Supporting Information

δ-amination of Alkyl Alcohols via Energy Transfer Photocatalysis

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1. General Considerations

1.1 General: For purple and blue light irradiation a Kessil PR160-purple LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 390 nm), a Kessil PR160-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) or a Kessil PR160-blue LED LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 456 nm) was placed 4 cm away from the reaction vials. NMR spectra (^{1}H, ^{13}C, ^{19}F) were acquired on a Bruker Avance 300 and 500 MHz spectrometers. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, δ_H = 7.26 ppm, δ_C = 77.16 ppm). ^{13}C NMR and ^{19}F spectra were acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), bs (broad singlet). Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (60 Å porosity, 250 μm thickness) in heptane/EtOAc as the eluent, and visualized using bromocresol, ninhydrin, vanillin, *p*-anisaldehyde stain, and/or UV light. Reactions were monitored by ^{1}H NMR, and/or TLC. Flash column chromatography was accomplished using silica gel Merck-60 from Aldrich. High Resolution Mass Spectrometry (HRMS) were registered in a spectrometer Bruker maXis IITM (Q-TOF) or a GCT Agilent Technologies 6890 N using Atmospheric Pressure Chemical Ionization (APCI) or Electrospray Ionization (ESI) method. Melting points (°C) were measure using Büchi Melting Point B-540 apparatus in open capillary tubes, and the values are uncorrected. UV/vis measurements were measured in a 1 cm quartz cuvette using a JASCO V-660 UV/vis spectrophotometer. The continuous-flow experiment was carried out using a homemade flow setup with a syringe pump (Chemyx Fusion 100), two Kessil lamps, and 1.36 mL perfluoroalcoxy (PFA) reactor coil (inner diameter: 1.6 mm, external diameter 3.0 mm). Photoredox-catalyzed reactions were performed using 8 mL Screw Neck Vial (clear glass, 45 x 14.7 mm) with screw cap 13 mm black Sil/PTFE septum.

1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Dry acetone, AcOEt, DMA, DMF and DMSO were obtained from ThermoFisher and used as received. MeCN, THF and CH_2Cl_2 were purchased and dried using a solvent delivery system. Alcohols, triphenylphosphine, *N*-hydroxyphtalimide, DIAD, DMAP, hydrazine hydrate, pyruvic acid, and EDC·HCl were purchased from commercial suppliers and used as received. Diphenylmethanone oxime[1] and 6-(2-isopropyl-5-methylphenoxy)hexan-1-ol[2] were synthesized following reported procedures. All the pbotocatalyst were purchased from commercial suppliers and used as received, except for 4CzIPN[3] and 5CzBN[4], which were synthesized following reported procedures.

[1] Y. Gao, J. Liu, Z. Li, T. Guo, S. Xu, H. Zhu, F. Wei, S. Chen, H. Gebru, K. Guo. *J. Org. Chem.* **2018**, *83*, 2040-2049.

[2] W. Yu, T. Gill, L. Wang, Y. Du, H. Ye, X. Qu, J.-T. Guo, A. Cuconati, K. Zhao, T. M. Bloc, X. Xu, J. Chang. *J. Med. Chem.* **2012**, *55*, 6061-6075.

[3] M. Garreau, F. Le Vaillant, J. Waser, *Angew. Chem. Int. Ed.* **2019**, *58*, 8182-8186.

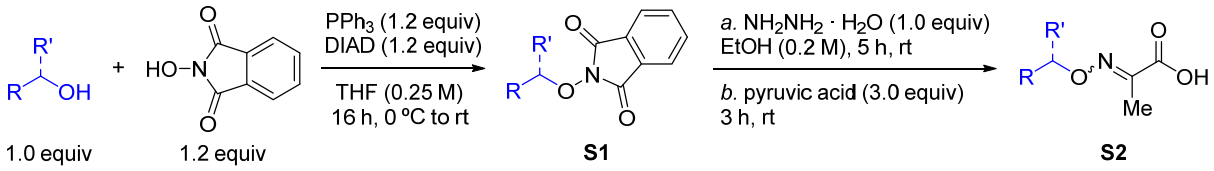
[4] J. Lu, B. Pattengale, Q. Liu, S. Yang, W. Shi, S. Li, J. Huang, J. Zhang. *J. Am. Chem. Soc.* **2018**, *140*, 13719-13725

2. Synthesis of Starting Materials

2.1 General Procedure A: Synthesis of α-Oxime Acids and α-Hydrazone Acids

All the acids **S2** were synthesized from the corresponding alcohols, alkyl halides or tosyl amines, according to the literature procedure.[5]

- **General Procedure A1: Primary and Secondary Alcohols**

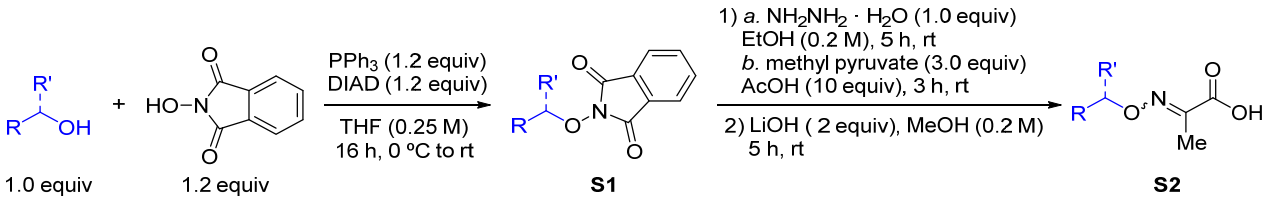


Synthesis of phtalimide **S1**. A solution of the correspondig alcohol (1.0 equiv), *N*-hydroxyphthalimide (1.2 equiv) and triphenylphosphine (1.20 eq.) in THF (0.25 M) under a nitrogen atmosphere was cooled to 0 ºC with an icebath. Diisopropylazodicarboxylate (1.2 equiv) was added dropwise to the solution at 0 ºC. The resulting mixture was stirred at 0 ºC for 10 minutes, after that the icebath was removed, and the reaction was stirred at room temperature for 16 h or until the reaction was complete by TLC analysis. Then, the reaction mixture was concentrated under reduced pressure, and the crude mixture was subjected to purification by flash column chromatography using heptane/ethyl acetate as the mobile phase. The resultant phthalimide **S1** was then used directly for the next step.

Synthesis of α-oxime acids **S2**. To a stirred suspension of the previous phtalimide **S1** (1.0 equiv) in absolute ethanol (0.2 M), hydrazine (1.0 M in THF,1.0 equiv) was added in a single portion. The mixture was stirred at room temperature for 5 hours, and the formation of a white precipitate was observed. The white solid was filtered off through a plug of Celite, and the filter pad was washed with a minimal amount of absolute ethanol. Then, pyruvic acid (3.0 equiv) was added to the solution, and the resulting mixture was stirred for 3 h at room temperature. Upon completion, the reaction mixture was concentrated under reduced preassure, and poured into 10% aq HCl soln. The mixture was poured into a separatory funnel, and extracted with AcOEt (2x20 mL). The combined organic layers were extracted with an aq NaOH soln (2 M, 4x20 mL). The combined basic aq layers were washed with AcOEt (2x20 mL), carefully acidified to pH 1 with con HCl, and extracted with AcOEt (3x20 mL). The combined organic layers were washed with satd NaCl soln, dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The resultanting α-oxime Acids **S2** was then used directly for the next step without further purification because problems in its isolation. (NOTE: No special caution for avoid O_2 in this reaction.)

[5] a) T. Kang, H. Kim, J. G. Kim, S. Chang. *Chem. Commun.* **2014**, *50*, 12073-12075; b) A. N. Herron, D. Liu, G. Xia, J.-Q. Yu. *J. Am. Chem. Soc.* **2020**, *142*, 2766-2770; c) A. N. Herron, C.-P. Hsu, J.-Q. Yu. *Org. Lett.* **2022**, *24*, 3652-3656.

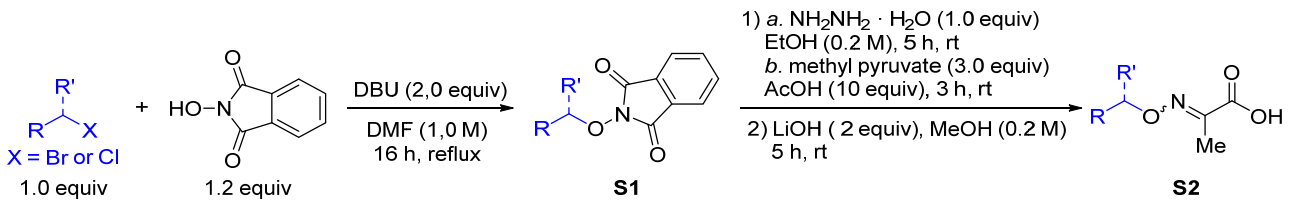
- **General Procedure A2: Primary and Secondary Alcohols**[5a,b]



Synthesis of phtalimide **S1**. A solution of the correspondig alcohol (1.0 equiv), *N*-hydroxyphthalimide (1.2 equiv) and triphenylphosphine (1.20 eq.) in THF (0.25 M) under a nitrogen atmosphere was cooled to 0 ºC with an icebath. Diisopropylazodicarboxylate (1.2 equiv) was added dropwise to the solution at 0 ºC. The resulting mixture was stirred at 0 ºC for 10 minutes, after that the icebath was removed, and the reaction was stirred at room temperature for 16 h or until the reaction was complete by TLC analysis. Then, the reaction mixture was concentrated under reduced pressure, and the crude mixture was subjected to purification by flash column chromatography using heptane/ethyl acetate as the mobile phase. The resultant phthalimide **S1** was then used directly for the next step.

Synthesis of α-oxime acids **S2**. To a stirred suspension of the previous phtalimide **S1** (1.0 equiv) in absolute ethanol (0.2 M), hydrazine (1.0 M in THF, 1.0 equiv) was added in a single portion. The mixture was stirred at room temperature for 5 hours, and the formation of a white precipitate was observed. The white solid was filtered off through a plug of Celite, and the filter pad was washed with a minimal amount of absolute ethanol. Then, methyl pyruvate (3.0 equiv) and acetic acid (10.0 equiv) were added to the solution, and the resulting mixture was stirred for 12 h at room temperature. Upon completion, the reaction mixture was concentrated under reduced preassure, and washed with water. The crude mixture was subjected to purification by flash column chromatography (5-10 % AcOEt in heptane) to obtain the corresponding intermediate oxime ester. Then, this ester was dissolved in mixture of methanol/H_2O (0.2 M, 3:1), and LiOH (3.0 equiv) was added. The resulting mixture was stirred at room temperature until the reaction was complete by TLC analysis (3-5 h). The reaction was concentrated under reduced pressure, acidified using a 10% aq HCl soln, and extracted with AcOEt (2x20 mL). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure, obtaining the pure product **S2**. (NOTE: No special caution for avoid O_2 in this reaction.).

- **General Procedure A3: Alkyl Halides**[5a,b]

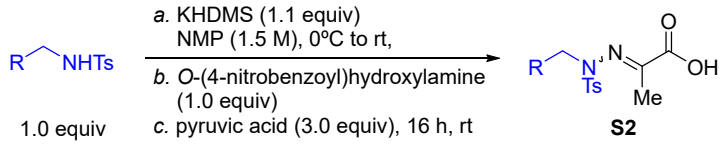


Synthesis of phtalimide **S1**. To a solution of the corresponding alkyl halide (1.0 equiv) and *N*-hydroxyphthalimide (1.2 equiv) in DMF (1.0 M), DBU (2.0 equiv) was added, and the resulting mixture was stirred at 90ºC for 3 h. The reaction was quenched with a 10% aq HCl soln, and extracted with AcOEt (3x20 mL). The combined organic

layers were washed with with satd NaCl soln three times, dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture of **S1** was used to the next step without further purification. (NOTE: No special caution for avoid O_2 and H_2O in this reaction.).

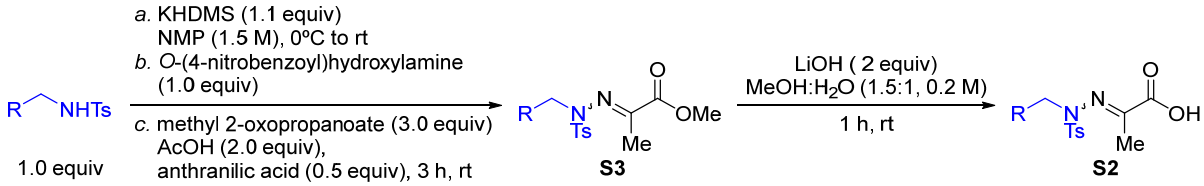
Synthesis of α-oxime acids **S2**. To a stirred suspension of the previous phtalimide **S1** (1.0 equiv) in absolute ethanol (0.2 M), hydrazine (1.0 M in THF, 1.0 equiv) was added in a single portion. The mixture was stirred at room temperature for 5 hours, and the formation of a white precipitate was observed. The white solid was filtered off through a plug of Celite, and the filter pad was washed with a minimal amount of absolute ethanol. Then, methyl pyruvate (3.0 equiv) and acetic acid (10.0 equiv) were added to the solution, and the resulting mixture was stirred for 12 h at room temperature. Upon completion, the reaction mixture was concentrated under reduced preassure, and washed with water. The crude mixture was subjected to purification by flash column chromatography (5-10 % AcOEt in heptane) to obtain the corresponding oxime ester. Then, this ester was dissolved in mixture of methanol/H_2O (0.2 M, 3:1), and LiOH (3.0 equiv) was added. The resulting mixture was stirred at room temperature until the reaction was complete by TLC analysis (3-5 h). The reaction was concentrated under reduced pressure, acidified using a 10% aq HCl soln, and extracted with AcOEt (2x20 mL). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure, obtaining the pure product **S2**. (NOTE: No special caution for avoid O_2 in this reaction.).

- **General Procedure A4: Tosyl Amines**[5c]



To a solution of the corresponding tosyl amine (1.0 equiv) in dry NMP (Aldrich SureSeal™, 1.5 M), a 1.0 M solution of potassium hexamethyldisilazide in THF (1.1 equiv) was added at 0ºC under inert atmosphere. The mixture was stirred at room temperature for 10-15 min, darkening with the time. Then, *O*-(4-nitrobenzoyl)hydroxylamine (1.00 eq.) was added, and the resulting mixture was stirred for other additional 15 min (monitoring by TLC because the hydrazide product usually stains yellow/orange using vanillin stain). The reaction was quenched with water (50 mL), and extracted with AcOEt (3 x 30 mL). The combined organic layers were washed with with satd NaCl soln three times, dried (Na_2SO_4), and the volatiles were removed under reduced pressure. (NOTE: This hydrazide is unstable and cannot be stored. It must be used immediately for the next step). Then, pyruvic acid (3.0 equiv) was added to a solution of the previous crude mixture in MeOH (0.2 M), and the mixture was stirred 18 h at room temperature. Upon completion, the reaction mixture was concentrated under reduced preassure, and washed with water. The organic layer was dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The resultanting α-hydrazone acid **S2** was then used directly for the next step without further purification because problems in its isolation. (NOTE: No special caution for avoid O_2 in this reaction).

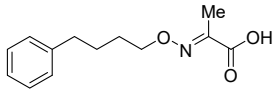
- **General Procedure A5: Tosyl Amines**[5c]



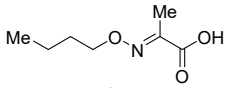
Synthesis of **S2**. To a solution of the corresponding tosyl amine (1.0 equiv) in dry NMP (Aldrich SureSeal™, 1.5 M), a 1.0 M solution of potassium hexamethyldisilazide in THF (1.1 equiv) was added at 0ºC under inert atmosphere. The mixture was stirred at room temperature for 10-15 min, darkening with the time. Then, *O*-(4-nitrobenzoyl)hydroxylamine (1.00 eq.) was added, and the resulting mixture was stirred for other additional 15 min (monitoring by TLC because the hydrazide product usually stains yellow/orange using vanillin stain). The reaction was quenched with water (50 mL), and extracted with AcOEt (3 x 30 mL). The combined organic layers were washed with with satd NaCl soln three times, dried (Na_2SO_4), and the volatiles were removed under reduced pressure. (NOTE: This hydrazide is unstable and cannot be stored. It must be used immediately for the next step). Then, methyl pyruvate (2.00 eq.), anthranilic acid (0.50 eq.) and acetic acid (2.00 eq.) were added to a solution of the previous crude mixture in MeOH (0.2 M), and the mixture was stirred 18 h at room temperature. Upon completion, the reaction mixture was concentrated under reduced preassure, and washed with water. The crude mixture was subjected to purification by flash column chromatography (5-10 % AcOEt in heptane) to obtain the corresponding oxime ester. Then, this ester was dissolved in mixture of methanol/H_2O (0.2 M, 3:1), and LiOH (3.0 equiv) was added. The resulting mixture was stirred at room temperature until the reaction was complete by TLC analysis (3-5 h). The reaction was concentrated under reduced pressure, acidified using a 10% aq HCl soln, and extracted with AcOEt (2x20 mL). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure, obtaining the pure product **S2**. (NOTE: No special caution for avoid O_2 in this reaction).

S2a-e, **S2l-m**, **S2o** and **S2x** were synthesized following the *General Procedure A2*, and all of them are already reported.X[5a,b,6] **S2g-h** were synthesized following the *General Procedure A1*. **S2s-u** were synthesized following the *General Procedure A5*, and all of them are already reported.[5c] **S2v-w** were synthesized following the *General Procedure A4*.

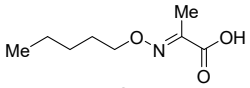
[6] a) G. Xia, J. Weng, L. Liu, P. Verma, Z. Li, J.-Q. Yu. *Nature Chemistry* **2019**, *11*, 571-577; b) Z. Liu, Y. Pan, P. Zou, H. Huang, Y. Chen, Y. Chen. *Org. Lett.* **2022**, *24*, 5951-5956.



