Supporting information

Regulating the Exciton Binding Energy of Covalent Triazine Frameworks for Enhancing Photocatalysis

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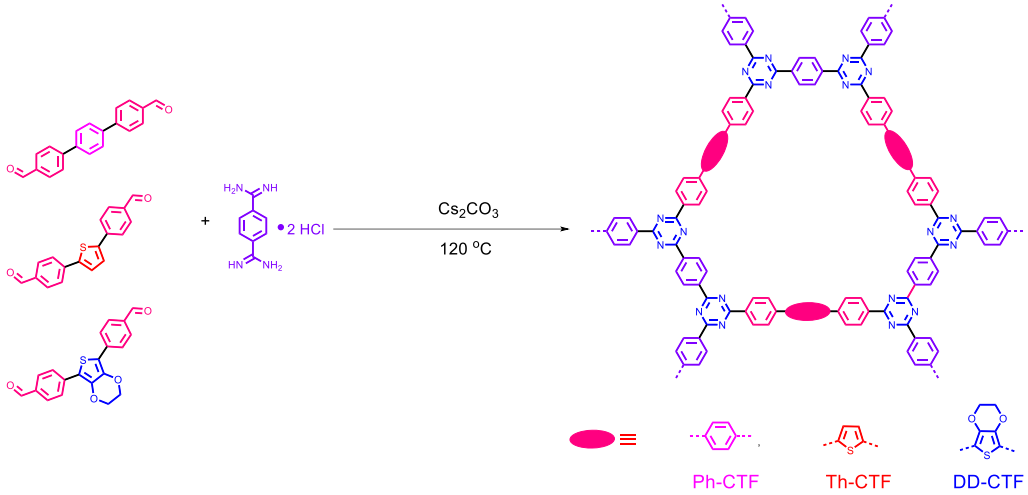
1. Preparation procedures

1.1 Synthesis of intermediates, Ph-CTF, Th-CTF , and DD-CTF



Scheme S1. Synthesis routes of Ph-CTF, Th-CTF, and DD-CTF

1.1.1 Preparation of 4,4'-(thiophene-2,5-diyl)dibenzaldehyde

A mixture of 2,5-dibromothiophene (1.93 g, 0.01 mol), (4-formylphenyl)boronic acid (3.75g, 0.025 mol), K_2CO_3 (2.76 g, 0.02 mol), $Pd[P(C_6H_5)_3]_4$ (115 .5 mg, 0.1 mmol) and H_2O (3.0 mL) in 1,4-dioxane (45.0 mL) was heated to 100 °C under N_2 for 24h. After cooling to room temperature, the reaction mixture was concentrated to remove the solvent and the residue was purified by flash column chromatography to obtain as a white solid in 61 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 10.0 (s, 2H), 7.92-7.90 (d, *J* = 8.0 Hz, 4H), 7.79-7.78 (d, *J* = 8.0 Hz, 4H), 7.48 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 191.5, 143.9, 139.5, 135.5, 130.6, 126.4, 126.0 ppm.

1.1.2 Preparation of 4,4'-(2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-diyl)dibenz-aldehyde

A mixture of 5,7-dibromo-2,3-dihydrothieno[3,4-b][1,4]dioxine (2.98 g, 0.01 mol), (4-formylphenyl)boronic acid (3.75g, 0.025 mol), K_2CO_3 (2.76 g, 0.02 mol), $Pd[P(C_6H_5)_3]_4$ (115 .5 mg, 0.1 mmol) and H_2O (3.0 mL) in 1,4-dioxane (45.0 mL) was heated to 100 °C under N_2 for 24h. After cooling to room temperature, the reaction mixture

was concentrated to remove the solvent and the residue was purified by flash column chromatography to obtain as a white solid in 53 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.99 (s, 2H), 7.94-7.92 (d, *J* = 8.0 Hz, 4H), 7.89-7.88 (d, *J* = 4.0 Hz, 4H), 4.45 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 191.6, 140.7, 138.6, 134.5, 130.3, 126.3, 116.4, 64.8 ppm.

1.1.3 Preparation of Th-CTF

In a typical synthesis, terephthalamidine dihydrochloride (235.2 mg, 1.0 mmol), 4,4'-(thiophene-2,5-diyl)dibenzaldehyde (146.0 mg, 0.5 mmol), and Cs_2CO_3 (716.8 mg, 2.2 mmol) were dissolved in dimethyl sulfoxide (DMSO) (20.0 mL) and H_2O (0.2 mL) and then heated to 60 °C, 80 °C, and 100°C for 12h in a 50 mL round-bottom flask fitted with a condenser under N_2 atmosphere, separately. The above mixtures were continued to be heated at 120 and 150 °C for 1.5 days respectively before the reaction was complete. The resulting precipitate was filtered and washed with deionized water to remove the inorganic salt, which was further purified by Soxhlet extraction with methanol and THF, respectively. Finally, after being dried at 80 °C under vacuum, a yellow power was obtained and denoted as Th-CTF in 80% yield. Ph-CTF and DD-CTF were obtained according to the same procedures as Th-CTF by performing [1,1':4',1''-terphenyl]-4,4''-dicarbaldehyde and 4,4'-(2,3-dihydrothieno[3,4-b][1,4]dioxine5,7diyl)diben-zaldehyde as the starting monomers.

1.2 General procedures for photocatalysis

Procedure I for photocatalytic Ugi reaction.

Typically, a mixture of *N,N,4*-trimethylaniline (40.6 mg, 0.30 mmol), H_2O (0.2 mL), DD-CTF (20 mg), and ethyl 2-isocyanoacetate (67.87 mg, 0.60 mmol) in CH_3CN (3.0 mL) were stirred at room temperature under O_2 atmosphere (1.0 atm) while irradiated with 14 W blue LEDs

(0.2 W/cm^2). After the reaction completion monitoring by TLC, the solvent was removed to give the residues, which could be further obtained by flash column chromatography with petroleum ether/ethyl acetate as the eluent.

Procedure II for photocatalytic synthesis of Thiocarbamates.

A mixture of 4-methylbenzenethiol (37.3 mg, 0.30 mmol), ethyl 2-isocyanoacetate (67.87 mg, 0.60 mmol), H_2O (0.2 mL), and DD-CTF (20 mg) in ethyl acetate (3.0 mL) were stirred at room temperature in the presence of O_2 atmosphere while irradiated with 14 W blue LEDs (0.2 W/cm^2). Upon the completion of reaction as monitored by TLC, the solvent was then removed under vacuum to give the residues, which could be further obtained by flash column chromatography with PE/EA (10:1-1:1) as the eluent.

Procedure III for photocatalytic oxidative S-P(O) coupling

Typically, a mixture of 4-methylbenzenethiol (37.3 mg, 0.30 mmol), diphenylphosphine oxide (121.3 mg, 0.60 mmol), and DD-CTF (20 mg) in DMF (3.0 mL) were stirred at room temperature under O_2 atmosphere (1.0 atm) while irradiated with 14 W blue LEDs (0.2 W/cm^2). After the reaction completion monitoring by TLC, the solvent was removed to give the residues, which could be further obtained by flash column chromatography with petroleum ether/ethyl acetate as the eluent.

2.Measurements

The ^{1}H and ^{13}C NMR spectra were measured with the deuterated solvents (Bruker AM-400 MHz NMR spectrometer). The corresponding Fourier transform infrared (FT-IR) spectra were measured in the 400-4000 cm^{-1} region (VARIAN 1000 FT-IR spectrometer). The solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker AVANCE III 400 MHz spectrometer. To calculate the surface area and pore volume of the polymers, the Brunauer-Emmett Teller (BET) approach was employed with the application rate of 77 K and the specimens dried in vacuum at 100°C during 14 h prior to measurement (Micromeritics ASAP 2020M). The distribution of the pore size of the polymers were acquired by means of sorption branching (non-local density functional theory approach, NLDFT). The surfaces of the polymers were characterized by an acceleration pressure from 8.0 kV (FEI SIRION200). The UV-Vis adsorption spectra of the powders in the solid state were obtained on a Scan UV-Vis spectrophotometer (U-4100 spectrometer). The Mott-Schottky analysis and electrochemical impedance spectrum (EIS) were carried out at a dark galvanic workstation at room temperature (CHI760E). Optical current testing of the obtained CTFs such as photocurrent response was conducted on a VersaSTAT 3 galvanic workstation and a 300W Xe lamp. Analysis of temporally dependent luminescence spectra of physical specimens was conducted using the FLS-980 fluorescence lifetime chromatograph. DFT calculations were carried out in the Gaussian 09W program package. Gaussian View 5.0 was used for visualization. The geometry calculation was optimized with the B3LYP/6-31G(d) theory level.

3. Characterization

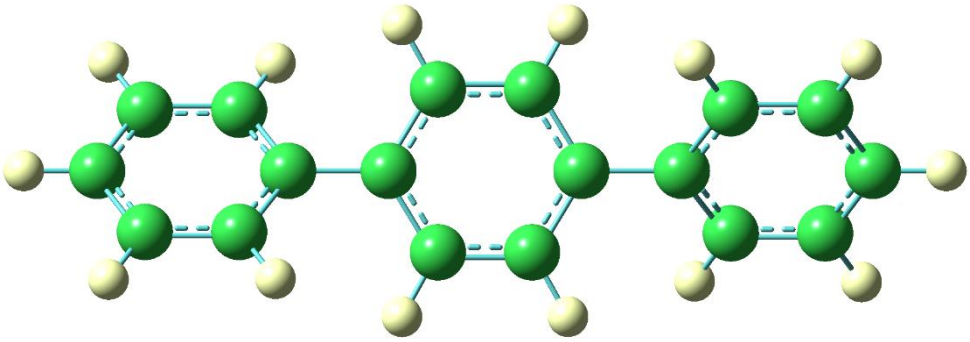


Figure S1. Diagram of molecular dipoles for 1,1':4',1''-terphenyl units (0.000 Debye).

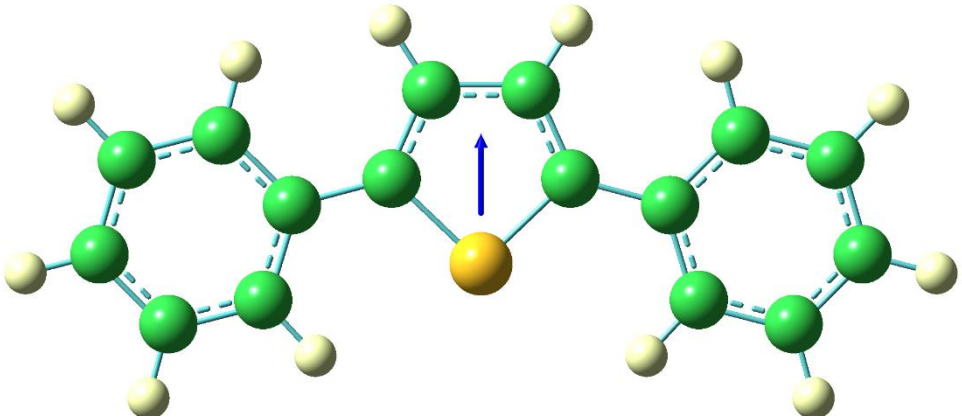


Figure S2. Diagram of molecular dipoles for 1,1':4',1''-terphenyl units (0.5586 Debye).

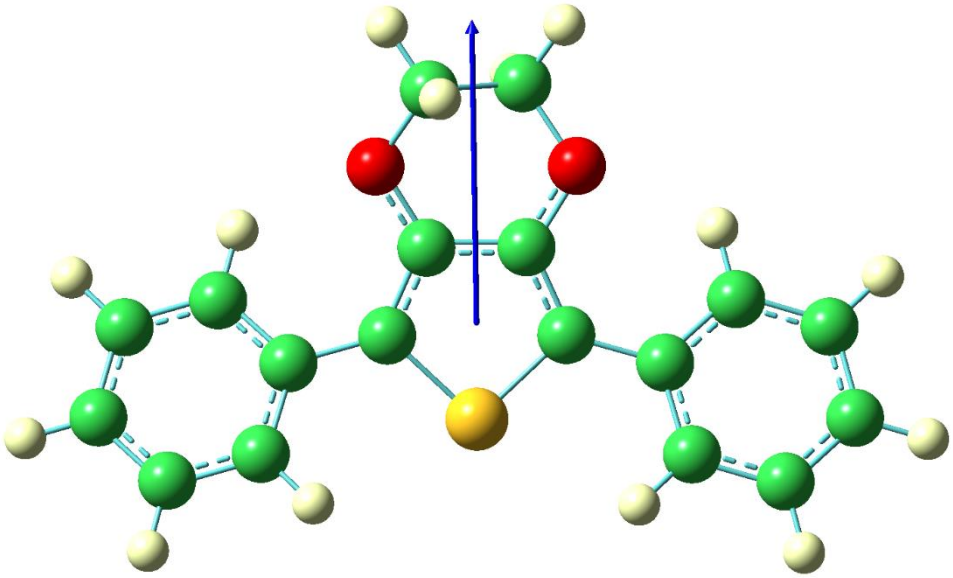


Figure S3. Diagram of molecular dipoles for 1,1':4',1''-terphenyl

units (2.7542 Debye).

