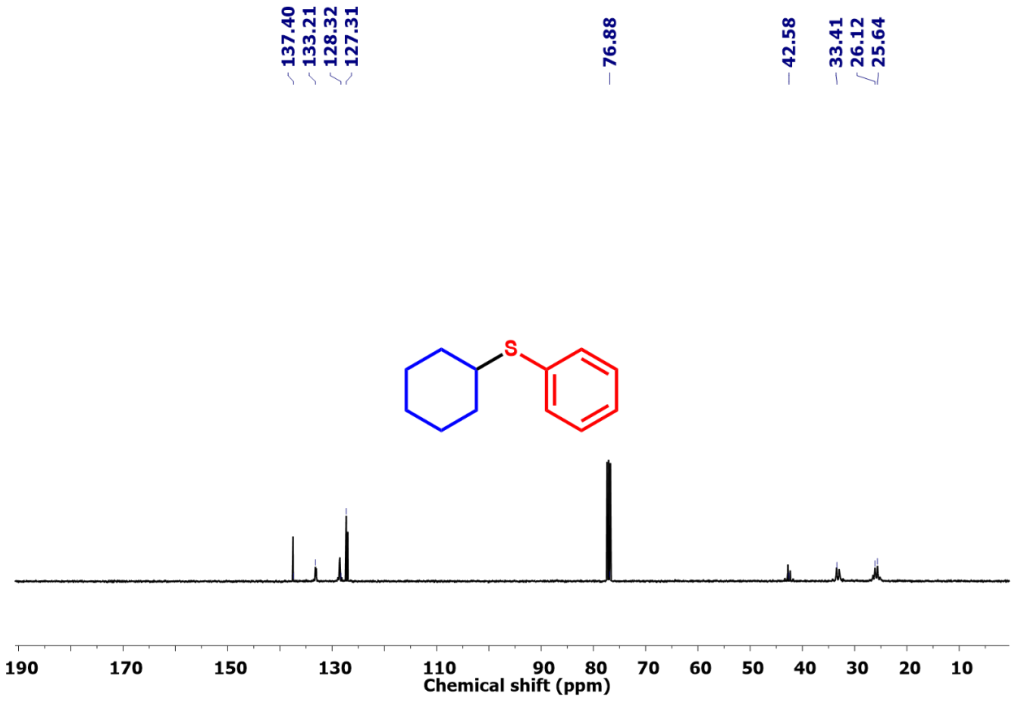
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **22c**.

Cyclohexylthio-benzene (23c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (145 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, 2H), 7.54 (t, 1H), 7.42 (t, 2H), 3.76-3.70 (s, 1H), 2.04-1.97 (m, 2H), 1.78-1.73 (m, 2H), 1.64-1.22 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.7, 128.4, 128.1, 126.3, 36.4, 33.6, 32.0, 31.7, 29.7, 22.0, 13.9. Compound **23c** is consistent with literature reports.[21]



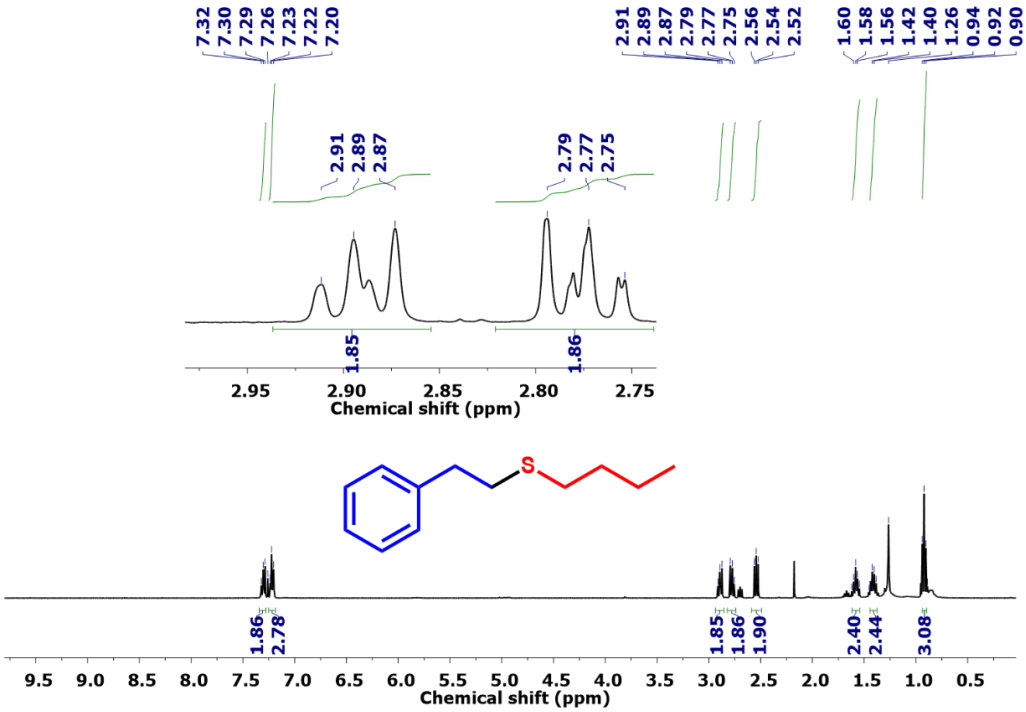
^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **23c**.