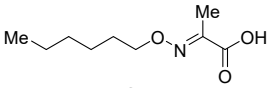
S2a



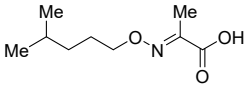
S2b



S2c



S2d



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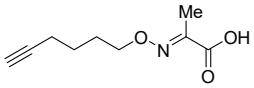
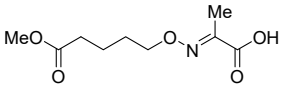
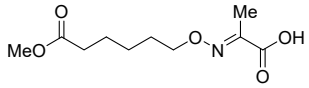


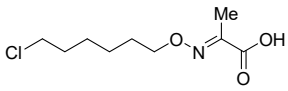
S2f



S2g



S2h



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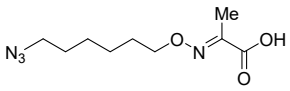

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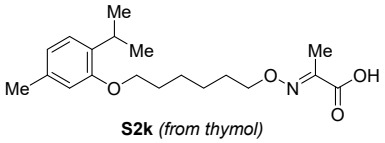
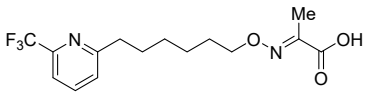


S2k *(from thymol)*



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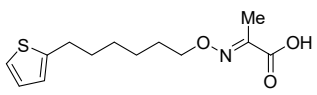

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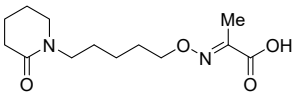
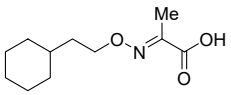
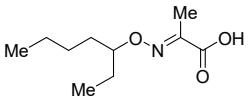


S2n



S2o



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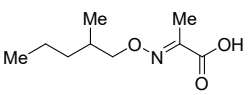

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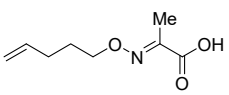

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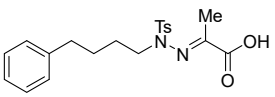

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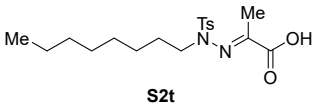

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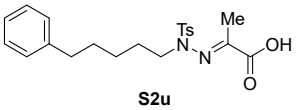

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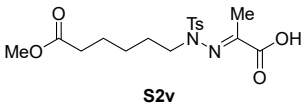

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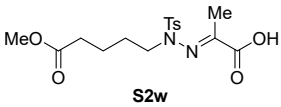
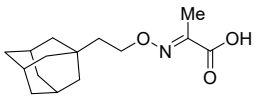
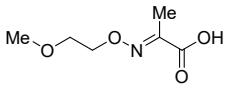


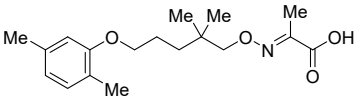
S2w



S2x



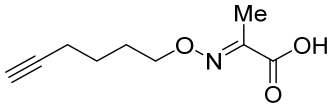
S2y



S2z

2.2 Characterization Data:

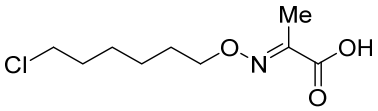
2-((hex-5-yn-1-yloxy)imino)Propanoic Acid (S2f)



Prepared according to the *General Procedure A2* from hex-5-yn-1-ol (491 mg, 5.00 mmol, 1.0 equiv). The title compound **S2f** was obtained as a colorless oil (706 mg, 3.85 mmol, 77%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 4.30 (t, *J* = 6.4 Hz, 2H), 2.26 (td, *J* = 7.0, 2.7 Hz, 2H), 2.07 (s, 3H), 1.97 (t, *J* = 2.7 Hz, 1H), 1.91 – 1.82 (m, 2H), 1.68 – 1.58 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 165.9, 148.0, 83.8, 75.4, 68.8, 27.9, 24.7, 18.0, 10.5. **HRMS (ESI)** calcd for $C_9H_{13}NO_3$ $[M+H]^+$: 309.0357, found 309.0354.

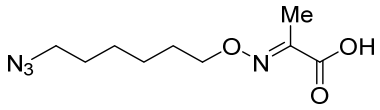
2-(((6-chlorohexyl)oxy)imino)Propanoic Acid (S2i)



Prepared according to the *General Procedure A2* from 6-chlorohexan-1-ol (683 mg, 5.00 mmol, 1.0 equiv). The title compound **S2i** was obtained as a pale brown oil (786 mg, 3.55 mmol, 71%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 4.27 (t, *J* = 6.6 Hz, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.06 (s, 3H), 1.87 – 1.67 (m, 4H), 1.55 – 1.37 (m, 4H). **^{13}C NMR** (76 MHz, $CDCl_3$), δ (ppm) = 165.7, 147.8, 75.7, 44.7, 32.2, 28.6, 26.3, 24.9, 10.3. **HRMS (APCI)** calcd for $C_9H_{17}ClNO_3$ $[M+H]^+$: 222.0891, found 222.0892.

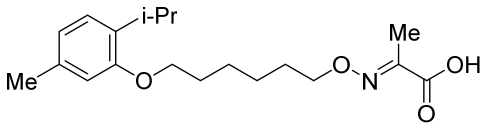
2-(((6-azidohexyl)oxy)imino)Propanoic Acid (S2j)



Prepared according to the *General Procedure A2* from 6-azidohexan-1-ol (430 mg, 3.0 mmol, 1.0 equiv). The title compound **S2j** was obtained as a yellow oil (679 mg, 2.97 mmol, 99%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 4.27 (t, *J* = 6.6 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.06 (s, 3H), 1.73 (q, *J* = 6.6 Hz, 2H), 1.62 (p, *J* = 6.8 Hz, 2H), 1.46 – 1.38 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 165.2, 148.0, 76.0, 51.3, 28.8, 28.7, 26.4, 25.4, 10.5. **HRMS (ESI)** calcd for $C_{22}H_{25}N_5O_3$ $[M+H]^+$: 309.0357, found 309.0354.

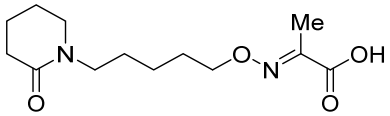
2-(((6-(2-isopropyl-5-methylphenoxy)hexyl)oxy)imino)Propanoic Acid (S2k)



Prepared according to the *General Procedure A2* from 6-(2-isopropyl-5-methylphenoxy)hexan-1-ol (604 mg, 2.4 mmol, 1.0 equiv). The title compound **S2k** was obtained as a yellow oil (548 mg, 1.63 mmol, 68%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = = 9.41 (s, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.67 (s, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.97 (t, *J* = 6.2 Hz, 2H), 3.30 (hept, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.08 (s, 3H), 1.93 – 1.70 (m, 4H), 1.67 – 1.40 (m, 4H), 1.22 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 165.1, 156.2, 147.9, 136.3, 134.1, 125.9, 121.01, 112.2, 76.3, 67.6, 29.4, 29.0, 26.7, 26.1, 25.6, 22.9(2C), 21.5, 10.5. **HRMS (ESI)** calcd for $C_{19}H_{30}NO_4$ $[M+H]^+$: 336.2169, found 336.2170.

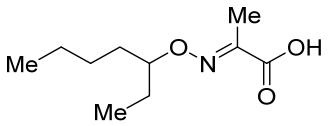
2-(((5-(2-oxopiperidin-1-yl)pentyl)oxy)imino)Propanoic Acid (S2n)



Prepared according to the *General Procedure A3* from 1-(5-chloropentyl)piperidin-2-one (801 mg, 3.93 mmol, 1.0 equiv). The title compound **S2n** was obtained as a yellow oil (282 mg, 1.05 mmol, 27%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 9.51 (s, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 3.42 – 3.31 (m, 2H), 3.31 – 3.22 (m, 2H), 2.41 (d, *J* = 5.8 Hz, 2H), 2.03 (s, 3H), 1.85 – 1.66 (m, 6H), 1.66 – 1.49 (m, 2H), 1.42 – 1.29 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 170.9, 164.9, 148.7, 75.5, 47.9, 47.2, 31.8, 28.7, 26.6, 23.1, 23.0, 21.0, 10.8. **HRMS (ESI)** calcd for $C_{26}H_{31}N_3O_4$ $[M+H]^+$: 309.0357, found 309.0354.

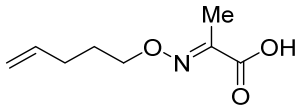
2-((heptan-3-yloxy)imino)Propanoic Acid (S2p)



Prepared according to the *General Procedure A2* from heptan-3-ol (581 mg, 5.00 mmol, 1.0 equiv). The title compound **S2p** was obtained as a yellow oil (505 mg, 2.5 mmol, 50%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 4.20 (p, *J* = 6.1 Hz, 1H), 2.06 (s, 3H), 1.74 – 1.53 (m, 4H), 1.40 – 1.22 (m, 4H), 0.99 – 0.82 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 165.9, 147.4, 87.0, 32.6, 27.3, 26.4, 22.6, 13.8, 10.4, 9.2. **HRMS (ESI)** calcd for $C_{10}H_{20}NO_3$ $[M+H]^+$: 202.1438, found 202.1437.

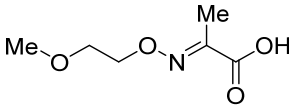
2-((pent-4-en-1-yloxy)imino)Propanoic Acid (S2r)



Prepared according to the *General Procedure A2* from pent-4-en-1-ol (431 mg, 5.00 mmol, 1.0 equiv). The title compound **S2r** was obtained as a yellow oil (400 mg, 2.33 mmol, 47%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 6.83 (s, 1H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.91 (m, 2H), 4.28 (t, *J* = 6.6 Hz, 2H), 2.18 – 2.09 (m, 2H), 2.04 (s, 3H), 1.87 – 1.73 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 164.8, 148.1, 137.6, 115.4, 75.7, 29.9, 28.2, 10.5. **HRMS (ESI)** calcd for $C_8H_{14}NO_3$ $[M+H]^+$: 172.0968, found 172.0967.

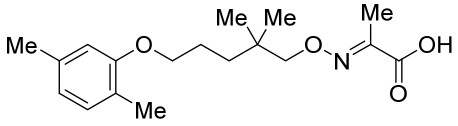
2-((2-methoxyethoxy)imino)Propanoic Acid (S2y)



Prepared according to the *General Procedure A2* from pent-4-en-1-ol (381 mg, 5.00 mmol, 1.0 equiv). The title compound **S2y** was obtained as a yellow oil (526 mg, 3.26 mmol, 65%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 10.19 (s, 1H), 4.26 – 4.19 (m, 2H), 3.59 – 3.48 (m, 2H), 3.23 (s, 3H), 1.86 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 164.8, 148.6, 74.3, 70.4, 58.4, 10.5. **HRMS (ESI)** calcd for $C_6H_{12}NO_4$ $[M+H]^+$: 162.0761, found 162.0764.

2-(((5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl)oxy)imino)Propanoic Acid (S2z)

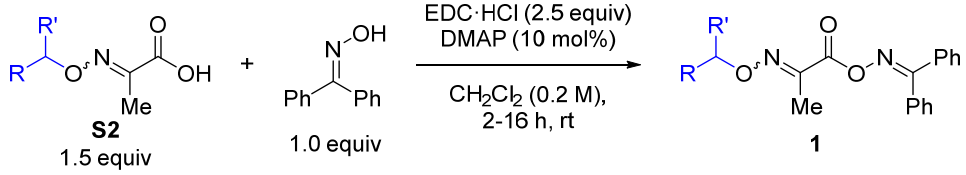


Prepared according to the *General Procedure A2* from 5-(2,5-dimethylphenoxy)-2,2-dimethylpentan-1-ol (512 mg, 2.10 mmol, 1.0 equiv). The title compound **S2z** was obtained as a yellow oil (113 mg, 0.35 mmol, 17%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 (s, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.64 (s, 1H), 4.09 (s, 2H), 3.94 (t, *J* = 6.2 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 2.09 (s, 3H), 1.90 – 1.71 (m, 2H), 1.58 – 1.43 (m, 2H), 1.01 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 164.9, 157.1, 148.0, 136.6, 130.4, 123.6, 120.85, 112.2, 84.8, 68.4, 35.7, 34.5, 24.5(2C), 24.2, 21.5, 15.8, 10.5. **HRMS (ESI)** calcd for $C_{18}H_{28}NO_4$ $[M+H]^+$: 322.2013, found 322.2012.

2.3 General Procedure B: Synthesis of Bifunctional reagents 1

All the bifunctional oximes **1** were synthesized from the corresponding α-oxime acid or α-hydrazone acid, according to the literature procedure.[7]



To a stirred solution of diphenylmethanone oxime (1.0 equiv), the corresponding α-oxime acid **S2** (1.5 equiv), and 4-dimethylaminopyridine (10 mol%) in CH_2Cl_2 (0.2 M), *N*-(3-dimetilaminopropilo)-*N*′-etilcarbodiimida hydrochloride (2.5 equiv) was added. The reaction was monitored by TLC analysis, and upon completion (2 – 16 h), the mixture was poured into a separatory funnel and washed with 10% aq HCl soln (4x20 mL). The organic layer was washed with satd NaCl soln, dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by flash column chromatography to obtain **1**. (NOTE: No special caution for avoid O_2 and H_2O in this reaction.).

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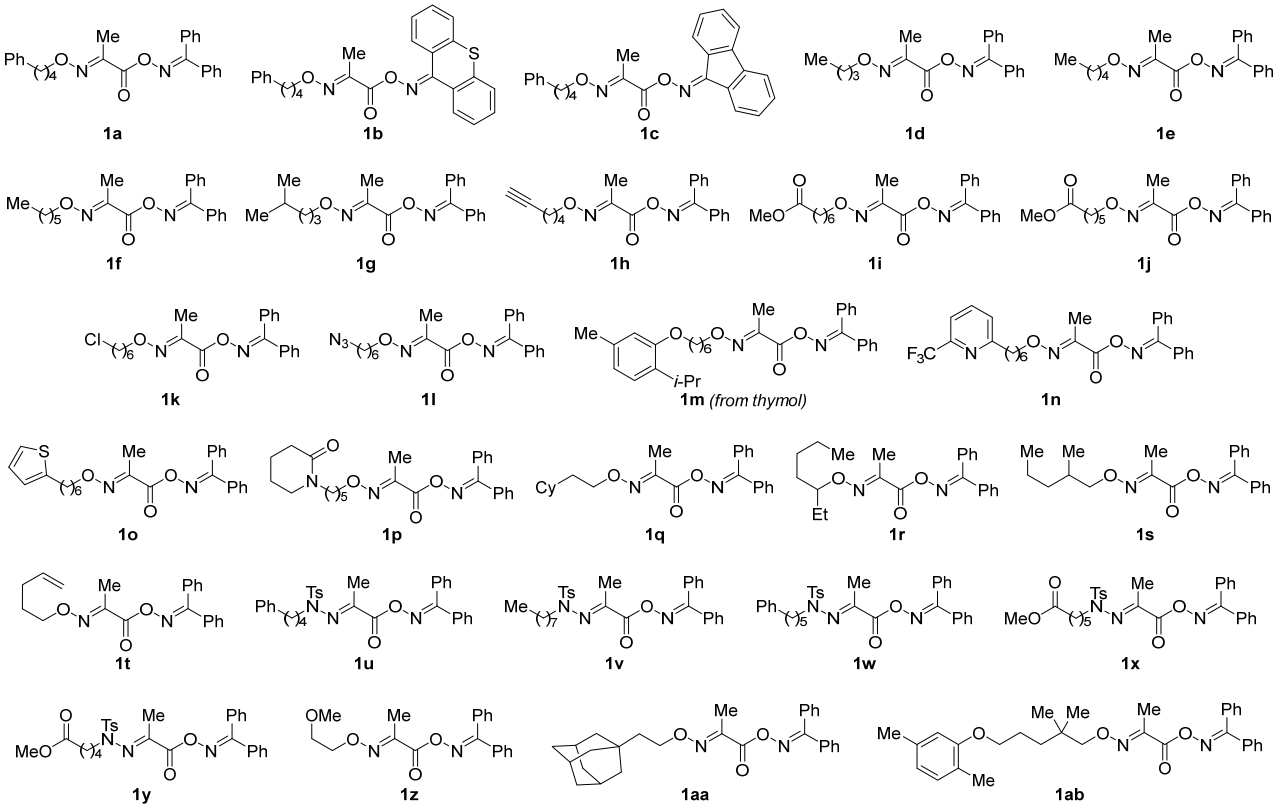
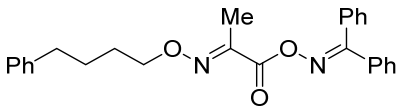
[7] J. Majhi, R. K. Dhungana, Á. Rentería-Gómez, M. Sharique, L. Li, W. Dong, O. Gutierrez, G. A. Molander. *J. Am. Chem. Soc.* **2022**, *144*, 15871-15878.



2.4 Characterization Data:

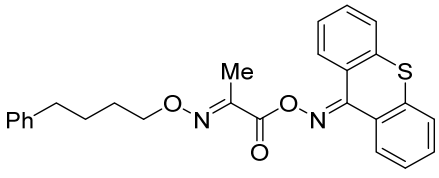
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(4-Phenylbutyl) 2-Oxime (1a)



Prepared according to the *General Procedure B* from α-oxime acid **S1a** (1.8 g, 7.50 mmol, 1.5 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1a** was obtained as a white solid (1.7 g, 4.17 mmol, 84%).

mp = 63 – 64 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.55 – 7.45 (m, 2H), 7.36 – 7.22 (m, 8H), 7.19 – 7.11 (m, 2H), 7.10 – 7.00 (m, 3H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 6.8 Hz, 2H), 1.83 (s, 3H), 1.60 – 1.49 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.4, 147.4, 142.3, 134.8, 132.5, 131.1, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (6C), 128.1 (2C), 125.9, 75.6, 35.7, 28.7, 27.7, 11.3. **HRMS (APCI)** calcd for $C_{26}H_{27}N_2O_3$ $[M+H]^+$: 415.2016, found 415.2021.

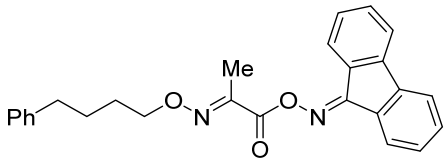
9*H*-Thioxanthen-9-one *O*-(2-((4-phenylbutoxy)imino)Propanoyl) Oxime (1b)



Prepared according to the *General Procedure B* from α-oxime acid **S1a** (130 mg, 0.47 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1b** was obtained as a yellow oil (180 mg, 0.40 mmol, 58%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 8.46 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.16 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.50 – 7.35 (m, 4H), 7.35 – 7.25 (m, 3H), 7.23 – 7.17 (m, 3H), 4.34 (t, *J* = 6.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.91 – 1.69 (m, 4H).**^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 161.4, 155.5, 147.6, 142.2, 135.1, 133.3, 132.6, 130.2, 129.9, 129.1, 128.5(4C), 128.2, 127.0, 126.6, 126.0, 125.5(2C), 125.1, 75.8, 35.7, 28.8, 27.7, 11.4. **HRMS (ESI)** calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$: 445.1580, found 445.1586.

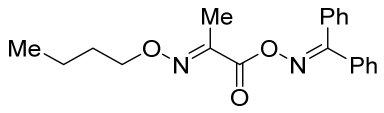
9*H*-Fluoren-9-one *O*-(2-((4-phenylbutoxy)imino)Propanoyl) Oxime (1c)



Prepared according to the *General Procedure B* from α-oxime acid **S2a** (316 mg, 1.45 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1c** was obtained as a yellow solid (313 mg, 0.76 mmol, 85%).

mp = 66 – 67 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) =8.70 (dt, *J* = 7.8, 1.0 Hz, 1H), 8.02 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.64 (ddt, *J* = 8.4, 7.5, 1.0 Hz, 2H), 7.48 (qd, *J* = 7.5, 1.0 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.27 – 7.19 (m, 3H), 4.44 (t, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.24 (s, 3H), 1.98 – 1.89 (m, 2H), 1.89 – 1.78 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 161.4, 159.8, 147.8, 142.6, 142.2, 141.6, 134.3, 132.7, 131.9, 131.5, 130.4, 128.6, 128.5(5C), 126.0, 123.7, 120.2(2C), 76.0, 35.7, 28.9, 27.8, 11.4. **HRMS (ESI)** calcd for $C_{26}H_{25}N_2O_3$ $[M+H]^+$: 413.1860, found 413.1861.