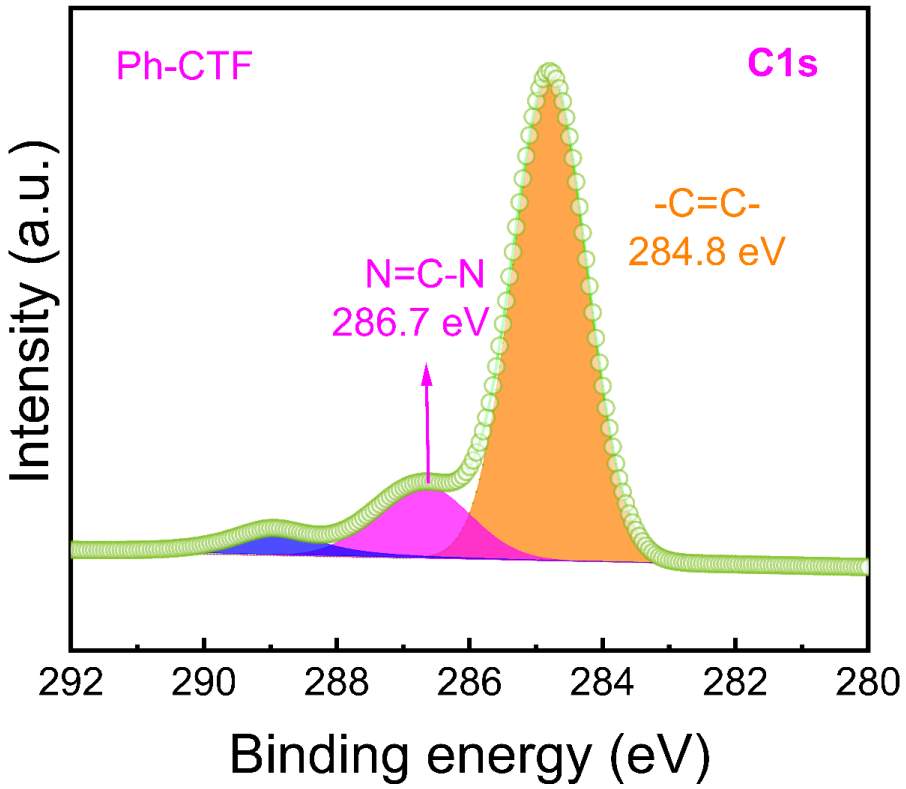


Figure S4. High-resolution XPS C1 s spectrum of Ph-CTF

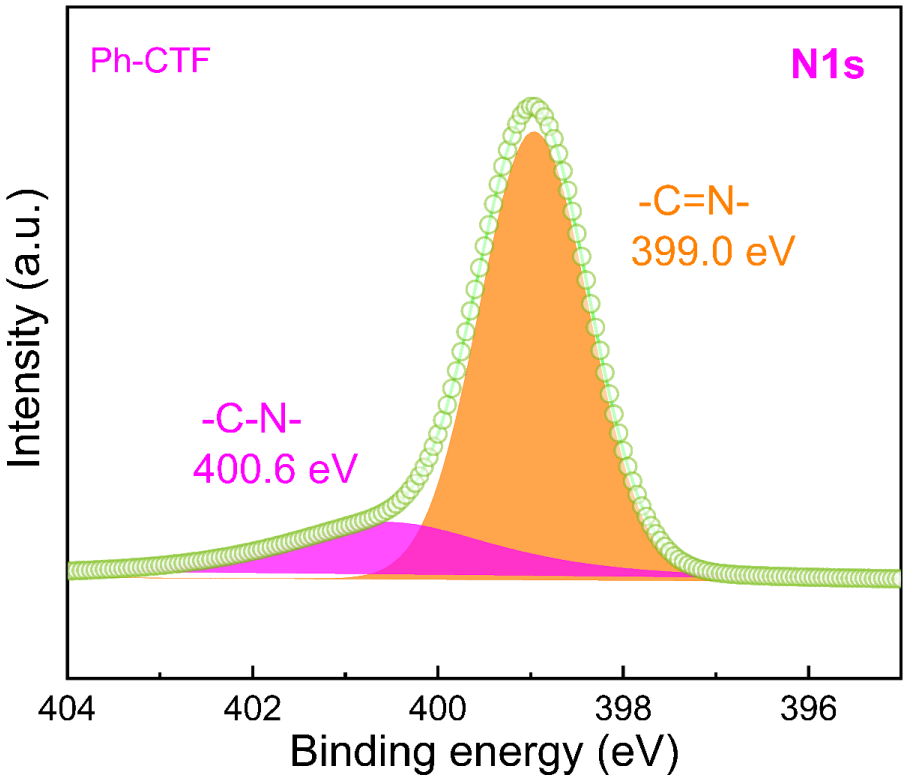


Figure S5. High-resolution XPS N1 s spectrum of Ph-CTF

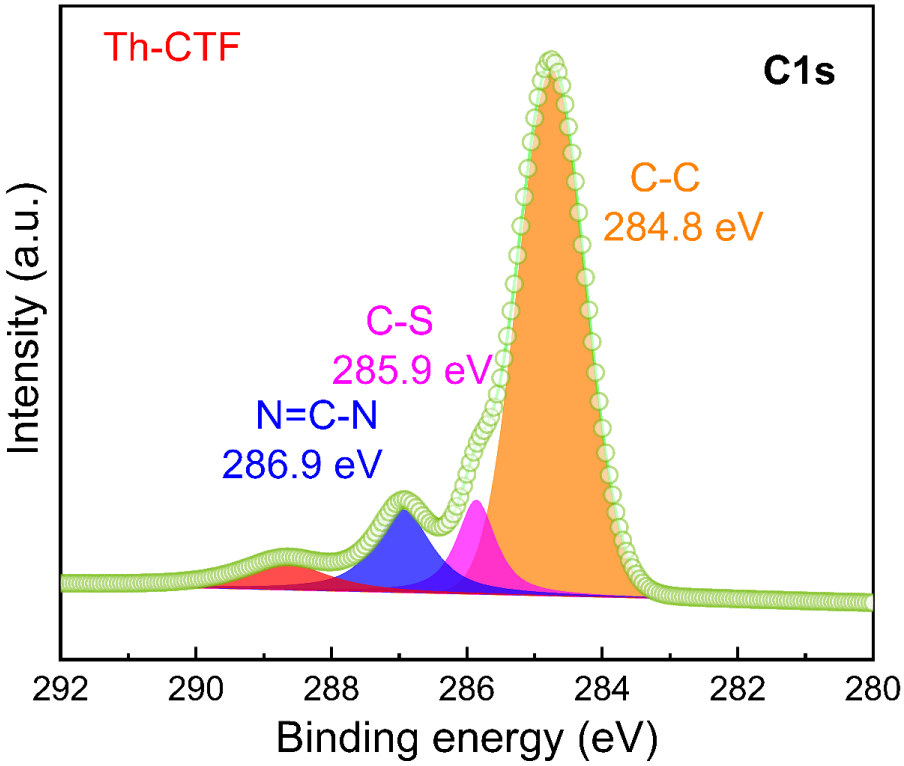


Figure S6. High-resolution XPS C1 s spectrum of Th-CTF

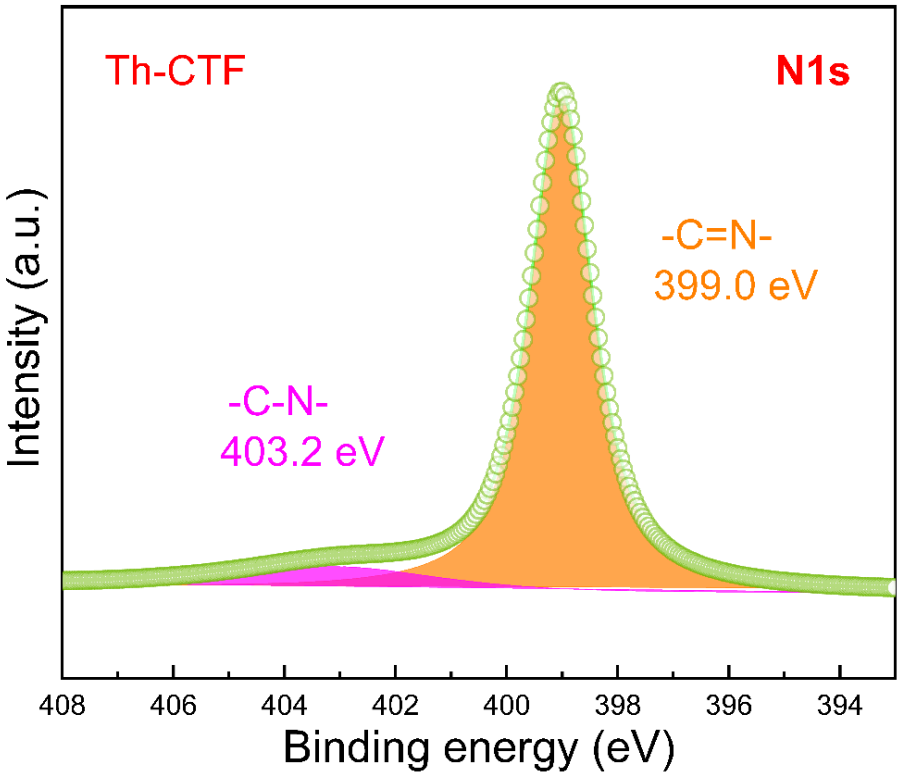


Figure S7. High-resolution XPS N1 s spectrum of Th-CTF

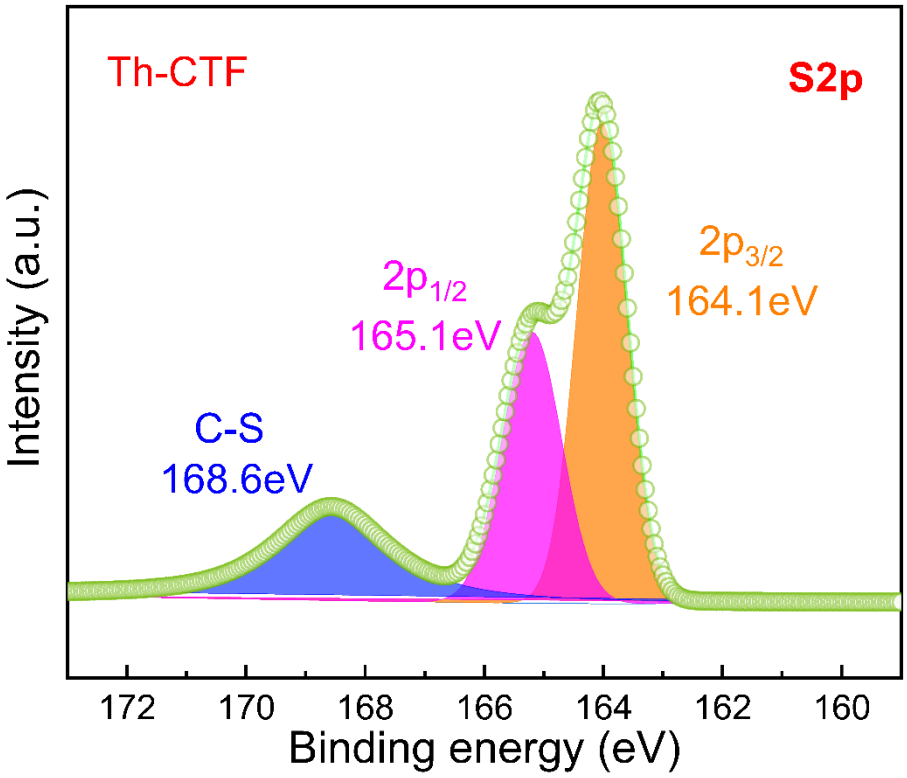


Figure S8. High-resolution XPS S 2p spectrum of Th-CTF

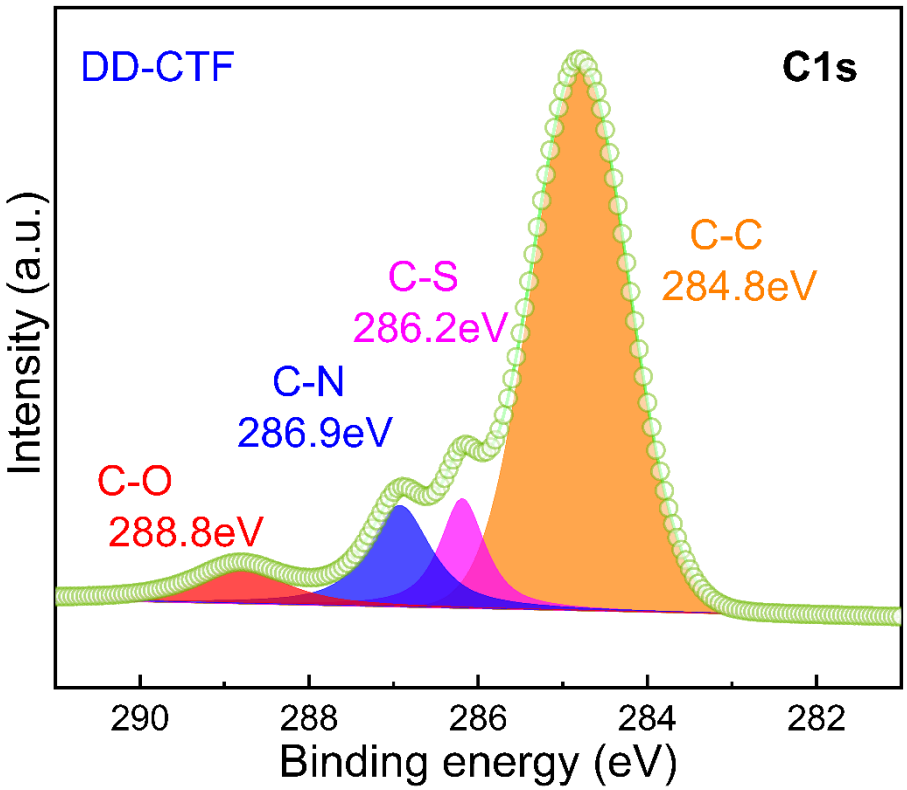


Figure S9. High-resolution XPS C1 s spectrum of DD-CTF

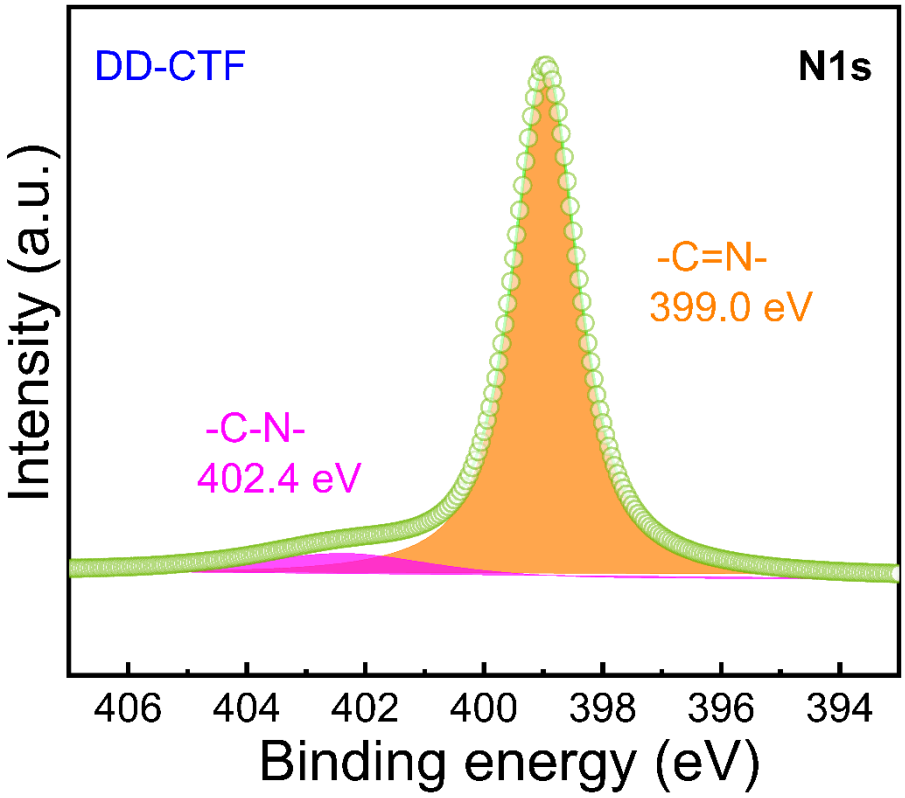


Figure S10. High-resolution XPS N1 s spectrum of DD-CTF

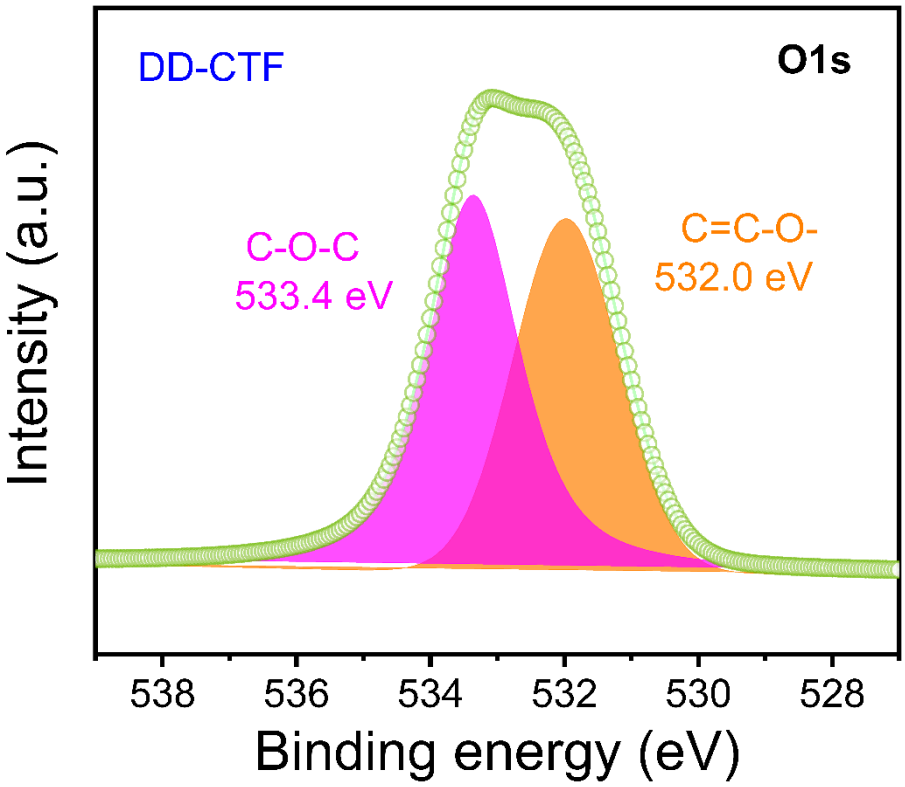


Figure S11. High-resolution XPS O1 s spectrum of DD-CTF

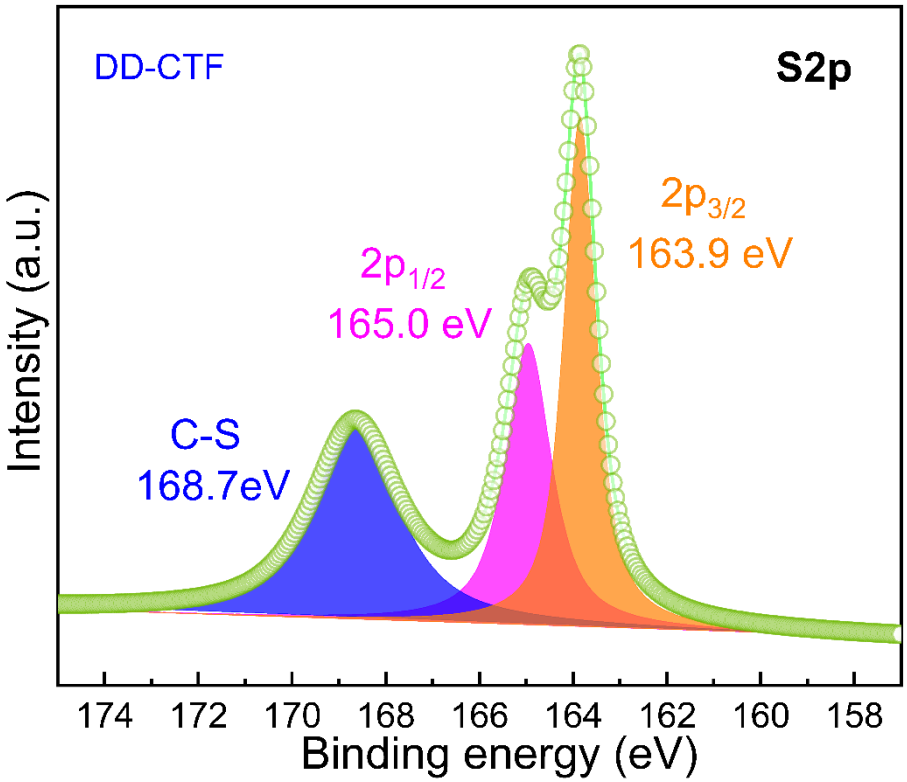


Figure S12. High-resolution XPS S 2p spectrum of DD-CTF

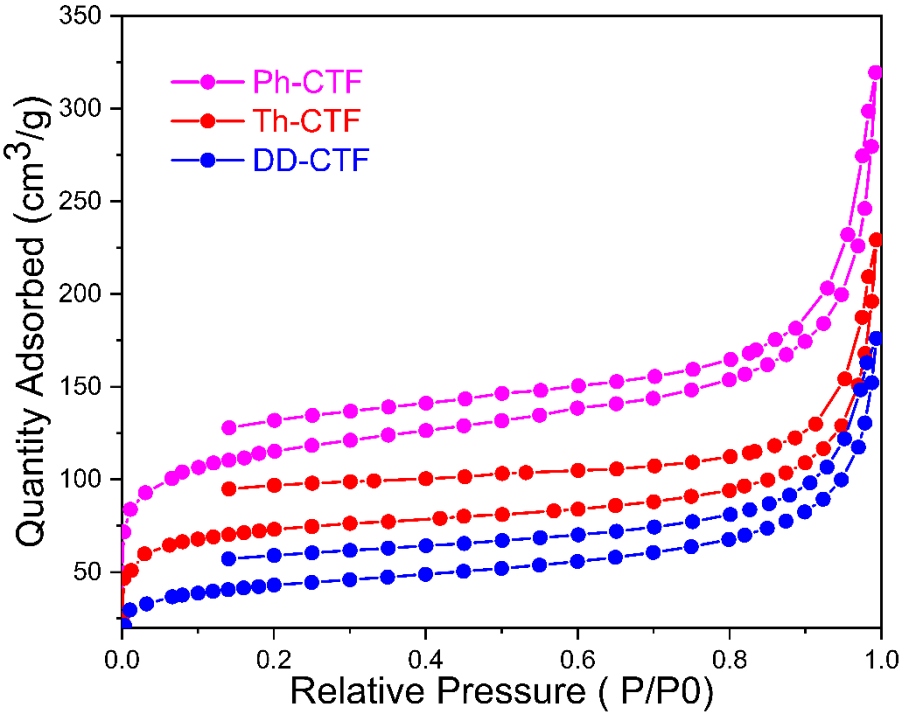


Figure S13. Nitrogen sorption isotherms of Ph-CTF, Th-CTF and DD-CTF at 77 K

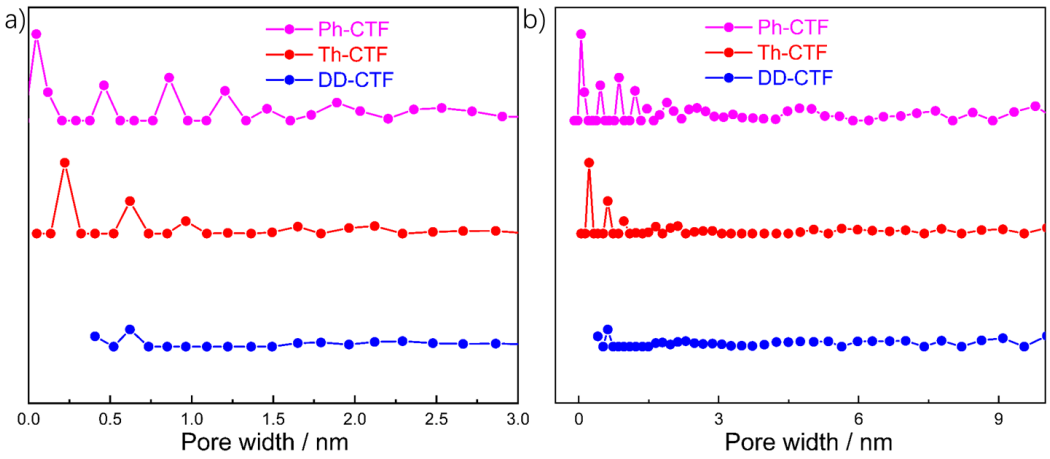


Figure S14. Pore size distributions of Ph-CTF, Th-CTF and DD-CTF

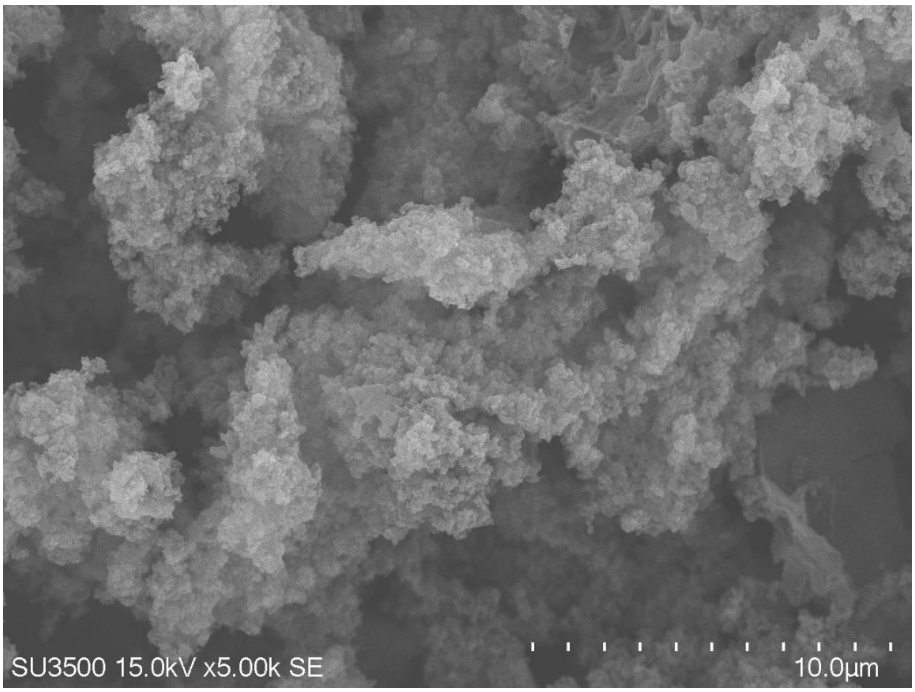


Figure S15. SEM of Ph-CTF

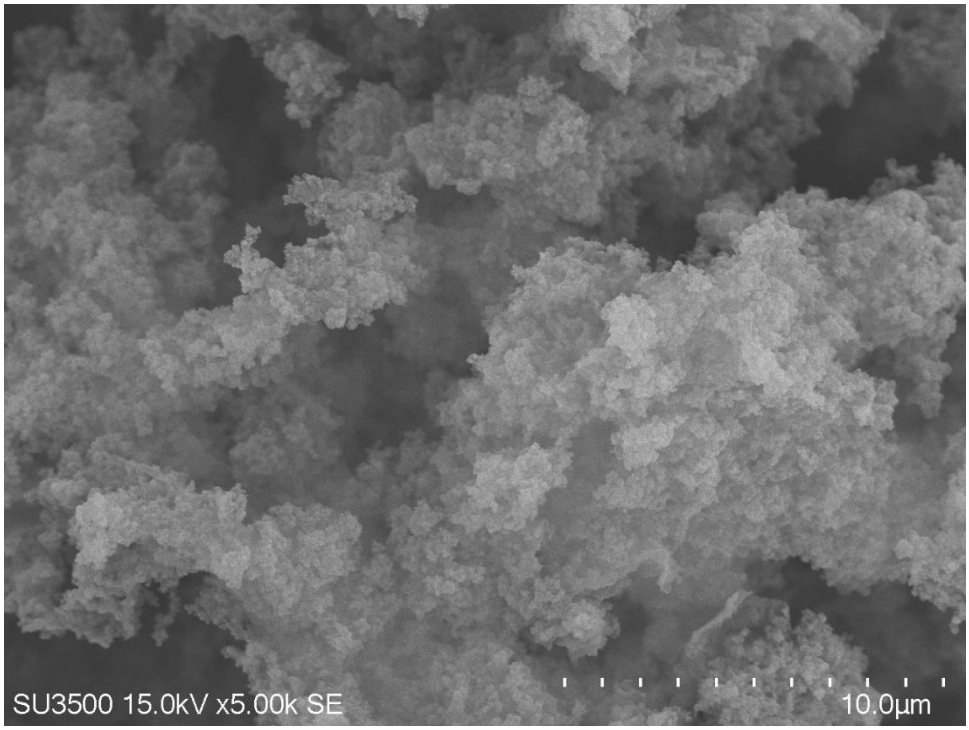


Figure S16. SEM of Th-CTF

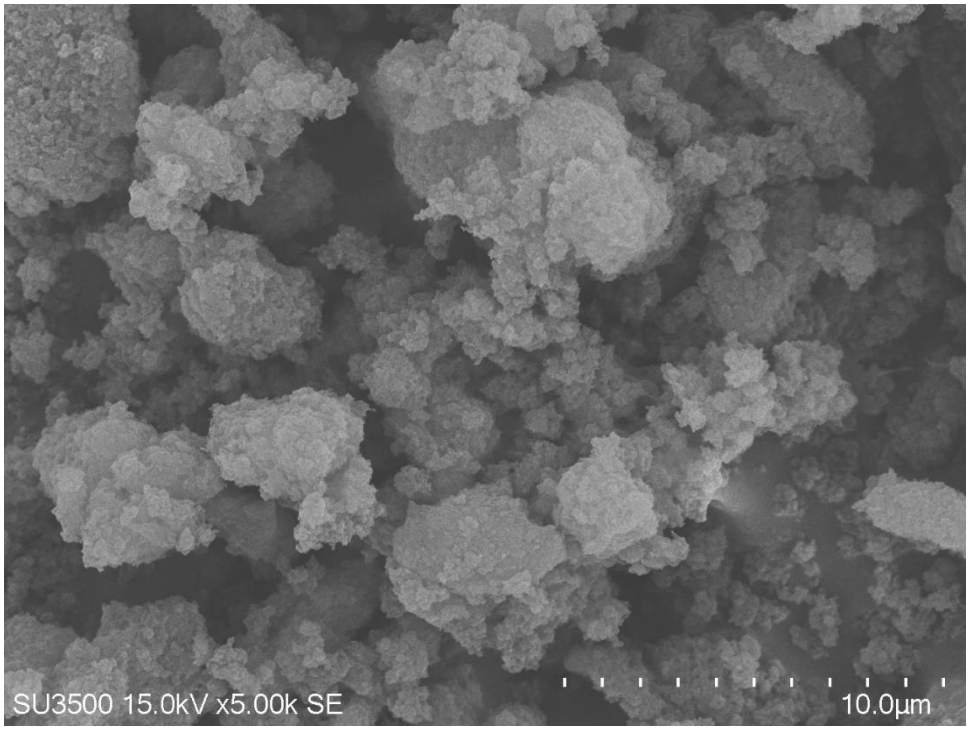


Figure S17. SEM of DD-CTF

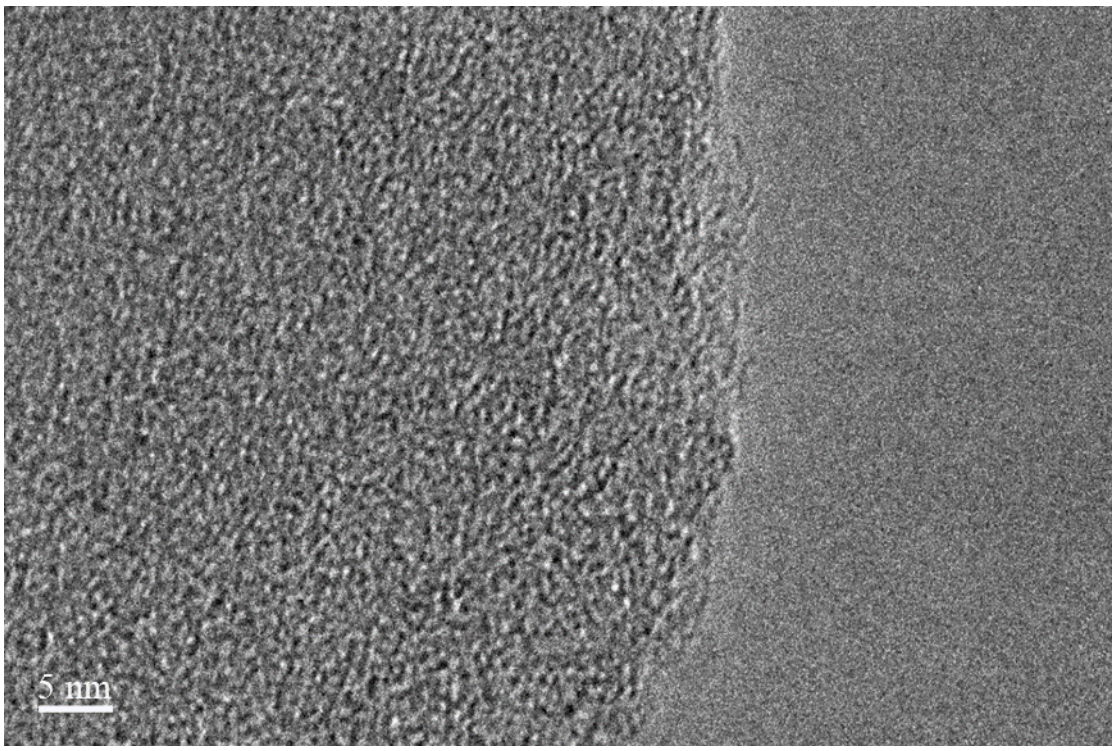


Figure S18. TEM of Ph-CTF

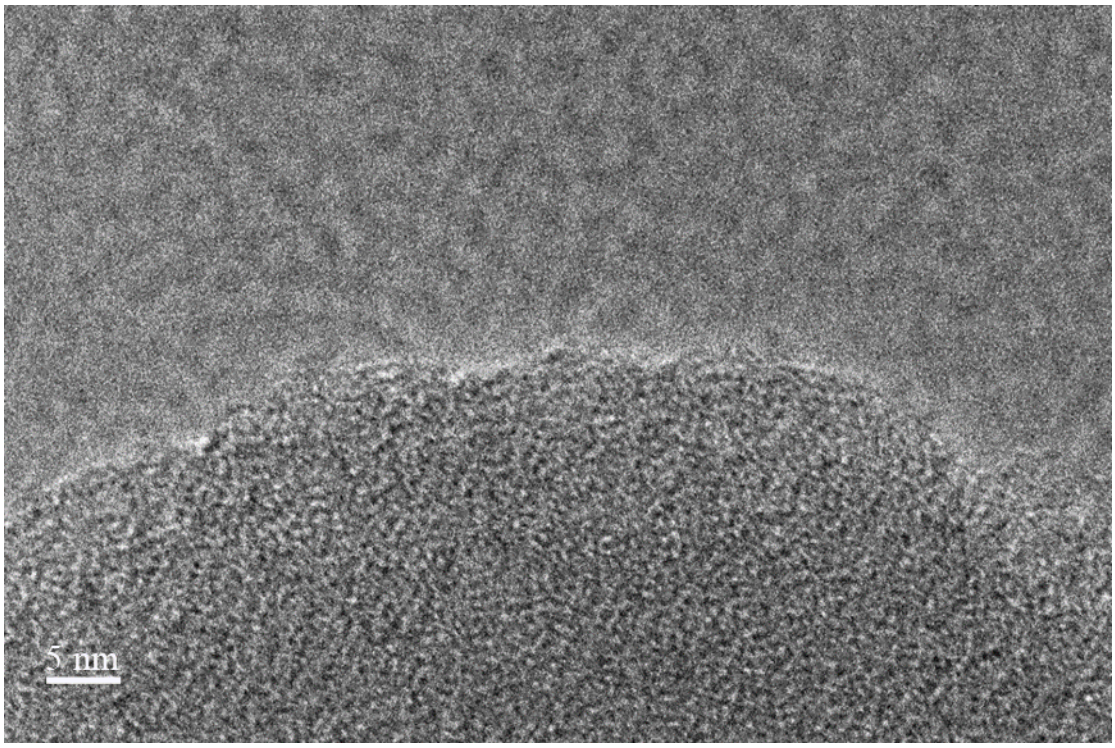


Figure S19. TEM of Th-CTF

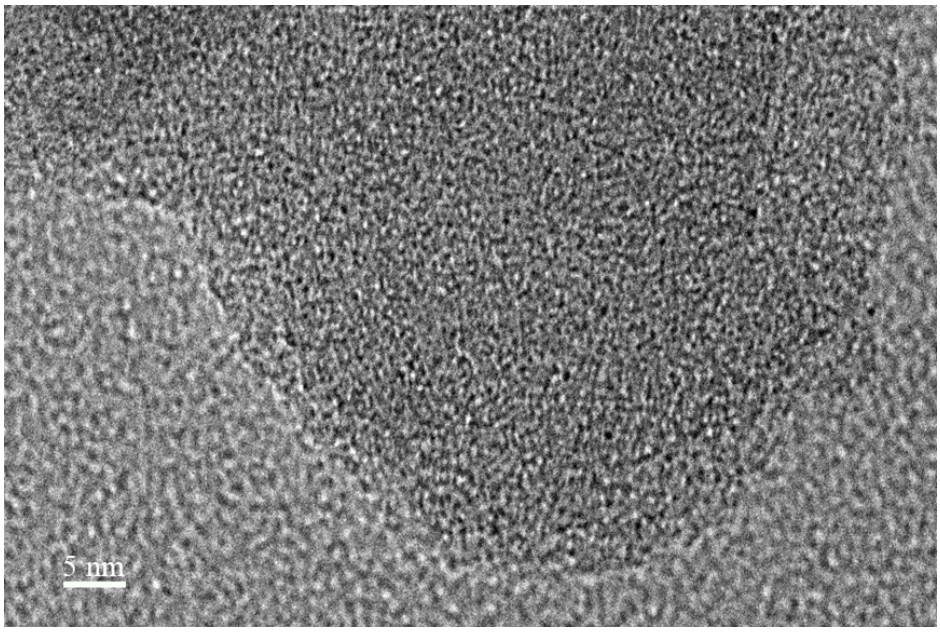


Figure S20. TEM of DD-CTF

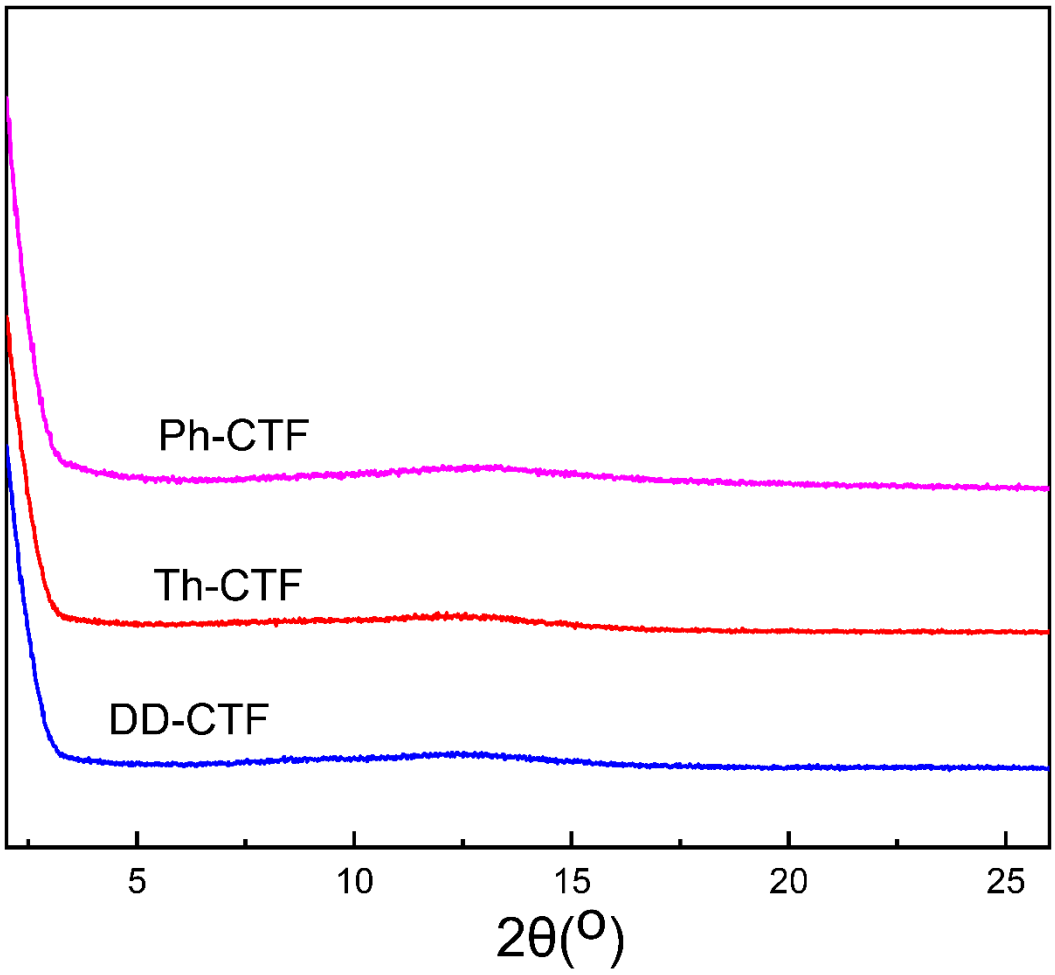


Figure S21. XRD of Ph-CTF, Th-CTF, and DD-CTF

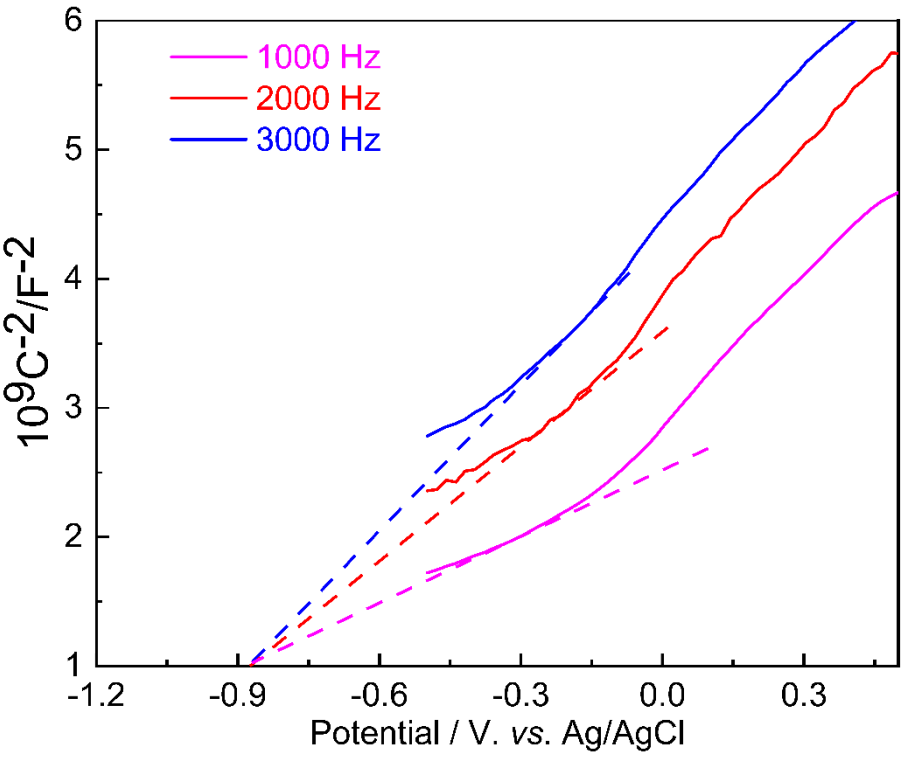


Figure S22. Mott-Schottky plots for Ph-CTF in 0.2 M Na_2SO_4 aqueous solution at 1000, 2000 and 3000 Hz

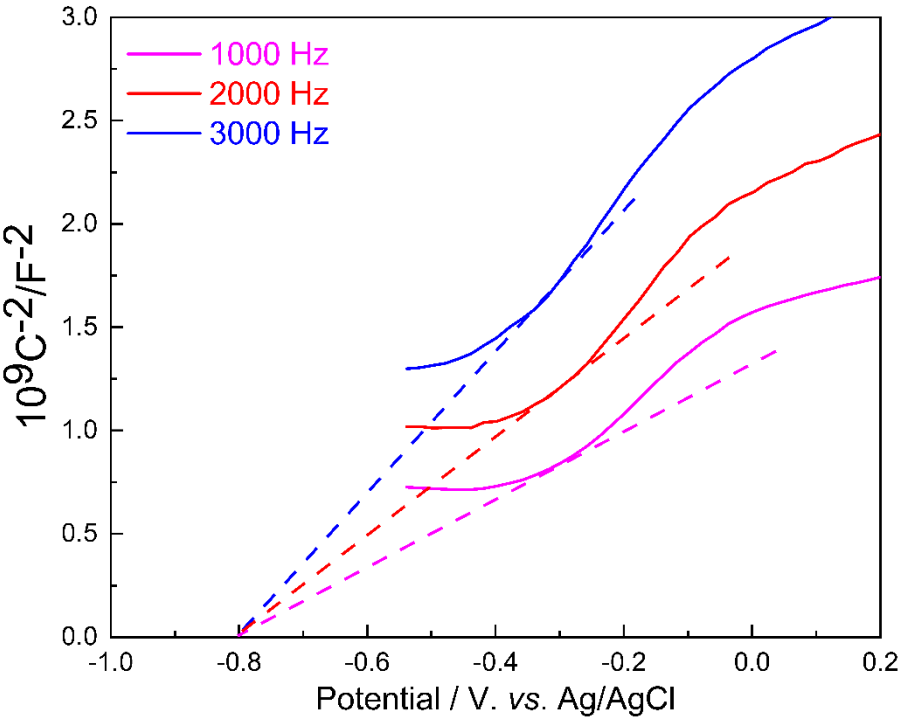


Figure S23. Mott-Schottky plots for Th-CTF in 0.2 M Na_2SO_4 aqueous solution at 1000, 2000 and 3000 Hz

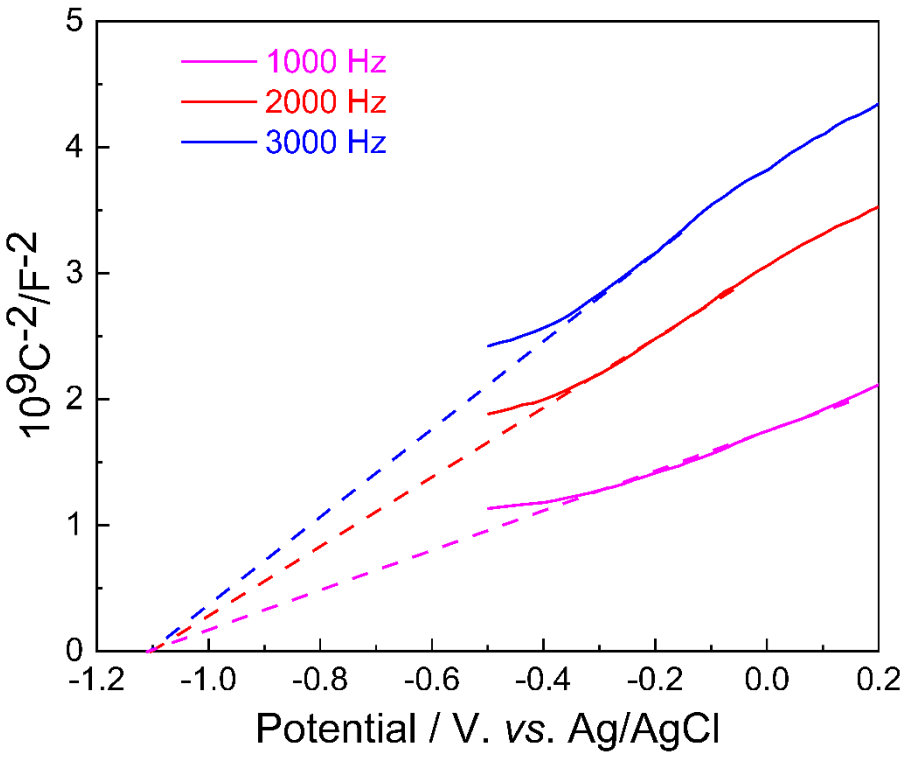


Figure S24. Mott-Schottky plots for DD-CTF in 0.2 M Na_2SO_4 aqueous solution at 1000, 2000 and 3000 Hz