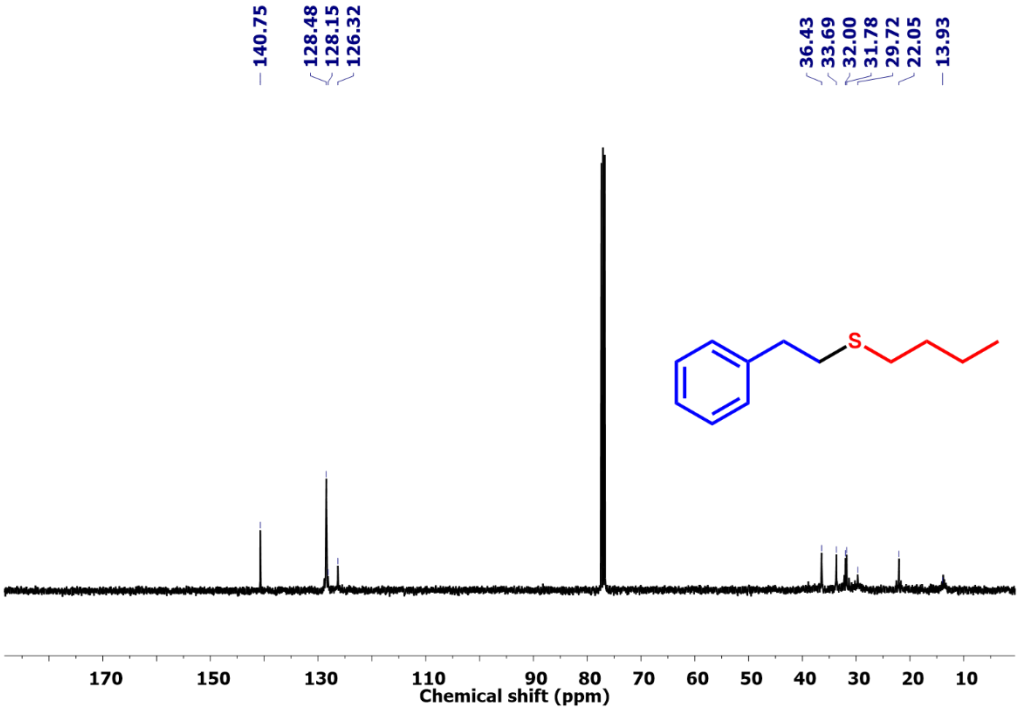
^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **23c**.

2-(Butylthio)ethyl]-benzene (24c)

Purified by column chromatography (hexane), yielding a yellow oily liquid (65 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (t, 2H), 7.23-7.20 (t, 3H), 2.89 (t, 2H), 2.77 (t, 2H), 2.54 (t, 2H), 1.62-1.55 (m, 2H), 1.45-1.38 (m, 2H), 0.94-0.89 (m, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 140.7, 128.4, 128.1, 126.3, 36.4, 33.6, 32.0, 31.7, 29.7, 22.0, 13.9. Compound **24c** is consistent with literature reports.[21]



^{1}H NMR ($CDCl_3$, 400 MHz) of Compound **24c**.