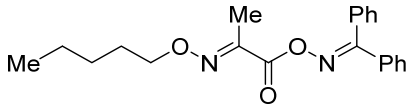
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-Butyl 2-Oxime (1d)



Prepared according to the *General Procedure B* from α-oxime acid **S2b** (1.1 mg, 6.84 mmol, 1.5 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1d** was obtained as a white solid (638 mg, 1.89 mmol, 41%).

mp = 64 – 65 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.58 (m, 2H), 7.51 – 7.33 (m, 8H), 4.17 (t, *J* = 6.7 Hz, 2H), 1.96 (s, 3H), 1.68 – 1.57 (m, 2H), 1.42 – 1.31 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.2, 161.5, 147.3, 134.8, 132.5, 131.1, 129.9, 129.6 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 75.7, 31.2, 19.1, 14.0, 11.3. **HRMS (ESI)** calcd for $C_{20}H_{22}N_2O_3$ $[M+H]^+$: 309.0357, found 309.0354.

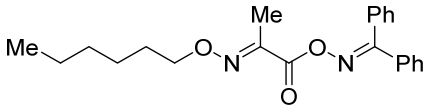
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-Pentyl 2-Oxime (1e)



Prepared according to the *General Procedure B* from α-oxime acid **S2c** (338 mg, 2.00 mmol, 1.5 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1e** was obtained as a white solid (375 mg, 1.07 mmol, 82%).

mp = 41 – 43 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) =7.66 – 7.56 (m, 2H), 7.51 – 7.31 (m, 8H), 4.16 (t, *J* = 6.7 Hz, 2H), 1.96 (s, 3H), 1.64 (p, *J* = 7.0 Hz, 2H), 1.41 – 1.21 (m, 4H), 1.01 – 0.73 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.0, 161.3, 147.2, 134.7, 132.4, 131.0, 129.8, 129.5(2C), 129.3(2C), 128.4(2C), 128.0(2C), 75.8, 28.7, 27.9, 22.5, 14.0, 11.2. **HRMS (ESI)** calcd for $C_{21}H_{24}N_2O_3$ $[M+H]^+$: 309.0357, found 309.0354.

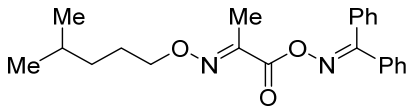
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-Hexyl 2-Oxime (1f)



Prepared according to the *General Procedure B* from α-oxime acid **S2d** (815 mg, 4.35 mmol, 1.5 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1f** was obtained as a white solid (530 mg, 1.45 mmol, 50%).

mp = 45 – 46 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.68 – 7.58 (m, 2H), 7.50 – 7.33 (m, 8H), 4.15 (t, *J* = 6.8 Hz, 2H), 1.96 (s, 3H), 1.69 – 1.58 (m, 2H), 1.38 – 1.24 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.2, 161.5, 147.4, 134.9, 132.5, 131.1, 129.9, 129.6 (2C), 129.5 (2C), 128.6 (2C), 128.1 (2C), 76.0, 31.7, 29.1, 25.6, 22.7, 14.2, 11.3. **HRMS (APCI)** calcd for $C_{22}H_{26}N_2O_3$ $[M]^+$: 366.1938, found 366.1940.

1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(4-Methylpentyl) 2-Oxime (1g)

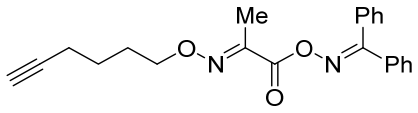


Prepared according to the *General Procedure B* from α-oxime acid **S2e** (478 mg, 2.55 mmol, 1.5 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1g** was obtained as a white solid (458 mg, 1.25 mmol, 74%).

mp = 31 – 33 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.66 – 7.58 (m, 2H), 7.51 – 7.32 (m, 8H), 4.14 (t, *J* = 6.9 Hz, 2H), 1.95 (d, *J* = 2.2 Hz, 3H), 1.71 – 1.56 (m, 4H), 1.56 – 1.50 (m, 1H), 1.20 (q, *J* = 7.5 Hz, 2H), 0.89 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.4, 147.3, 134.8, 132.4, 131.1, 129.9, 129.5

(2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 76.2, 34.9, 27.9, 27.0, 22.6 (2C), 11.3. **HRMS (ESI)** calcd for $C_{22}H_{26}N_2O_3$ $[M+H]^+$: 309.0357, found 309.0354.

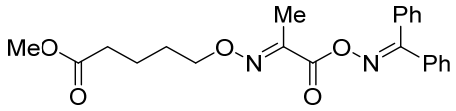
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-Hex-5-yn-1-yl 2-Oxime (1h)



Prepared according to the *General Procedure B* from α-oxime acid **S2f** (522 mg, 2.85 mmol, 1.5 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1h** was obtained as a white solid (599 mg, 1.65 mmol, 87%).

mp = 81 – 82 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.66 – 7.59 (m, 2H), 7.52 – 7.33 (m, 8H), 4.19 (t, *J* = 6.4 Hz, 2H), 2.21 (td, *J* = 7.0, 2.7 Hz, 2H), 1.96 (s, 3H), 1.96 (d, *J* = 5.3 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.63 – 1.56 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.2, 161.4, 147.6, 134.8, 132.5, 131.1, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 84.2, 75.2, 68.8, 28.2, 24.9, 18.3, 11.3. **HRMS (ESI)** calcd for $C_{22}H_{22}N_2O_3$ $[M+H]^+$: 309.0357, found 309.0354.

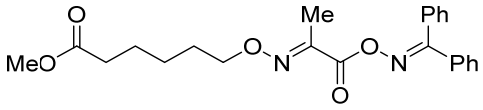
Methyl 5-Methyl-4-oxo-1,1-diphenyl-3,7-dioxa-2,6-diazadodeca-1,5-dien-12-oate (1i)



Prepared according to the *General Procedure B* from α-oxime acid **S2g** (1.8 g, 5.00 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1i** was obtained as a yellow oil (465 mg, 1.17 mmol, 36%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.69 – 7.62 (m, 2H), 7.53 – 7.36 (m, 8H), 4.26 – 4.16 (m, 2H), 3.70 (s, 3H), 2.39 – 2.33 (m, 2H), 1.99 (s, 3H), 1.74 – 1.67 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 173.4, 165.7, 160.9, 147.2, 134.4, 132.0, 130.8, 129.6, 129.1 (2C), 129.0 (2C), 128.2 (2C), 127.8 (2C), 74.8, 51.2, 33.3, 28.2, 21.0, 10.9. **HRMS (ESI)** calcd for $C_{22}H_{25}N_2O_5$ $[M+H]^+$: 397.1758, found 397.1745.

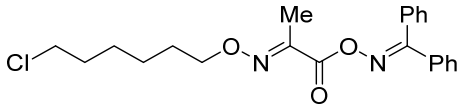
Methyl 5-Methyl-4-oxo-1,1-diphenyl-3,7-dioxa-2,6-diazatrideca-1,5-dien-13-oate (1j)



Prepared according to the *General Procedure B* from α-oxime acid **S2h** (1.2 g, 5.00 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1j** was obtained as a yellow oil (600 mg, 1.46 mmol, 43%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.64 – 7.57 (m, 2H), 7.48 – 7.31 (m, 8H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.66 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.94 (s, 3H), 1.72 – 1.57 (m, 4H), 1.41 – 1.29 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 174.1, 166.1, 161.3, 147.4, 134.7, 132.4, 131.1, 129.9, 129.5 (2C), 129.3 (2C), 128.5 (2C), 128.1 (2C), 75.5, 51.6, 34.0, 28.7, 25.4, 24.7, 11.2. **HRMS (ESI)** calcd for $C_{23}H_{27}N_2O_5$ $[M+H]^+$: 411.1914, found 411.1907.

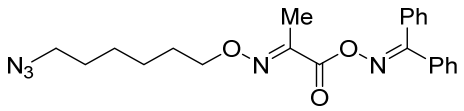
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(6-Chlorohexyl) 2-Oxime (1k)



Prepared according to the *General Procedure B* from α-oxime acid **S2i** (786 mg, 3.71 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1k** was obtained as a colorless oil (671 mg, 1.67 mmol, 68%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.57 (m, 2H), 7.51 – 7.33 (m, 8H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 1.95 (s, 3H), 1.85 – 1.67 (m, 2H), 1.71 – 1.60 (m, 2H), 1.54 – 1.29 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.0, 161.2, 147.3, 134.6, 132.3, 131.0, 129.8, 129.4 (2C), 129. 3(2C), 128.4 (2C), 128.0 (2C), 75.5, 45.0, 32.4, 28.8, 26.6, 25.1, 11.2. **HRMS (ESI)** calcd for $C_{22}H_{25}ClN_2O_3$ $[M+H]^+$: 309.0357, found 309.0354.

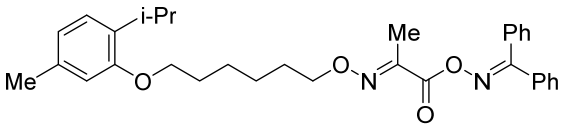
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(6-Azidohexyl) 2-Oxime (1l)



Prepared according to the *General Procedure B* from α-oxime acid **S2j** (679 mg, 2.97 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1l** was obtained as a colorless oil (647 mg, 1.60 mmol, 80%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.57 (m, 2H), 7.49 – 7.33 (m, 8H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 1.95 (s, 3H), 1.71 – 1.57 (m, 4H), 1.45 – 1.30 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.2, 161.4, 147.5, 134.8, 132.5, 131.1, 129.9, 129.6 (2C), 129.4 (2C), 128.6 (2C), 128.1 (2C), 75.7, 51.5, 29.0, 28.9, 26.6, 25.5, 11.3. **HRMS (ESI)** calcd for $C_{22}H_{25}N_5O_3$ $[M+H]^+$: 309.0357, found 309.0354.

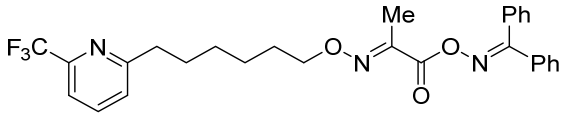
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(6-(2-isopropyl-5-methylphenoxy)Hexyl) 2-Oxime (1m)



Prepared according to the *General Procedure B* from α-oxime acid **S2k** (548 mg, 1.63 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1m** was obtained as a yellow oil (300 mg, 0.58 mmol, 53%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.60 (m, 2H), 7.52 – 7.34 (m, 8H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.75 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.67 (s, 1H), 4.20 (t, *J* = 6.6 Hz, 2H), 3.97 (t, *J* = 6.3 Hz, 2H), 3.31 (hept, *J* = 6.9 Hz, 1H), 2.33 (s, 3H), 1.98 (s, 3H), 1.88 – 1.77 (m, 2H), 1.70 (p, *J* = 6.9 Hz, 2H), 1.59 – 1.49 (m, 2H), 1.49 – 1.38 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.4, 156.3, 147.4, 136.4, 134.8, 134.2, 132.5, 131.1, 129.9, 129.6 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 126.0, 121.1, 112.3, 75.8, 67.8, 29.5, 29.1, 26.8, 26.2, 25.7, 22.9 (2C), 21.5, 11.3. **HRMS (ESI)** calcd for $C_{32}H_{39}N_2O_4$ $[M+H]^+$: 515.2904, found 515.2909.

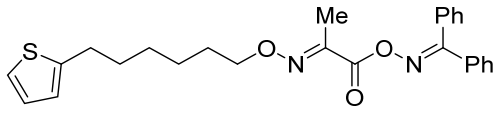
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(6-(6-(trifluoromethyl)pyridin-2-yl)Hexyl) 2-Oxime (1n)



Prepared according to the *General Procedure B* from α-oxime acid **S2l** (2.0 g, 6.10 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1n** was obtained as a colorless oil (1.2 g, 2.34 mmol, 57%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.76 (t, *J* = 7.8 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.53 – 7.30 (m, 10H), 4.15 (t, *J* = 6.6 Hz, 2H), 2.93 – 2.75 (m, 2H), 1.94 (s, 3H), 1.83 – 1.69 (m, 2H), 1.68 – 1.57 (m, 2H), 1.43 – 1.33 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 165.6, 162.9, 160.9, 147.1 (q, *J* = 33.9 Hz), 146.9, 137.3, 134.3, 131.9, 130.7, 129.6, 129.1 (2C), 128.9 (2C), 128.1 (2C), 127.7 (2C), 125.3, 121.4 (q, *J* = 274.2 Hz), 117.3 (q, *J* = 3.0 Hz), 75.3, 37.6, 29.2, 28.7, 28.5, 25.2, 10.8. **^{19}F NMR** (282 MHz, $CDCl_3$) -67.99. **HRMS (ESI)** calcd for $C_{28}H_{28}F_3N_3O_3$ $[M+H]^+$: 309.0357, found 309.0354.

1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(6-(thiophen-2-yl)Hexyl) 2-Oxime (1o)

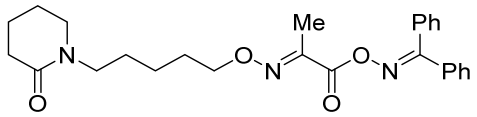


Prepared according to the *General Procedure B* from α-oxime acid **S2m** (1.3 g, 4.70 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1o** was obtained as a yellow oil (700 mg, 1.60 mmol, 50%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.64 – 7.57 (m, 2H), 7.50 – 7.33 (m, 8H), 7.11 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.78 (dq, *J* = 3.3, 1.0 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 2.93 – 2.65 (m, 2H), 1.95 (s, 3H), 1.75 – 1.55 (m, 4H), 1.40 – 1.26 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.4, 147.3, 145.6,

134.7, 132.3, 131.1, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.0 (2C), 126.7, 124.1, 122.9, 75.8, 31.7, 29.9, 29.0, 28.9, 25.6, 11.3. **HRMS (ESI)** calcd for $C_{26}H_{28}N_2O_3S$ $[M+H]^+$: 309.0357, found 309.0354.

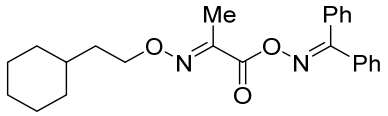
1-(5-methyl-4-oxo-1,1-diphenyl-3,7-dioxa-2,6-diazadodeca-1,5-dien-12-yl)Piperidin-2-one (1p)



Prepared according to the *General Procedure B* from α-oxime acid **S2n** (282 mg, 1.05 mmol, 1.5 equiv). After chromatographic purification (from 10% AcOEt in heptane to 100% AcOEt), the title compound **1p** was obtained as a yellow oil (280 mg, 0.62 mmol, 89%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.66 – 7.57 (m, 2H), 7.52 – 7.31 (m, 8H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.41 – 3.31 (m, 2H), 3.30 – 3.20 (m, 2H), 2.41 – 2.33 (m, 2H), 1.94 (s, 3H), 1.82 – 1.74 (m, 4H), 1.71 – 1.61 (m, 2H), 1.59 – 1.47 (m, 2H), 1.38 – 1.23 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 169.4, 165.9, 161.1, 147.2, 134.5, 132.2, 130.9, 129.7, 129.3 (2C), 129.2 (2C), 128.3 (2C), 127.9 (2C), 75.4, 47.7, 46.8, 32.2, 28.7, 26.7, 23.2, 23.0, 21.3, 11.1. **HRMS (ESI)** calcd for $C_{26}H_{31}N_3O_4$ $[M+H]^+$: 309.0357, found 309.0354.

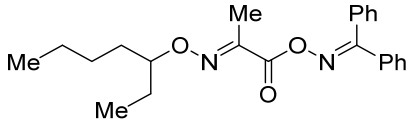
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(2-Cyclohexylethyl) 2-Oxime (1q)



Prepared according to the *General Procedure B* from α-oxime acid **S2o** (1.1 g, 4.96 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1q** was obtained as a white solid (660 mg, 1.68 mmol, 51%).

mp = 43 – 45 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.66 – 7.58 (m, 2H), 7.51 – 7.33 (m, 8H), 4.20 (t, *J* = 6.9 Hz, 2H), 1.95 (s, 3H), 1.77 – 1.64 (m, 5H), 1.54 (q, *J* = 6.9 Hz, 2H), 1.38 – 1.13 (m, 4H), 1.02 – 0.77 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.4, 147.2, 134.8, 132.4, 131.0, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 74.1, 36.4, 34.7, 33.4 (2C), 26.6, 26.3 (2C), 11.3. **HRMS (ESI)** calcd for $C_{24}H_{29}N_2O_3$ $[M+H]^+$: 393.2173, found 393.2179.

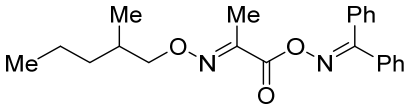
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-Heptan-3-yl 2-Oxime (1r)



Prepared according to the *General Procedure B* from α-oxime acid **S2p** (505 mg, 2.50 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1r** was obtained as a colorless oil (369 mg, 0.97 mmol, 57%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.64 – 7.56 (m, 2H), 7.46 – 7.25 (m, 8H), 4.06 (q, *J* = 6.8 Hz, 1H), 1.97 (s, 3H), 1.68 – 1.47 (m, 4H), 1.33 – 1.21 (m, 4H), 0.92 – 0.80 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 165.5, 161.4, 146.4, 134.7, 132.3, 130.8, 129.6, 129.4 (2C), 129.1 (2C), 128.3 (2C), 127.8 (2C), 86.4, 32.6, 27.4, 26.4, 22.6, 13.9, 11.0, 9.5. **HRMS (ESI)** calcd for $C_{23}H_{29}N_2O_3$ $[M+H]^+$: 381.2173, found 381.2167.

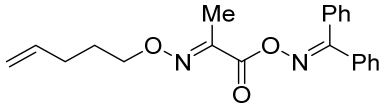
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(2-Methylpentyl) 2-Oxime (1s)



Prepared according to the *General Procedure B* from α-oxime acid **S2q** (737 mg, 3.90 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1s** was obtained as a yellow oil (510 mg, 1.40 mmol, 54%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.57 (m, 2H), 7.51 – 7.32 (m, 8H), 4.05 (dd, *J* = 10.5, 6.1 Hz, 1H), 3.95 (dd, *J* = 10.5, 7.0 Hz, 1H), 1.97 (s, 3H), 1.88 – 1.72 (m, 1H), 1.41 – 1.03 (m, 4H), 0.95 – 0.84 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.5, 147.3, 134.8, 132.5, 131.1, 129.9, 129.6 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 81.2, 35.7, 32.8, 20.0, 16.8, 14.4, 11.3. **HRMS (ESI)** calcd for $C_{22}H_{27}N_2O_3$ $[M+H]^+$: 367.2016, found 367.2014.

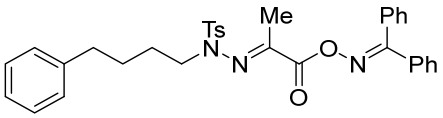
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-Pent-4-en-1-yl 2-Oxime (1t)



Prepared according to the *General Procedure B* from α-oxime acid **S2r** (400 mg, 2.34 mmol, 1.0 equiv). After chromatographic purification (3-5% AcOEt in heptane), the title compound **1t** was obtained as a white solid (478 mg, 1.36 mmol, 88%).

mp = 29 – 31 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.66 – 7.56 (m, 2H), 7.52 – 7.33 (m, 8H), 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10 – 4.90 (m, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.16 – 2.03 (m, 2H), 1.96 (s, 3H), 1.83 – 1.64 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.2, 161.4, 147.5, 137.9, 134.7, 132.4, 131.1, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 115.2, 75.1, 30.0, 28.3, 11.3. **HRMS (ESI)** calcd for $C_{21}H_{23}N_2O_3$ $[M+H]^+$: 351.1703, found 351.1705.