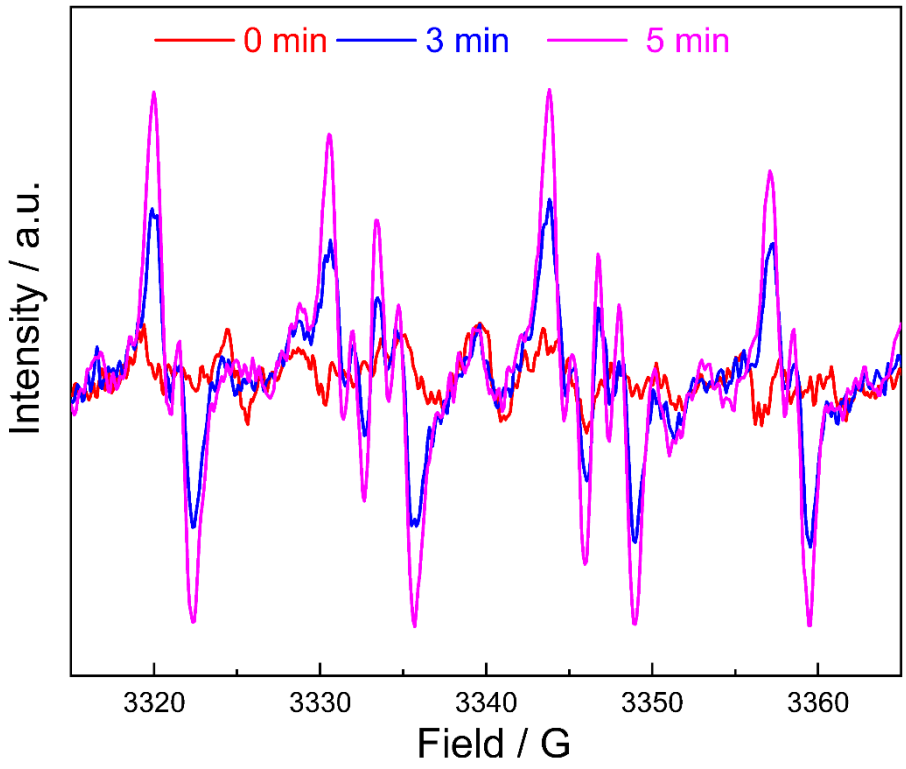


Figure S25. EPR spectra of DMPO- $O_2^{\bullet-}$ for DD-CTF

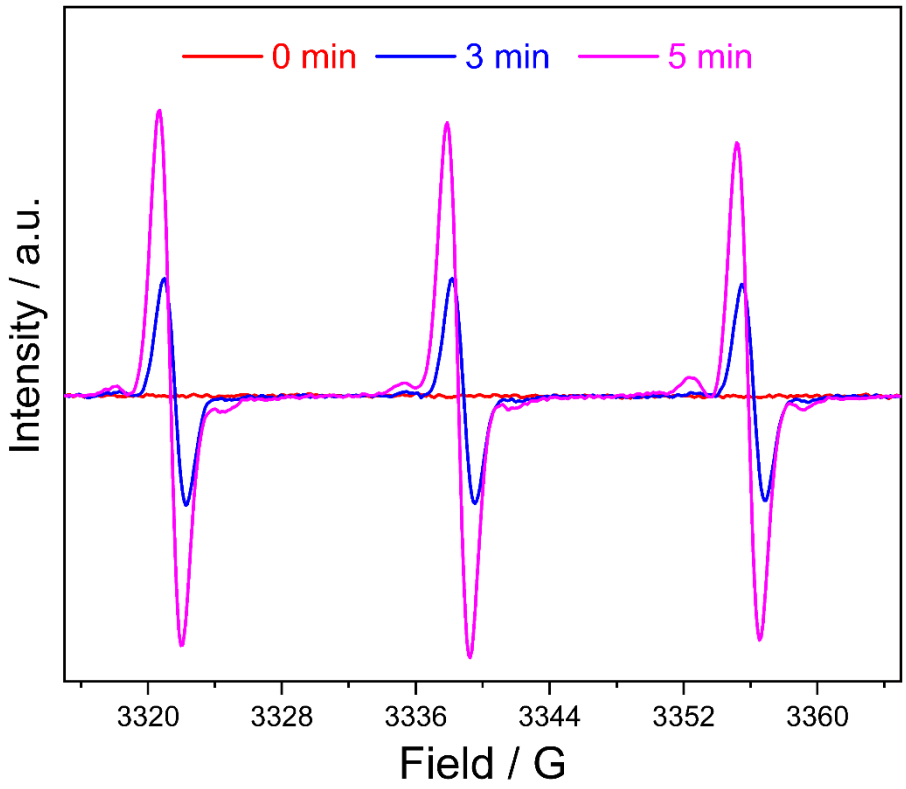


Figure S26. EPR spectra of TEMP-$^1O_2$ for DD-CTF

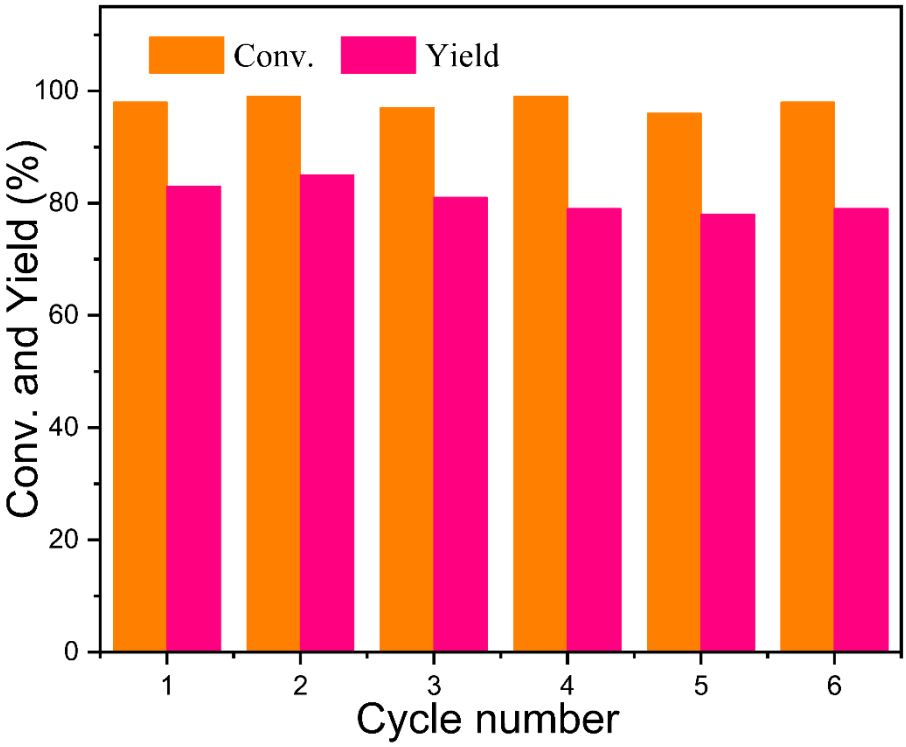


Figure S27. Recycle experiments with DD-CTF for Ugi reactions

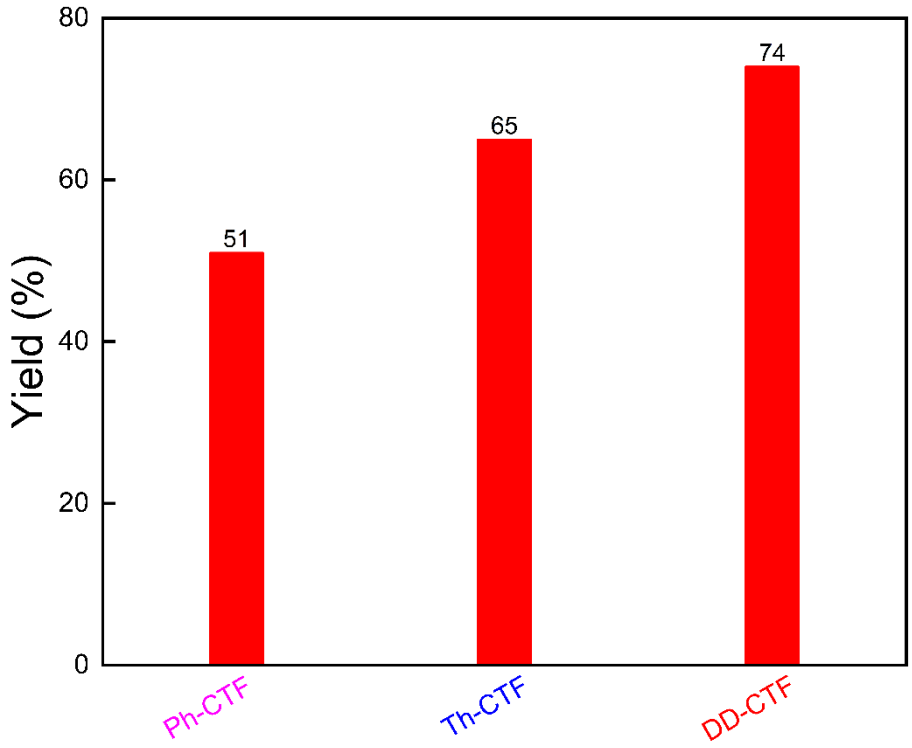


Figure S28. Photocatalyst Screening for Thiocarbamates.

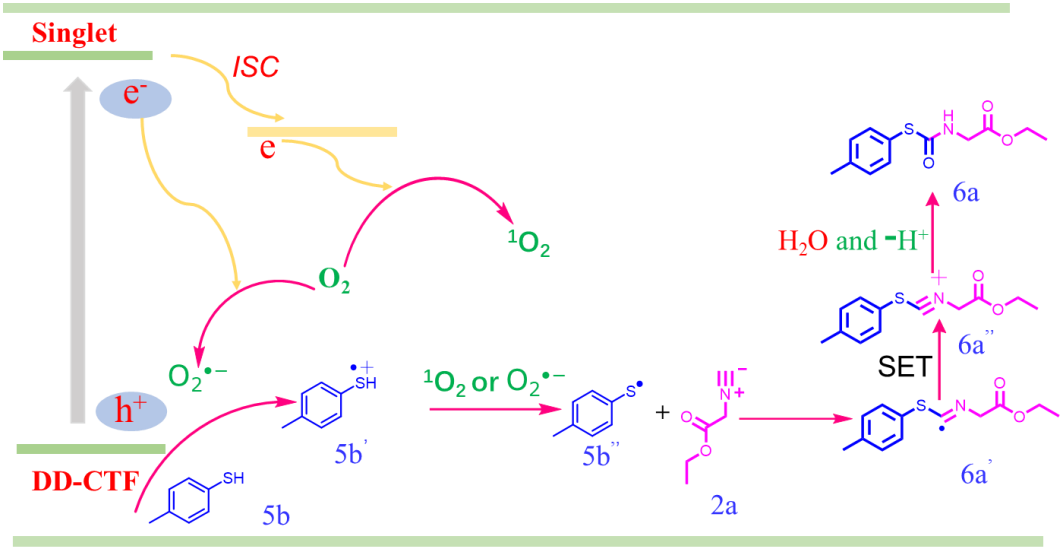


Figure S29. Proposed photocatalytic mechanism for thiocarbamates

Table S1. Optimization of Reaction Conditions

5a 6a 7c

Entry	Photocatalyst	Reaction condition variations	Yield (%)
1	Ph-CTF	DMF	77
2	Th-CTF	DMF	86
3	DD-CTF	DMF	94
4	DD-CTF	CH_3CN	68
5	DD-CTF	THF	56
6	DD-CTF	$CHCl_3$	37
7	DD-CTF	H_2O	17
8	DD-CTF	CH_3OH	29
9	DD-CTF	no O_2	<10
10	-	DMF	Trace
11	DD-CTF	KI	22%
12	DD-CTF	$Na_2C_2O_4$	Trace
13	DD-CTF	$O_2^{\bullet-}$ scavenger	16%
14	DD-CTF	$^1O_2$ scavenger	11%
15	DD-CTF	TEMPO	trace
16	DD-CTF	BHT	trace

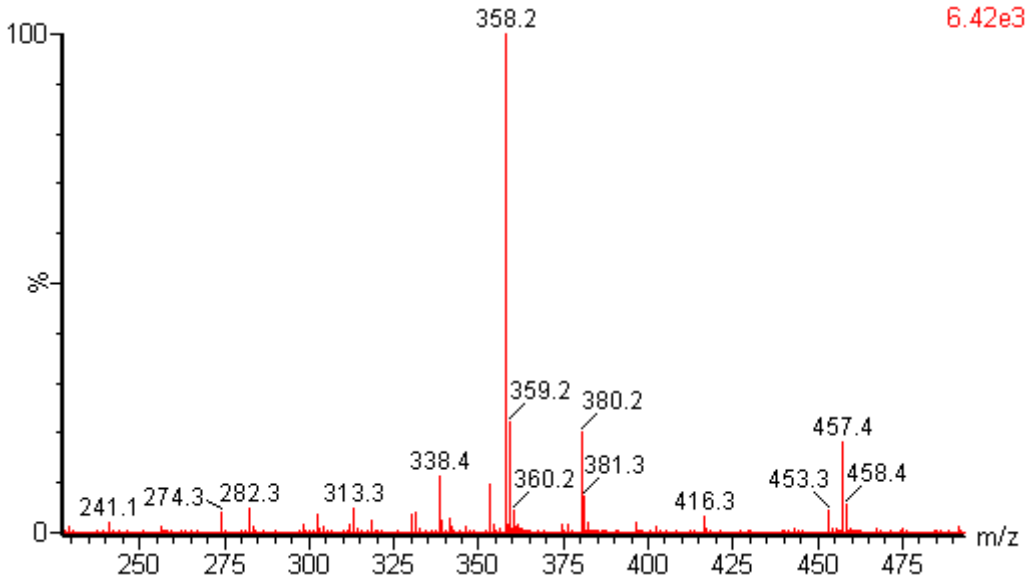
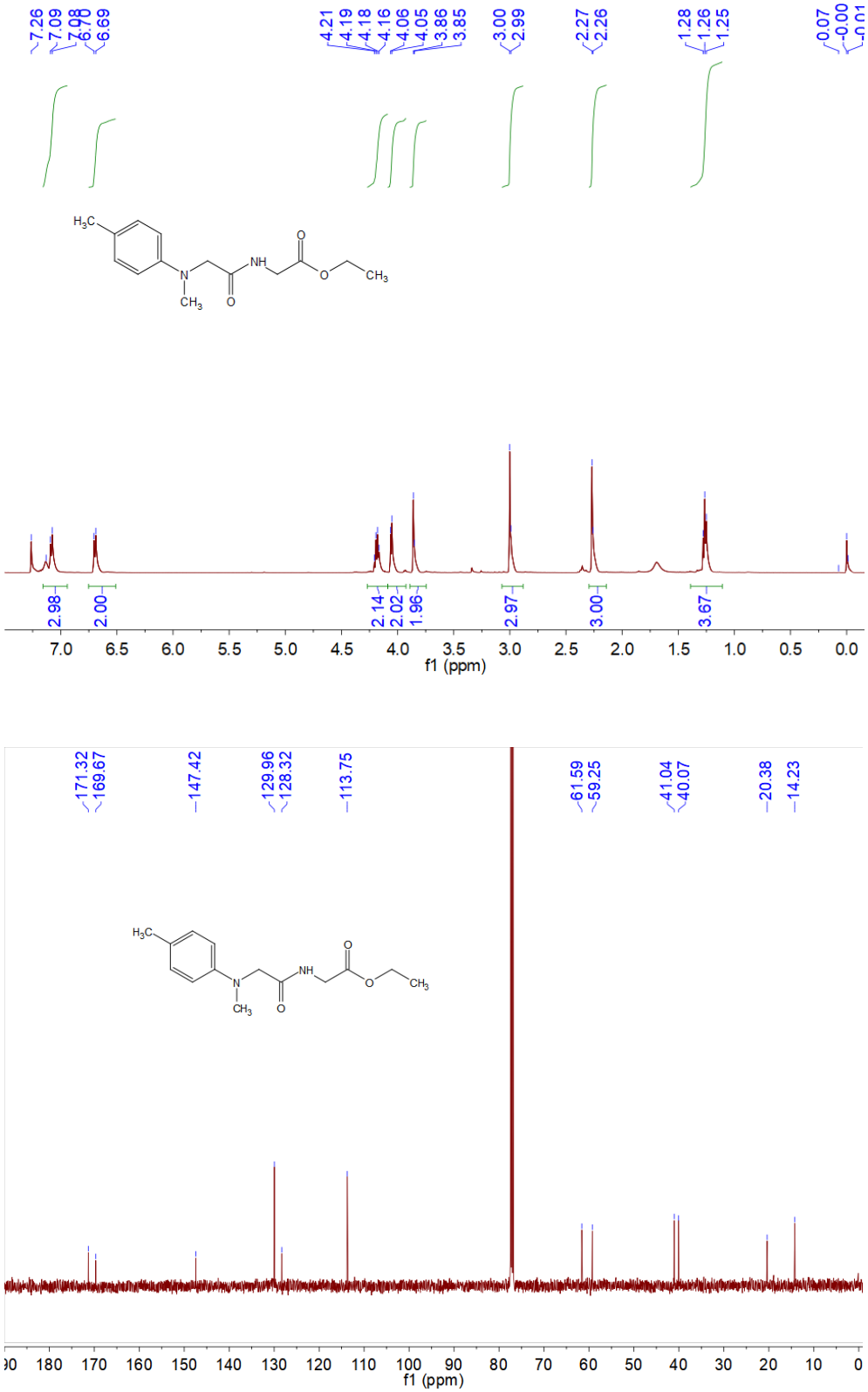


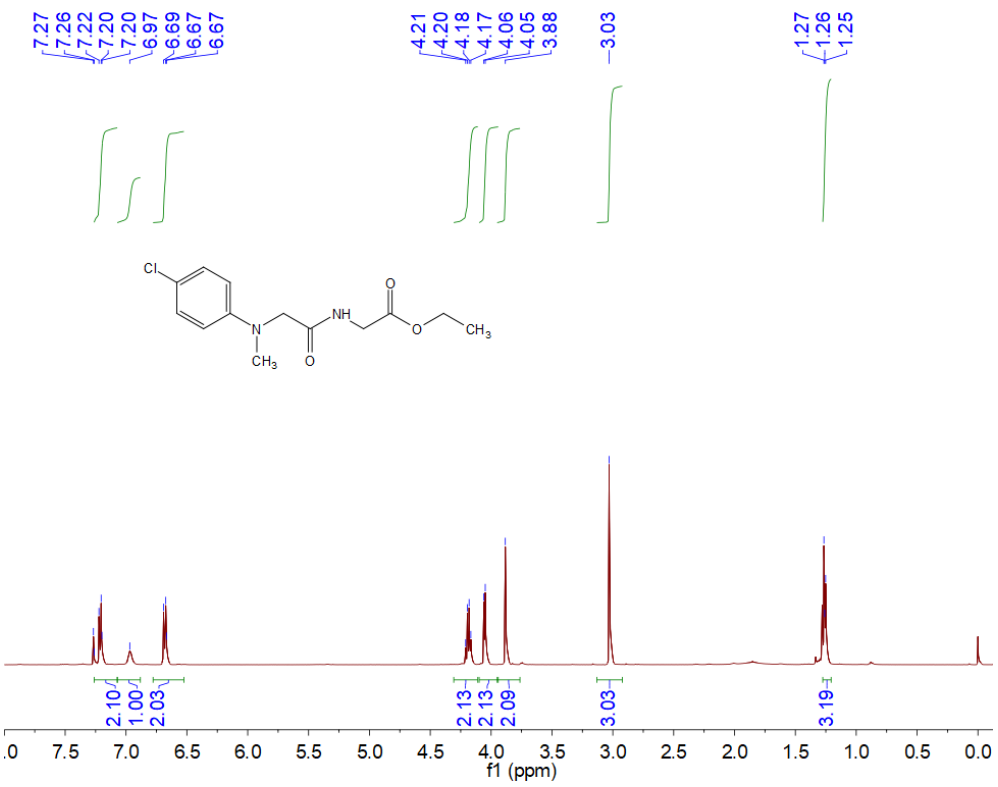
Figure S30. a radical capture experiment with TEMPO for diphenyl-phosphine oxide

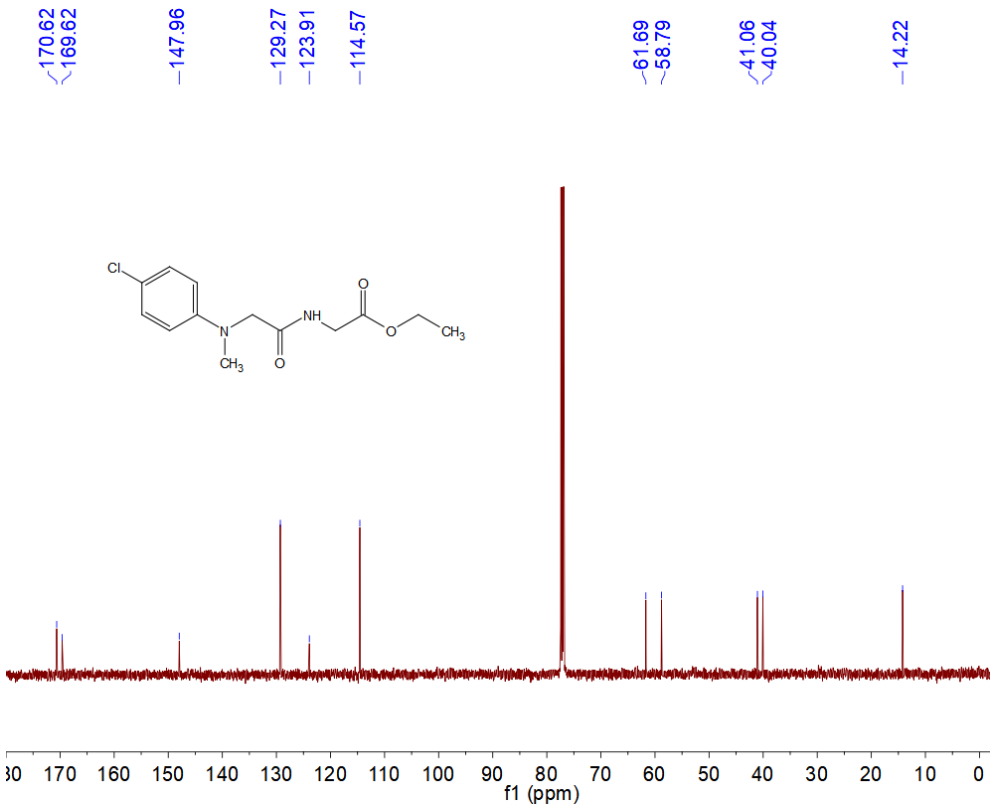
4.^{1}HNMR and ^{13}CNMR spectra



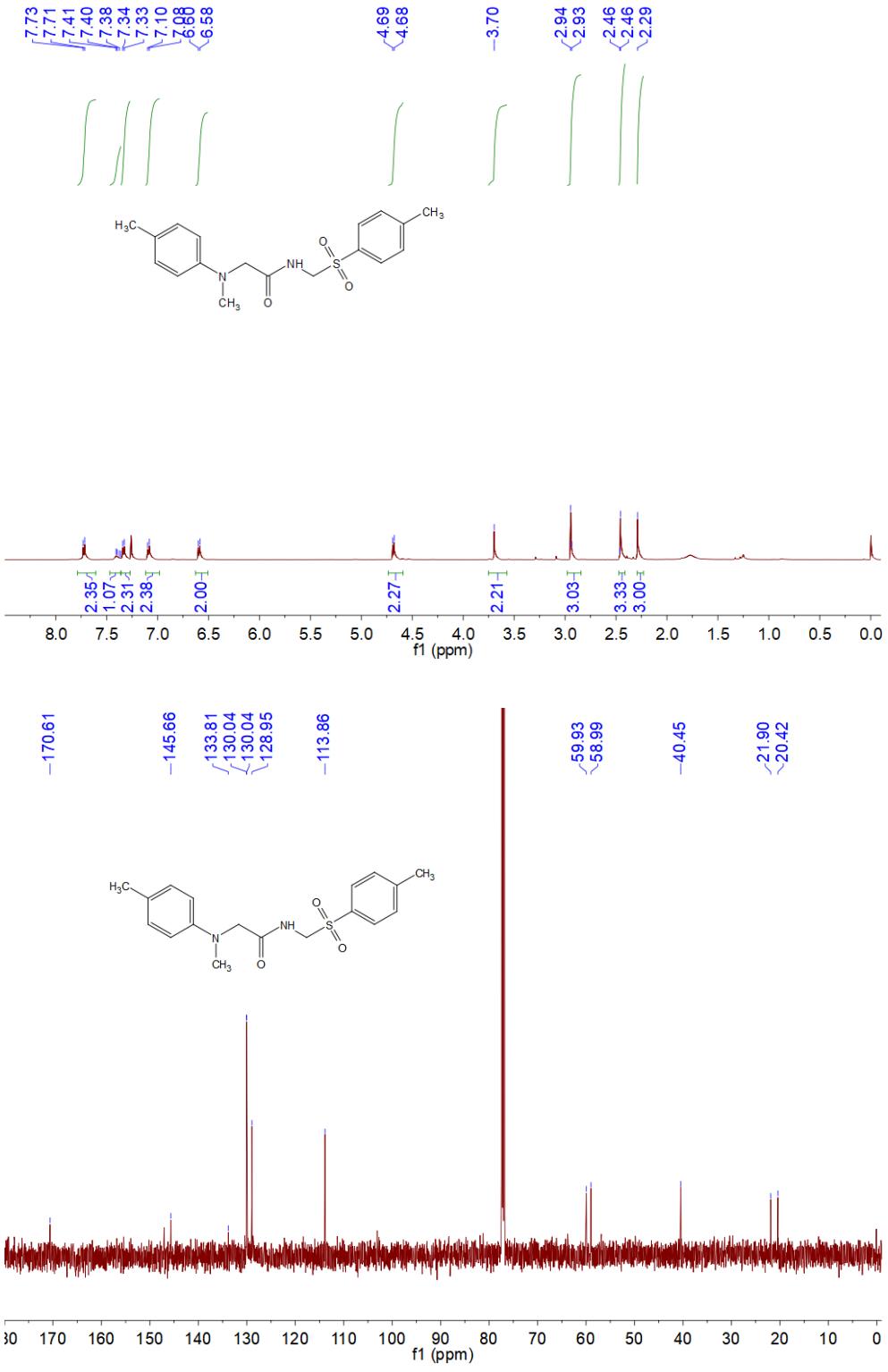
***Ethyl N-methyl-N-(p-tolyl)glycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13 (s, 1H), 7.09-7.08(d, J = 4.0 Hz, 2H), 7.70-7.08(d, J = 4.0 Hz, 2H), 4.21-4.16 (m, 2H), 4.06-4.05 (d, J = 4.0 Hz, 2H), 3.00 (s, 3H), 2.26 (s, 3H),1.28-1.25 (m, 3H).^{13}C NMR ($CDCl_3$, 100 MHz):

δ 171.3,169.7, 147.4, 130.0, 128.3, 113.8, 61.6, 59.2, 41.0. 41.1, 20.4, 14.2.

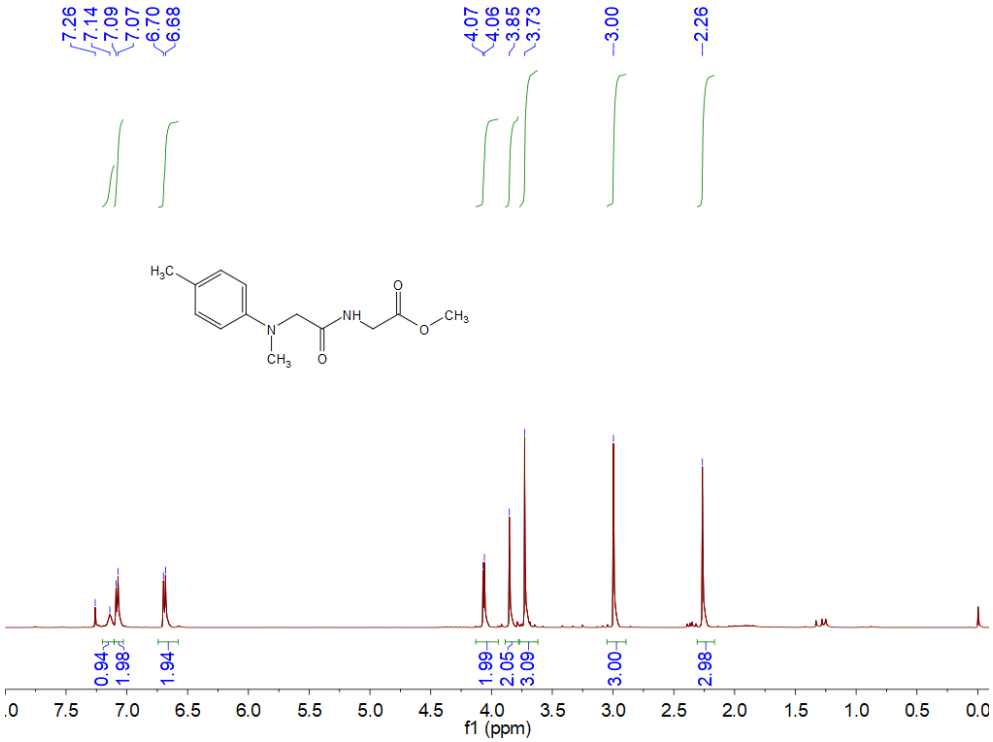


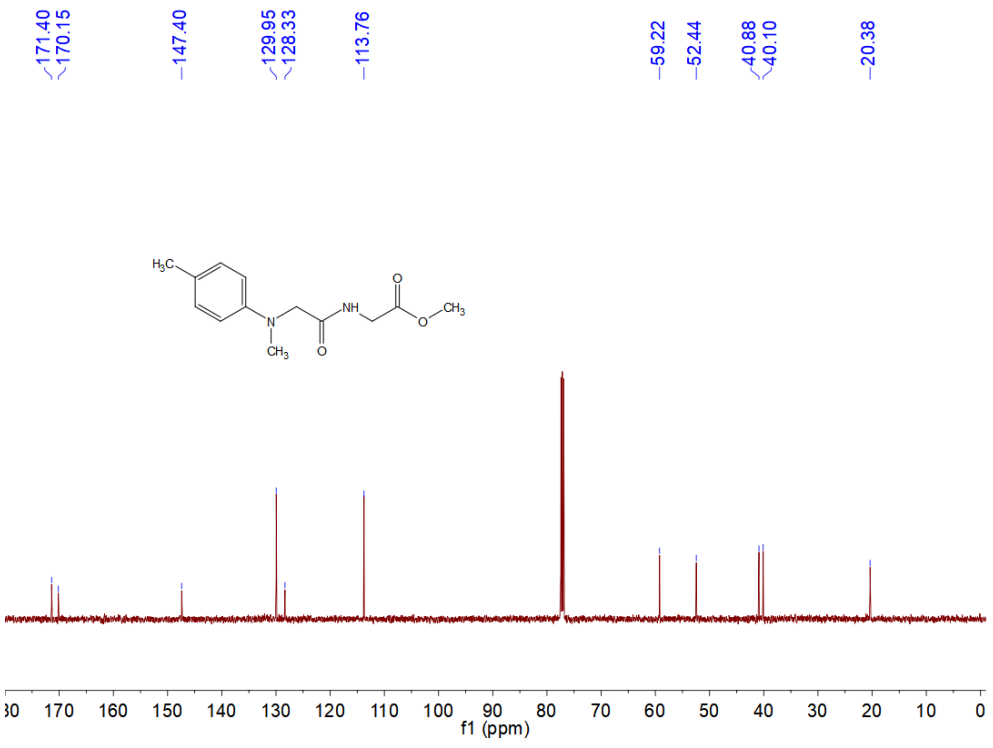


***Ethyl N-(4-chlorophenyl)-N-methylglycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26-7.22(d, J = 8.0 Hz, 2H), 7.20 (s, 1H), 6.69-6.678(d, J = 8.0 Hz, 2H), 4.21-4.17 (m, 2H), 4.06-4.05 (d, J = 4.0 Hz, 2H), 3.88 (s, 2H), 3.00 (s, 3H) ,(1.27-1.25 (m, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 169.6, 148.0, 129.3, 123.9, 114.6, 61.7, 58.8,41.1, 40.0, 14.2.