^{13}C NMR ($CDCl_3$, 100 MHz) of Compound **24c**.

References:

1 J. Xiong, Z. You, S. Lei, K. Zhao, Q. Bian, Y. Xiao and B. Cheng, *ACS Sustain. Chem. Eng.*, 2020, **8**, 13488–13496.

2 M. U. S. Bhat, M. A. Ganie, S. Kumar, M. A. Rizvi, S. Raheem and B. A. Shah, *J. Org. Chem.*, 2024, **89**, 4607–4618.

3 S. Mondal, R. Patra, J. Ray and D. Sarma, *ACS App. Nano Mat.*, 2025, **7**, 26765-26776.

4 K. Van Aken, L. Strekowski and L. Patiny, *Beilstein J. Org. Chem.*, 2006, **2**, 1–7.

5 W. Song, K. Dong and M. Li, *Org. Lett.*, 2020, **22**, 371–375.

6 H. Liu, L. Zhao, Y. Yuan, Z. Xu, K. Chen, S. Qiu and H. Tan, *ACS Catal.*, 2016, **6**, 1732–1736.

7 Y. Xiao, Y. K. Chun, S. C. Cheng, C. O. Ng, M. K. Tse, N. Y. Lei, R. Liu and C. C. Ko, *Catal. Sci. Technol.*, 2021, **11**, 556–562.

8 D. V. Wagle, H. Zhao and G. A. Baker, *Acc. Chem. Res.*, 2014, **47**, 2299–2308.

9 C. Liu, X. Qin, W. Yuan, H. Li, S. Sun, H. Li, T. Xu and Z. Yin, *Org.Lett.*, 2025, **27**, 5417-5422.

10 Y. Q. Miao, J. X. Kang, Y. N. Ma and X. Chen, *Green Chem.*, 2021, **23**, 3595–3599.

11 M. Wu, S. Huang, H. Hou, J. Lin, M. Lin, S. Zhou, Z. Zheng, W. Sun and F. Ke, *RSC Adv.*, 2022, **12**, 14724–14728.

12 T. McCallum and L. Barriault, *J. Org. Chem.*, 2015, **80**, 2874–8.

13 J. W. Ren, C. S. Han, H. X. Zhang, Q. H. Zhang, X. T. Song and J. H. Sun, *Org. Chem. Front.*, 2024, **11**, 4449–4455.

14 C. Liu and B. Zhang, *RSC Adv.*, 2015, **5**, 61199–61203.

15 N. Katta, M. Ojha, A. Murugan, S. Arepally and D. S. Sharada, *RSC Adv.*, 2020, **10**, 12599–12603.

16 J. Singh and A. Sharma, *New J. Chem.*, 2022, **46**, 16220–16242.

17 X. Chen, Z. Lian and S. Kramer, *Angew. Chemie - Int. Ed.*, 2023, ***62***, e202217638.

18 S. S. Shah, M. Shee, Y. Venkatesh, A. K. Singh, S. Samanta and N. D. P. Singh, *Chem. - A Eur. J.*, 2020, **26**, 3703–3708.

19 C. Jian, Z. Li, Y. Mao, Y. Zhu, W. Yu, J. Wu and S. Li, *Org. Lett. 2025,* **27**, 2576-2581.

20 C. Q. Qin, X. N. Liu, M. Z. Gu, Y. B. Xu, G. S. Chen and Y. L. Liu, *New J. Chem.*, 2024, **49**, 366–370.

21 H. Ali, B. Mahto, A. Barhoi and S. Hussain, *ACS Appl. Nano Mater.*,2025, **8**, 5001-5013.

22 H. Ali, B. Mahto, A. Barhoi and S. Hussain, *Nanoscale*, 2023, **15**, 14551–14563.

23 Li, Y., Cai, J., Hao, M. and Li, Z., *Green Chem.*,2019, **21**, 2345-2351.

24 Kuciński, K., Pawluć, P. and Hreczycho, G., *Adv. Synth. & Cat.*, 2015, **18**, 3936-3942.