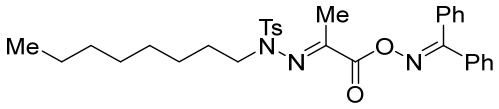
***N'*-(1-(((diphenylmethylene)amino)oxy)-1-oxopropan-2-ylidene)-4-Methyl-*N*-(4-phenylbutyl)benzenesulfonohydrazide (1u)**



Prepared according to the *General Procedure B* from α-hydrazone acid **S2s** (1.8 g, 4.60 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1u** was obtained as a yellow oil (421 mg, 0.74 mmol, 24%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.70 – 7.57 (m, 2H), 7.53 – 7.32 (m, 10H), 7.26 – 7.21 (m, 2H), 7.19 – 7.13 (m, 3H), 7.13 – 7.05 (m, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 1.55 (p, *J* = 7.6 Hz, 2H), 1.29 (p, *J* = 7.2 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 170.6, 167.1, 161.6, 144.3, 141.9, 134.4, 132.1, 131.8, 131.4, 130.2, 129.5, 129.5 (2C), 129.4 (2C), 128.9, 128.6 (2C), 128.4 (2C), 128.4 (2C), 128.2 (2C), 125.9, 52.5, 35.3, 28.4, 27.3, 21.7, 18.0. **HRMS (ESI)** calcd for $C_{33}H_{33}N_3O_4S$ $[M+H]^+$: 309.0357, found 309.0354.

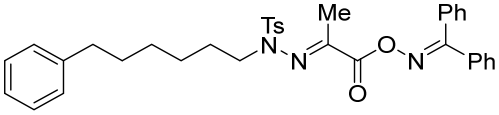
***N'*-(1-(((diphenylmethylene)amino)oxy)-1-oxopropan-2-ylidene)-4-Methyl-*N*-octylbenzenesulfonohydrazide (1v)**



Prepared according to the *General Procedure B* from α-hydrazone acid **S2t** (1.1 g, 3.10 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1v** was obtained as a yellow oil (600 mg, 1.10 mmol, 53%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.64 – 7.58 (m, 2H), 7.52 – 7.35 (m, 10H), 7.20 – 7.14 (m, 2H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 1.28 – 1.15 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 170.4, 167.2, 161.7, 144.3, 134.5, 132.2, 132.0, 131.4, 130.2, 129.5 (4C), 129.5 (2C), 129.0 (2C), 128.6 (2C), 128.3 (2C), 52.9, 31.8, 29.2 (2C), 27.9, 26.7, 22.7, 21.7, 18.0, 14.2. **HRMS (ESI)** calcd for $C_{31}H_{37}N_3O_4S$ $[M+H]^+$: 309.0357, found 309.0354.

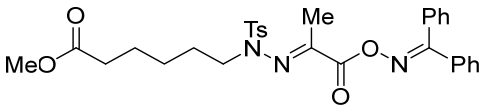
***N'*-(1-(((diphenylmethylene)amino)oxy)-1-oxopropan-2-ylidene)-4-Methyl-N-(6-phenylhexyl)benzenesulfonohydrazide (1w)**



Prepared according to the *General Procedure B* from α-hydrazone acid **S2u** (743 mg, 1.86 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1w** was obtained as a yellow oil (275 mg, 0.46 mmol, 38 %).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.60 (m, 2H), 7.56 – 7.37 (m, 10H), 7.31 – 7.26 (m, 2H), 7.21 – 7.11 (m, 5H), 3.13 – 2.99 (m, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 2.37 (s, 3H), 1.63 – 1.47 (m, 2H), 1.36 – 1.20 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 170.4, 167.0, 161.6, 144.3, 142.2, 134.4, 132.0, 131.7, 131.3, 130.1, 129.5 (2C), 129.4 (2C), 129.4 (2C), 128.8 (2C), 128.5 (2C), 128.4 (2C), 128.3 (2C), 128.1 (2C), 125.7, 52.6, 35.6, 30.8, 27.7, 26.1, 21.6, 17.9. **HRMS (ESI)** calcd for $C_{35}H_{37}N_3O_4S$ $[M+H]^+$: 309.0357, found 309.0354.

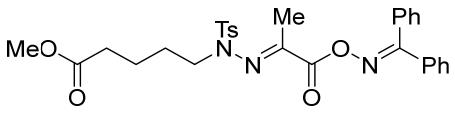
Methyl 6-(2-(1-(((diphenylmethylene)amino)oxy)-1-oxopropan-2-ylidene)-1-tosylhydrazineyl)Hexanoate (1x)



Prepared according to the *General Procedure B* from α-hydrazone acid **S2v** (700 mg, 1.82 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1x** was obtained as a yellow oil (390 mg, 0.69 mmol, 57%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.56 (m, 2H), 7.54 – 7.32 (m, 10H), 7.22 – 7.13 (m, 2H), 3.65 (s, 3H), 3.10 – 2.97 (m, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 2.24 (t, *J* = 7.4 Hz, 2H), 1.58 – 1.44 (m, 2H), 1.29 – 1.19 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 173.9, 170.6, 167.1, 161.6, 144.4, 134.4, 132.1, 131.7, 131.4, 130.2, 129.5 (2C), 129.4 (2C), 129.4 (2C), 128.9 (2C), 128.6 (2C), 128.2 (2C), 52.5, 51.6, 33.8, 27.6, 26.2, 24.5, 21.7, 18.0. **HRMS (ESI)** calcd for $C_{30}H_{33}N_3O_6S$ $[M+H]^+$: 309.0357, found 309.0354.

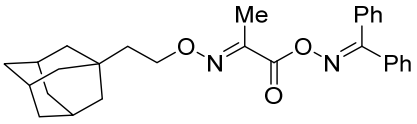
Methyl 5-(2-(1-(((diphenylmethylene)amino)oxy)-1-oxopropan-2-ylidene)-1-tosylhydrazineyl)Pentanoate (1y)



Prepared according to the *General Procedure B* from α-hydrazone acid **S2w** (545 mg, 1.40 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1y** was obtained as a yellow oil (416 mg, 0.75 mmol, 80%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.57 (m, 2H), 7.54 – 7.33 (m, 10H), 7.21 – 7.15 (m, 2H), 3.64 (s, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.47 (m, 2H), 1.36 – 1.20 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 173.5, 170.7, 167.0, 161.5, 144.4, 134.3, 132.0, 131.7, 131.4, 130.1, 129.5 (2C), 129.5 (2C), 129.4 (2C), 128.8 (2C), 128.5 (2C), 128.2 (2C), 52.3, 51.6, 33.3, 27.2, 21.9, 21.6, 18.0. **HRMS (ESI)** calcd for $C_{29}H_{31}N_3O_6S$ $[M+H]^+$: 309.0357, found 309.0354.

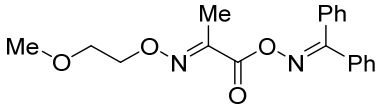
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(2-((3r,5r,7r)-adamantan-1-yl)ethyl) 2-Oxime (1z)



Prepared according to the *General Procedure B* from α-oxime acid **S2x** (616 mg, 2.33 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1z** was obtained as a yellow oil (700 mg, 1.54 mmol, 99%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.59 (m, 2H), 7.50 – 7.34 (m, 8H), 4.24 (t, *J* = 7.2 Hz, 2H), 1.95 (s, 6H), 1.77 – 1.57 (m, 6H), 1.51 (d, *J* = 2.9 Hz, 6H), 1.43 (t, *J* = 7.2 Hz, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.0, 161.4, 147.1, 134.7, 132.4, 131.0, 129.9, 129.5 (2C), 129.3 (2C), 128.5 (2C), 128.1 (2C), 72.1, 42.8, 42.7 (3C), 37.1 (3C), 31.8, 28.7 (3C), 11.4. **HRMS (ESI)** calcd for $C_{28}H_{33}N_2O_3$ $[M+H]^+$: 445.2440, found 445.2463.

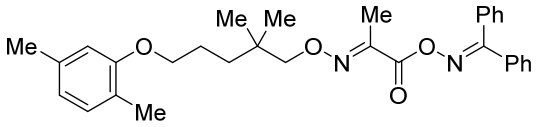
1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(2-Methoxyethyl) 2-Oxime (1aa)



Prepared according to the *General Procedure B* from α-oxime acid **S2y** (526 mg, 3.26 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1aa** was obtained as a white solid (524 mg, 1.54 mmol, 71%).

mp = 73 – 75 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.58 (m, 2H), 7.54 – 7.30 (m, 8H), 4.37 – 4.22 (m, 2H), 3.64 – 3.57 (m, 2H), 3.35 (s, 3H), 1.99 (s, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.2, 161.21, 148.2, 134.7, 132.4, 131.1, 129.9, 129.4 (2C), 129.3 (2C), 128.5 (2C), 128.1 (2C), 74.8, 70.7, 59.1, 11.4. **HRMS (ESI)** calcd for $C_{15}H_{14}ClO_3S$ $[M+H]^+$: 309.0357, found 309.0354.

1-(((diphenylmethylene)amino)oxy)Propane-1,2-dione *O*-(5-(2,5-dimethylphenoxy)-2,2-Dimethylpentyl) 2-Oxime (1ab)



Prepared according to the *General Procedure B* from α-oxime acid **S2z** (113 mg, 0.35 mmol, 1.5 equiv). After chromatographic purification (3% AcOEt in heptane), the title compound **1ab** was obtained as a yellow oil (117 mg, 0.23 mmol, 99%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.68 – 7.63 (m, 2H), 7.51 – 7.36 (m, 8H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.64 (s, 1H), 4.02 (s, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 2.01 (s, 3H), 1.85

– 1.73 (m, 2H), 1.51 – 1.42 (m, 2H), 0.96 (s, 6H).**^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.1, 161.4, 157.1, 147.1, 136.5, 134.7, 132.4, 131.1, 130.4, 129.9, 129.5 (2C), 129.4 (2C), 128.5 (2C), 128.1 (2C), 123.5, 120.7, 112.0, 84.3, 68.4, 35.6, 34.5, 24.5 (2C), 24.2, 21.5, 15.9, 11.3. **HRMS (ESI)** calcd for $C_{31}H_{37}N_2O_4$ $[M+H]^+$: 501.2748, found 501.2746.

3. δ-Amination: Reaction Workflow, Optimization and Characterization

3.1 Reaction Workflow:

All photoredox reactions were performed with a Kessil PR160-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm). The lamp was placed 4 cm away from the reaction vials, and cooled at 25ºC by an external fan. A typical reaction setup is shown below.

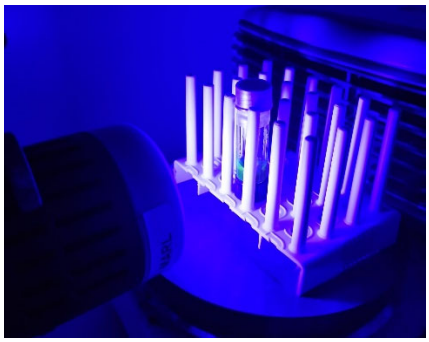


Figure S1. *Reaction setup for the visible light-assisted synthesis of 1,5-aminoalcohols and 1,5-diamines*

3.2 Reaction Optimization:

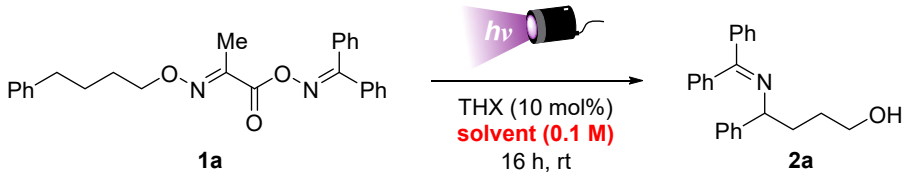
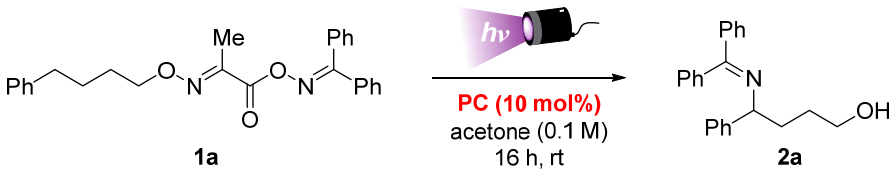


Table 1. Solvent[a]

Entry	Solvent	3a (%)[b]
1	**Acetone**	**50**
2	AcOEt	47
3	MeCN	49
4	CH_2Cl_2	39
5	MeOH	32
6	DMSO	36
7	DMF	nr

[a]Optimization reactions were performed using **1a** (0.10 mmol) and THX (10 mol%), in dry degassed solvent (1.0 mL, c = 0.1 M) under purple Kessil irradiation (λ_{max} = 390 nm) for 16 h at rt. [b]Yields were determined by ^{1}H-NMR analysis using trimethoxybenzene as internal standard. Abbreviations: THX, thioxanthone; nr, no reaction.



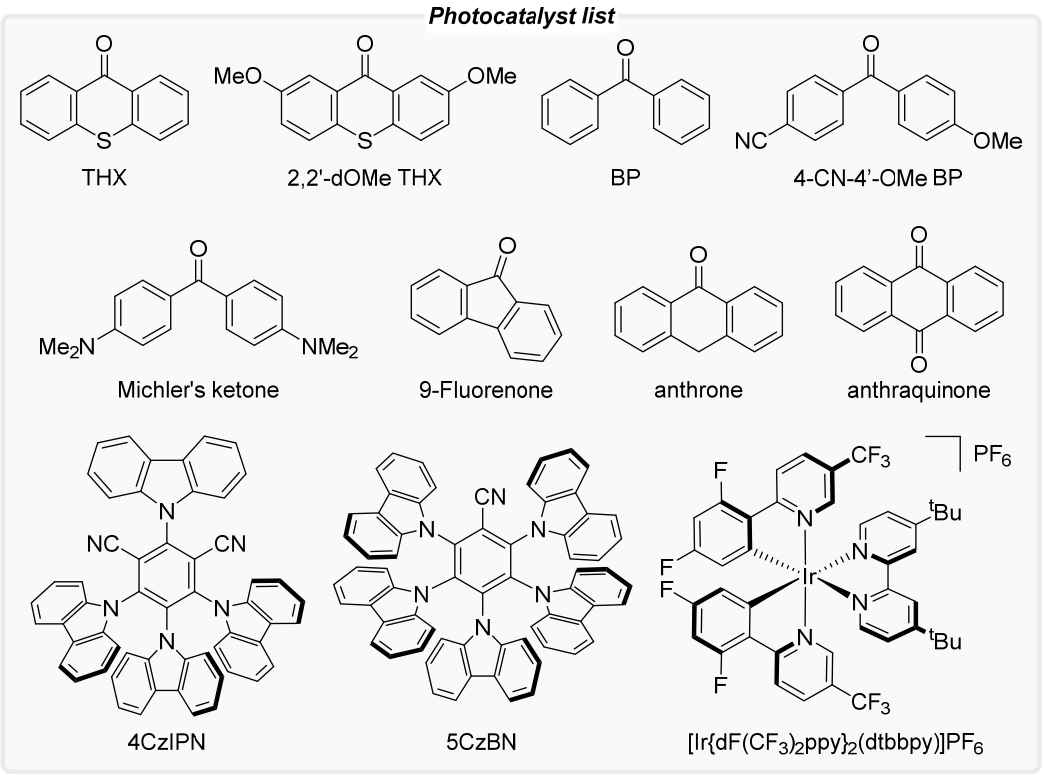


Table 2. Photocatalyst[a]

Entry	PC	3a (%)[b]
1	THX	47
2	2,2'-dOMe THX	41
3	benzophenone	44
4	4-CN-4'-OMe BP	41
5	Mickler's ketone	23
6	9-Fluorenone	18
7	anthrone	29
8	anthraquinone	32
9	4CzIPN	13
10	5BzCN	46
11	THX	44[c]
12	4CzIPN	12[c]
13	**5BzCN**	**46[c]**
14	[Ir{dF(CF$_3$)ppy}$_2$(dtbpy)]PF$_6$	46[c]

[a]Optimization reactions were performed using **1a** (0.10 mmol) and PC (10 mol%), in dry degassed acetone (1.0 mL, c = 0.1 M) under purple Kessil irradiation (λ_{max} = 390 nm) for 16 h at rt [b]Yields were determined by ^{1}H-NMR analysis using trimethoxybenzene as internal standard. [c]Under blue Kessil irradiation (λ_{max} = 456 nm).

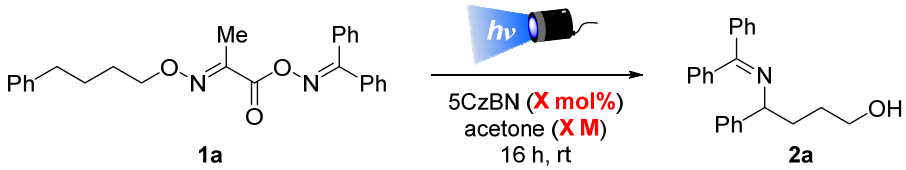


Table 3. Catalyst loading and concentration[a]

Entry	Catalyst loading (mol%)	Concentration (M)	3a (%)[b]
1	10	0.1	46
2	20	0.1	40
3	5	0.1	46
4	5	0.2	37
5	5	0.05	46
6	2.5	0.1	47
7	**1**	**0.1**	**46**

[a]Optimization reactions were performed using **1a** (0.10 mmol) and 5CzBN, in dry degassed acetone under blue Kessil irradiation (λ_{max} = 456 nm) for 16 h at rt. [b]Yields were determined by ^{1}H-NMR analysis using trimethoxybenzene as internal standard.

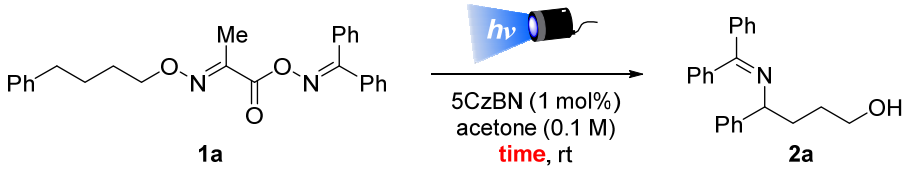


Table 4. Reaction time[a]

Entry	Time (h)	blue Kessil (λ_{max} nm)	3a (%)[b]
1	48	456	49
2	24	456	52
3	16	456	47
4	16	427	52
5	**2**	427	**52**

[a]Optimization reactions were performed using **1a** (0.10 mmol), and 5CzBN (1 mol%), in dry degassed acetone (1.0 mL, c = 0.1 M) under blue Kessil irradiation at rt. [b]Yields were determined by ^{1}H-NMR analysis using trimethoxybenzene as internal standard.