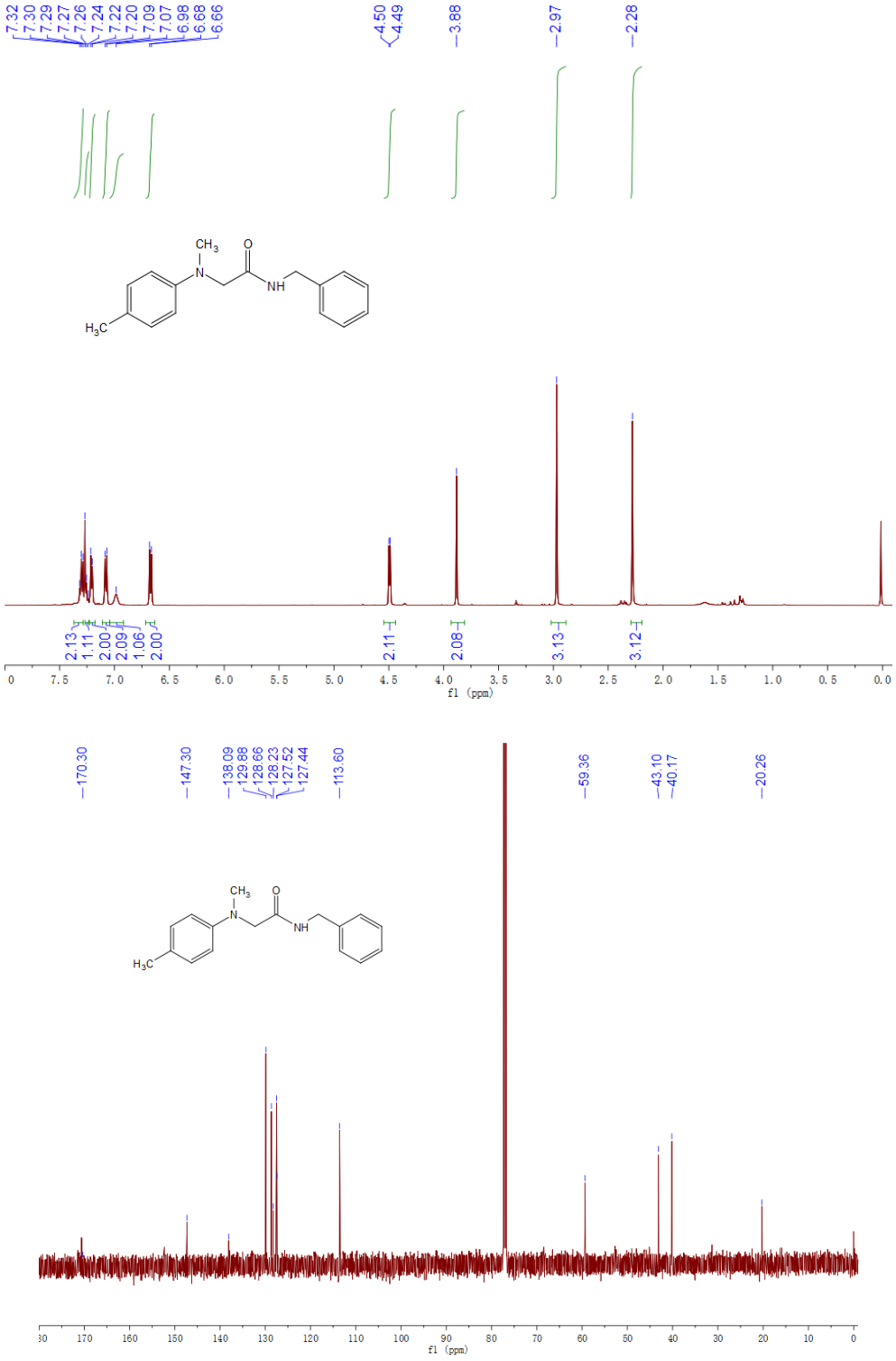


***2-(methyl(p-tolyl)amino)-N-(tosylmethyl)acetamide*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.71(d, J = 8.0 Hz, 2H), 7.41 (s, 1H), 7.34-7.33(d, J = 8.0 Hz, 2H), 7.10-7.08(d, J = 8.0 Hz, 2H), 6.60-6.58 (d, J = 8.0 Hz, 2H), 4.69-4.68 (d, J = 4.0 Hz, 2H), 3.70 (s, 2H), 2.94 (s, 3H), 2.46 (s, 3H), 2.29 (s, 3H)..^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 145.7, 133.8,130.0, 128.9, 113.9, 59.9, 59.0, 40.4, 21.9, 20.4.



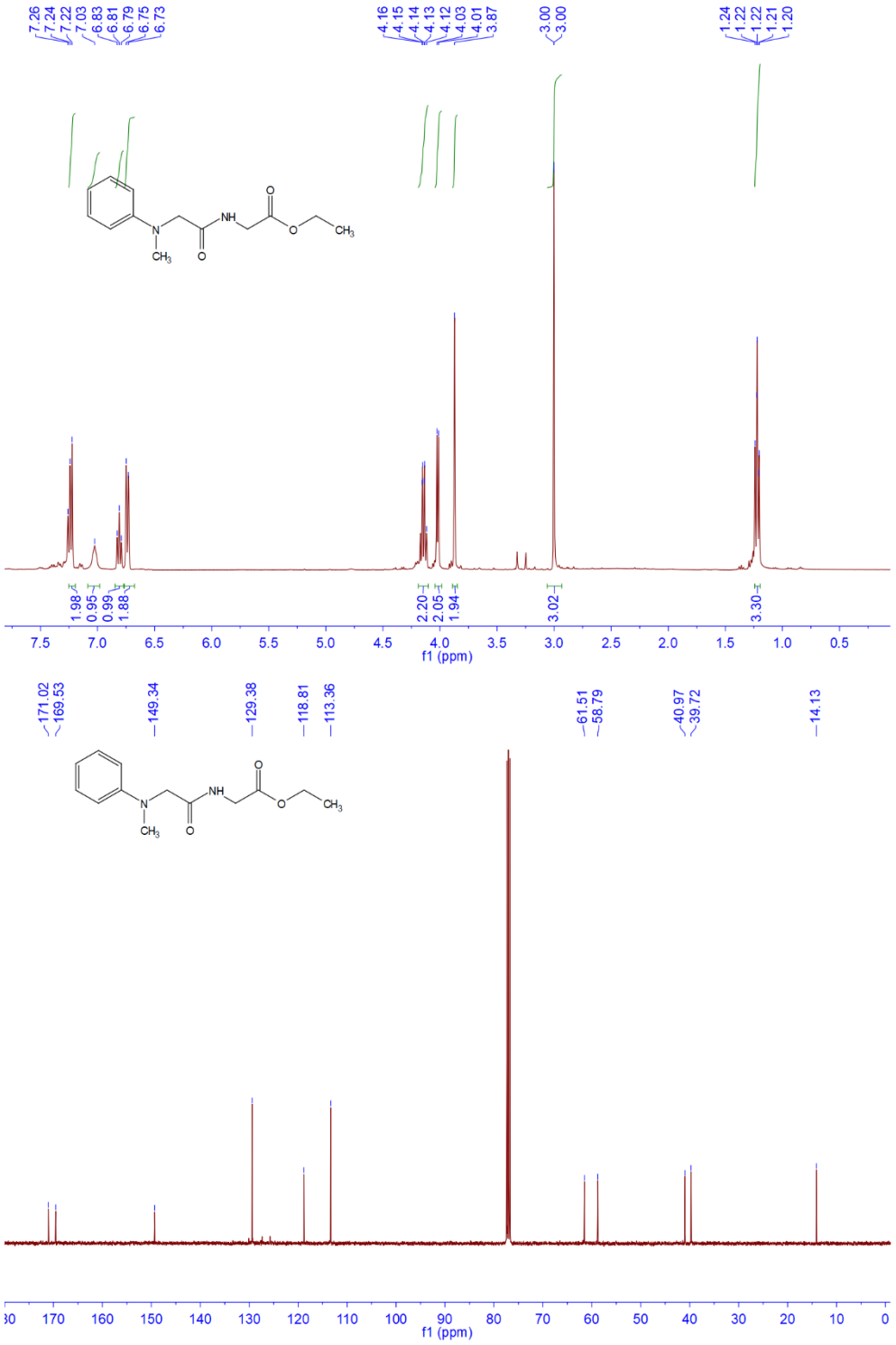


***Methyl N-methyl-N-(p-tolyl)glycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14 (s, 1H), 7.09-7.07(d, J = 8.0 Hz, 2H), 7.70-6.68(d, J = 8.0 Hz, 2H), 4,07-4.06 (d, J = 4.0 Hz, 2H), 3.85 (s, 2H), 3.73 (s, 3H), 3.00 (s, 3H), 2.26 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 170.1, 147.4, 129.9, 128.3,113.8, 59.2, 52.4, 40.9, 40.1, 20.4.



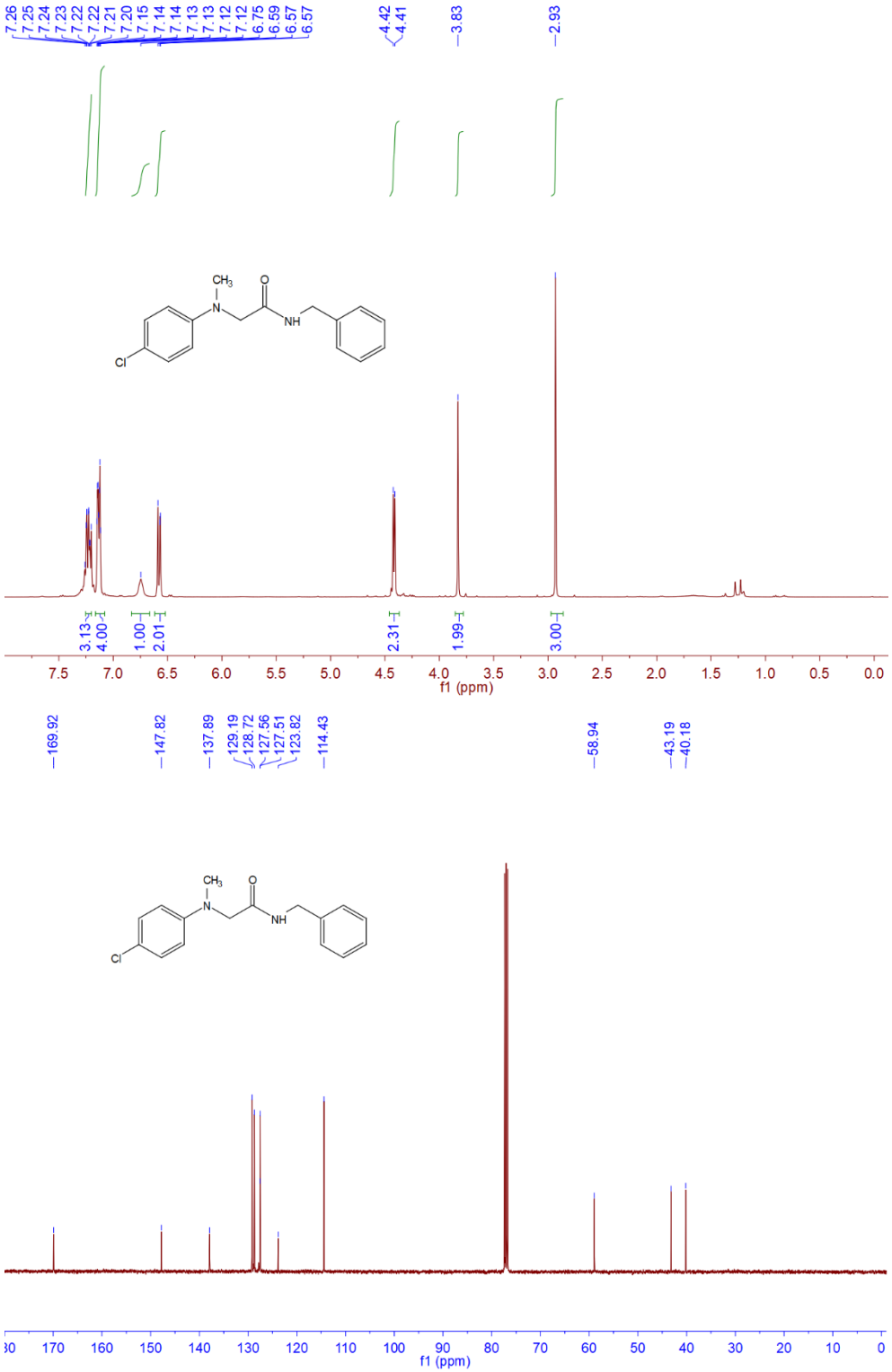
***N*-benzyl-2-(methyl(p-tolyl)amino)acetamide:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.24 (m, 3H), 7.21 (d, J = 8.0 Hz, 2H), 7.08 (m, J

= 8.0 Hz, 2H), 6.98 (s, 1H), 6.67(d, *J* = 8.0 Hz, 2H), 4.50 (d, 2H) , 3.88 (s, 2H), 2.97 (s, 3H), 2.28 (s, 3H)ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 169.2, 166.3, 142.9., 137.1, 131.2, 130.8, 127.4, 127.2, 126.9, 99.9, 61.7, 42.6, 21.1, 14.1.



***Ethyl N-methyl-N-phenylglycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.24-7.22 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 1H), 6.83-6.79 (t, *J* = 8.0 Hz, 1H), 6.70-6.73(d, *J* = 8.0 Hz, 2H), 4.16-4.12 (m, 2H),

4.03-4.01(d, *J* = 8.0 Hz, 2H), 3.87 (s, 2H), 3.0 (s, 3H),1.24-1.20 (t, *J* = 8.0 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 171.0,169.5, 149.3, 129.4, 118.8, 113.4, 61.5, 58.8, 41.0. 39.7, 14.1.

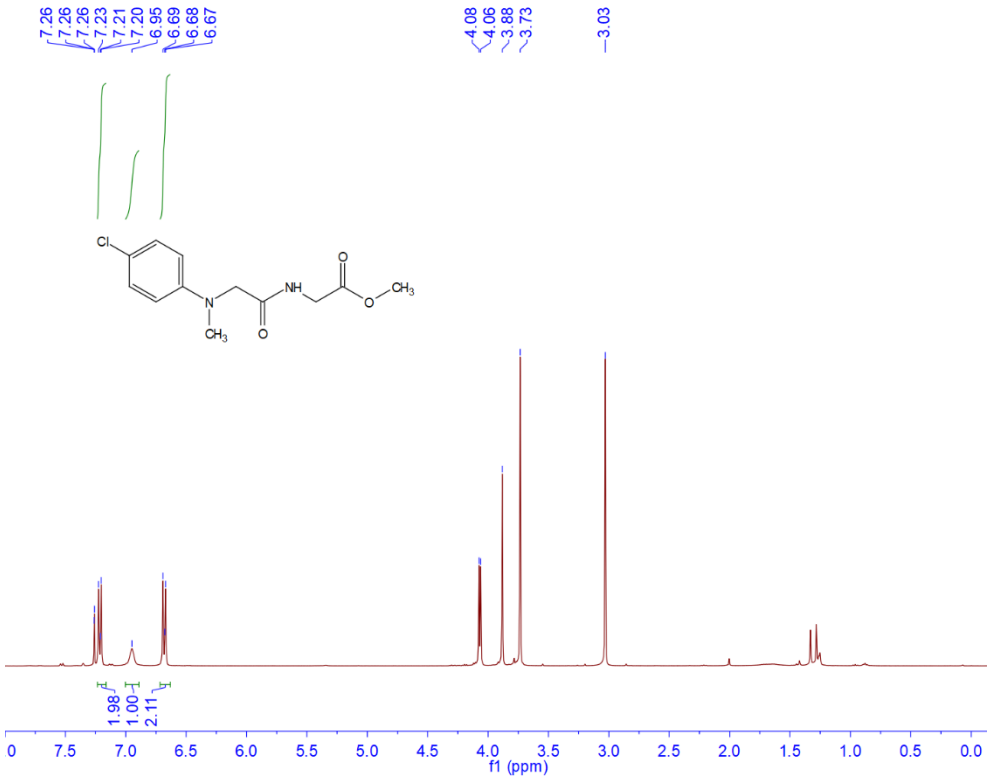


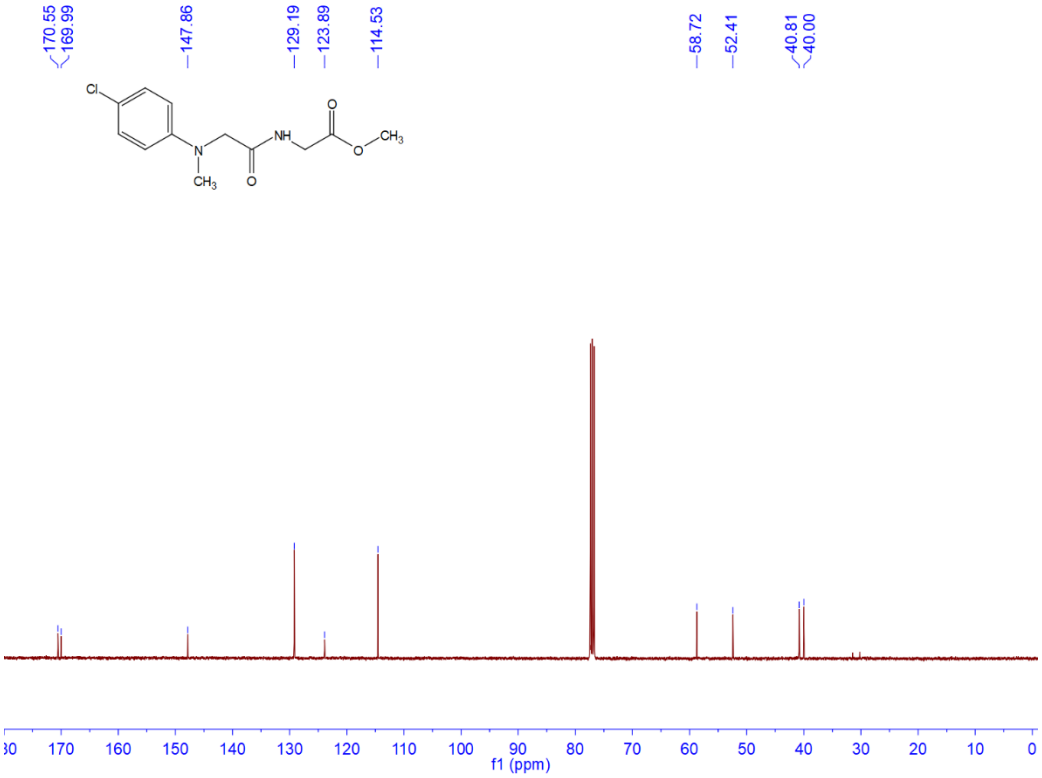
N-benzyl-2-((4-chlorophenyl)(methyl)amino)acetamide: ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.25-7.20 (m, 3H), 7.15-7.12 (m, 2H), 6.75 (s, 1H), 6.59-6.57 (d, *J* = 8.0 Hz, 2H), 4.42-4.41(d, *J* = 4.0 Hz, 2H), 3.83 (s, 2H), 2.93 (s, 3H), 2.28 (s, 3H)ppm. ^{13}C NMR ($CDCl_3$,

100 MHz): δ 169.9, 147.8, 137.9, 129.2, 128.7, 127.6, 127.5, 123.8, 114.4, 58.9, 42.2, 40.2.

2-((4-chlorophenyl)(methyl)amino)-N-(tosylmethyl)acetamide: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.69 (d, J = 8.0 Hz, 2H), 7.34-7.32 (d, J = 8.0 Hz, 2H), 7.24-7.20 (m, 3H), 6.58-6.56 ((d, J = 8.0 Hz, 2H), 6.59-6.57 (d, J = 4.0 Hz, 2H), 4.69-4.68B(d, J = 4.0 Hz, 2H), 2.98 (s, 3H), 2.46 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 147.5, 145.7, 133.7, 130.0, 129.3,

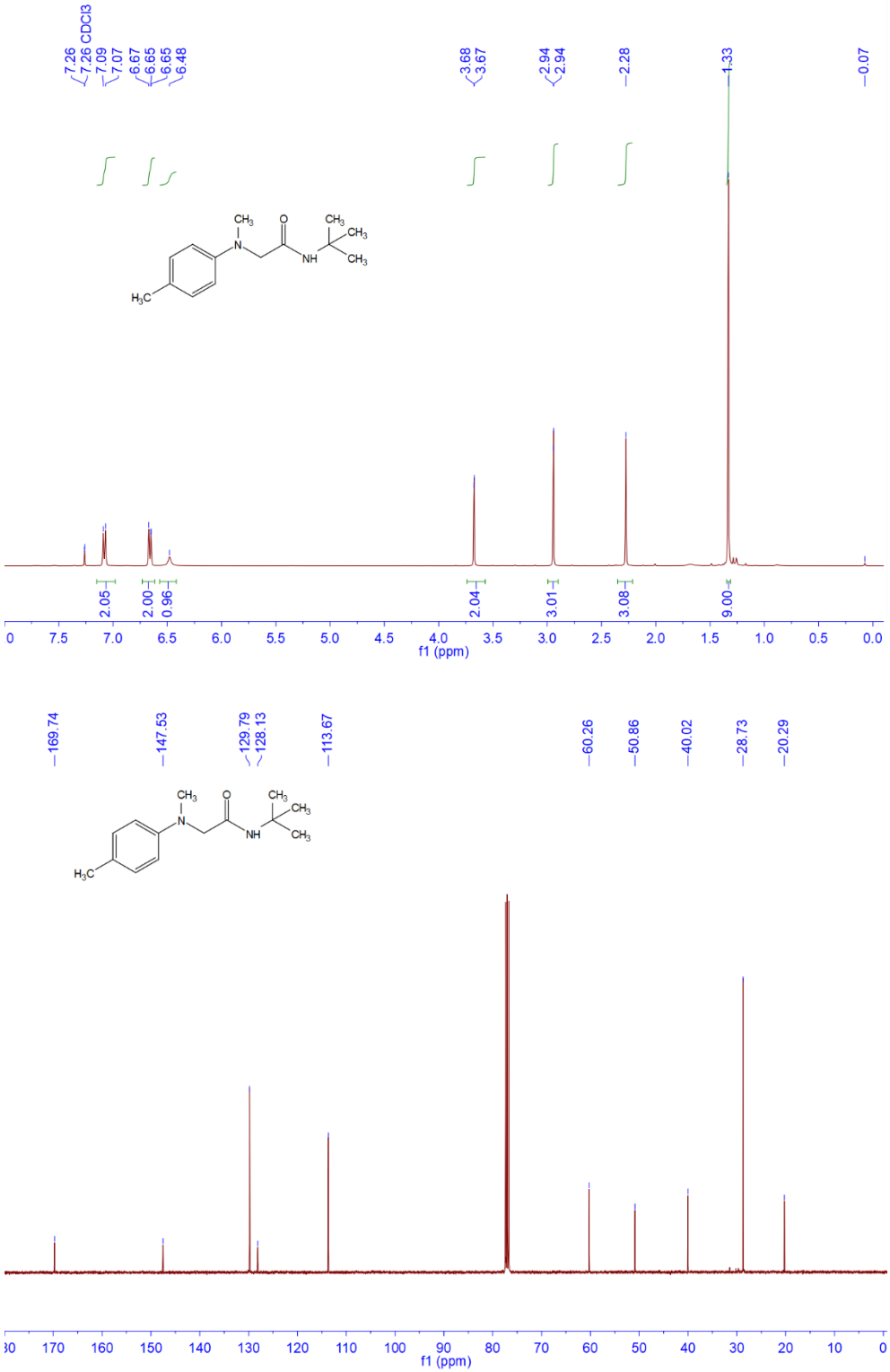
128.8, 124.3, 114.6, 59.8, 58.5, 40.3, 21.8.





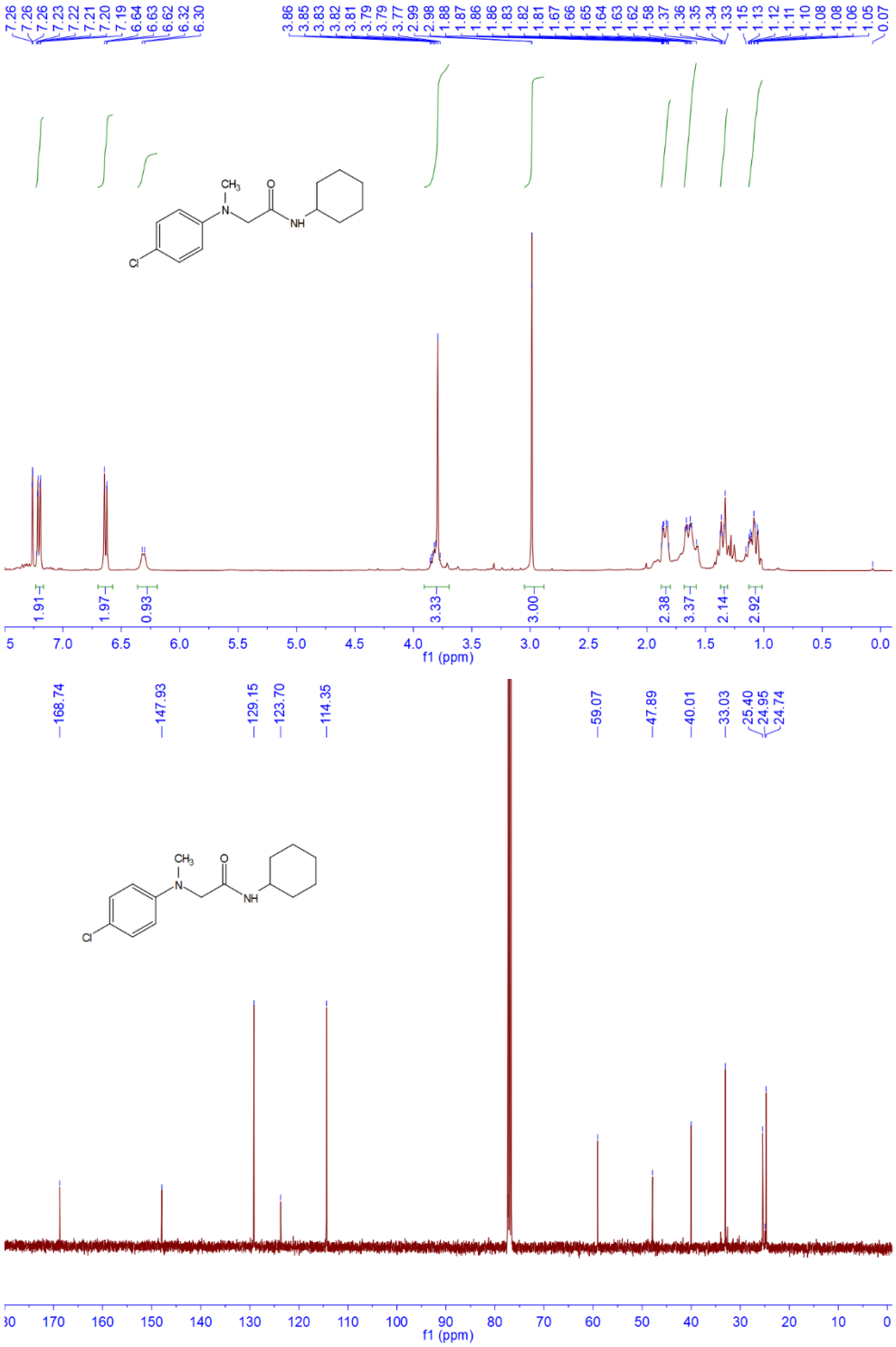
***Methyl N-(4-chlorophenyl)-N-methylglycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23-7.20 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H),

6.69-6.67 (d, *J* = 8.0 Hz, 2H), 4.08-4.06 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 2H), 3.73(s, 3H), 3.03 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 170.6, 170.0, 147.9, 129.2, 123.9, 114.5, 58.7, 52.4, 40.8, 40.0.



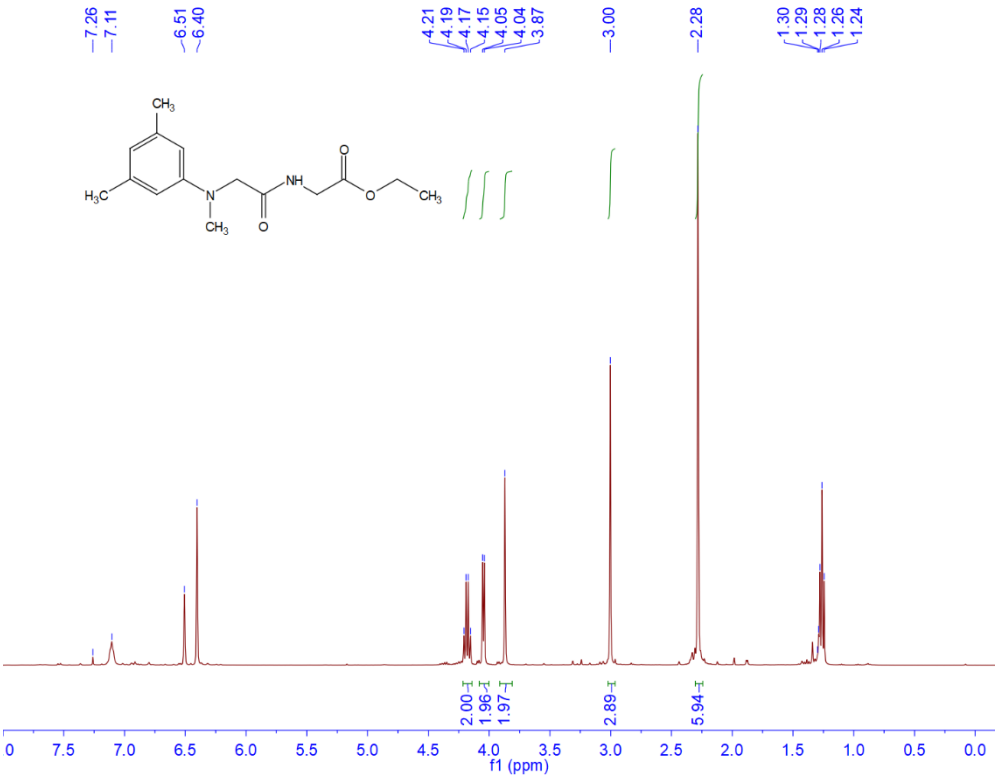
***N-(tert-butyl)-2-(methyl(p-tolyl)amino)acetamide*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.09-7.07 (d, *J* = 8.0 Hz, 2H), 6.67-6.65 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 3.68 (s, 2H), 2.94 (s, 2H), 2.28 (s, 3H),

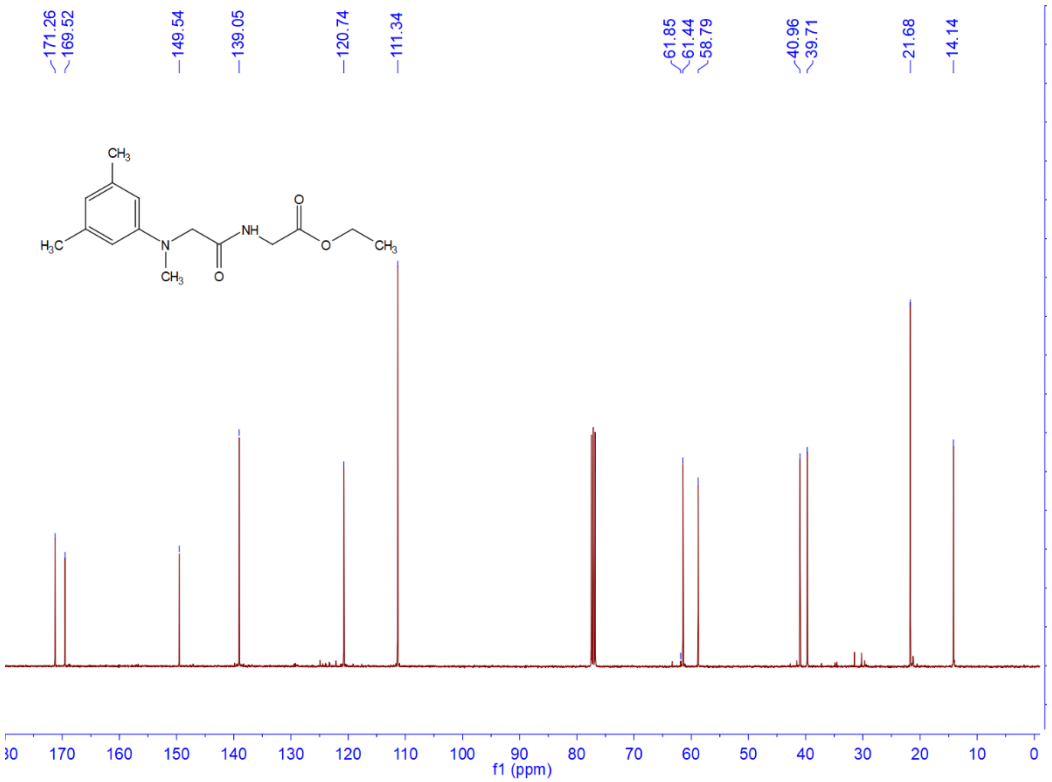
1.33 (s, 9H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 147.4, 147.5, 129.8, 128.1, 113.7, 60.3, 50.9, 40.0, 28.7, 20.3.



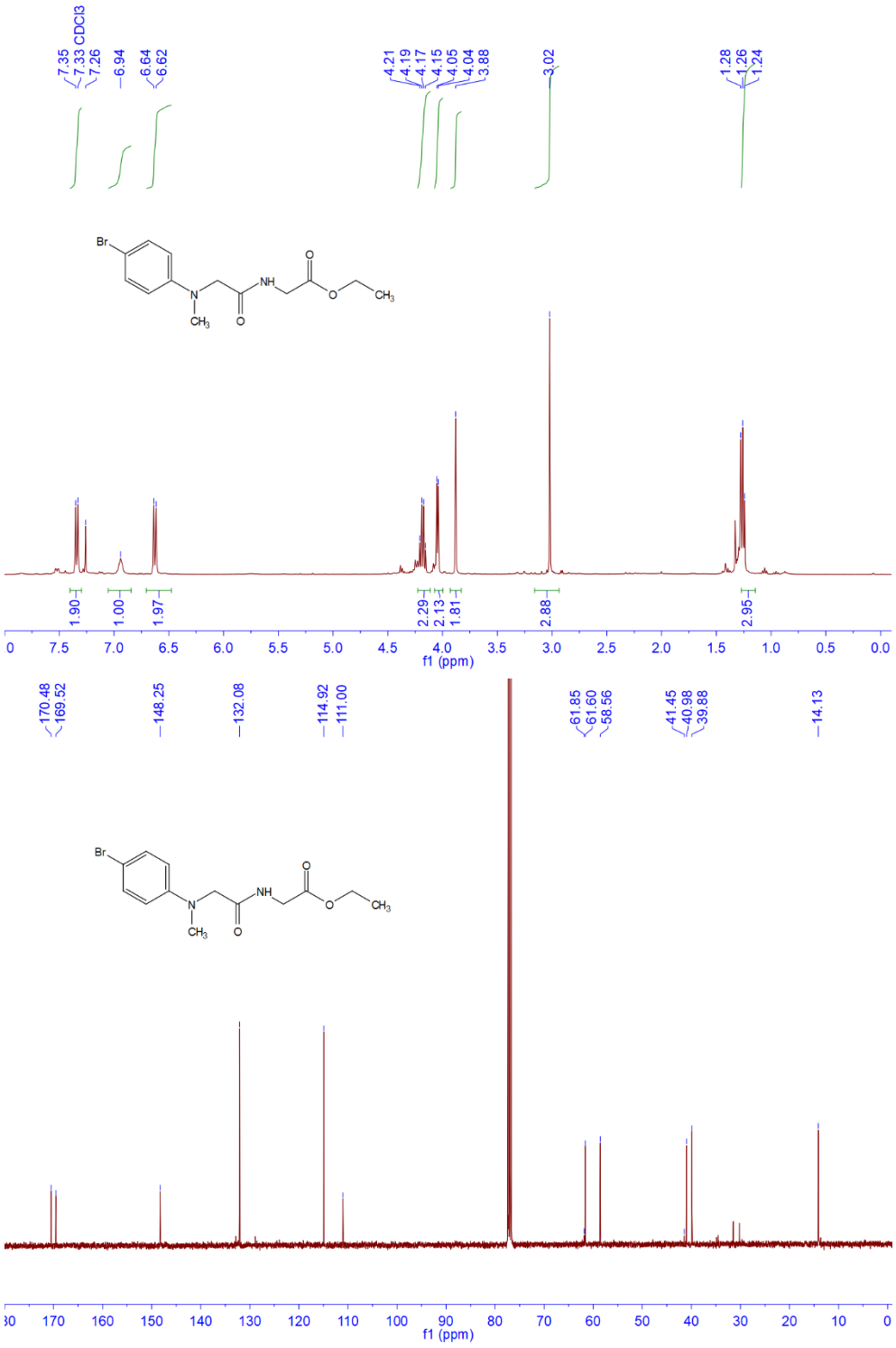
***2-((4-chlorophenyl)(methyl)amino)-N-cyclohexylacetamide*:**
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23-7.21 (d, J = 8.0 Hz, 2H), 7.21-7.19 (d, J = 8.0 Hz, 2H), 3.86 (m+s, 3H), 2.98 (s, 3H),. 1.88-1.81 (m, 2H), 1.67-1.58 (m, 3H), 1.37-1.33 (m, 2H), 1.15-1.05 (m, 3H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.7, 147.9, 129.1, 123.7, 114.3, 59.0, 47.9, 40.0, 33.0, 25.4, 25.0, 24.7.

***N-cyclohexyl-2-(methyl(p-tolyl)amino)acetamide*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08-7.06 (d, J = 8.0 Hz, 2H), 6.66-6.64 (d, J = 8.0 Hz, 2H), 6.54 (s, 1H), 3.87-3.79 (m, 1H), 3.77 (s, 2H), 2.95 (s, 3H), 2.27 (s, 3H). 1.88-1.83 (m, 2H), 1.68-1.56 (m, 3H), 1.39-1.30(m, 2H), 1.16-1.03 (m, 3H) ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 147.5, 129.8, 128.1, 113.5, 59.5, 47.8, 39.9, 33.0, 25.4, 24.8, 20.3.

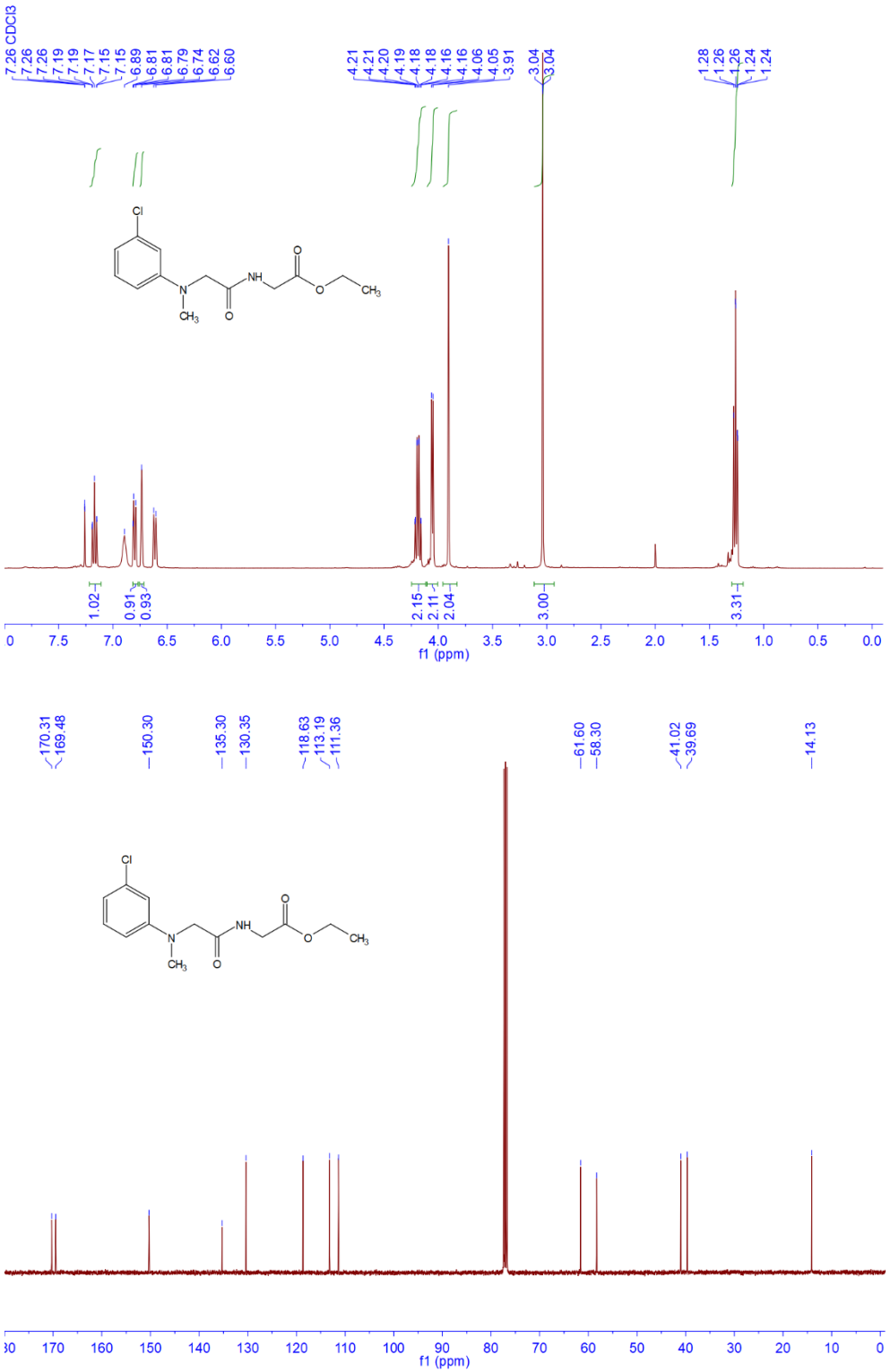




***Ethyl N-(3,5-dimethylphenyl)-N-methylglycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11 (s, 1H), 6.51 (s, 3H), 6.40 (s, 6H), 4.21-4.15 (dd, J = 8.0 Hz, 2H),4.05-4.04 (d, J = 8.0 Hz, 2H). 3.87 (s, 2H), 3.00 (s, 3H), 2.28 (s, 6H) ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.3, 169.5, 149.5, 139.0, 120.7, 111.3, 61.4, 58.8, 41.0, 39.7, 21.7, 14.1.

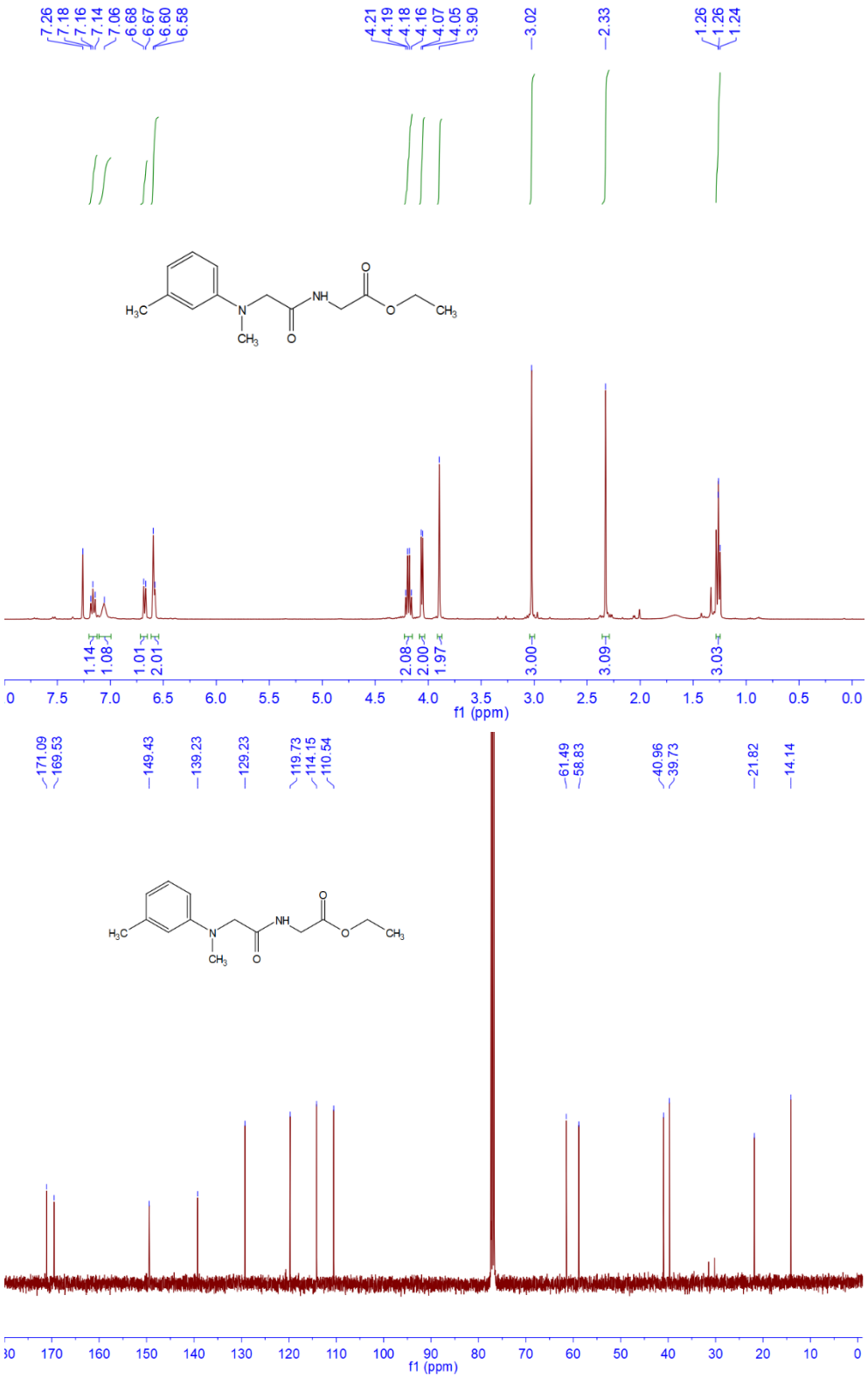


***Ethyl N-(4-bromophenyl)-N-methylglycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.33 (d, J = 8.0 Hz, 2H), 6.94 (s, 1H), 6.64-6.62 (d, J = 8.0 Hz, 2H), 4.21-4.15 (q, J = 8.0 Hz, 1H), 4.05-4.04 (d, J = 8.0 Hz, 2H), 3.88 (s, 2H), 2.95 (s, 3H), 3.02 (s, 3H). 1.28-1.24 (t, J = 8.0 Hz, 3H) ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 169.5, 148.2, 132.0, 114.9, 111.0, 61.8,61.6, 58.6, 41.4, 41.0, 39.9, 14.1.



***Ethyl N-(3-chlorophenyl)-N-methylglycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.19-7.15 (m, 1H), 6.89 (s, 1H), 6.81-6.79 (d, J = 8.0 Hz, 2H), 6.74 (s, 1H), 6.62-6.60 (d, J = 8.0 Hz, 2H), 4.21-4.16 (d, J = 8.0 Hz, 2H), 4.06-4.05 (d, J = 4.0 Hz, 2H), 3.91 (s, 2H), 1.28-1.24 (t, J = 8.0 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4,

169.5, 148.2, 132.0, 114.9, 111.0, 61.8,61.6, 58.6, 41.4, 41.0, 39.9, 14.1.



***Ethyl N-methyl-N-(m-tolyl)glycylglycinate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18-7.14 (d, J = 8.0 Hz, 2H), 7.06 (s, 1H), 6.68-6.67 (d, J

= 8.0 Hz, 1H), 6.60-6.58 (d, *J* = 8.0 Hz, 2H), 4.21-4.16 (d, *J* = 8.0 Hz, 2H), 4.07-4.05 (d, *J* = 8.0 Hz, 2H), 3.02 (s, 3H),2.33 (s, 3H), 1.26-1.24 (t, *J* = 8.0 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 171.1, 169.5, 149.4, 139.2, 129.2, 119.7, 114.1, 110.5, 61.5, 58.8, 40.9, 58.8, 40.9, 39.7, 21.8, 14.1.

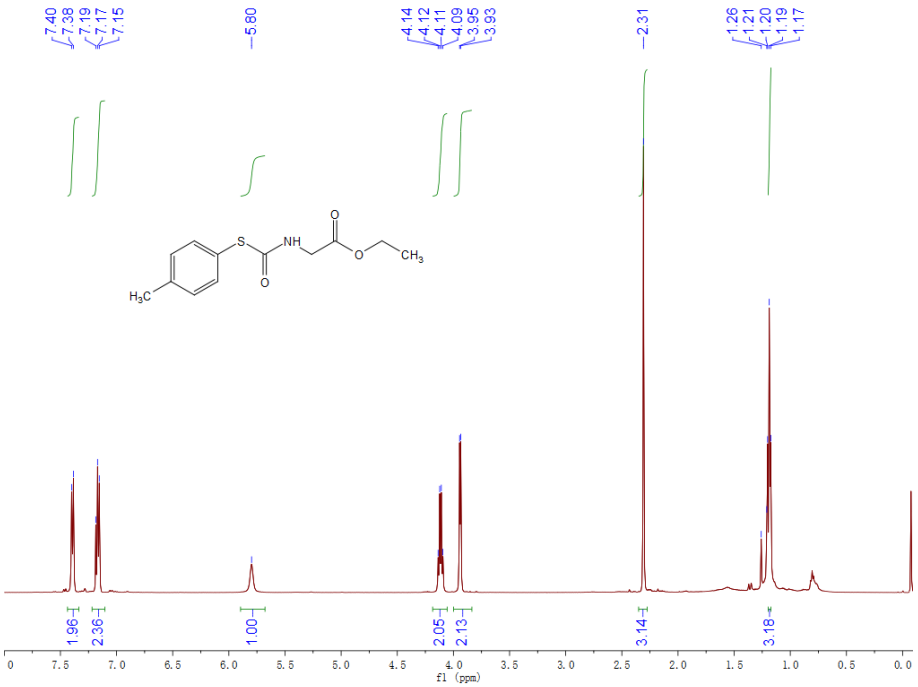


Figure S16. ^{1}H NMR for ethyl 2-(p-tolylthiocarbonylamino)acetate

Ethyl 2-(p-tolylthiocarbonylamino)acetate: Compound 4a was obtained in 78 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.39 (d, 2H), 7.16 (d, 2H), 5.87 (s, 1H), 4.11 (q, 2H), 3.94 (d, 2H), 2.31 (s, 3H), 1.19 (t, 3H).

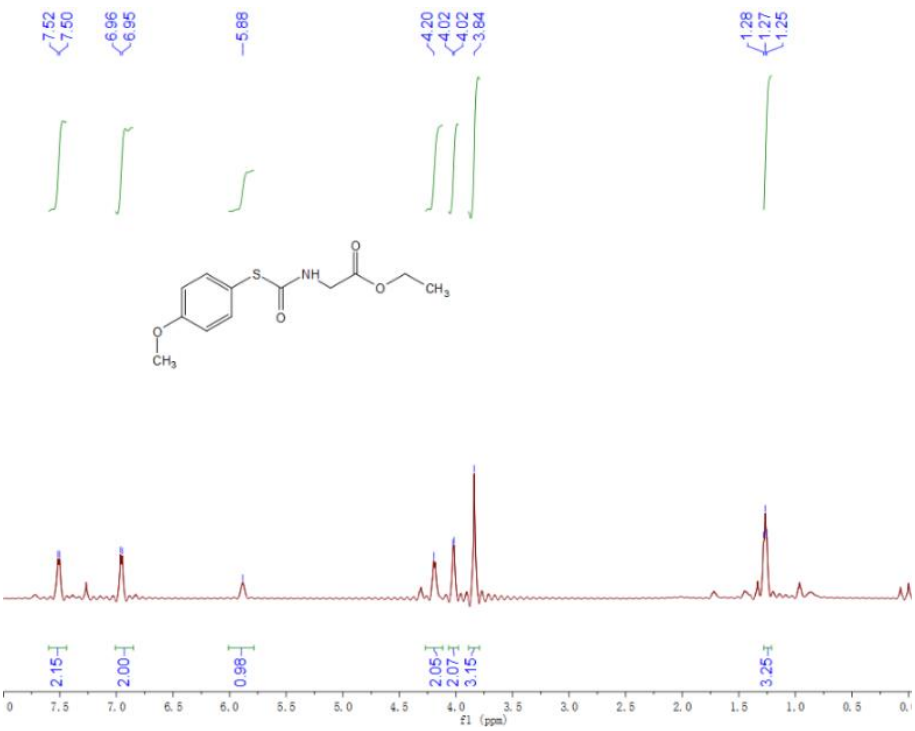


Figure S17. ^{1}H NMR for ethyl 2-((4-methoxyphenylthio)Carbonylami -no)acetate

Ethyl 2-((4-methoxyphenylthio)carbonylamino)acetate: Compound 4b was obtained in 62 % yield according to the general procedure. white solid, ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.50 (d, 2H), 6.95 (d, 2H), 5.88 (s, 1H), 4.20 (q, 2H), 4.02 (d, 2H), 3.84 (s, 3H), 1.27 (t, 3H).

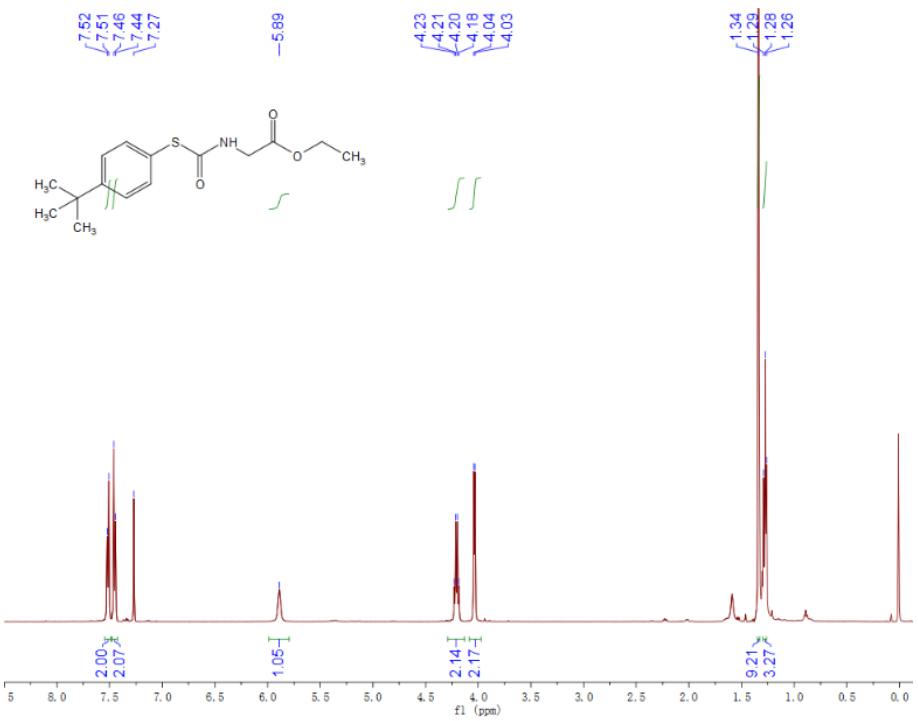


Figure S18. ^{1}H NMR for ethyl (((4-(tert-butyl)phenyl)thio)carbonyl) -glycinate

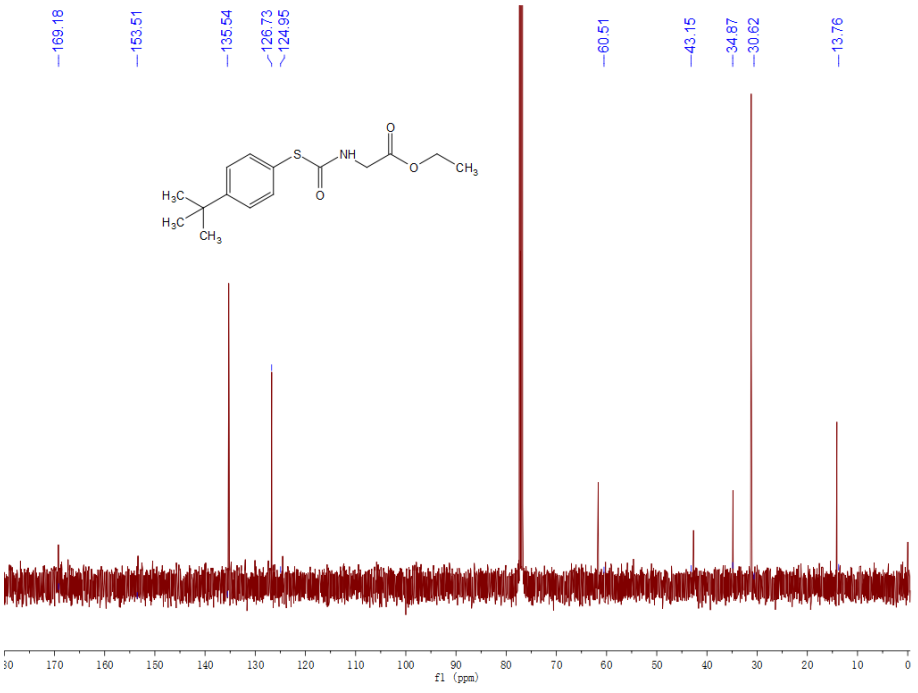


Figure S19. ^{13}C NMR for ethyl (((4-(tert-butyl)phenyl)thio)carbonyl) -glycinate

Ethyl (((4-(tert-butyl)phenyl)thio)carbonyl)glycinate: Compound 4c was obtained in 56 % yield according to the general procedure. ^{1}H

NMR ($CDCl_3$, 400 MHz, ppm): δ 7.52-7.51 (d, 2H), 7.46-7.42 (d, 2H), 5.89 (s, 1H)), 4.20 (q, 2H), 4.03 (d, 2H),1.31 (s, 9H) 1.29-2.26 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 169.1, 153.5, 135.5, 126.7, 124.9, 60.5, 43.1, 34.8,30.6, 13.7.

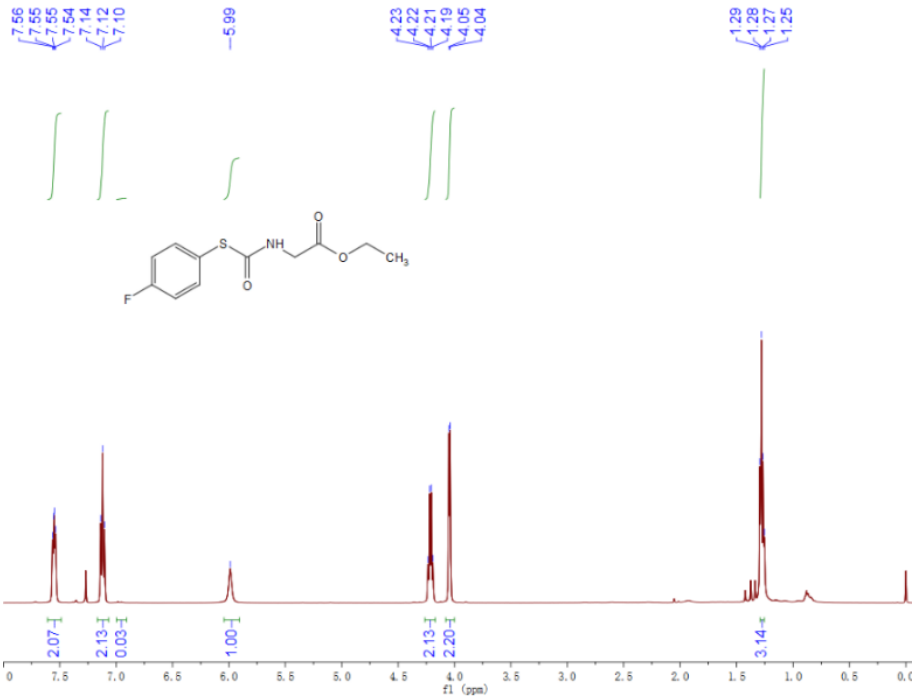


Figure S20. ^1H NMR for ethyl 2-((4-fluorophenylthio)carbonylamino) -acetate.

Ethyl 2-((4-fluorophenylthio)carbonylamino)acetate: Compound 4d was obtained in 77 % yield according to the general procedure. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.56-7.54 (m, 2H), 7.14-7.10 (m, 2H), 5.99 (s, 1H), 4.21 (q, 2H), 4.04 (d, 2H), 1.28 (t, 3H).

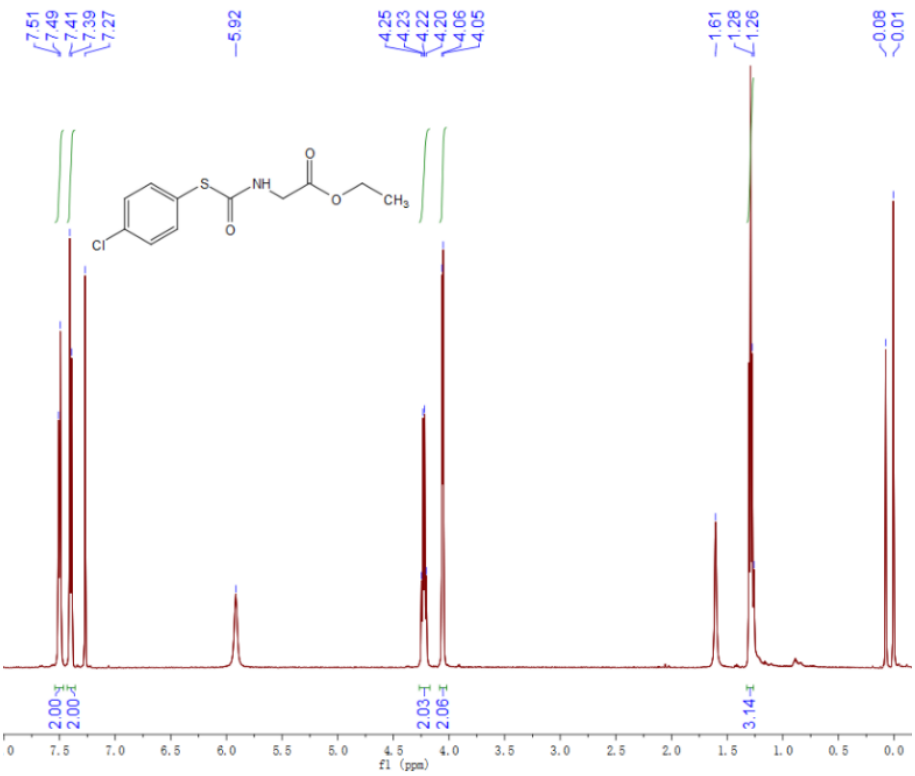


Figure S21. ^{1}H NMR for ethyl 2-((4-chlorophenylthio)carbonylamino) acetate

Ethyl 2-((4-chlorophenylthio)carbonylamino)acetate: Compound 4e was obtained in 92 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.49 (d, 2H), 7.39 (d, ,2H), 5.92 (s, 1H), 4.23 (q, 2H), 4.05 (d, 2H), 1.27 (t, 3H).