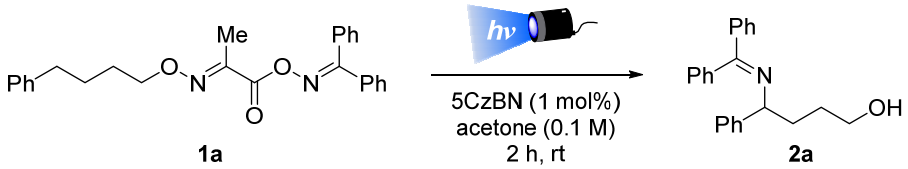
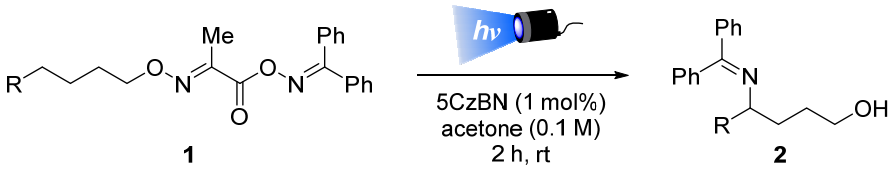


Table 5. Control experiments[a]

Entry	Controls	3a (%)[b]
1	No light	nr[c]
2	No PC	nr
3	Open-to-air	50

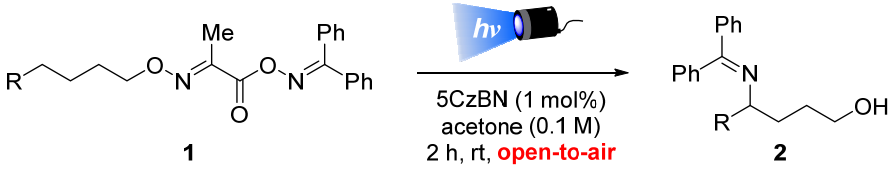
[a]Optimization reactions were performed using **1a** (0.10 mmol), and 5CzBN (1 mol%), in dry degassed acetone (1.0 mL, c = 0.1 M) under blue Kessil irradiation (λ_{max} = 427 nm) for 2 h at rt. [b]Yields were determined by ^{1}H-NMR analysis using trimethoxybenzene as internal standard. [c]16 h. Abbreviations: nr, no reaction.

3.3 General Procedure C for the visible light-assisted amine functionalization:



To an 8 mL vial equipped with a magnetic stir bar was added the bifunctional reagent **1** (0.20 mmol, 1.0 equiv) and 5BzCN (1.9 mg, 2.00 µmol, 1 mol%). The vial was sealed with a cap containing a Sil/PTFE septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, anhydrous degassed acetone (2.0 mL, c = 0.1 M) was added via syringe. The reaction mixture was irradiated with a Kessil PR160-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) for 2 h as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials, and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography to afford compound **2**.

3.4 General Procedure D for the visible light-assisted amine functionalization:

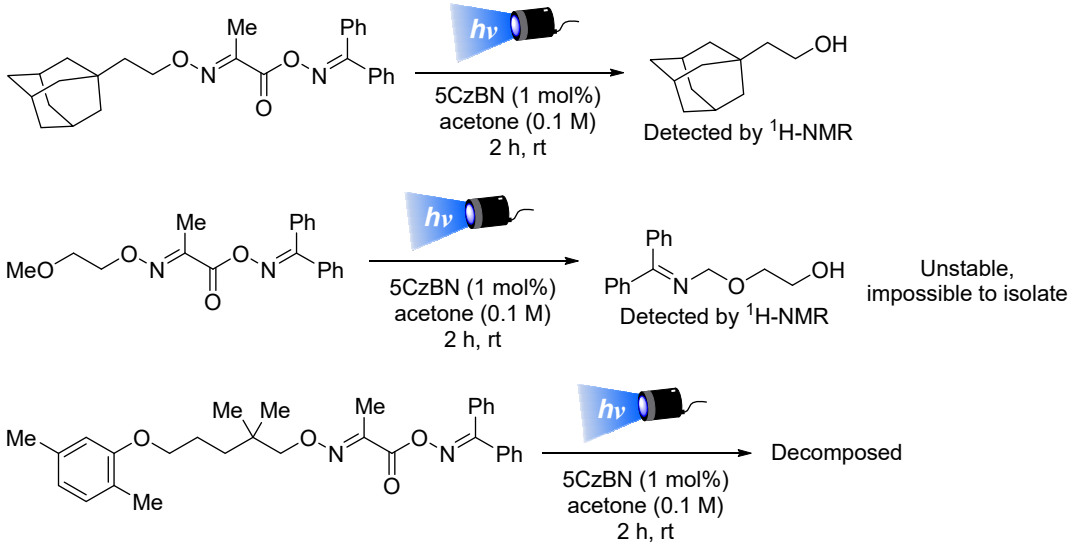


To an 8 mL vial equipped with a magnetic stir bar was added the bifunctional reagent **1** (0.25 mmol, 1.0 equiv), 5BzCN (2 mg, 2.30 µmol, 1 mol%) and acetone (2.5 mL, c = 0.1 M). The vial was sealed with a cap containing a Sil/PTFE septum, and the reaction mixture was irradiated with a Kessil PR160-blue LED lamp (30 W High

Luminous DEX 2100 LED, λ_{max} = 427 nm) for 2 h as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials, and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography to afford compound **2**.

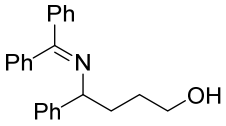
3.5 Unsuccessful bifunctional oximes 1:

All the crude mixtures were analyzed by ^{1}H-NMR.



3.6 Characterization Data:

4-((diphenylmethylene)amino)-4-Phenylbutan-1-ol (2a)



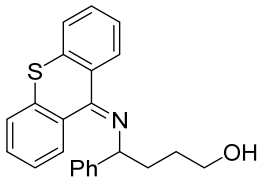
Prepared according to the *General Procedure C* from oxime **1a** (83 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (10-15% AcOEt in heptane), the title compound **2a** was obtained as a yellow oil (33 mg, 0.10 mmol, 50%).

Prepared according to the *General Procedure D* from oxime **1a** (104 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-15% AcOEt in heptane), the title compound **2a** was obtained as a yellow oil (43 mg, 0.13 mmol, 52%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.70 – 7.61 (m, 2H), 7.43 – 7.27 (m, 8H), 7.26 – 7.15 (m, 3H), 7.06 – 6.99 (m, 2H), 4.43 (dd, *J* = 7.4, 4.8 Hz, 1H), 3.63 – 3.52 (m, 2H), 2.41 (bs, 1H), 2.08 – 1.97 (m, 1H), 1.92 – 1.81 (m, 1H), 1.61 – 1.43 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.9, 144.8, 139.8, 137.1, 130.2, 128.8 (2C),

128.5 (3C), 128.4 (2C), 128.3 (2C), 127.8 (2C), 127.2 (2C), 126.8, 66.0, 63.1, 36.2, 29.4. **HRMS (ESI)** calcd for $C_{23}H_{24}NO$ $[M+H]^+$: 330.1852, found 330.1854.

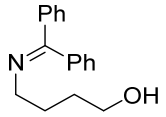
4-((9H-thioxanthen-9-ylidene)amino)-4-phenylbutan-1-ol (2b)



Prepared according to the *General Procedure C* from oxime **1b** (44.5 mg, 0.10 mmol, 1.0 equiv). After chromatographic purification (5% to 20% AcOEt in heptane), the title compound **2b** was obtained as a yellow oil (19.7 mg, 0.05 mmol, 54%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 8.11 – 8.01 (m, 1H), 7.63 – 7.52 (m, 3H), 7.50 – 7.39 (m, 5H), 7.38 – 7.28 (m, 3H), 7.25 – 7.17 (m, 1H), 5.05 (dd, *J* = 6.8, 4.2 Hz, 1H), 3.58 – 3.34 (m, 2H), 2.17 – 2.02 (m, 1H), 1.91 – 1.77 (m, 1H), 1.53 – 1.38 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 159.5, 144.9, 136.6, 136.3, 133.0, 129.3, 129.0, 128.9 (3C), 128.3, 127.7, 127.5, 127.2, 127.1, 127.0 (2C), 125.6, 125.4, 64.8, 62.8, 37.5, 28.7. **HRMS (ESI)** calcd for $C_{23}H_{22}NOS$ $[M+H]^+$: 360.1417, found 360.1400.

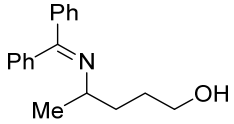
4-((diphenylmethylene)amino)Butan-1-ol (2d)



Prepared according to the *General Procedure C* from oxime **1d** (68 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-20% AcOEt in heptane), the title compound **2d** was obtained as a yellow oil (10 mg, 0.04 mmol, 20%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.61 – 7.53 (m, 2H), 7.50 – 7.41 (m, 3H), 7.40 – 7.30 (m, 3H), 7.20 – 7.14 (m, 2H), 3.71 (t, *J* = 5.4 Hz, 2H), 3.40 (t, *J* = 5.7 Hz, 2H), 1.79 – 1.71 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 169.0, 139.5, 136.8, 130.3, 128.7 (2C), 128.7, 128.6 (2C), 128.4 (2C), 127.9 (2C), 63.0, 53.8, 32.1, 29.2. **HRMS (ESI)** calcd for $C_{15}H_{14}ClO_3S$ $[M+H]^+$: 253.0357, found 253.0354.

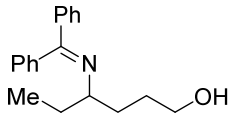
4-((diphenylmethylene)amino)Pentan-1-ol (2e)



Prepared according to the *General Procedure C* from oxime **1e** (71 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-20% AcOEt in heptane), the title compound **2e** was obtained as a yellow oil (14 mg, 0.05 mmol, 27%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.54 (m, 2H), 7.51 – 7.40 (m, 3H), 7.40 – 7.29 (m, 3H), 7.19 – 7.13 (m, 2H), 3.72 – 3.48 (m, 3H), 3.03 (bs, 1H, OH), 1.85 – 1.71 (m, 1H), 1.67 – 1.51 (m, 3H), 1.19 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.0, 139.9, 137.3, 130.1, 128.6 (2C), 128.6 (2C), 128.4, 128.3 (2C), 127.7 (2C), 63.1, 56.8, 35.1, 29.2, 21.6. **HRMS (ESI)** calcd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1696, found 268.1691.

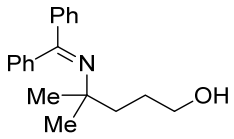
4-((diphenylmethylene)amino)Hexan-1-ol (2f)



Prepared according to the *General Procedure C* from dioxime **1f** (73 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-20% AcOEt in heptane), the title compound **2f** was obtained as a yellow oil (20 mg, 0.07 mmol, 36%).

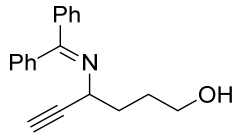
^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.62 – 7.55 (m, 2H), 7.50 – 7.40 (m, 3H), 7.39 – 7.30 (m, 3H), 7.20 – 7.13 (m, 2H), 3.69 – 3.48 (m, 2H), 3.38 – 3.27 (m, 1H), 2.66 (bs, 1H, OH), 1.90 – 1.43 (m, 6H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.4, 140.0, 137.4, 130.1, 128.6 (2C), 128.5 (2C), 128.3, 128.3 (2C), 128.0 (2C), 63.3, 62.7, 33.3, 29.0, 28.5, 11.2. **HRMS (ESI)** calcd for $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852, found 282.1846.

4-((diphenylmethylene)amino)-4-Methylpentan-1-ol (2g)



Prepared according to the *General Procedure C* from dioxime **1g** (73 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-10% AcOEt in heptane), the title compound **2g** was obtained as an unstable yellow oil (4 mg, 0.01 mmol, 6%). Due to the instability of **2g**, the product was isolated with benzophenone deriving from its decomposition. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) =7.42 – 7.37 (m, 5H), 7.36 – 7.31 (m, 5H), 3.78 – 3.67 (m, 1H), 3.60 (t, *J* = 6.0 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.66 – 1.59 (m, 2H), 0.99 (s, 7H). **HRMS (APCI)** calcd for $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852, found 282.1852.

4-((diphenylmethylene)amino)Hex-5-yn-1-ol (2h)

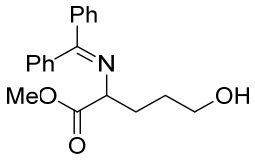


Prepared according to the *General Procedure C* from dioxime **1h** (73 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (10-20% AcOEt in heptane), the title compound **2h** was obtained as a pale yellow solid (23 mg, 0.08 mmol, 41%).

Prepared according to the *General Procedure C* from dioxime **1h** (91 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (10-20% AcOEt in heptane), the title compound **2h** was obtained as a pale yellow solid (22 mg, 0.08 mmol, 31%).

mp = 87 – 89 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$), δ (ppm) = 7.64 – 7.56 (m, 2H), 7.53 – 7.42 (m, 3H), 7.41 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 4.25 – 4.14 (m, 1H), 3.77 – 3.55 (m, 2H), 2.85 (s, 1H), 2.33 (d, *J* = 2.3 Hz, 1H), 1.96 – 1.82 (m, 2H), 1.80 – 1.62 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 170.3, 139.4, 136.2, 130.7, 129.0 (3C), 128.7 (2C), 128.3 (2C), 127.9 (2C), 84.4, 72.0, 62.7, 53.5, 34.0, 29.1. **HRMS (APCI)** calcd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1536.

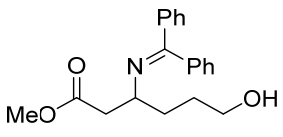
Methyl 2-((diphenylmethylene)amino)-5-Hydroxypentanoate (2i)



Prepared according to the *General Procedure C* from dioxime **1i** (79 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-10% AcOEt in heptane), the title compound **2i** was obtained as a yellow oil (28 mg, 0.09 mmol, 46%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 – 7.58 (m, 2H), 7.51 – 7.42 (m, 3H), 7.40 – 7.28 (m, 3H), 7.22 – 7.11 (m, 2H), 4.16 (dd, *J* = 7.2, 4.5 Hz, 1H), 3.71 (s, 3H), 3.67 – 3.53 (m, 2H), 2.65 (bs, 1H, OH), 2.14 – 2.00 (m, 1H), 1.98 – 1.84 (m, 1H), 1.71 – 1.47 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 172.6, 171.3, 139.3, 136.3, 130.7, 129.0(2C), 128.9, 128.8(2C), 128.3(2C), 127.8(2C), 64.8, 62.5, 52.2, 30.9, 29.3. **HRMS (ESI)** calcd $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found 312.1587.

Methyl 3-((diphenylmethylene)amino)-6-Hydroxyhexanoate (2j)

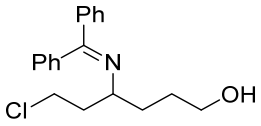


Prepared according to the *General Procedure C* from dioxime **1j** (82 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-15% AcOEt in heptane), the title compound **2j** was obtained as a yellow oil (26 mg, 0.08 mmol, 41%).

Prepared according to the *General Procedure D* from dioxime **1j** (103 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (5-15% AcOEt in heptane), the title compound **2j** was obtained as a yellow oil (17 mg, 0.05 mmol, 20%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.58 – 7.53 (m, 2H), 7.49 – 7.41 (m, 3H), 7.39 – 7.29 (m, 3H), 7.23 – 7.18 (m, 2H), 3.94 – 3.83 (m, 1H), 3.60 (s, 3H), 3.59 – 3.55 (m, 1H), 3.54 – 3.47 (m, 1H), 2.86 (bs, 1H, OH), 2.70 (dd, *J* = 15.0, 7.7 Hz, 1H), 2.58 (dd, *J* = 15.0, 5.5 Hz, 1H), 1.78 – 1.70 (m, 1H), 1.69 – 1.52 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 172.3, 168.6, 139.8, 136.8, 130.3, 128.7 (2C), 128.7, 128.5 (2C), 128.3 (2C), 127.9 (2C), 62.9, 57.9, 51.6, 40.5, 33.3, 28.9. **HRMS (ESI)** calcd for $C_{20}H_{24}NO_3$ $[M+H]^+$: 326.1751, found 326.1746.

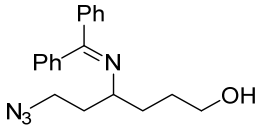
6-Chloro-4-((diphenylmethylene)amino)hexan-1-ol (2k)



Prepared according to the *General Procedure C* from oxime **1k** (80 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-20% AcOEt in heptane), the title compound **2k** was obtained as a yellow oil (31 mg, 0.10 mmol, 48%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.63 – 7.56 (m, 2H), 7.51 – 7.43 (m, 3H), 7.40 – 7.30 (m, 3H), 7.23 – 7.13 (m, 2H), 3.68 – 3.47 (m, 4H), 3.46 – 3.34 (m, 1H), 2.69 (bs, 1H, OH), 2.32 – 2.16 (m, 1H), 2.06 – 1.89 (m, 1H), 1.80 – 1.70 (m, 1H), 1.67 – 1.55 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 169.3, 139.3, 136.5, 130.6, 128.8 (3C), 128.6 (2C), 128.4 (2C), 127.9 (2C), 62.9, 58.4, 42.4, 38.5, 33.2, 28.9. **HRMS (ESI)** calcd for $C_{19}H_{23}ClNO$ $[M+H]^+$: 316.1463, found 316.1462.

6-Azido-4-((diphenylmethylene)amino)hexan-1-ol (2l)

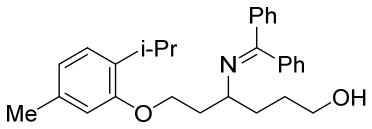


Prepared according to the *General Procedure C* from dioxime **1l** (82 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-15% AcOEt in heptane), the title compound **2l** was obtained as a yellow oil (18 mg, 0.06 mmol, 28%).

Prepared according to the *General Procedure D* from dioxime **1l** (98 mg, 0.25 mmol, 1.0 equiv). After a chromatographic purification (5-15% AcOEt in heptane), the title compound **2l** was obtained as a yellow oil (14 mg, 0.04 mmol, 18%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.63 – 7.53 (m, 2H), 7.51 – 7.42 (m, 3H), 7.41 – 7.29 (m, 3H), 7.18 – 7.12 (m, 2H), 3.67 – 3.46 (m, 3H), 3.33 – 3.23 (m, 1H), 3.22 – 3.09 (m, 1H), 2.86 (bs, 1H, OH), 2.05 – 1.91 (m, 1H), 1.88 – 1.48 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 168.6, 139.6, 136.9, 130.4, 128.7 (2C), 128.6 (3C), 128.3 (2C), 127.8 (2C), 63.0, 58.4, 48.8, 34.6, 33.4, 29.0. **HRMS (ESI)** calcd for $C_{19}H_{22}N_4O$ $[M+H]^+$: 309.0357, found 309.0354.