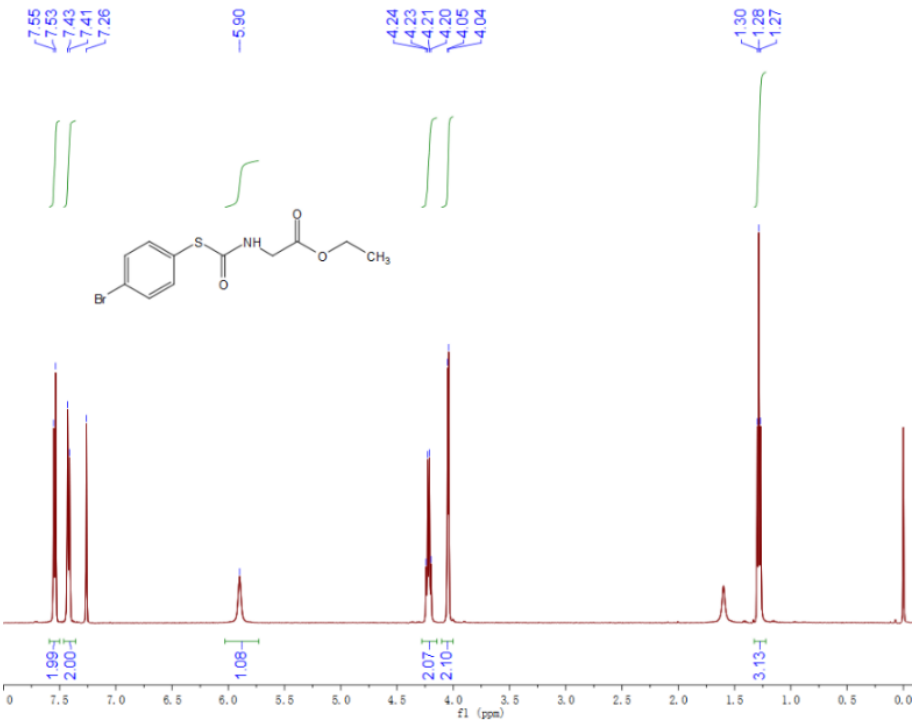


Figure S22. ^{1}H NMR for ethyl 2-((4-bromophenylthio)carbonylamino) acetate.

Ethyl 2-((4-bromophenylthio)carbonylamino)acetate: Compound 4f was obtained in 82 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.54 (d, 2H), 7.41 (d, 2H), 5.90 (s, 1H), 4.23 (q, 2H), 4.04 (d, 2H), 1.28 (t, 3H).

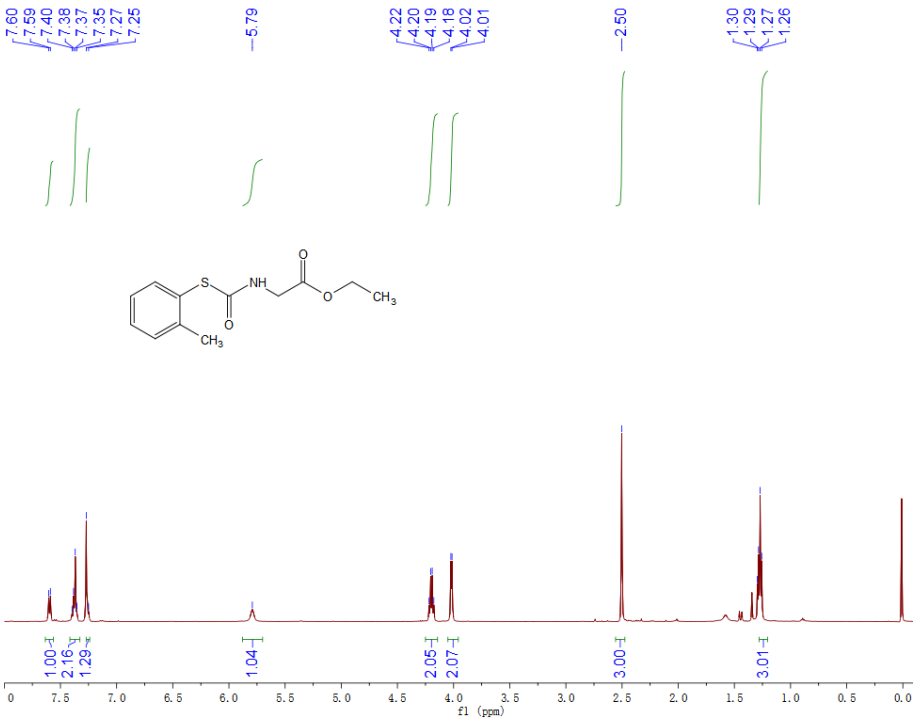


Figure S23. ^{1}H NMR for ethyl ((o-tolylthio)carbonyl)glycinate

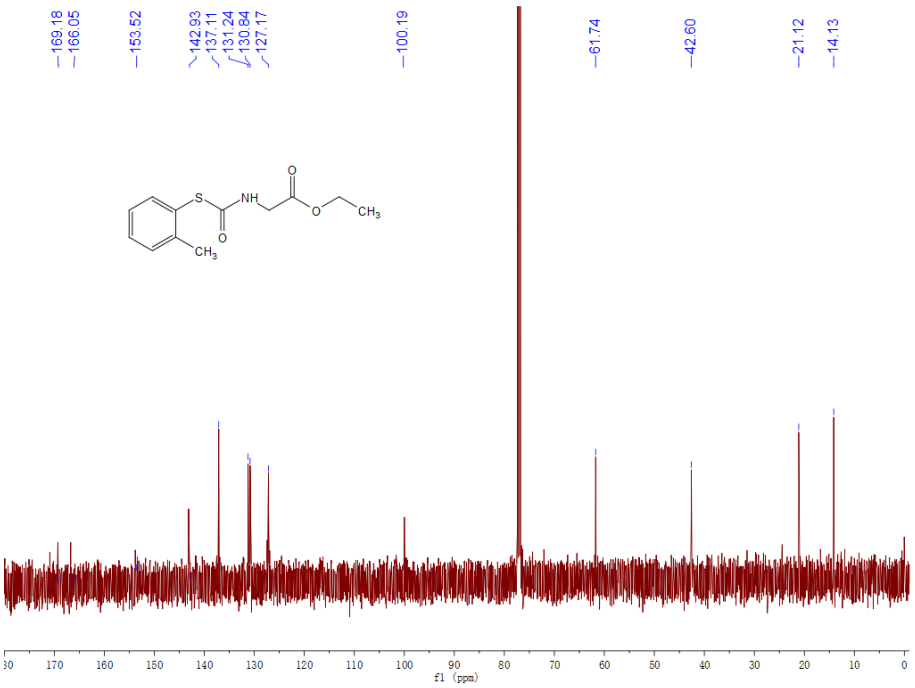


Figure S24. ^{13}C NMR for ethyl ((o-tolylthio)carbonyl)glycinate

Ethyl ((o-tolylthio)carbonyl)glycinate: Compound 4g was obtained in 56 % yieldaccording to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.60(d, 1H), 7.40-7.35 (m, 2H), 7.27-2.25(m, 1H), 5.79 (s, 1H)), 4.20 (q, 2H), 4.02 (d, 2H), 2.50 (s, 3H) 1.30-1.26 (t,

3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 170.3, 147.3, 138.1, 129.9, 128.7, 128.2, 127.5, 127.4, 113.6, 59.4, 43.1, 40.17, 20.3

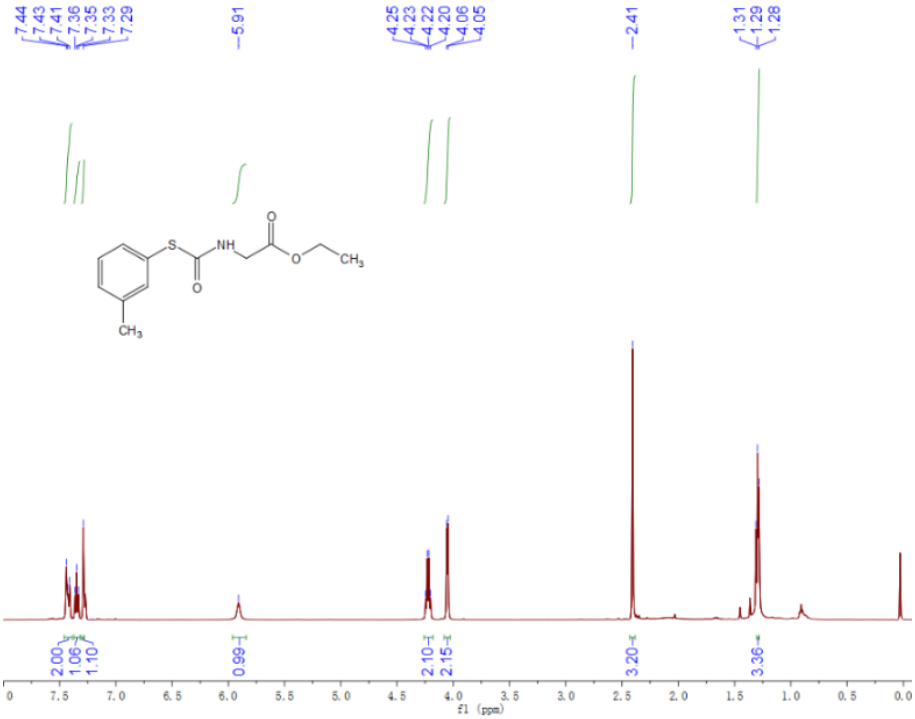


Figure S25. ^{1}H NMR for ethyl 2-(m-tolylthiocarbonylamino)acetate Ethyl 2-(m-tolylthiocarbonylamino)acetate: Compound 4h was obtained in 74 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.44-7.41 (m, 2H), 7.35 (t, 1H), 7.29 (s, 1H), 5.91 (s, 1H), 4.23 (q, 2H), 4.05 (d, 2H), 2.41 (s, 3H), 1.29 (t, 3H);

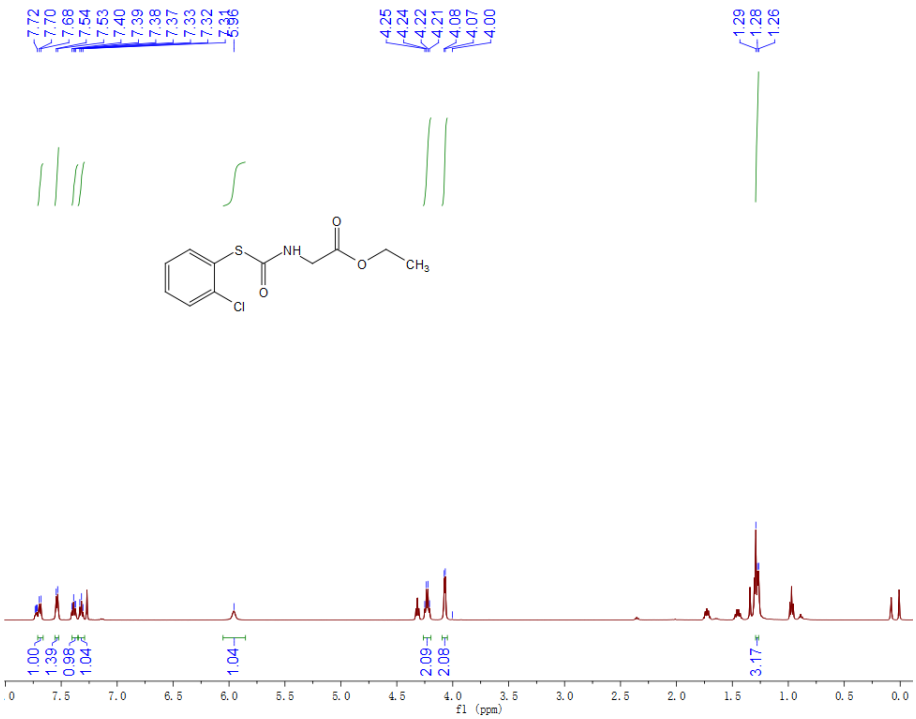


Figure S26. ^{1}H NMR for ethyl 2-((2-chlorophenylthio)carbonylamino) acetate

Ethyl 2-((2-chlorophenylthio)carbonylamino)acetate: Compound 4i was obtained in 66 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.68 (dd, 7.6 Hz, 1H), 7.53 (d, 1H), 7.40-7.37 (m 1H), 7.33-7.30 (m, 1H), 5.96 (s, 1H), 4.24 (q, 2H), 4.07 (d, 2H), 1.28 (t, 3H).

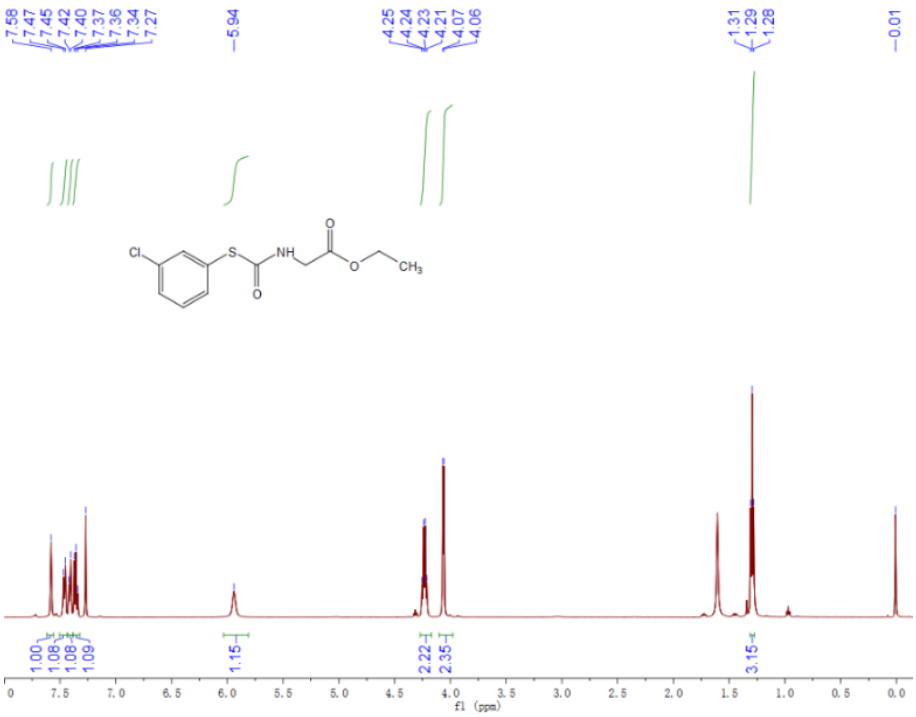


Figure S27. ^{1}H NMR for ethyl 2-((3-chlorophenylthio)carbonylamino) acetate

Ethyl 2-((3-chlorophenylthio)carbonylamino)acetate: Compound 4j was obtained in 83 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.58 (s, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.37-7.34 (m, 1H), 7.36 (t, 1H), 5.94 (s, 1H), 4.24 (q, 2H), 4.07 (d, 2H), 1.29 (t, J = 7.1 Hz, 3H).

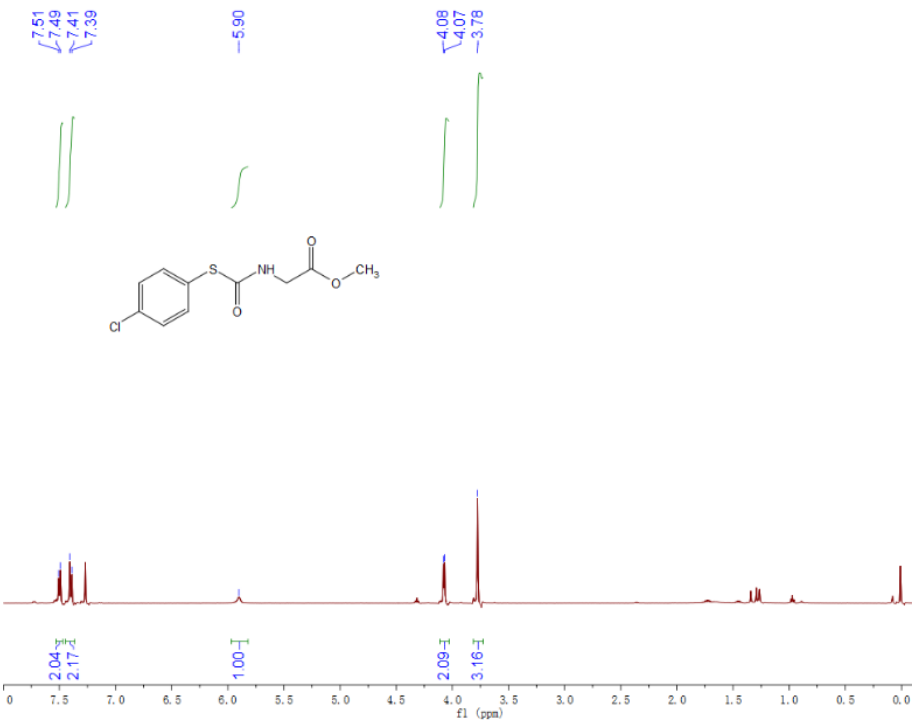


Figure S28. ^{1}H NMR for methyl (((4-chlorophenyl)thio)carbonyl) glycinate

Methyl (((4-chlorophenyl)thio)carbonyl)glycinate: Compound 4k was obtained in 88 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.51-7.49 (d, 2H), 7.41-7.39 (d, 1H), 5.91 (s, 1H)), 4.07 (d, 2H), 3.78 (s, 3H).

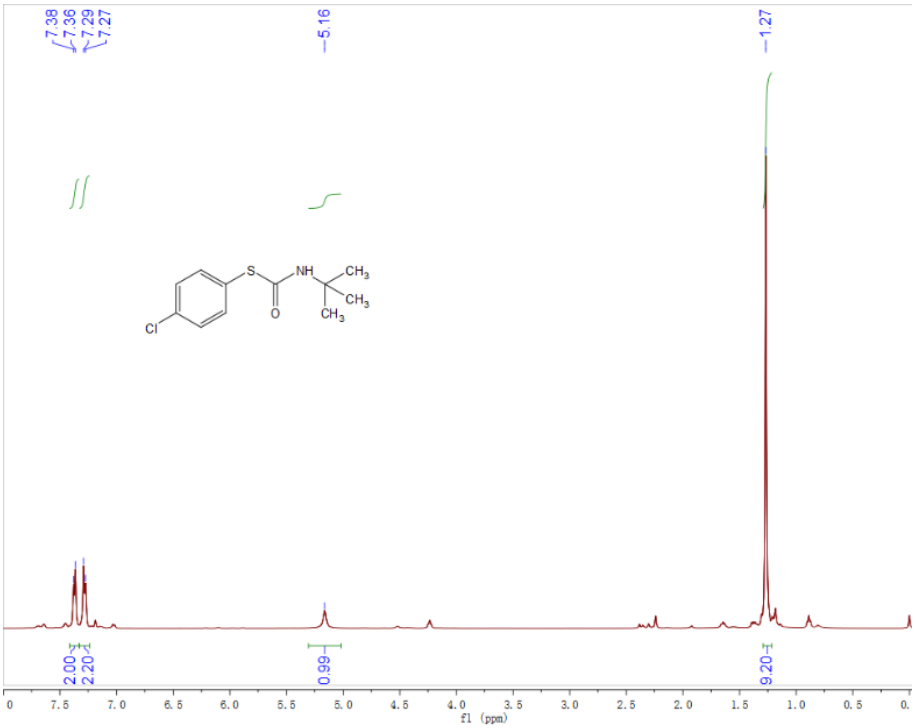


Figure S29. ^{1}H NMR for *S*-4-chlorophenyl *tert*-butylcarbamothioate *S*-4-chlorophenyl *tert*-butylcarbamothioate: Compound 4l was obtained in 63 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.38 (d, 2H), 7.29 (d, 2H), 5.16 (s, 1H), 1.27 (s, 9H).

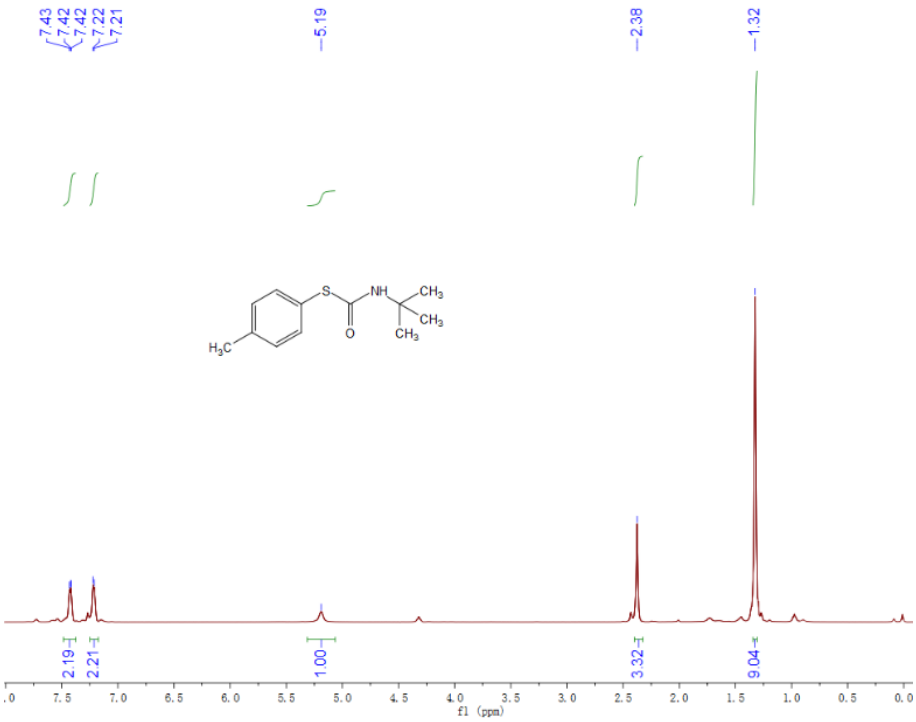


Figure S30. ^{1}H NMR for *S*-p-tolyl *tert*-butylcarbamothioate

S-p-tolyl tert-butylcarbamothioate: Compound 40 was obtained in 58 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.43 (d, 2H), 7.21 (d, 2H), 5.19 (s, 1H), 2.32 (s, 3H), 1.38 (s, 9H).

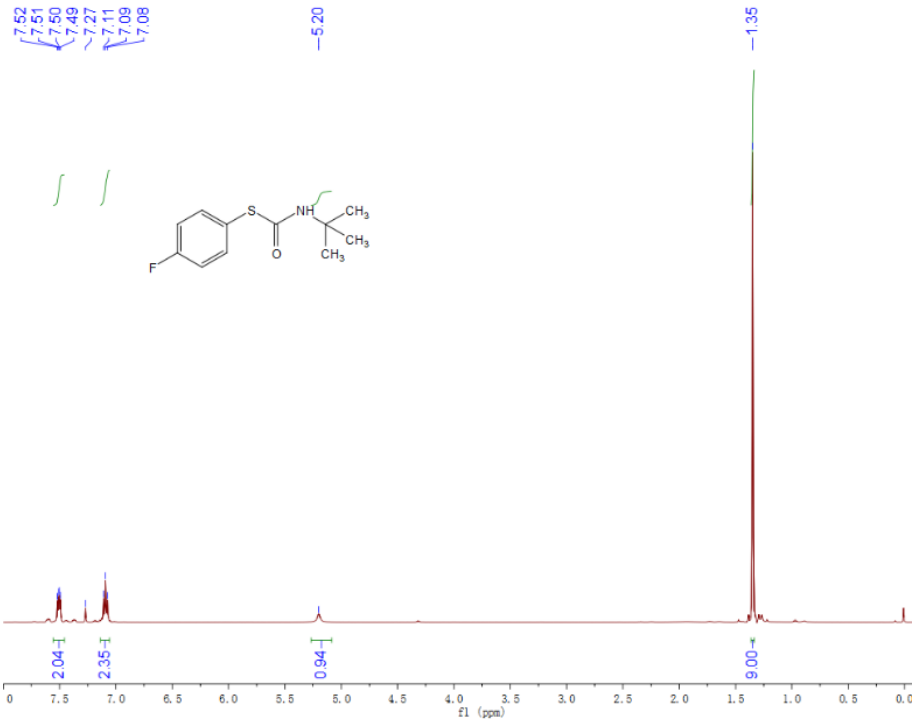


Figure S31. ^{1}H NMR for *S*-(4-fluorophenyl) tert-butylcarbamothioate *S*-(4-fluorophenyl)tert-butylcarbamothioate: Compound 4p was obtained in 61% yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm):δ 7.51−7.48 (m, 2H), 7.08 (t, 2H), 5.19 (s, 1H), 1.34 (s, 9H).

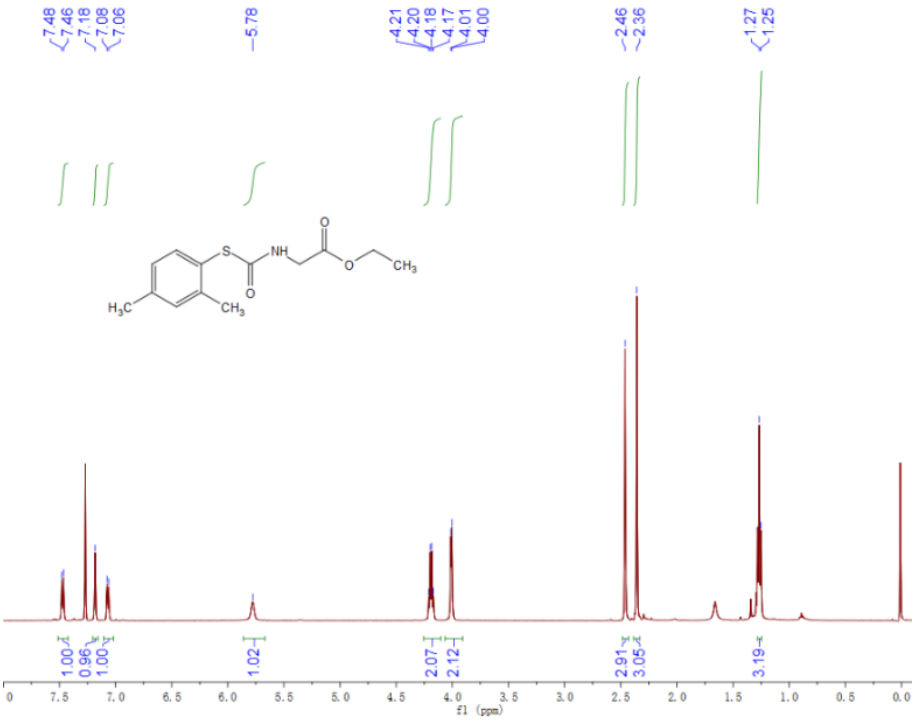


Figure S32. ^{1}H NMR for ethyl (((2,4-dimethylphenyl)thio)carbonyl) glycinate

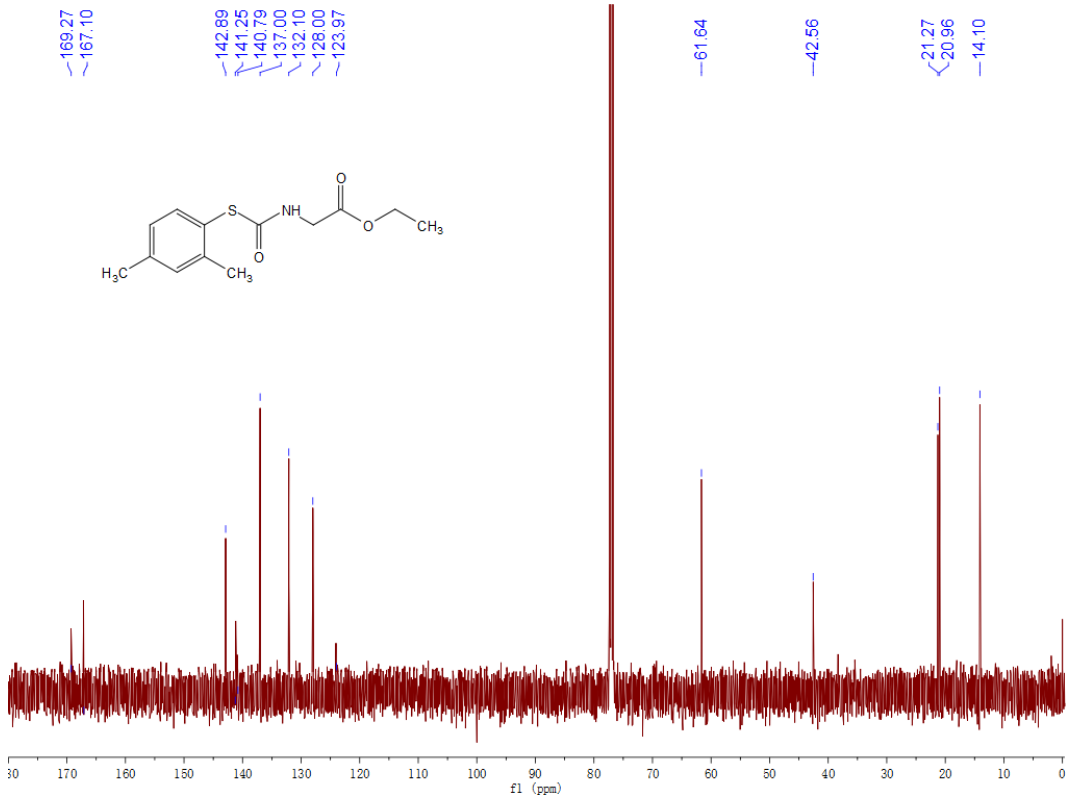


Figure S33. ^{13}C NMR for ethyl (((2,4-dimethylphenyl)thio)carbonyl) glycinate

Ethyl (((2,4-dimethylphenyl)thio)carbonyl)glycinate: Compound 4q was obtained in 75 % yield according to the general procedure . ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.47 (d, 1H), 7.18 (s, 1H), 7.07 (d, 1H), 7.33-7.30 (m, 1H), 5.78 (s, 1H), 4.20 (q, 2H), 4.01 (d, 2H), 2.46 (s, 1H), 2.36 (s, 1H),1.25 (t, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.2, 167.2, 142.9, 141.2, 140.9, 137.0, 132.1, 128.0,124.1, 61.6, 42.6, 21.3, 20.9, 14.1.