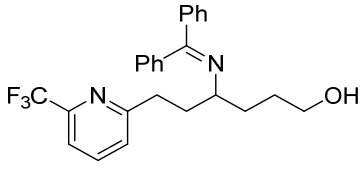
4-((diphenylmethylene)amino)-6-(2-isopropyl-5-methylphenoxy)Hexan-1-ol (2m)



Prepared according to the *General Procedure C* from oxime **1m** (103 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-30 % AcOEt in heptane), the title compound **2m** was obtained as a yellow oil (28 mg, 0.07 mmol, 33%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.63 – 7.56 (m, 2H), 7.41 – 7.30 (m, 6H), 7.12 – 7.07 (m, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.58 (s, 1H), 3.98 – 3.85 (m, 2H), 3.80 – 3.73 (m, 1H), 3.70 – 3.51 (m, 2H), 2.94 (hept, *J* = 6.8 Hz, 1H), 2.30 (s, 3H), 2.19 – 2.02 (m, 2H), 1.84 – 1.74 (m, 1H), 1.72 – 1.59 (m, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 168.2, 156.0, 139.8, 137.0, 136.3, 134.0, 130.3, 128.7 (2C), 128.6 (2C), 128.4, 128.3 (2C), 127.8 (2C), 125.8, 121.0, 111.9, 64.7, 63.1, 58.1, 35.3, 33.3, 29.0, 26.4, 23.0, 22.5, 21.5. **HRMS (ESI)** calcd for $C_{29}H_{35}NO_2$ $[M+H]^+$: 309.0357, found 309.0354.

4-((diphenylmethylene)amino)-6-(6-(trifluoromethyl)pyridin-2-yl)Hexan-1-ol (2n)

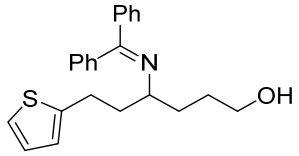


Prepared according to the *General Procedure C* from oxime **1n** (102 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-25% AcOEt in heptane), the title compound **2n** was obtained as a green oil (22 mg, 0.05 mmol, 26%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.69 (t, *J* = 7.8 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.35 – 7.30 (m, 2H), 7.28 – 7.26 (m, 1H), 7.14 – 7.10 (m, 2H), 3.66 – 3.58 (m, 1H), 3.56 – 3.48 (m, 2H), 2.87 – 2.78 (m, 1H), 2.77 – 2.69 (m, 1H), 2.12 – 2.00 (m, 2H), 1.83 – 1.75 (m, 1H), 1.71 – 1.56 (m,

3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 168.0, 163.2, 147.7 (q, *J* = 34.1 Hz), 139.7, 137.5, 137.1, 130.3, 128.7 (2C), 128.6 (2C), 128.5, 128.3 (2C), 127.8 (2C), 125.6, 121.7 (q, *J* = 274.4 Hz), 117.7 (q, *J* = 3.1 Hz), 63.1, 60.6, 35.3 (2C), 33.5, 28.9. **^{19}F NMR** (282 MHz, $CDCl_3$) -68.03. **HRMS (ESI)** calcd for $C_{25}H_{25}F_3N_2O$ $[M+H]^+$: 309.0357, found 309.0354.

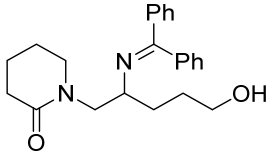
4-((diphenylmethylene)amino)-6-(thiophen-2-yl)hexan-1-ol (2o)



Prepared according to the *General Procedure C* from oxime **1o** (90 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-20% AcOEt in heptane), the title compound **2o** was obtained as a yellow oil (21 mg, 0.06 mmol, 30%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.62 – 7.56 (m, 2H), 7.46 – 7.29 (m, 6H), 7.16 – 7.10 (m, 2H), 7.07 (dd, *J* = 5.2, 1.0 Hz, 1H), 6.86 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.68 (dd, *J* = 3.4, 1.0 Hz, 1H), 3.67 – 3.45 (m, 3H), 2.85 – 2.59 (m, 2H), 2.11 – 1.90 (m, 2H), 1.83 – 1.72 (m, 1H), 1.70 – 1.46 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 168.0, 145.2, 139.5, 136.9, 130.5, 128.8, 128.6 (2C), 128.6 128.4 (2C), 127.9 (2C), 126.8 (2C), 124.0, 123.0, 63.1, 60.7, 37.5, 33.2, 29.0, 27.0. **HRMS (ESI)** calcd for $C_{23}H_{25}NOS$ $[M+H]^+$: 309.0357, found 309.0354.

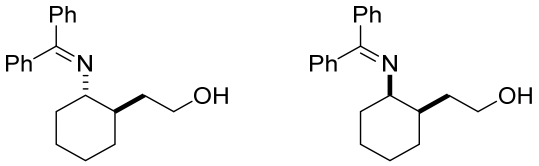
1-(2-((diphenylmethylene)amino)-5-hydroxypentyl)Piperidin-2-one (2p)



Prepared according to the *General Procedure C* from oxime **1p** (90 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (0-2% *i*-PrOH in AcOEt), the title compound **2p** was obtained as a yellow oil (17 mg, 0.05 mmol, 24%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.55 – 7.48 (m, 2H), 7.41 – 7.24 (m, 6H), 7.08 – 6.99 (m, 2H), 3.86 – 3.71 (m, 2H), 3.59 – 3.39 (m, 2H), 3.26 – 3.07 (m, 3H), 2.33 – 2.18 (m, 2H), 1.74 – 1.57 (m, 6H), 1.59 – 1.48 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 169.8, 168.6, 139.5, 136.5, 130.3, 128.7, 128.6 (2C), 128.5 (2C), 128.3 (2C), 127.7 (2C), 62.9, 59.9, 52.9, 50.1, 32.3, 31.1, 28.9, 23.4, 21.4. **HRMS (APCI)** calcd for $C_{23}H_{29}N_2O_2$ $[M+H]^+$: 365.2224, found 365.2216.

2-(2-((diphenylmethylene)amino)cyclohexyl)Ethan-1-ol (2q)



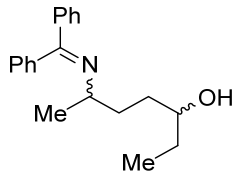
2q **2q'**

Prepared according to the *General Procedure C* from oxime **1q** (79 mg, 0.20 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1), and after a chromatographic purification (5-20% AcOEt in heptane) **2q** was obtained as a yellow oil (15 mg, 0.05 mmol, 25%) and **2q'** was obtained as a yellow oil (15 mg, 0.05 mmol, 25%).

^{1}H NMR (300 MHz, $CDCl_3$) of **2q**, δ (ppm) = 7.68 – 7.58 (m, 2H), 7.51 – 7.41 (m, 3H), 7.41 – 7.30 (m, 3H), 7.21 – 7.14 (m, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.99 (td, *J* = 10.0, 4.4 Hz, 1H), 1.96 (s, 1H, OH), 1.85 – 1.74 (m, 1H), 1.73 – 1.48 (m, 5H), 1.35 – 1.18 (m, 3H), 1.15 – 1.03 (m, 1H), 0.89 (qd, *J* = 12.7, 3.5 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) of **2q**, δ (ppm) = 167.4, 140.0, 137.4, 130.1, 128.6 (2C), 128.5 (2C), 128.3, 128.3 (2C), 127.7 (2C), 66.4, 61.6, 41.2, 37.6, 34.0, 31.5, 26.0, 24.8. **HRMS (ESI)** calcd for **2q** $C_{21}H_{26}NO$ $[M+H]^+$: 308.2009, found 308.2002

^{1}H NMR (300 MHz, $CDCl_3$) of **2q'**, δ (ppm) = 7.67 – 7.59 (m, 2H), 7.54 – 7.46 (m, 3H), 7.43 – 7.35 (m, 3H), 7.25 – 7.18 (m, 2H), 3.76 – 3.63 (m, 1H), 3.64 – 3.47 (m, 2H), 2.04 – 1.76 (m, 4H), 1.76 – 1.60 (m, 2H), 1.58 – 1.39 (m, 4H), 1.36 – 1.23 (m, 1H). **^{13}C NMR** (76 MHz, $CDCl_3$) of **2q'**, δ (ppm) = 167.2, 140.0, 137.3, 130.1, 128.7 (2C), 128.6 (2C), 128.4, 128.3 (2C), 127.8 (2C), 62.1, 62.0, 40.0, 35.1, 31.3, 30.3, 23.4, 23.2. **HRMS (ESI)** calcd for **2q'** $C_{21}H_{26}NO$ $[M+H]^+$: 308.2009, found 308.2003.

6-((diphenylmethylene)amino)Heptan-3-ol (2r)



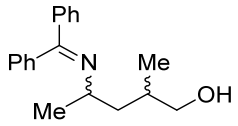
Prepared according to the *General Procedure C* from oxime **1r** (76 mg, 0.20 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1), and after a chromatographic purification (5-15% AcOEt in heptane) **2r** was obtained as a yellow oil (5 mg, 0.02 mmol, 9%) and **2r'** was obtained as a yellow oil (7 mg, 0.02 mmol, 12%).

^{1}H NMR (300 MHz, $CDCl_3$) of **2r**, δ (ppm) = 7.60 – 7.54 (m, 2H), 7.50 – 7.41 (m, 3H), 7.38 – 7.28 (m, 3H), 7.18 – 7.12 (m, 2H), 3.57 – 3.39 (m, 2H), 3.30 (bs, 1H), 1.76 – 1.55 (m, 3H), 1.53 – 1.38 (m, 4H), 1.15 (d, *J* = 6.3 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) of **2r**, δ (ppm) = 166.9, 139.9, 137.3, 130.1, 128.6 (4C),

128.4, 128.3 (2C), 127.7 (2C), 73.5, 57.1, 34.9, 33.3, 30.4, 21.6, 10.2. **HRMS (APCI)** calcd for **2r** $C_{20}H_{26}NO$ $[M+H]^+$: 296.2009, found 296.2009.

^{1}H NMR (300 MHz, $CDCl_3$) of **2r'**, δ (ppm) = 7.62 – 7.54 (m, 2H), 7.49 – 7.40 (m, 3H), 7.38 – 7.28 (m, 3H), 7.18 – 7.11 (m, 2H), 3.53 – 3.37 (m, 2H), 1.78 – 1.68 (m, 1H), 1.64 – 1.55 (m, 1H), 1.51 – 1.36 (m, 4H), 1.15 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) of **2r'**, δ (ppm) = 166.8, 140.0, 137.4, 130.0, 128.6 (4C), 128.3, 128.2 (2C), 127.8 (2C), 73.1, 57.1, 33.9, 33.4, 30.1, 22.1, 10.2. **HRMS (APCI)** calcd for **2r** $C_{20}H_{26}NO$ $[M+H]^+$: 296.2009, found 296.2009.

4-((diphenylmethylene)amino)-2-Methylpentan-1-ol (2s)

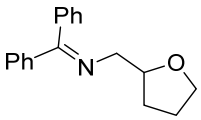


Prepared according to the *General Procedure C* from oxime **1s** (73 mg, 0.20 mmol, 1.0 equiv). The title compound was obtained as mixture of diastereomers (1:1), and after a chromatographic purification (5-15% AcOEt in heptane) **2s** was obtained as a yellow oil (6 mg, 0.02 mmol, 10%) and **2s'** was obtained as a yellow oil (10 mg, 0.03 mmol, 17%).

^{1}H NMR (300 MHz, $CDCl_3$) of **2s**, δ (ppm) = 7.57 – 7.51 (m, 2H), 7.49 – 7.42 (m, 4.1, 1.7 Hz, 3H), 7.39 – 7.29 (m, 3H), 7.21 – 7.13 (m, 2H), 5.02 (bs, 1H), 3.72 – 3.56 (m, 1H), 3.48 (dd, *J* = 11.1, 4.2 Hz, 1H), 3.32 (dd, *J* = 11.1, 8.0 Hz, 1H), 2.11 – 1.91 (m, 1H), 1.69 – 1.62 (m, 1H), 1.50 – 1.35 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) of **2s**, δ (ppm) = 167.2, 139.5, 137.0, 130.3, 128.7 (4C), 128.6, 128.4 (2C), 127.6 (2C), 68.8, 55.6, 43.9, 32.3, 21.0, 18.9. **HRMS (APCI)** calcd for **2s** $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852, found 282.1853.

^{1}H NMR (300 MHz, $CDCl_3$) of **2s'**, δ (ppm) = 7.60 – 7.54 (m, 2H), 7.50 – 7.41 (m, 3H), 7.37 – 7.28 (m, 3H), 7.20 – 7.14 (m, 2H), 3.59 – 3.44 (m, 1H), 3.42 (dd, *J* = 5.9, 4.9 Hz, 2H), 1.85 (ddd, *J* = 13.5, 9.6, 5.1 Hz, 1H), 1.68 – 1.51 (m, 1H), 1.33 – 1.23 (m, 2H), 1.14 (d, *J* = 6.3 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) of **2s'**, δ (ppm) = 167.2, 140.0, 137.3, 130.1, 128.6 (2C), 128.5 (2C), 128.4, 128.2 (2C), 127.8 (2C), 68.8, 55.3, 42.7, 33.6, 23.1, 17.4. **HRMS (APCI)** calcd for **2s'** $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852, found 282.1851.

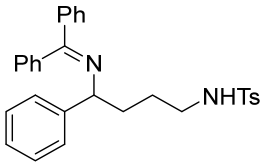
1,1-diphenyl-N-((tetrahydrofuran-2-yl)methyl)Methanimine (2t)



Prepared according to the *General Procedure C* from oxime **1t** (70 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (5-10% AcOEt in heptane), the title compound **2t** was obtained as a yellow oil (11 mg, 0.04 mmol, 21%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.58 (m, 2H), 7.48 – 7.39 (m, 3H), 7.38 – 7.28 (m, 3H), 7.21 – 7.14 (m, 2H), 4.31 – 4.20 (m, 1H), 3.88 – 3.71 (m, 2H), 3.53 (dd, *J* = 13.7, 5.8 Hz, 1H), 3.41 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.10 – 1.97 (m, 1H), 1.93 – 1.82 (m, 2H), 1.76 – 1.63 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 169.3, 134.0, 137.0, 130.2, 128.6 (4C), 128.5, 128.1 (2C), 128.0 (2C), 79.4, 68.4, 58.5, 29.7, 25.9. **HRMS (APCI)** calcd for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539, found 266.1538.

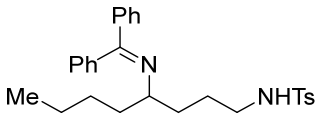
***N*-(4-((diphenylmethylene)amino)-4-phenylbutyl)-4-Methylbenzenesulfonamide (2u)**



Prepared according to the *General Procedure C* from oxime **1u** (114 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (3-20% AcOEt in heptane), the title compound **2u** was obtained as a yellow oil (39 mg, 0.08 mmol, 40%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.65 – 7.44 (m, 4H), 7.35 – 7.22 (m, 6H), 7.17 – 7.04 (m, 7H), 6.94 – 6.79 (m, 2H), 4.55 (t, *J* = 6.2 Hz, 1H), 4.19 (dd, *J* = 8.0, 4.9 Hz, 1H), 2.84 – 2.69 (m, 2H), 2.28 (s, 3H), 1.86 – 1.72 (m, 1H), 1.70 – 1.55 (m, 1H), 1.37 – 1.14 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.5, 144.6, 143.3, 139.7, 137.2, 136.9, 130.2, 129.7 (2C), 128.7 (2C), 128.5 (3C), 128.5 (2C), 128.2 (2C), 127.7 (2C), 127.1 (2C), 127.1 (2C), 126.9, 65.9, 43.3, 36.4, 26.6, 21.6. **HRMS (ESI)** calcd for $C_{30}H_{30}N_2O_2S$ $[M+H]^+$: 309.0357, found 309.0354.

***N*-(4-((diphenylmethylene)amino)octyl)-4-Methylbenzenesulfonamide (2v)**

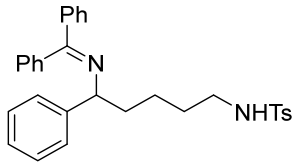


Prepared according to the *General Procedure C* from oxime **1v** (110 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (3-20% AcOEt in heptane), the title compound **2v** was obtained as a yellow oil (29 mg, 0.06 mmol, 30%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.63 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.45 – 7.30 (m, 6H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.03 (m, 2H), 4.86 (t, *J* = 6.2 Hz, 1H), 3.26 – 3.17 (m, 1H), 2.97 – 2.74 (m, 2H), 2.38 (s, 3H), 1.61 – 1.37 (m, 7H), 1.20 – 1.11 (m, 2H), 1.09 – 1.01 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.1, 143.2, 140.1, 137.5, 137.4, 130.0, 129.7 (2C), 128.6 (2C), 128.5 (2C), 128.3, 128.3

(2C), 127.9 (2C), 127.2 (2C), 61.3, 43.7, 36.1, 33.7, 28.7, 26.4, 22.9, 21.6, 14.2. **HRMS (ESI)** calcd for $C_{28}H_{34}N_2O_2S$ $[M+H]^+$: 309.0357, found 309.0354.

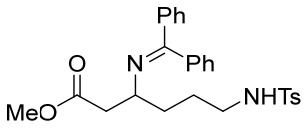
***N*-(5-((diphenylmethylene)amino)-5-phenylpentyl)-4-Methylbenzenesulfonamide (2w)**



Prepared according to the *General Procedure C* from oxime **1w** (116 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (3-20% AcOEt in heptane), the title compound **2w** was obtained as a yellow oil (16 mg, 0.03 mmol, 16%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.74 – 7.60 (m, 4H), 7.45 – 7.39 (m, 3H), 7.38 – 7.30 (m, 3H), 7.29 – 7.20 (m, 7H), 7.03 – 6.98 (m, 2H), 4.31 – 4.20 (m, 2H), 2.86 (q, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 1.89 – 1.76 (m, 1H), 1.75 – 1.66 (m, 1H), 1.63 – 1.53 (m, 1H), 1.40 – 1.31 (m, 2H), 1.14 – 1.05 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 166.9, 145.0, 143.4, 140.0, 137.1, 130.1, 129.8 (4C), 128.7, 128.5 (2C), 128.5 (2C), 128.2 (2C), 127.9 (2C), 127.2 (2C), 127.2 (2C), 126.8, 66.5, 43.2, 39.0, 29.6, 23.6, 21.7. **HRMS (ESI)** calcd for $C_{31}H_{32}N_2O_2S$ $[M+H]^+$: 309.0357, found 309.0354.

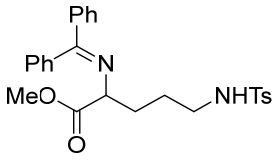
Methyl 3-((diphenylmethylene)amino)-6-((4-methylphenyl)sulfonamido)Hexanoate (2x)



Prepared according to the *General Procedure C* from oxime **1x** (113 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (3-15% AcOEt in heptane), the title compound **2x** was obtained as a yellow oil (24 mg, 0.05 mmol, 25%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.48 – 7.39 (m, 3H), 7.38 – 7.29 (m, 3H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.06 (m, 2H), 4.72 (t, *J* = 6.3 Hz, 1H), 3.82 – 3.71 (m, 1H), 3.60 (s, 3H), 2.96 – 2.71 (m, 2H), 2.65 – 2.42 (m, 2H), 2.38 (s, 3H), 1.68 – 1.50 (m, 2H), 1.46 – 1.34 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 172.1, 168.8, 143.4, 139.7, 137.2, 136.6, 130.4, 129.8 (2C), 128.8 (2C), 128.7, 128.6 (2C), 128.3 (2C), 127.9 (2C), 127.2 (2C), 57.8, 51.7, 43.3, 40.8, 33.3, 26.2, 21.6. **HRMS (ESI)** calcd for $C_{27}H_{30}N_2O_4S$ $[M+H]^+$: 309.0357, found 309.0354.

Methyl 2-((diphenylmethylene)amino)-5-((4-methylphenyl)sulfonamido)Pentanoate (2y)

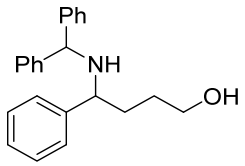


Prepared according to the *General Procedure C* from oxime **1y** (110 mg, 0.20 mmol, 1.0 equiv). After a chromatographic purification (10-20% AcOEt in heptane), the title compound **2y** was obtained as a yellow oil (19 mg, 0.04 mmol, 20%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.67 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.56 (m, 2H), 7.47 – 7.38 (m, 4H), 7.37 – 7.31 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.14 – 7.06 (m, 2H), 4.62 (bt, *J* = 5.9 Hz, 1H), 4.02 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.68 (s, 3H), 3.00 – 2.81 (m, 2H), 2.39 (s, 3H), 1.95 – 1.78 (m, 2H), 1.53 – 1.41 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 172.5, 171.3, 143.4, 139.3, 137.2, 136.3, 130.7, 129.8 (2C), 129.0 (3C), 128.8 (2C), 128.3 (2C), 127.8 (2C), 127.2 (2C), 64.6, 52.4, 43.1, 30.7, 26.3, 21.7. **HRMS (ESI)** calcd for $C_{26}H_{28}N_2O_4S$ $[M+H]^+$: 309.0357, found 309.0354.

3.7 Derivatization reactions

4-(benzhydrylamino)-4-Phenylbutan-1-ol (3)

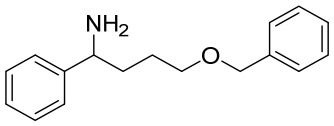


1,5-amine alcohol 3 was synthesis following a reported procedure.[8] To a solution of **2a** (50 mg, 0.15 mmol, 1.0 equiv) in dry MeOH (3.0 mL), was added $NaBH_4$ (144 mg, 3.79 mmol, 25.0 equiv) at 0ºC under inert atmosphere. The reaction was warmed up to room temperature, and stirred 16 h at the same temperature. Then, the reaction mixture was concentrated under reduced pressure, and the crude mixture was diluted in CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by flash column chromatography (10-15% AcOEt in heptane) to obtain the title compound **3** as a colorless oil (43 mg, 0.13 mmol, 86%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.40 – 7.32 (m, 6H), 7.32 – 7.23 (m, 6H), 7.21 – 7.15 (m, 3H), 4.59 (s, 1H), 3.72 – 3.55 (m, 2H), 3.49 (dd, *J* = 7.6, 5.8 Hz, 1H), 2.84 (ds, 2H), 1.86 – 1.72 (m, 2H), 1.73 – 1.59 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 144.3, 144.1, 142.7, 128.8 (2C), 128.7 (4C), 128.0 (2C), 127.3 (4C), 127.2, 127.0 (2C), 64.2, 63.2, 60.4, 36.2, 30.7. **HRMS (ESI)** calcd for $C_{23}H_{25}NO$ $[M+H]^+$: 309.0357, found 309.0354.

[8] R. Viswanathan, D. Mutnick, J. N. Johnston. *J. Am. Chem. Soc.* **2003**, *125*, 7266-7271.

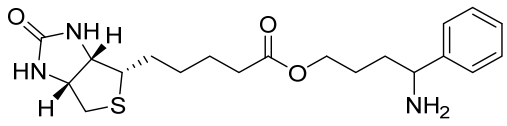
4-(benzyloxy)-1-Phenylbutan-1-amine (4)



Amine **4** was synthesized following reported procedures.[7,9] To a stirred solution of **2a** (50 mg, 0.15 mmol, 1.0 equiv) in dry THF (0.8 mL), NaH (60 % dispersion in mineral oil, 9 mg, 0.23 mmol, 1.5 equiv) was added at 0ºC under inert atmosphere. The reaction mixture was stirred at room temperature for 30 min, and then, benzyl bromide (29 mg, 20 µL, 0.17 mmol, 1.1 equiv) was added dropwise. The mixture was stirred for other 12 h, and quenched with H_20. The resulting suspension was diluted with AcOEt, and poured into a separatory funnel. The layers were separated and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure. In a round-bottom flask, the crude mixture was dissolved in THF (3.0 mL) and H_2O (0.2 mL), and pyridinium *p*-toluene sulfonate (46 mg, 0.18 mmol, 1.2equiv) was added. The reaction was stirred at room temperature for 18 h, and then, diluted with EtOAc and H_2O. The mixture was poured into a separatory funnel and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by flash column chromatography (0-10% *i*-PrOH in CH_2Cl_2) to obtain **5** as yellow oil (15 mg, 0.06 mmol, 38%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.39 – 7.25 (m, 10H), 4.60 (bs, 2H), 4.44 (s, 2H), 4.05 (t, *J* = 7.2 Hz, 1H), 3.49 – 3.33 (m, 2H), 2.09 – 1.84 (m, 2H), 1.65 – 1.43 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$), δ (ppm) = 140.9, 138.4, 129.0 (2C), 128.6 (2C), 128.3, 127.9 (2C), 127.8, 127.2 (2C), 73.1, 69.8, 56.4, 33.9, 26.5. **HRMS (ESI)** calcd for $C_{17}H_{21}NO$ $[M+H]^+$: 309.0357, found 309.0354.

4-Amino-4-phenylbutyl 5-((3a*S*,4*S*,6a*R*)-2-oxohexahydro-1*H*-thieno[3,4-*d*]imidazol-4-yl)Pentanoate (5)



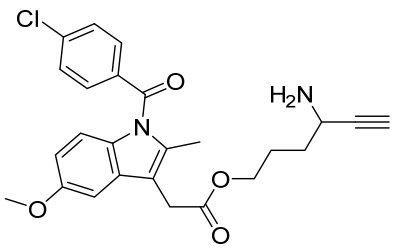
Amine **5** was synthesized following reported procedures.[7] To a stirred solution of **2a** (50 mg, 0.15 mmol, 1.0 equiv), biotin (56 mg, 0.23 mmol, 1.5 equiv), and 4-dimethylaminopyridine (2 mg, 0.02 mmol, 10 mol%) in CH_2Cl_2 (0.8 mL), *N*-(3-dimetilaminopropilo)-*N*′-etilcarbodiimida hydrochloride (73 mg, 0.38 mmol, 2.5 equiv) was added. The reaction was monitored by TLC analysis, and upon completion (16 h), the mixture was poured into a separatory funnel and washed with brine (2 x 20 mL). The organic layer was dried (Na_2SO_4), and the volatiles were removed under reduced pressure. In a round-bottom flask, the crude mixture was dissolved in THF (2.8 mL) and H_2O (0.2 mL), and pyridinium *p*-toluene sulfonate (46 mg, 0.18 mmol, 1.2equiv) was added. The reaction was stirred at

[9] N. Yasukawa, T. Kanie, M. Kuwata, Y. Monguchi, H. Sajiki, Y. Sawama. *Chem. Eur. J.* **2017**, *23*, 10974-10977.

room temperature for 18 h, and then, diluted with EtOAc and H_2O. The mixture was poured into a separatory funnel and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by flash column chromatography (0-20% *i*-PrOH in CH_2Cl_2) to obtain **5** as yellow oil (25 mg, 0.06 mmol, 42%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.40 – 7.29 (m, 5H), 6.12 (bs, 1H), 5.69 (bd, *J* = 15.4 Hz, 1H), 4.47 (dd, *J* = 8.0, 4.7 Hz, 1H), 4.27 (dd, *J* = 8.2, 4.4 Hz, 1H), 4.07 – 3.93 (m, 5H), 3.18 – 3.07 (m, 1H), 2.88 (dd, *J* = 12.8, 4.9 Hz, 1H), 2.72 (d, *J* = 13.2 Hz, 1H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.93 – 1.76 (m, 2H), 1.75 – 1.55 (m, 6H), 1.50 – 1.35 (m, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$), δ (ppm) = 173.8, 163.9, 144.0, 128.9 (2C), 127.7, 126.7 (2C), 64.1, 62.1, 60.3, 55.9, 55.7, 40.7, 34.7, 34.0, 28.4, 25.7, 25.5, 24.9. **HRMS (ESI)** calcd for $C_{20}H_{29}N_3O_3S$ $[M+H]^+$: 309.0357, found 309.0354.

4-Aminohex-5-yn-1-yl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)Acetate (6)



Amine **6** was synthesized following reported procedures.[7] To a stirred solution of **2a** (44 mg, 0.16 mmol, 1.0 equiv), indomethacin (85 mg, 0.24 mmol, 1.5 equiv), and 4-dimethylaminopyridine (2 mg, 0.02 mmol, 10 mol%) in CH_2Cl_2 (0.8 mL), *N*-(3-dimetilaminopropilo)-*N*′-etilcarbodiimida hydrochloride (76 mg, 0.40 mmol, 2.5 equiv) was added. The reaction was monitored by TLC analysis, and upon completion (16 h), the mixture was poured into a separatory funnel and washed with brine (2 x 20 mL). The organic layer was dried (Na_2SO_4), and the volatiles were removed under reduced pressure. In a round-bottom flask, the crude mixture was dissolved in THF (3.0 mL) and H_2O (0.2 mL), and pyridinium *p*-toluene sulfonate (48 mg, 0.19 mmol, 1.2equiv) was added. The reaction was stirred at room temperature for 18 h, and then, diluted with EtOAc and H_2O. The mixture was poured into a separatory funnel and the aqueous layer was extracted with EtOAc (10 mL x 2). The combined organic layers were dried (Na_2SO_4), and the volatiles were removed under reduced pressure. The crude mixture was subjected to purification by flash column chromatography (80-90% AcOEt in heptane) to obtain **5** as yellow oil (53 mg, 0.12 mmol, 74%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.66 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 3H), 3.66 (s, 2H), 3.51 (td, *J* = 6.9, 2.2 Hz, 1H), 2.38 (s, 3H), 2.26 (d, *J* = 2.2 Hz, 1H), 1.88 – 1.72 (m, 2H), 1.65 – 1.53 (m, 2H), 1.47 (bs, 2H). **^{13}C NMR** (76 MHz, $CDCl_3$), δ (ppm) = 171.0, 168.4, 156.2, 139.4, 136.1, 134.0, 131.3 (2C), 130.9, 130.8, 129.3 (2C), 115.1, 112.8, 111.7, 101.5, 87.2, 70.9, 64.8, 55.9, 43.1, 34.5, 30.5, 25.3, 13.5. **HRMS (APCI)** calcd for $C_{25}H_{26}ClN_2O_4$ $[M+H]^+$: 453.1576, found 453.1573.

3.8 Gram Scale Synthesis of 2a

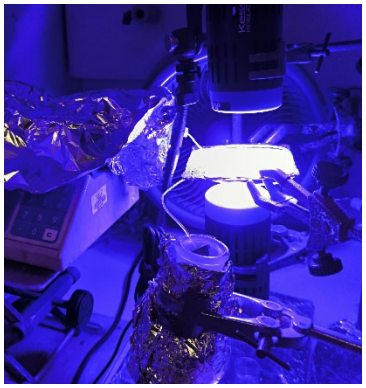
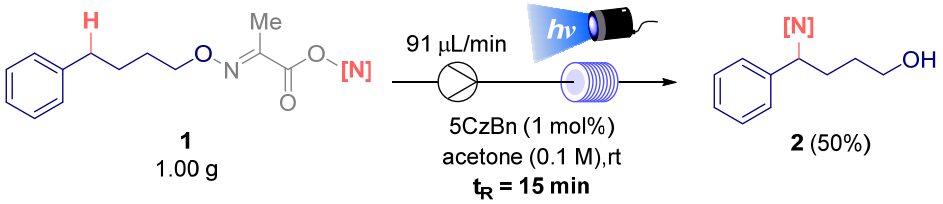


Figure S2. Gram scale synthesis reaction setup of **2a**.



To a 100mL round bottom flask equipped with a magnetic stir bar was added dioxime **1** (1.0 g, 2.41 mmol, 1.0 equiv) and 5BzCN (22 mg, 24.12 μmol, 1 mol%). The flask was sealed with a rubber septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, anhyd degassed acetone (24.0 mL, c = 0.1 M) was added via syringe. The reaction mixture was transferred to a 25 mL syringe and connected to our homemade flow system. The mixture was pumped through a PFA HPLC tube (total volume of the system: 1.36 mL), and irradiated with two Kessil PR160-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) for 4 h 24 min (residence time: 15 min, flow rate: 91 μL/min) as described in figure S2. The lamps were placed 2 cm away from the reaction system, and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by flash column chromatography (10-15% AcOEt in heptane). The title compound **2a** was obtained as a yellow oil (397 mg, 1.21 mmol, 50%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.70 – 7.61 (m, 2H), 7.43 – 7.27 (m, 8H), 7.26 – 7.15 (m, 3H), 7.06 – 6.99 (m, 2H), 4.43 (dd, *J* = 7.4, 4.8 Hz, 1H), 3.63 – 3.52 (m, 2H), 2.41 (bs, 1H), 2.08 – 1.97 (m, 1H), 1.92 – 1.81 (m, 1H), 1.61 – 1.43 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.9, 144.8, 139.8, 137.1, 130.2, 128.8 (2C), 128.5 (3C), 128.4 (2C), 128.3 (2C), 127.8 (2C), 127.2 (2C), 126.8, 66.0, 63.1, 36.2, 29.4. **HRMS (ESI)** calcd for $C_{23}H_{24}NO$ $[M+H]^+$: 330.1852, found 330.1854.

4 Mechanistic Investigations

4.1 UV/vis studies

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using JASCO V-660 UV/vis spectrophotometer. Absorption spectra of **1a** (2 mM) and 5CzBN (0.1 mM) were recorded in acetone.

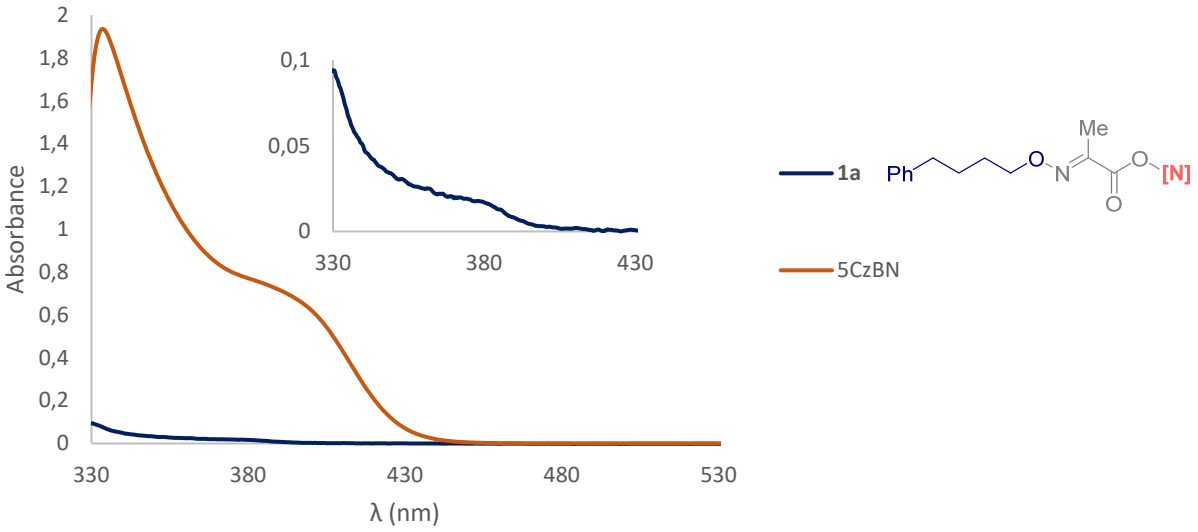
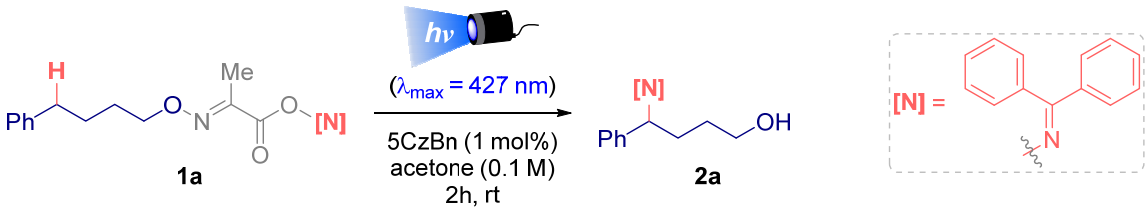


Figure S3. UV/vis absorption spectra of **1a** and 5CzBN.

4.2 Quantum yield

The quantum yield of the reaction was determined using the procedure reported previously:[9-10] bifunctional dioxime **1a** was used as a model substrate to calculated the quantum yield, using trimethoxybenzene as internal standard in a proportion 1:1 with **1a**.



The quantum yield of the reaction is defined as:

$$\Phi = \frac{\text{mol of product formed}}{\text{mol of photon flux} \times t \times f} \qquad (1)$$

where Φ is the quantum yield of the reaction, t is the time of the reaction (s), f is the incident light absorbed by the organophotocatalyst at 427 nm and the photon flux is calculated by standard ferrioxalate actinometry[11] (section C).

A) Incident light absorbed by 5CzBn (f)

The fraction of light, f, absorbed was determined according to *equation 2*:

$$f = 1 - 10^{-A} \qquad (2)$$

where A is the absorbance of the fully soluble 5CzBn in acetone at 427 nm. The absorbance of the organophotocatalyst was measured by adding a solution of 5CzBn (0.9 mg, 0.001 mmol) in acetone (1 mL) to a quartz cuvette equipped with a Teflon cap. The absorbance of the solution was recorded, and the absorbance value at 427 nm was determined to be 2.16507 (*figure S4*), indicating the fraction of light absorbed is 0.99316 according to equation 2.

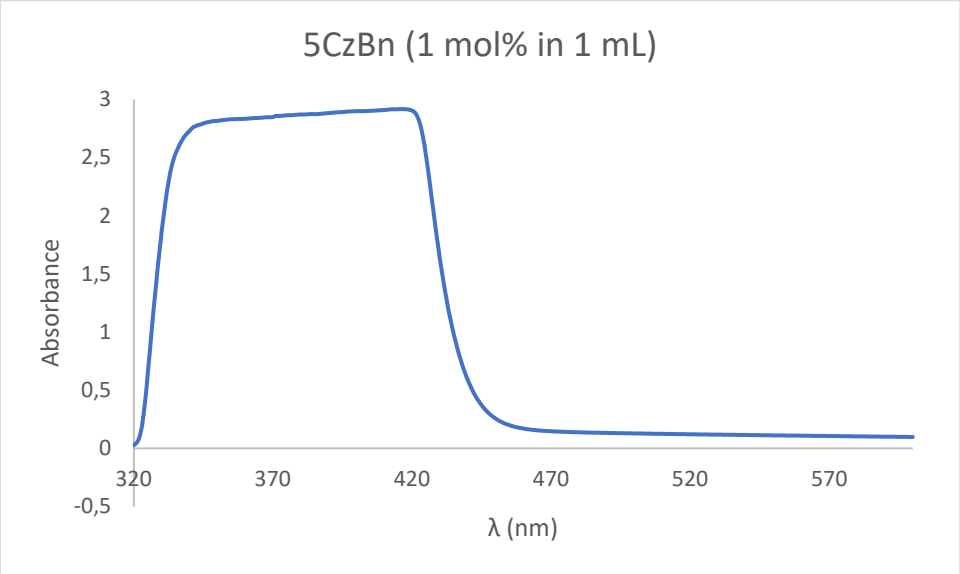


***Figure S4**. Absorption spectrum of 5CzBn in acetone.*

B) The photoredox reaction

The photoinduced transformation was performed as described in XX. Afterwards, 1,3,5-trimethoxybenzene was added as internal standard, and the volatiles were removed under vacuum. The yield of the reaction was determined by 1H NMR, where 6.5 µmols (13%) of the desired compound were detected after 300 s.