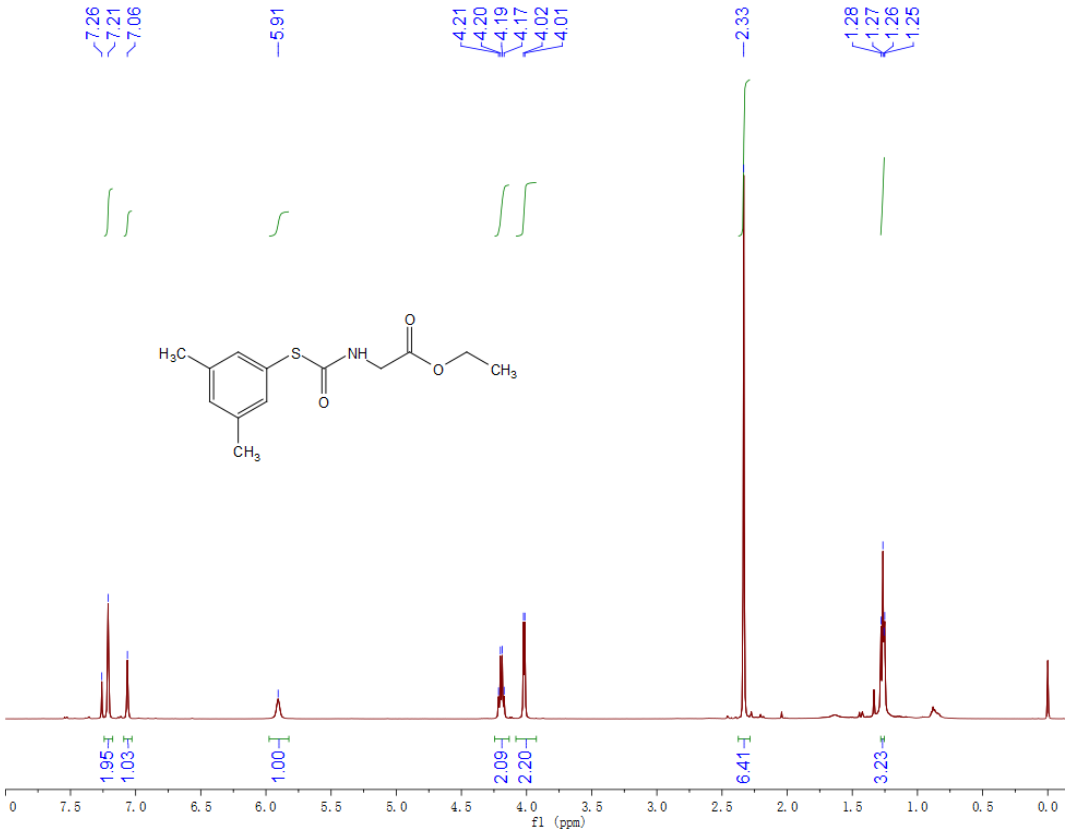


Figure S34. ^{1}H NMR for ethyl (((3,5-dimethylphenyl)thio)carbonyl) glycinate

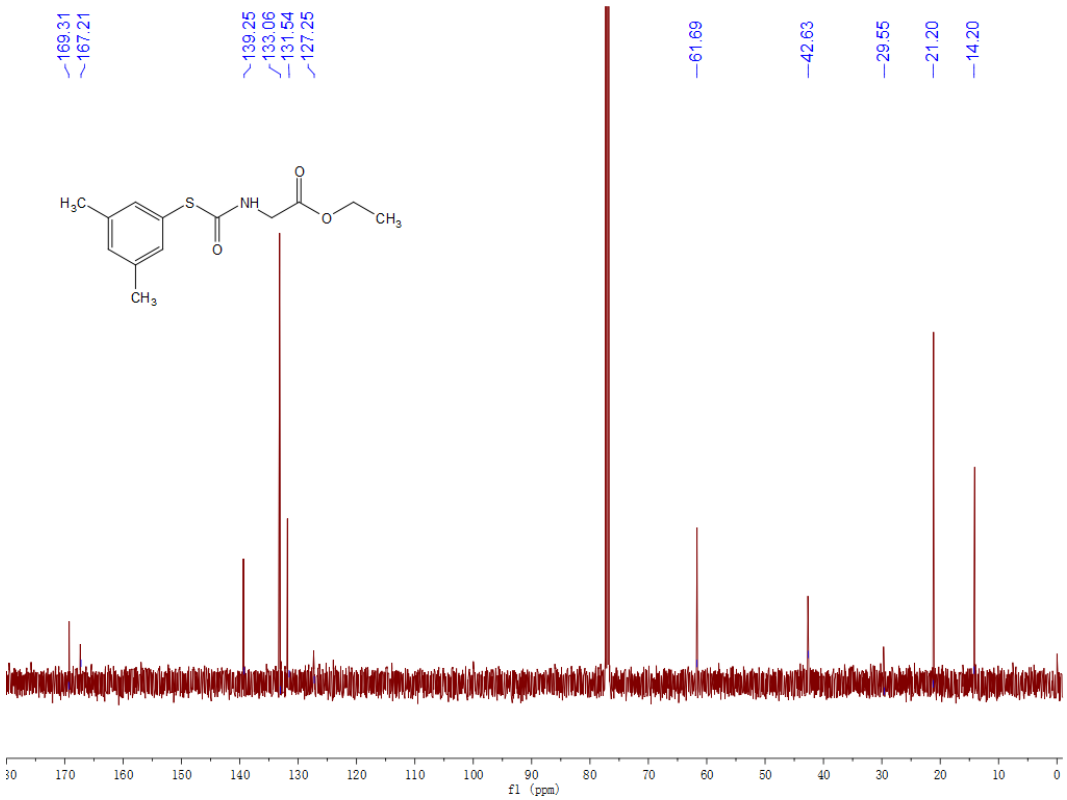
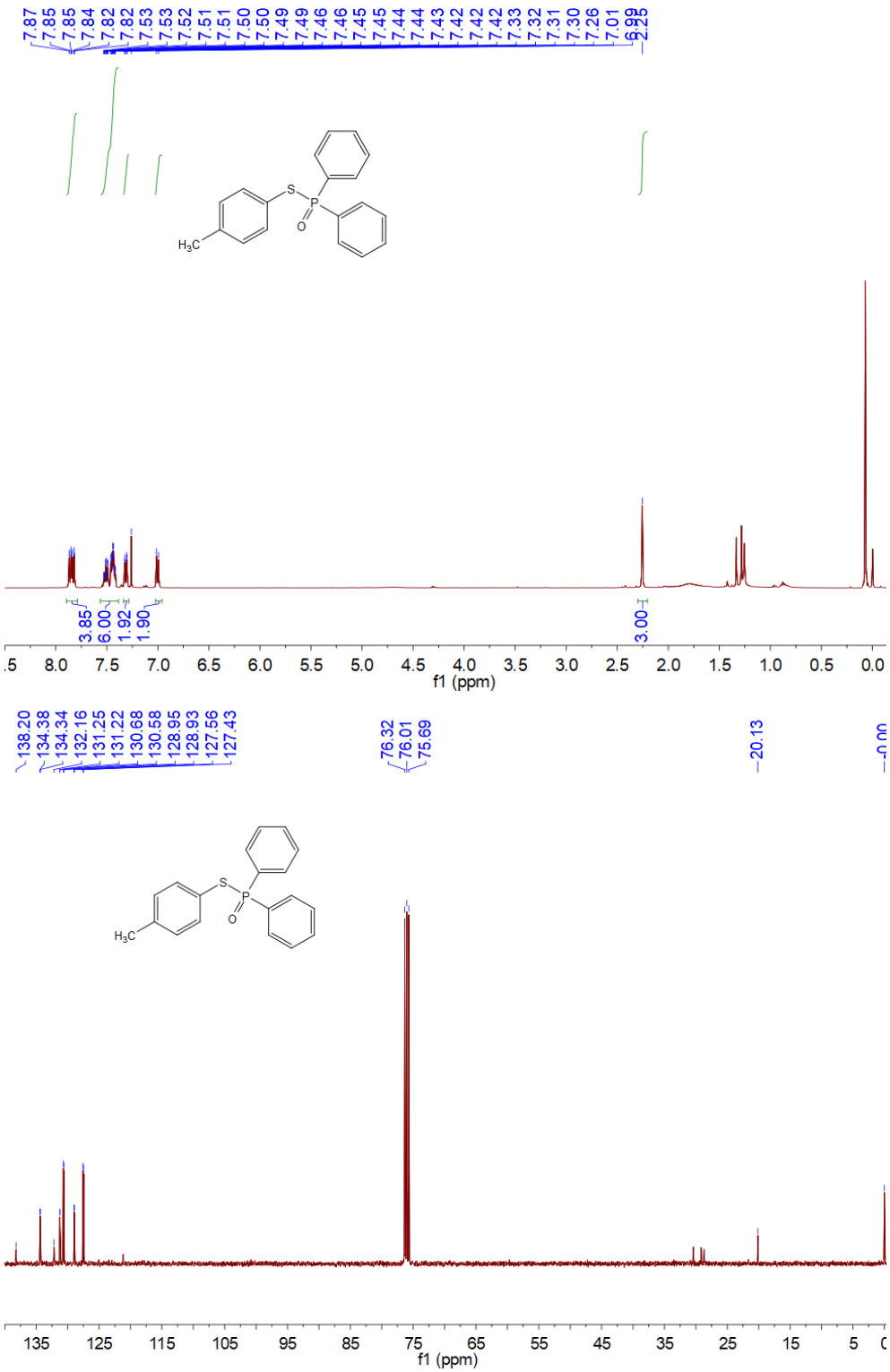
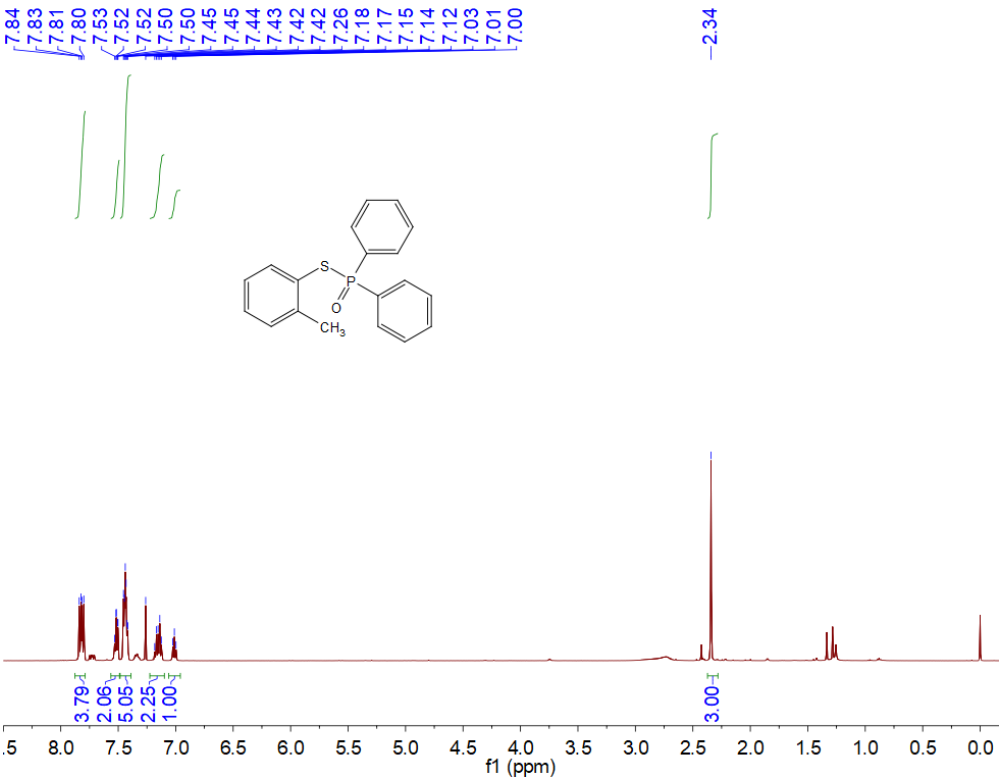


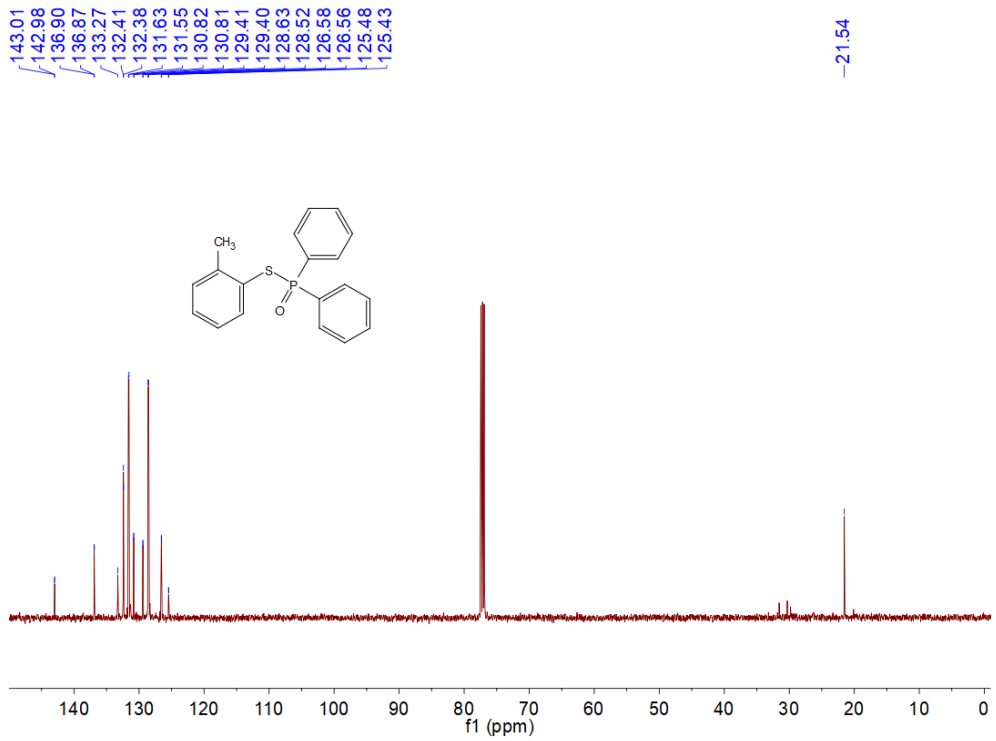
Figure S35. ^{13}C NMR for ethyl (((3,5-dimethylphenyl)thio)carbonyl) glycinate

Ethyl (((3,5-dimethylphenyl)thio)carbonyl)glycinate: Compound 4r was obtained in 82 % yield according to the general procedure. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.21(s, 2H), 7.06 (s, 1H), 5.91 (s, 1H)), 4.20 (q, 2H), 4.02 (d, 2H),2.33 (s, 6H) 1.28-1.25 (t, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.3, 167.2, 139.2, 133.0, 131.5,127.2, 61.7, 42.6, 29.5, 21.2, 14.2.



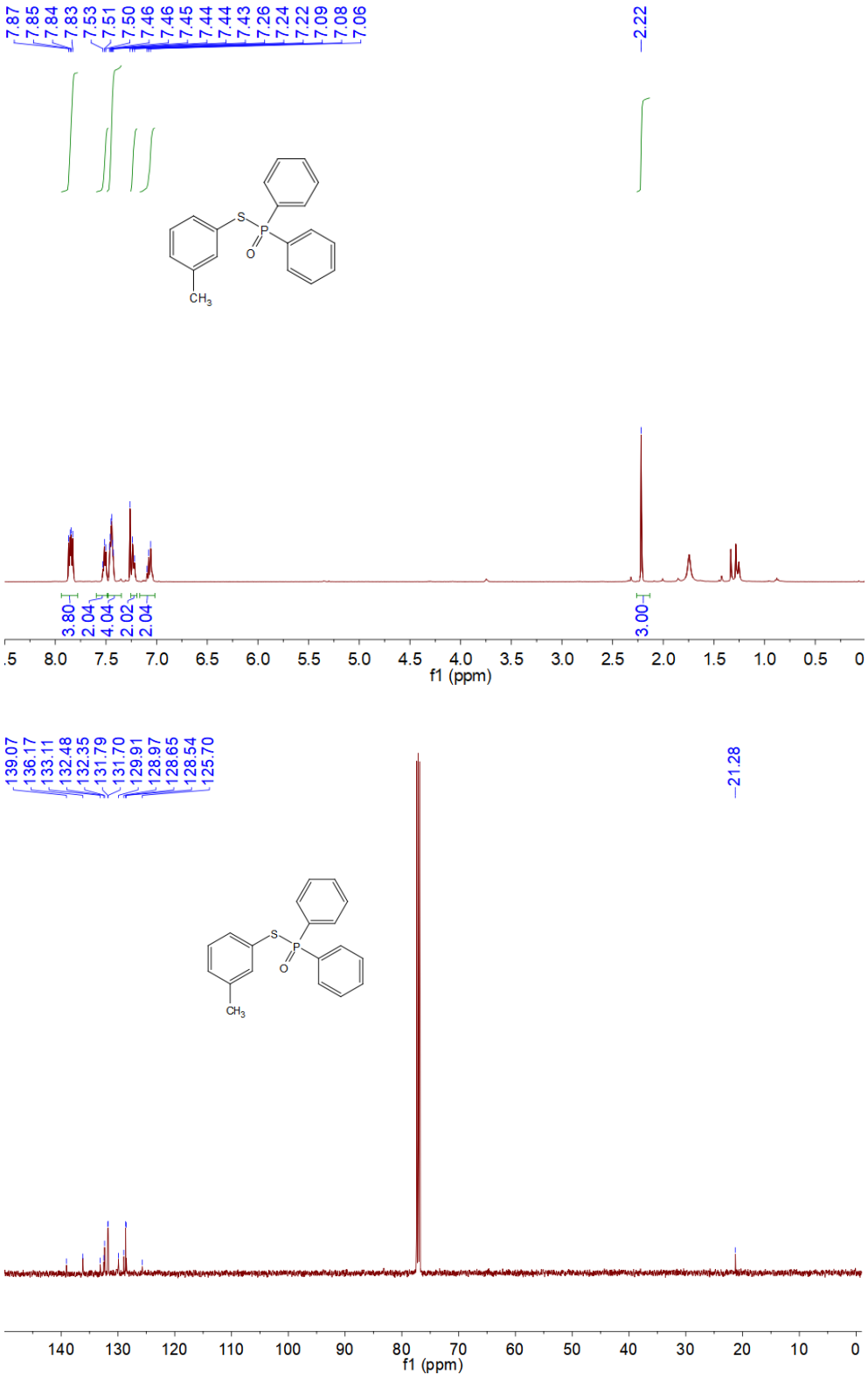
***S-(p-tolyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.82 (m, 4H), 7.53-7.42(m, 6H), 7.33-7.30 (dd, J = 4.0 Hz, 2H), 7.01-6.99 (d, J = 8.0 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 134.4, 134.3, 132.2, 131.2, 130.7, 130.6, 128.9, 127.6, 127.4, 20.1.





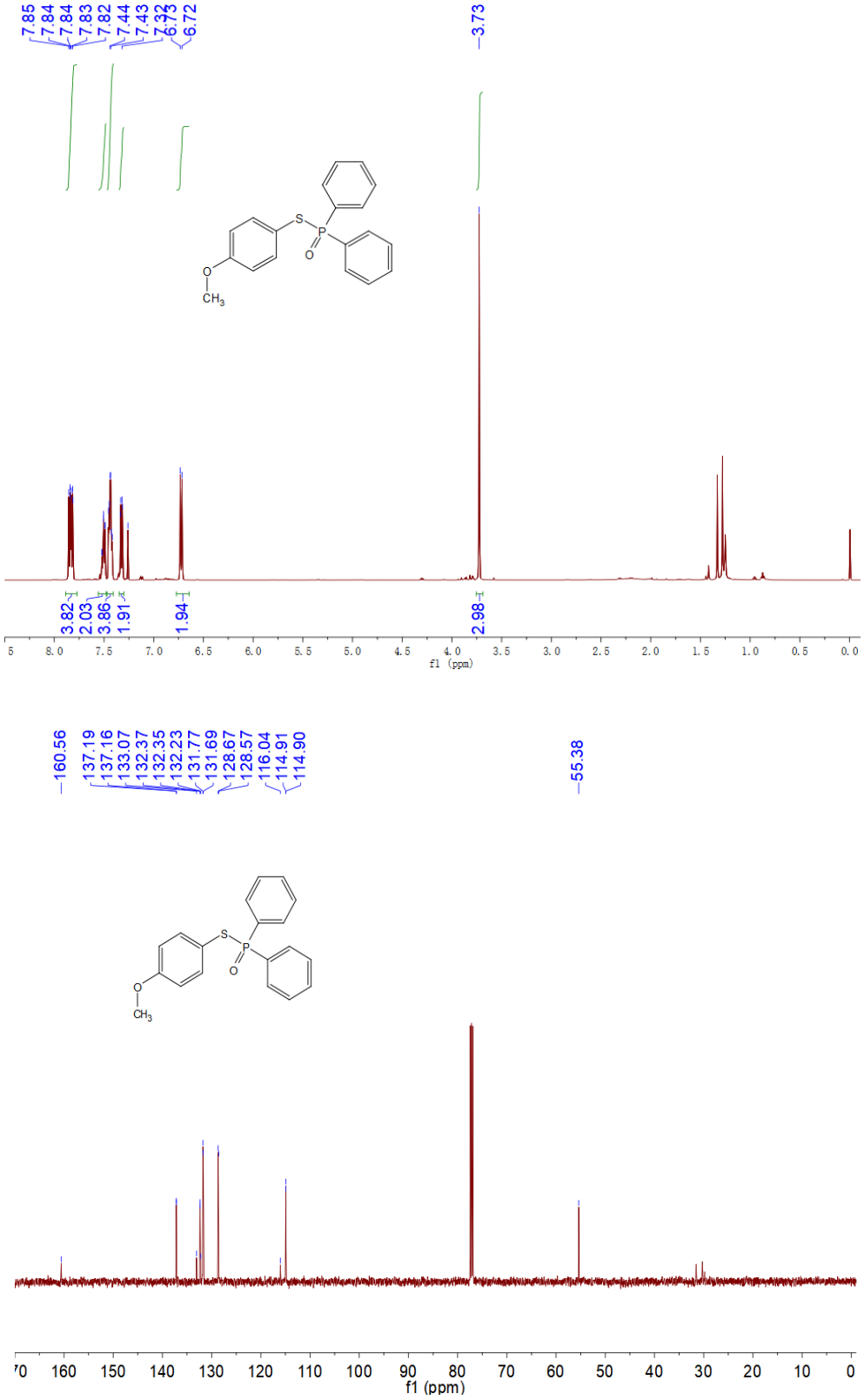
***S-(o-tolyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.84-7.80 (m, 4H), 7.53-7.50(m, 2H), 7.45-7.42 (m, 5H), 7.18-7.12 (m , 2H), 7.03-7.00 (m, 1H), 2.34(s, 3H). ^{13}C NMR ($CDCl_3$, 100

MHz): *δ* 143.0, 142.9, 136.9, 136.8, 133.3, 132.4, 131.6, 131.5, 130.8, 129.4, 128.6, 128.5, 126.6, 126.5, 125.5, 125.4, 21.5.



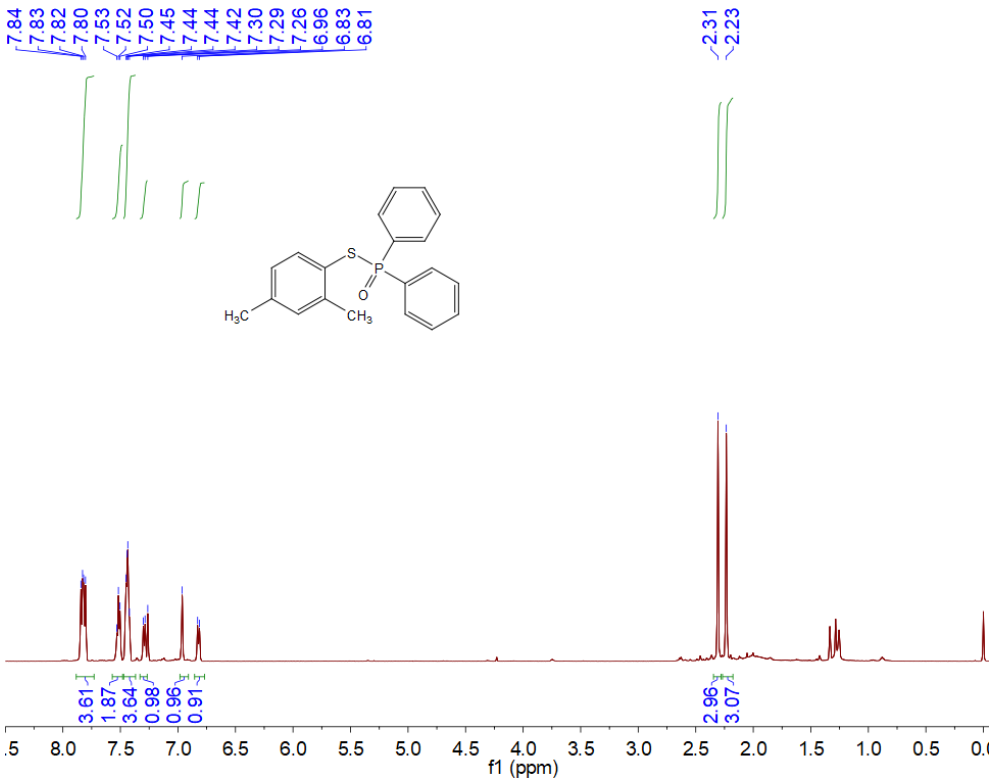
***S-(m-tolyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ 7.*87-7.83 (m, 4H), 7.53-7.50 (m, 2H), 7.46-7.42 (m, 4H), 7.24-

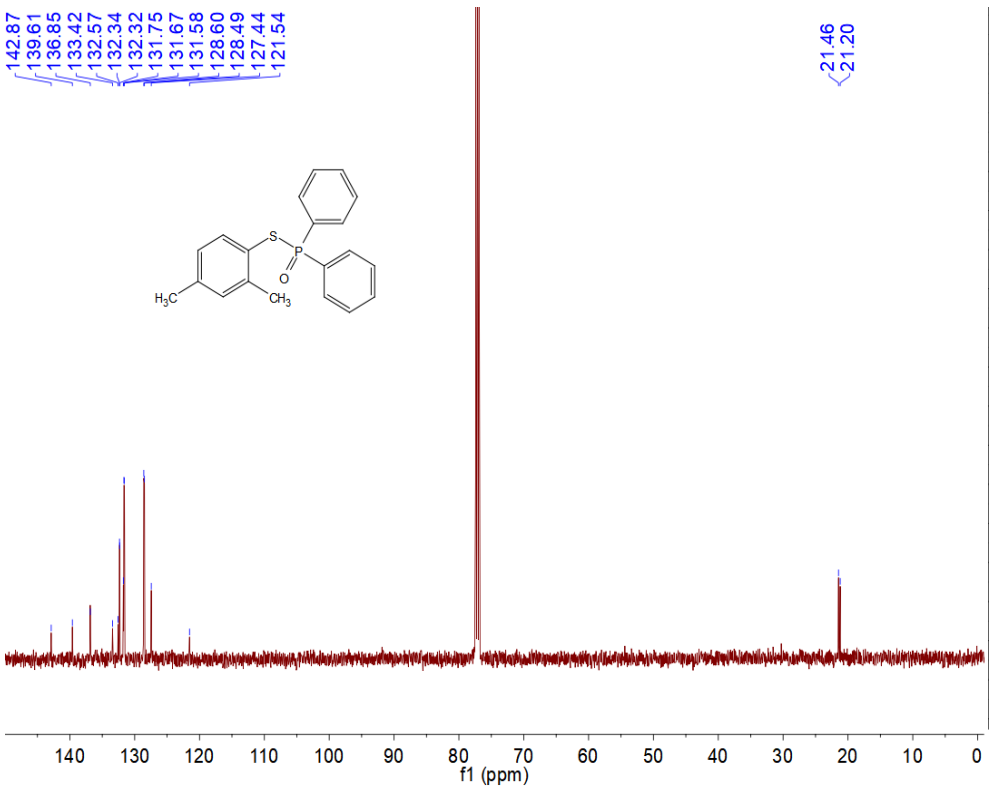
7.22 (d, *J* = 8.0 Hz, 2H),7.09-7.06 (m, 4H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 139.1, 136.2, 133.1, 132.4, 132.3, 131.8, 129.9, 128.9, 128.6, 128.5, 125.7, 21.3.



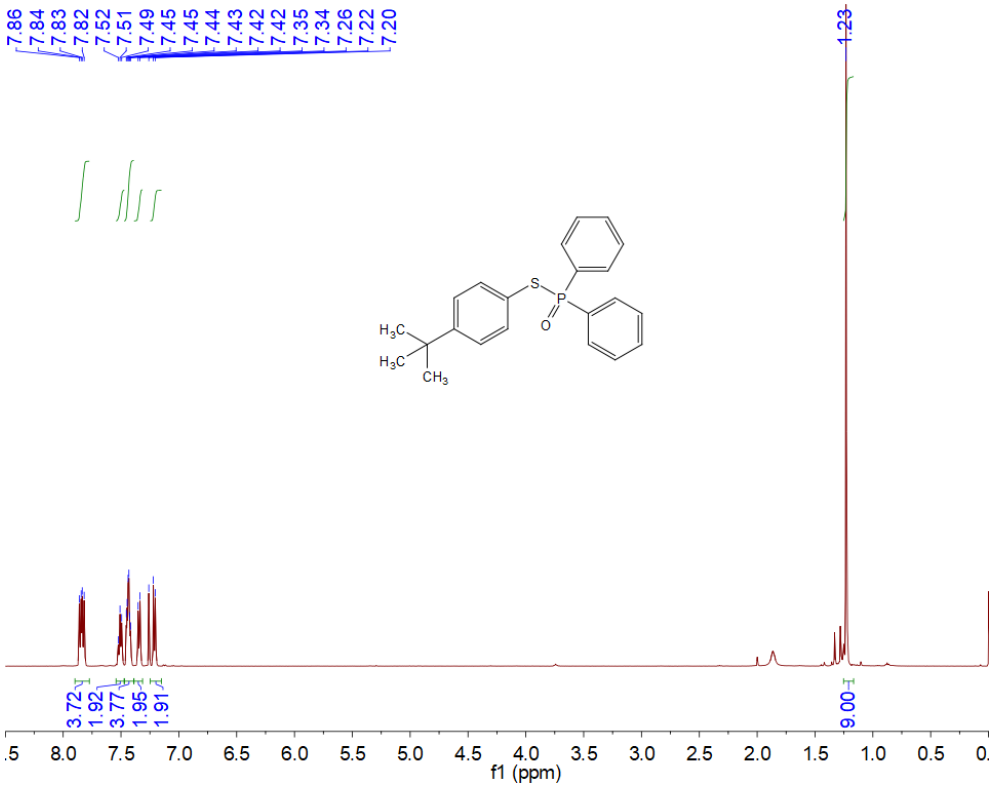
***S-(4-methoxyphenyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ 7.*85-7.81 (m, 4H), 7.52-7.49 (m, 2H), 7.45-

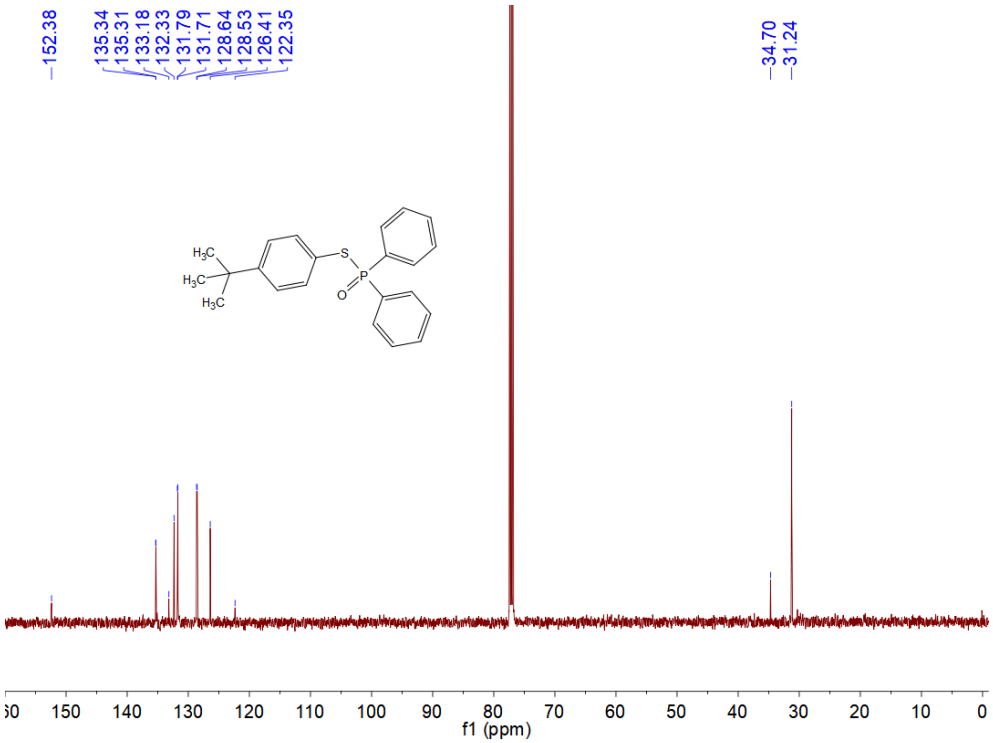
7.42 (m, 4H), 7.33-7.31 (d, *J* = 8.0 Hz, 2H),6.73-6.72 (m, 2H), 3.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 160.5, 137.2, 133.1, 132.4, 132.8, 132.7, 128.7, 128.6, 116.0, 114.9, 55.4.



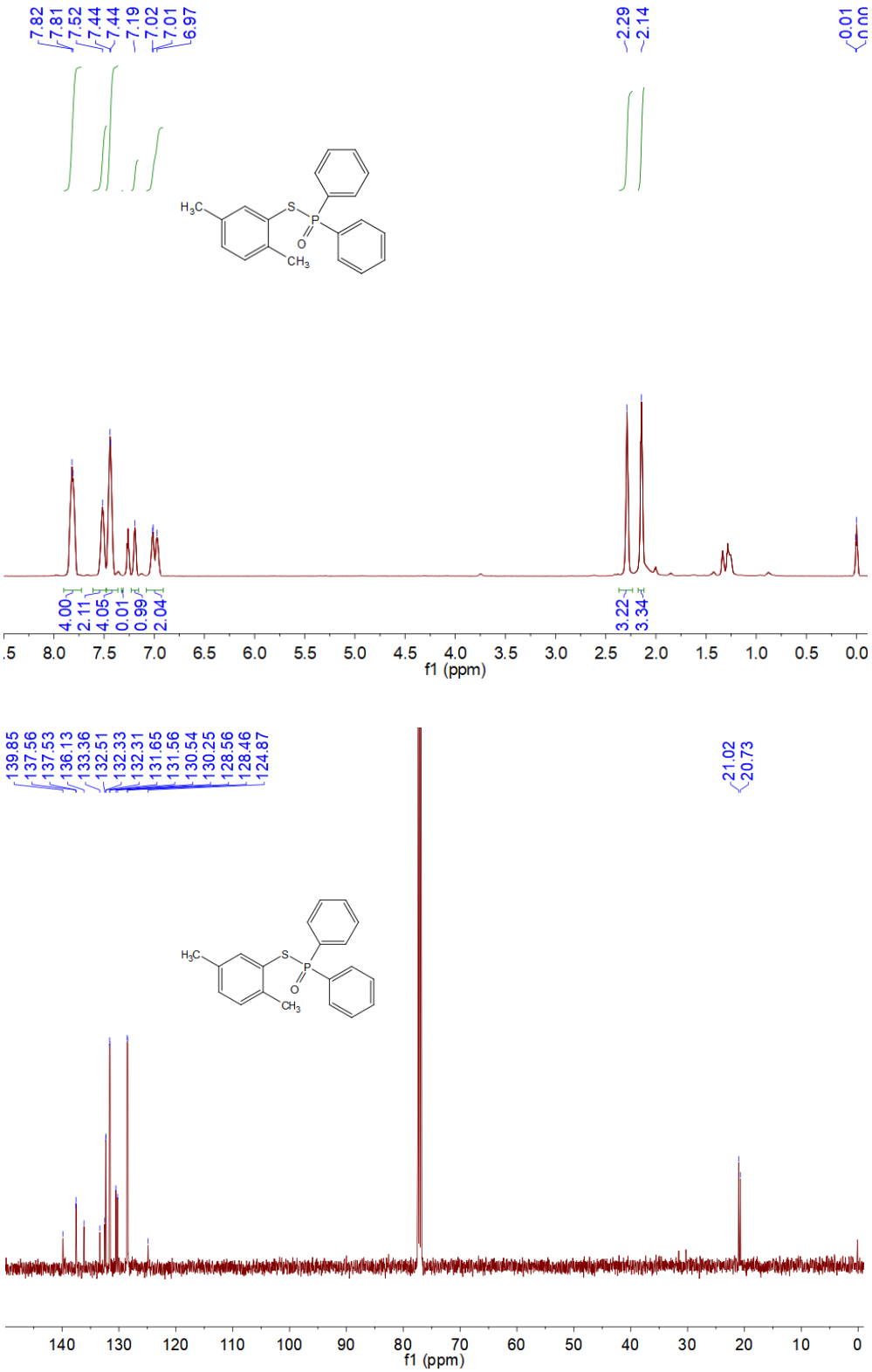


***S-(2,4-dimethylphenyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ 7.*84-7.80 (m, 4H), 7.53-7.50 (m, 2H), 7.30-7.29 (m, 1H), 6.96 (s, 1H), 6.83-6.81 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 1H), 2.31 (s, 1H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 142.9, 139.6, 136.9, 133.4, 132.6, 132.3, 131.7, 131.6, 131.5, 128.6, 128.5, 127.4,121.5, 21.4, 21.3.

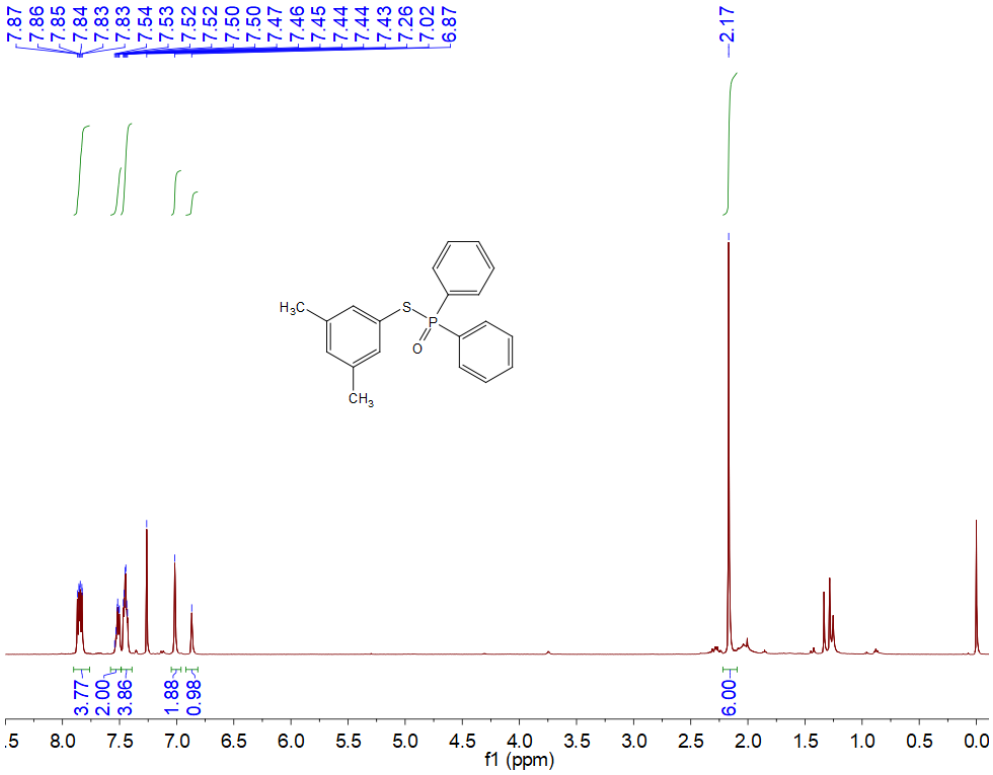


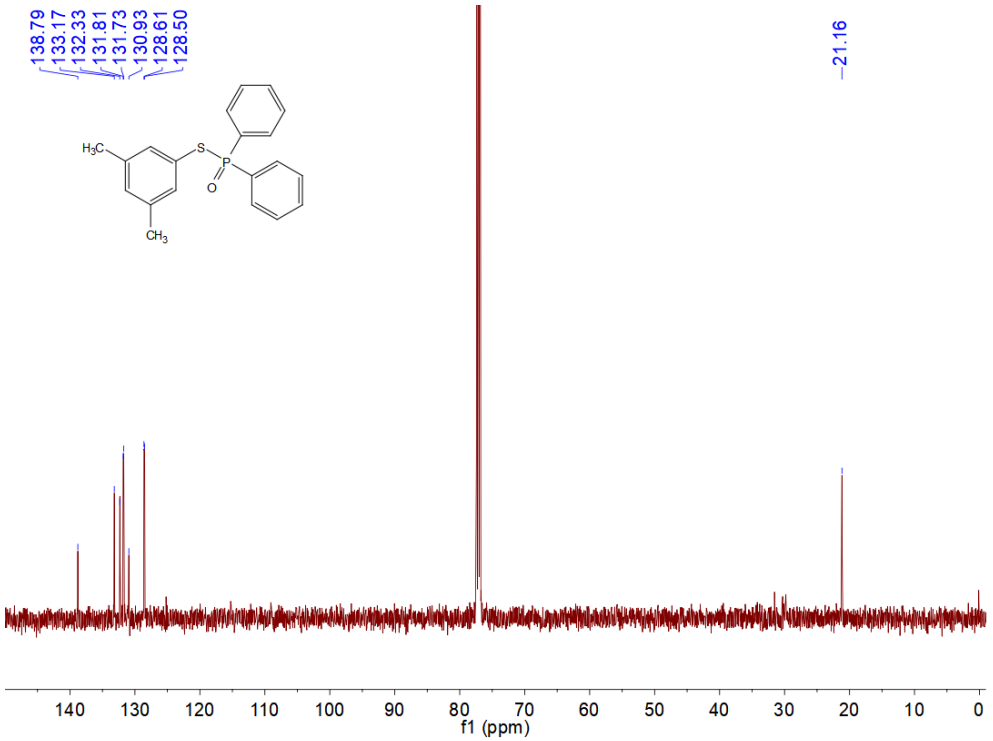


***S-(4-(tert-butyl)phenyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ 7.*86-7.82 (m, 4H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 4H), 7.35-7.34 (d, *J* = 8.0 Hz, 2H), 7.22-7,20 (d, *J* = 8.0 Hz, 2H), 1.23 (s, 9H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 152.4, 135.3, 132.3, 131.8. 131.7, 128.6, 128.5, 126.4, 122.4, 34.7, 31.2.



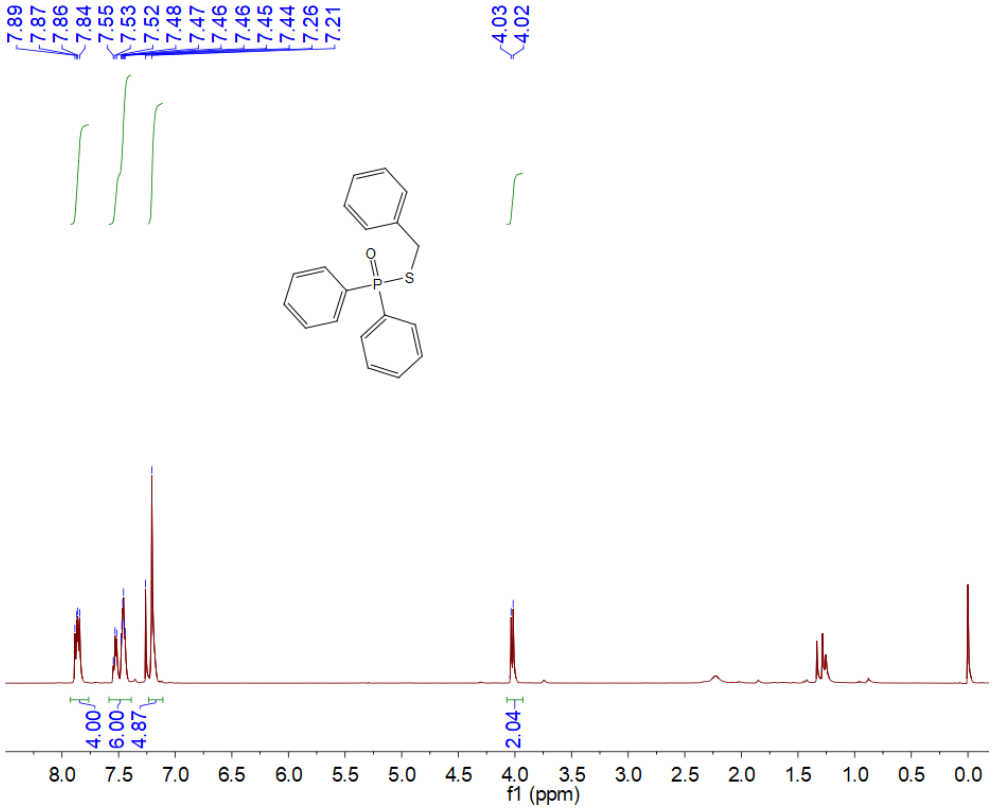
***S-(2,5-dimethylphenyl) diphenylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ 7*.82-7.81 (m, 4H), 7.52-7.44 (m, 6H), 7.19 (s, 1H), 7.02-6.97 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.14 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 139.8, 137.6, 136.1, 133.4, 132.5, 132.3, 131.7, 131.6, 130.5, 130.3, 128.6, 128.5, 124.9, 21.0,20.7.

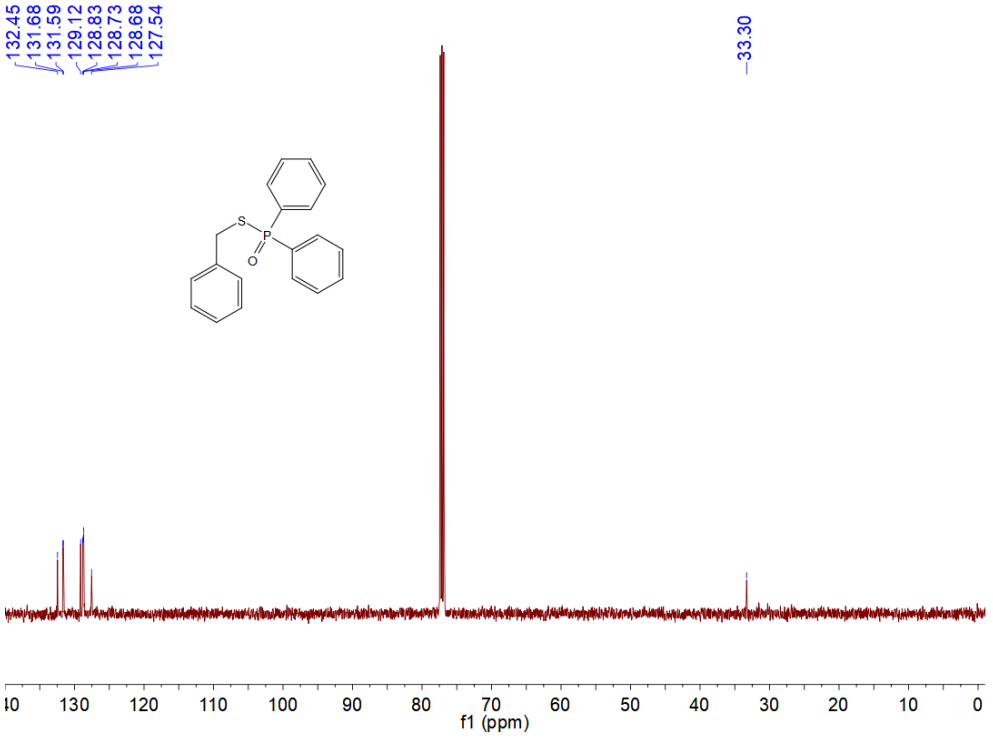




S-(3,5-dimethylphenyl) diphenylphosphinothioate: ^{1}H NMR ($CDCl_3$, 400 MHz): *δ 7.*87-7.83 (m, 4H), 7.53-7.50 (m, 2H), 7.47-7.43 (m, 4H), 7.02 (s, 1H),6.87 (s,1H), 2.17 (s, 6H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 138.8, 133.2, 132.3, 131.8, 131.7, 130.9, 128.6, 128.5,

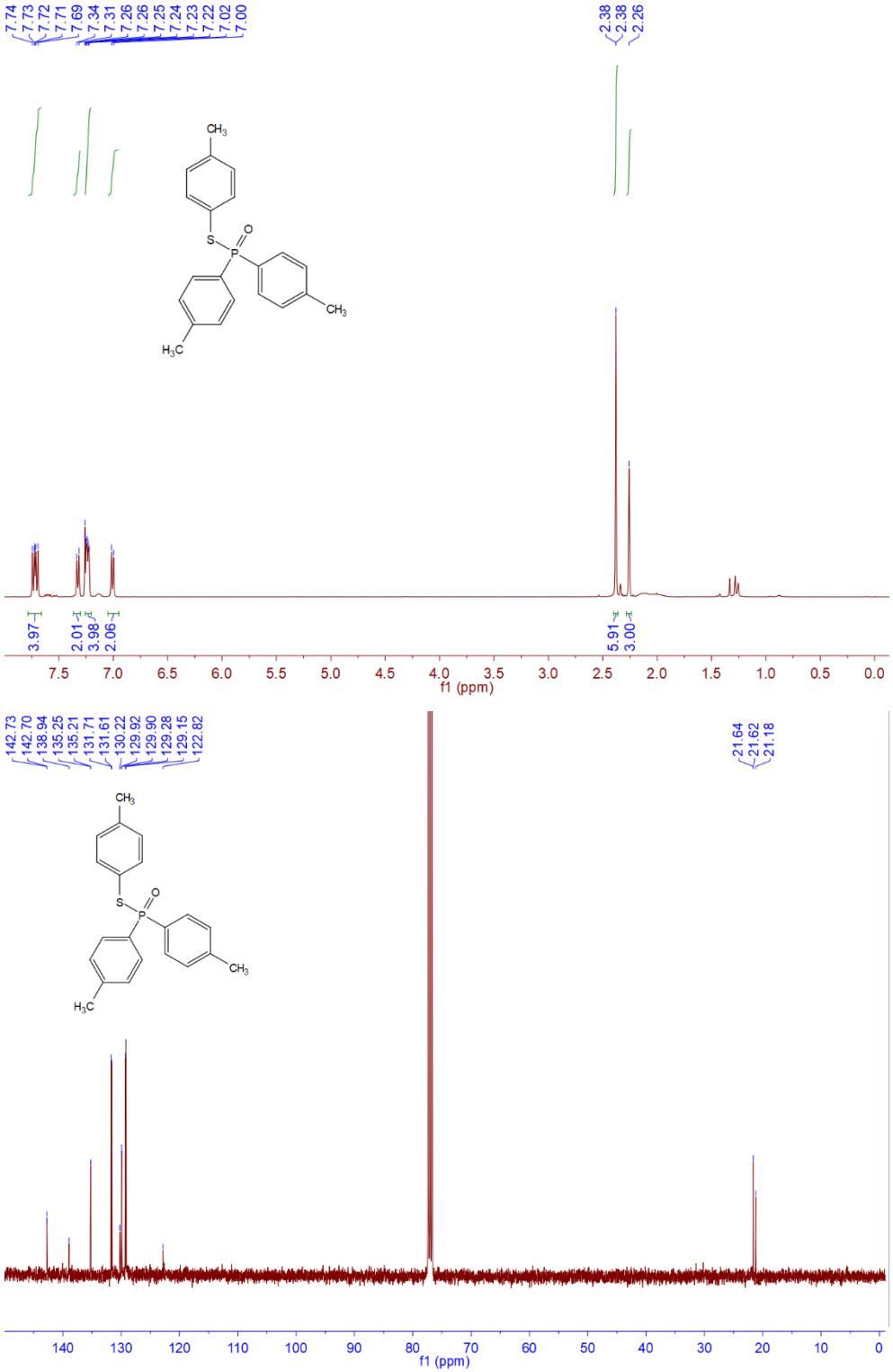
21.2.





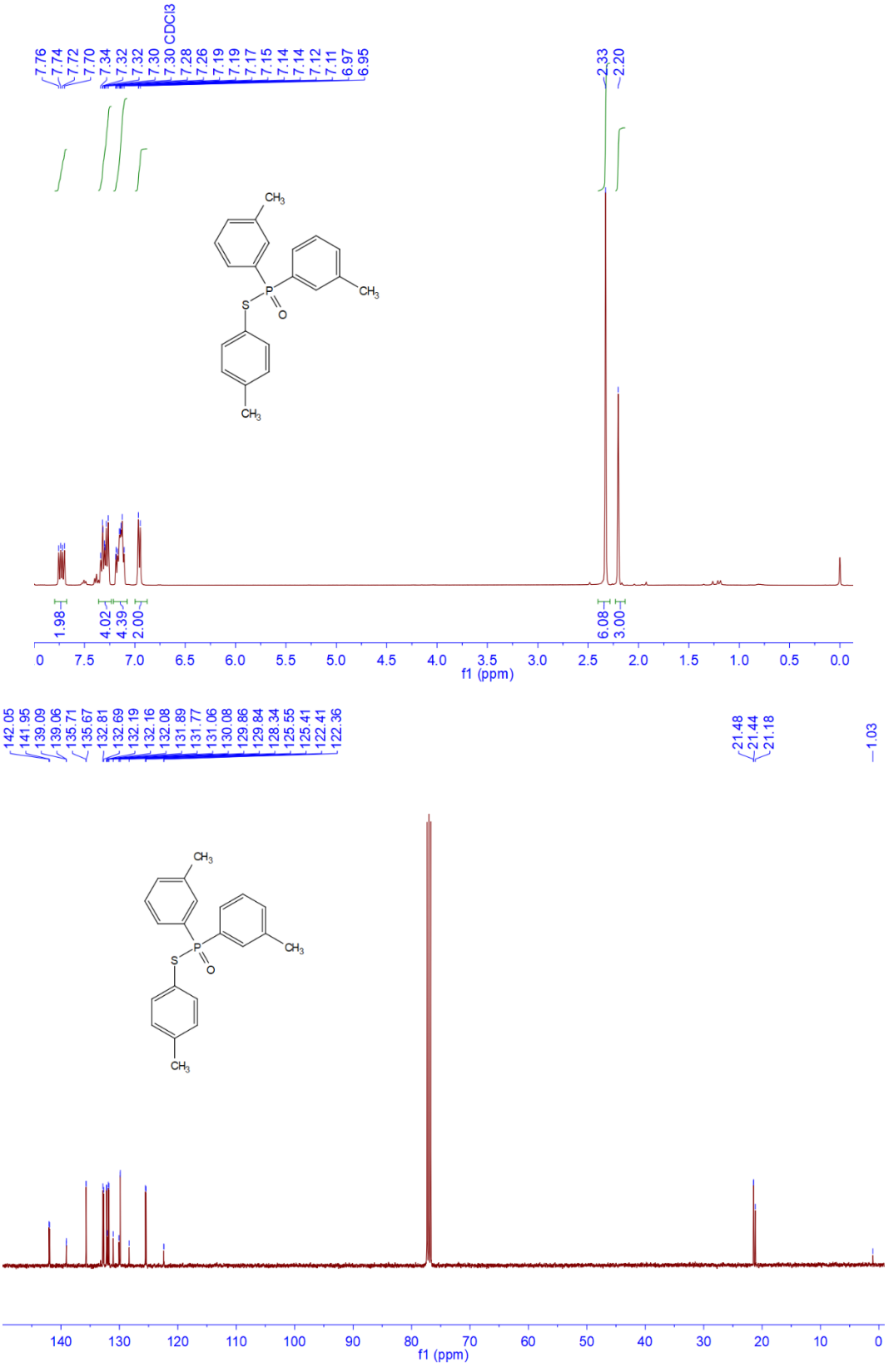
***S-benzyl diphenylphosphinothioate*: ^{1}H NMR ($CDCl_3$, 400 MHz):**

δ 7.89-7.84 (m, 4H), 7.55-7.44 (m, 6H), 7.21 (m, 5H), 4.02. (d, *J* = 4.0 Hz, 2H).^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 132.5, 131.7, 131.6, 129.1, 128.8, 128.7, 128.6, 127.5, 33.3.

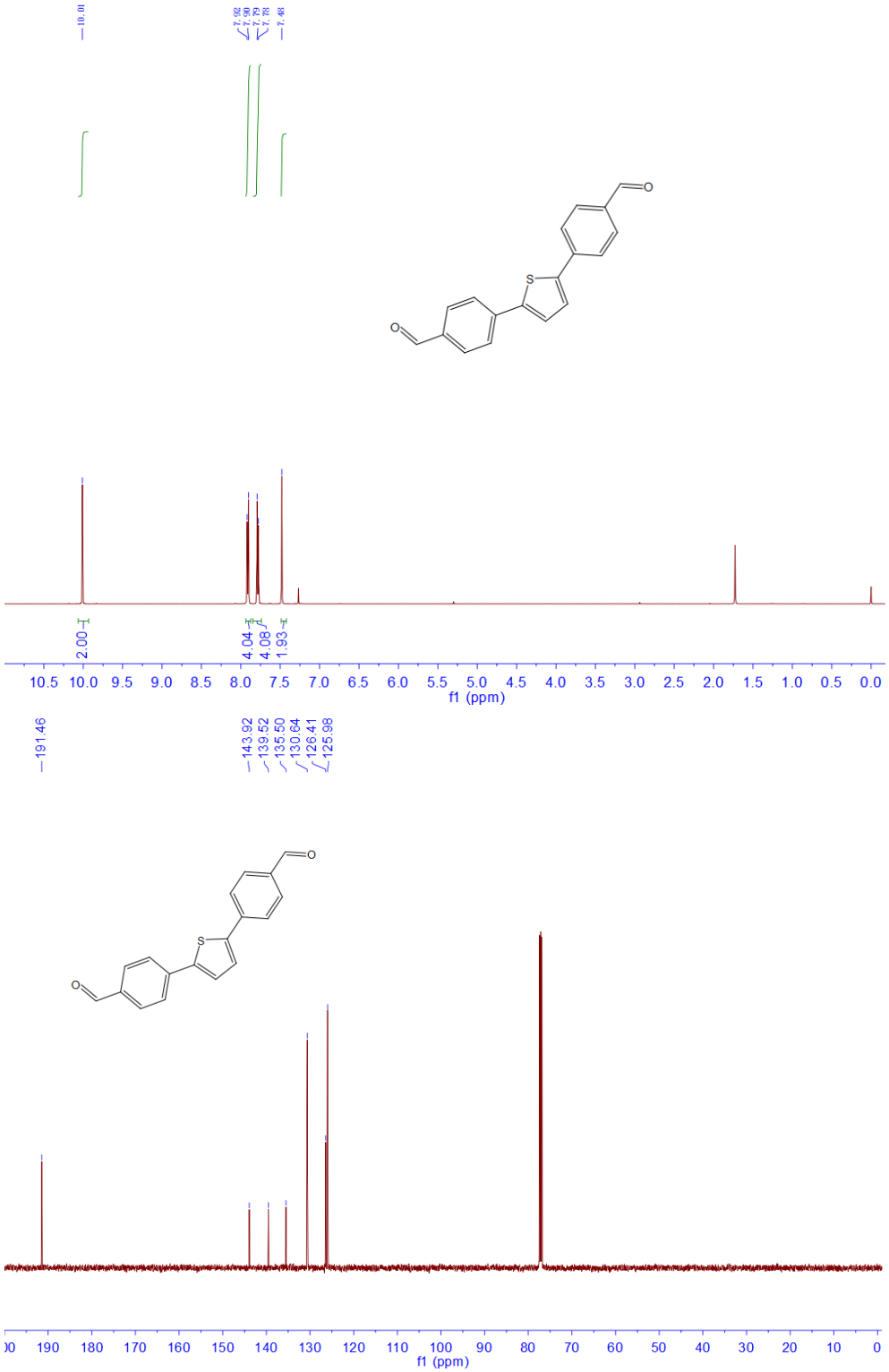


***S-(p-tolyl) di-p-tolylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): *δ* 7.74-7.69 (m, 4H), 7.33-7.31 (d, *J* = 8.0 Hz, 2H), 7.25-7.22 (m, 4H),7.02-7.00 (d, *J* = 4.0 Hz, 2H), 2.38 (s, 6H), 2.26 (s, 3H) .^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 142.7, 138.9, 135.2, 131.7, 131.6, 130.2,

129.9, 129.3, 129.2, 122.8, 21.6, 21.2.

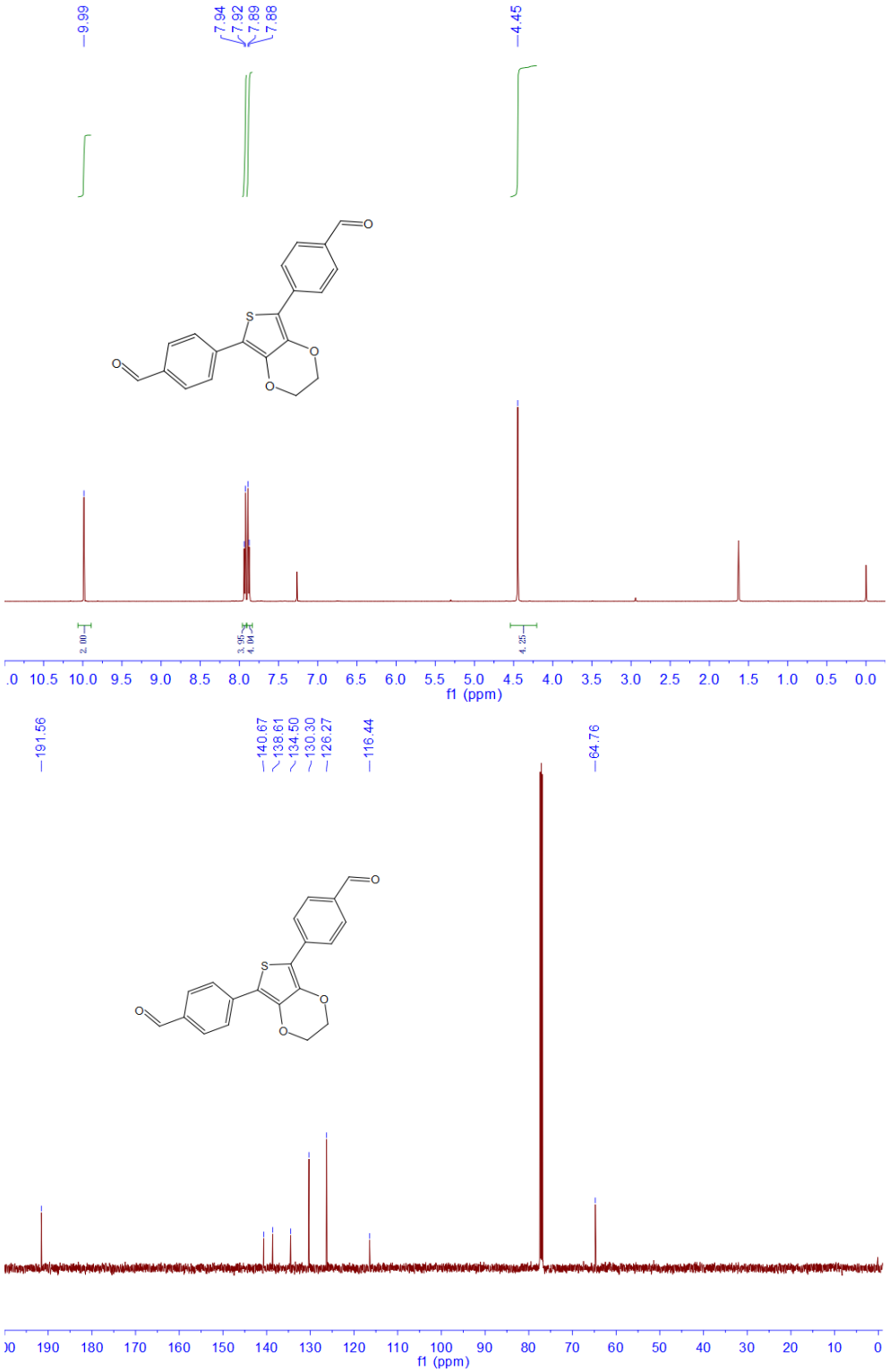


***S-(p-tolyl) di-m-tolylphosphinothioate*:** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.69 (q, J = 8.0 Hz, 2H), 7.34-7.28 (m, 4H), 7.19-7.11 (m, 4H),6.97-6.95 (d, J = 8.0 Hz, 2H), 2.33 (s, 6H), 2.20 (s, 3H) .^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.0,141.9, 139.0, 135.7, 132.8, 132.2, 131.0, 129.8, 128.3, 125.5, 125.4, 122.4. 21.5, 21.4, 21.2.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.0 (s, 2H), 7.92-7.90 (d, J = 8.0 Hz,

4H), 7.79-7.78 (d, *J* = 8.0 Hz, 4H), 7.48 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 191.5, 143.9, 139.5, 135.5, 130.6, 126.4, 126.0 ppm.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.99 (s, 2H), 7.94-7.92 (d, *J* = 8.0 Hz,

4H), 7.89-7.88 (d, J = 4.0 Hz, 4H), 4.45 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.6, 140.7, 138.6, 134.5, 130.3, 126.3, 116.4, 64.8 ppm.