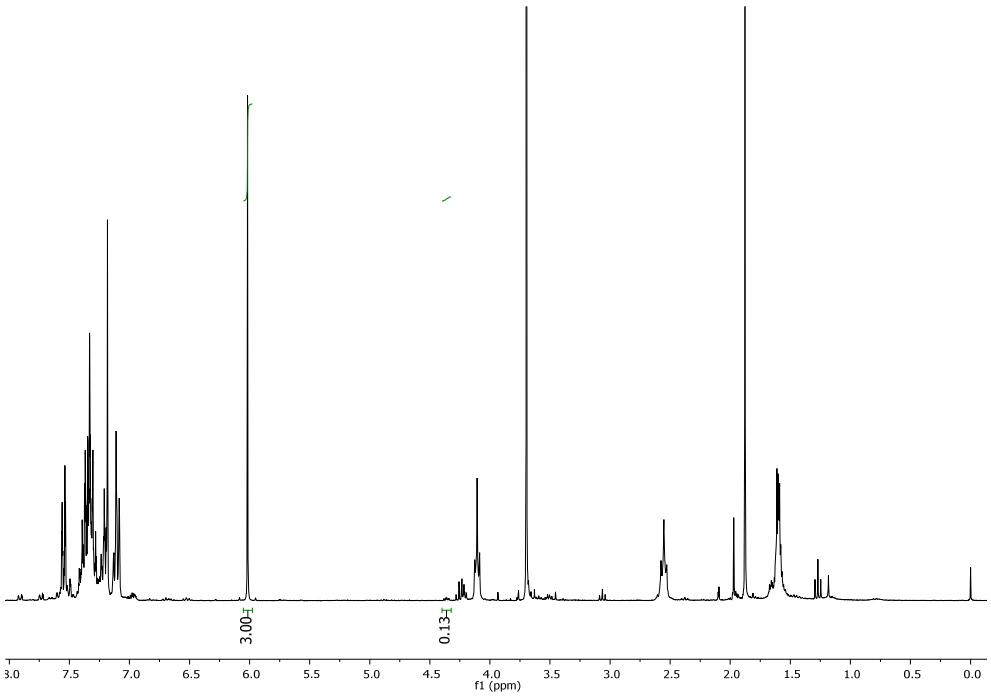


Figure S5*. Crude mixture with 1*,3,5-trimethoxybenzene after 5 min of irradiation at 427 nm*.*

C) Photon flux at 406 nm.

Standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer using equations 3 and 4.[9-11] For the ferrioxalate actinometer the production of iron(II) ions proceeds by the following reactions:[11]

$$[Fe(C_2O_4)_n]^{(3-2n)+} \xrightarrow{h\nu} Fe^{2+} + (n\text{-}1)(C_2O_4)^{2-} + C_2O_4^{-}$$

$$[Fe(C_2O_4)_n]^{(3-2n)+} + C_2O_4^{-} \longrightarrow Fe^{2+} + n(C_2O_4)^{2-} + 2CO_2$$

The moles of Fe^{2+} formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red $[Fe(phen)_3]^{2+}$ moiety (λ = 510 nm).[9-11] The photon flux is defined as:

$$\text{Photon flux} = \frac{\text{mol}\,(Fe^{2+})}{\Phi(Fe^{2+}) \times t \times f} \qquad (3)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.188 at λ = 406 nm),[11] t is the time (s), and f > 0.999, and the mol of Fe^{2+} are calculated according to *equation 4*.

$$\text{mol}\,(Fe^{2+}) = \frac{V \times \Delta A}{l \times \varepsilon} \qquad (4)$$

Where V is the total volume of the solution, ΔA is the difference in absorbance between irradiated and non-irradiated solutions, l is the path length (1.0 cm), ε is the molar absorptivity at 510 nm (11,110 L $mol^{-1}cm^{-1}$).[11]

D) ***Experimental.***

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

- *Ferrioxalate solution (0.15 M):* Potassium ferrioxalate hydrate (2.21 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (30 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.
- *Developer solution:* 1,10-Phenanthroline (50 mg) and sodium acetate (11.25 g) was added to a flask containing H_2SO_4 (50 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample. The buffered solution of phen (0.35 mL) was added to a ferrioxalate (2.0 mL) in a vial that had been covered with aluminum foil {lights of the laboratory were switched off}. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated was measured at 515 nm to be 0.0368 (*Figure 6*).

The absorbance of the irradiated sample. In a glass vial equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 75.0 s at λ = 427 nm. After irradiation, the buffered phen solution (0.35 mL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 515 nm to be 0.33385 (*figure S6*).

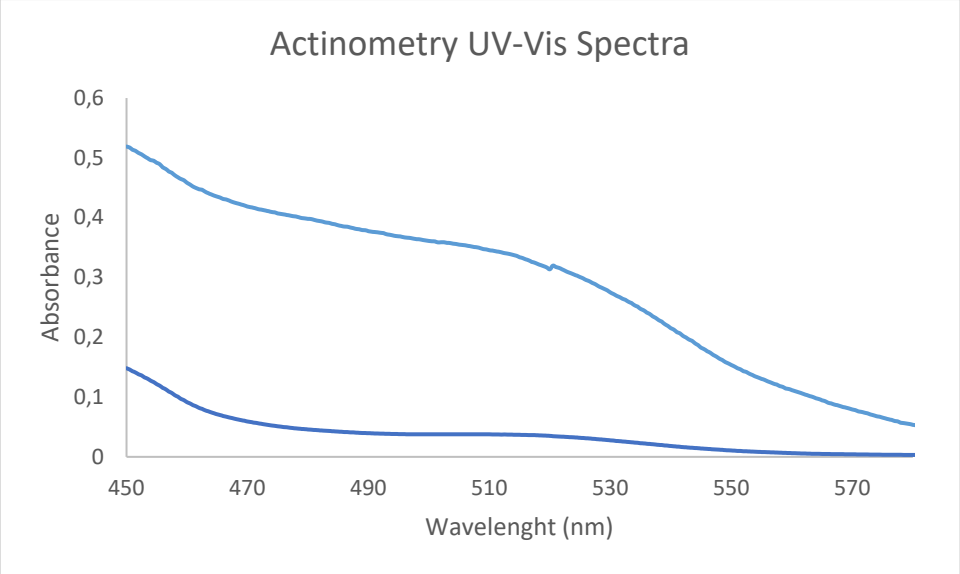


Figure S6*. Absorption spectra for irradiated and non-irradiated samples of red* $[Fe(phen)_3]^{2+}$.

Photon flux sample calculation. Sample calculation:

$$\text{mol}\ (Fe^{2+}) = \frac{\text{V} \times \Delta\text{A}}{\text{l} \times \varepsilon} \qquad (4)$$

$$\text{mol}\ (Fe^{2+}) = \frac{0.00235\ \text{L} \times 0.2970}{1.00\ cm \times 11.110\ \text{L}mol^{-1}cm^{-1}} = 6.3081\ \times\ 10^{-7}\ mol$$

$$\text{Photon flux} = \frac{\text{mol}\ (Fe^{2+})}{\Phi(Fe^{2+})\ \times\ \text{t}\ \times\ \text{f}} \qquad (3)$$

$$\text{Photon flux} = \frac{6.3081\ \times\ 10^{-7}\ mol}{1.188\ \times\ 75.0\ \text{s}\ \times\ 1.00} = 7{,}0797 \times 10^{-9}\ \text{einstein}\ \text{s}^{-1}$$

E) Quantum yield of the reaction.

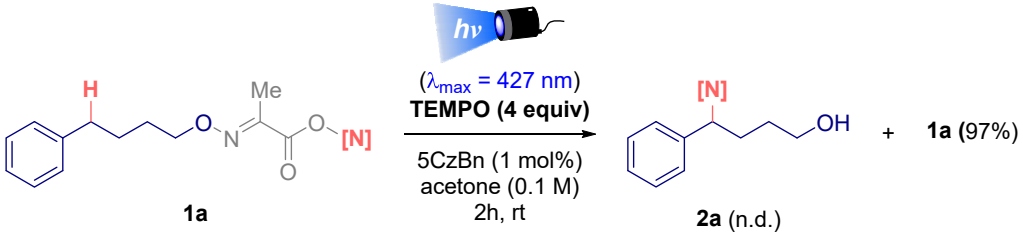
Therefore, the quantum yield of the reaction is determined to be:

$$\Phi = \frac{\text{mol of product formed}}{\text{mol of photon flux}\ \times\ \text{t}\ \times\ \text{f}} \qquad (1)$$

$$\Phi = \frac{6.5 \times 10^{-6}\ mol}{7{,}0797 \times 10^{-9}\ \text{einstein}\ \text{s}^{-1}\ \times\ 300\ \text{s} \times\ 0.99316} = \mathbf{3.09}$$

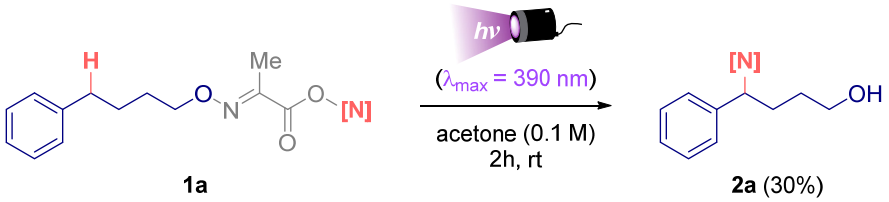
The quantum yield studies indicate that this is most likely a radical-chain process as evidenced by the Φ value. In other words, the quantum yield value indicated that 3 equivalents of product are formed for every photon absorbed. However, due to the low value, it is impossible to exclude a combination of radical chain and catalytic cycle mechanism.

4.3 TEMPO trapping experiment



To test the intermediacy of radical species, a trapping experiment was performed using TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger. The reaction was performed according to the *General Procedure C* using **1a** (42 mg, 0.1 mmol, 1 equiv) in the presence of TEMPO (78 mg, 0.50 mmol, 5.0 equiv). After chromatographic purification (5-20% AcOEt in heptane), the starting **1a** was recovered in 97% yield (40 mg, 0.97 mmol).

4.4 Direct excitation

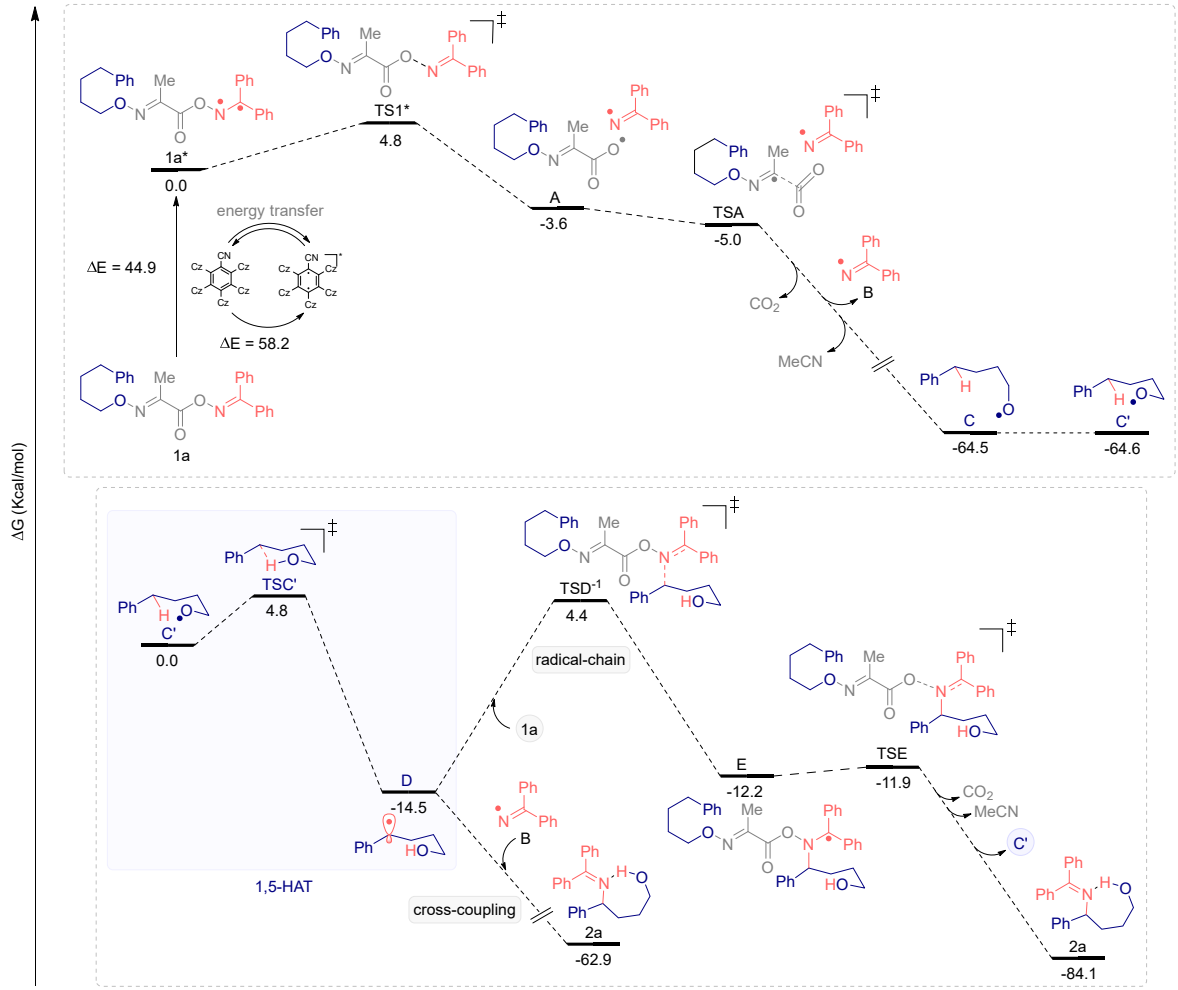


To an 8 mL vial equipped with a magnetic stir bar was added the bifunctional reagent **1a** (0.20 mmol, 1.0 equiv). The vial was sealed with a cap containing a Sil/PTFE septum, evacuated, and back-filled with nitrogen. After this process was repeated 3 times, anhydrous degassed acetone (2.0 mL, c = 0.1 M) was added via syringe. The reaction mixture was irradiated with a Kessil PR160-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) for 2 h as described in the "Workflow" section. The lamp was placed 4 cm away from the reaction vials, and cooled at room temperature by an external fan. Upon completion, the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography (10-15% AcOEt in heptane) to afford compound **2** as a yellow oil (20 mg, 0.06 mmol, 30%).

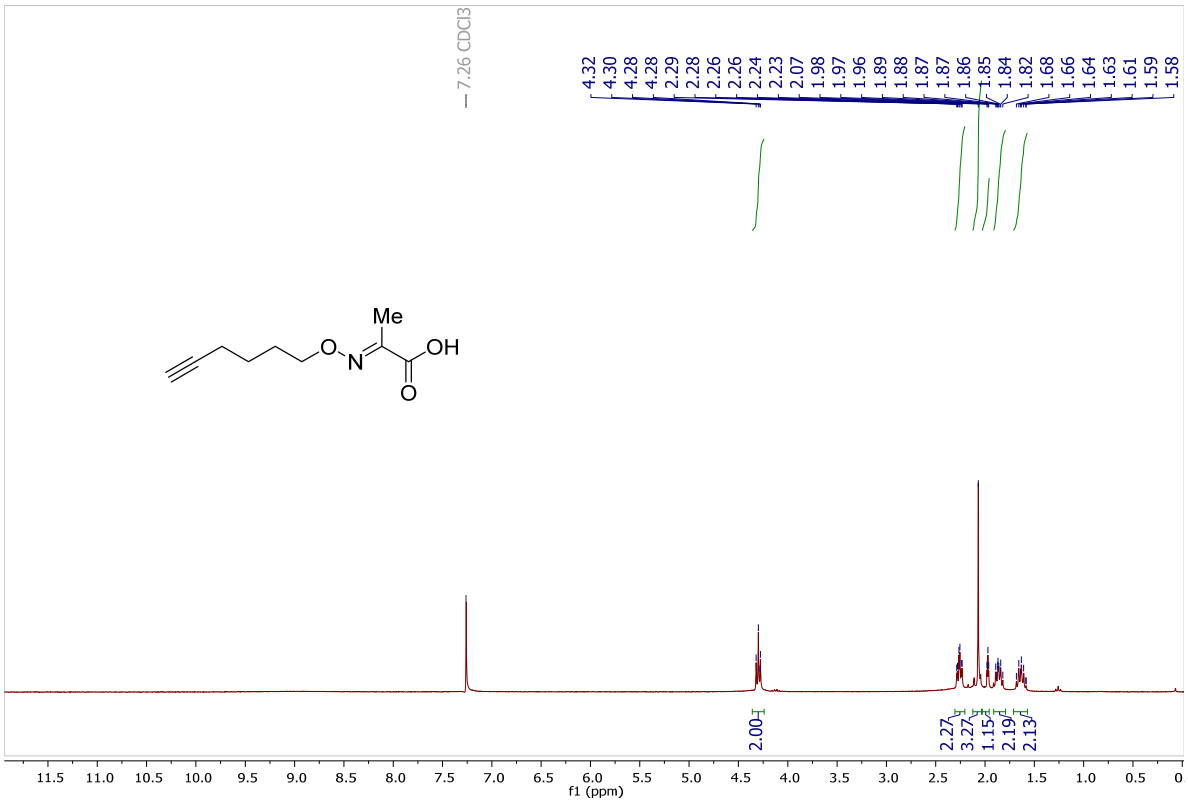
^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.70 – 7.61 (m, 2H), 7.43 – 7.27 (m, 8H), 7.26 – 7.15 (m, 3H), 7.06 – 6.99 (m, 2H), 4.43 (dd, *J* = 7.4, 4.8 Hz, 1H), 3.63 – 3.52 (m, 2H), 2.41 (bs, 1H), 2.08 – 1.97 (m, 1H), 1.92 – 1.81 (m, 1H), 1.61 – 1.43 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$), δ (ppm) = 167.9, 144.8, 139.8, 137.1, 130.2, 128.8 (2C), 128.5 (3C), 128.4 (2C), 128.3 (2C), 127.8 (2C), 127.2 (2C), 126.8, 66.0, 63.1, 36.2, 29.4. **HRMS (ESI)** calcd for $C_{23}H_{24}NO$ $[M+H]^+$: 330.1852, found 330.1854.

5 DFT

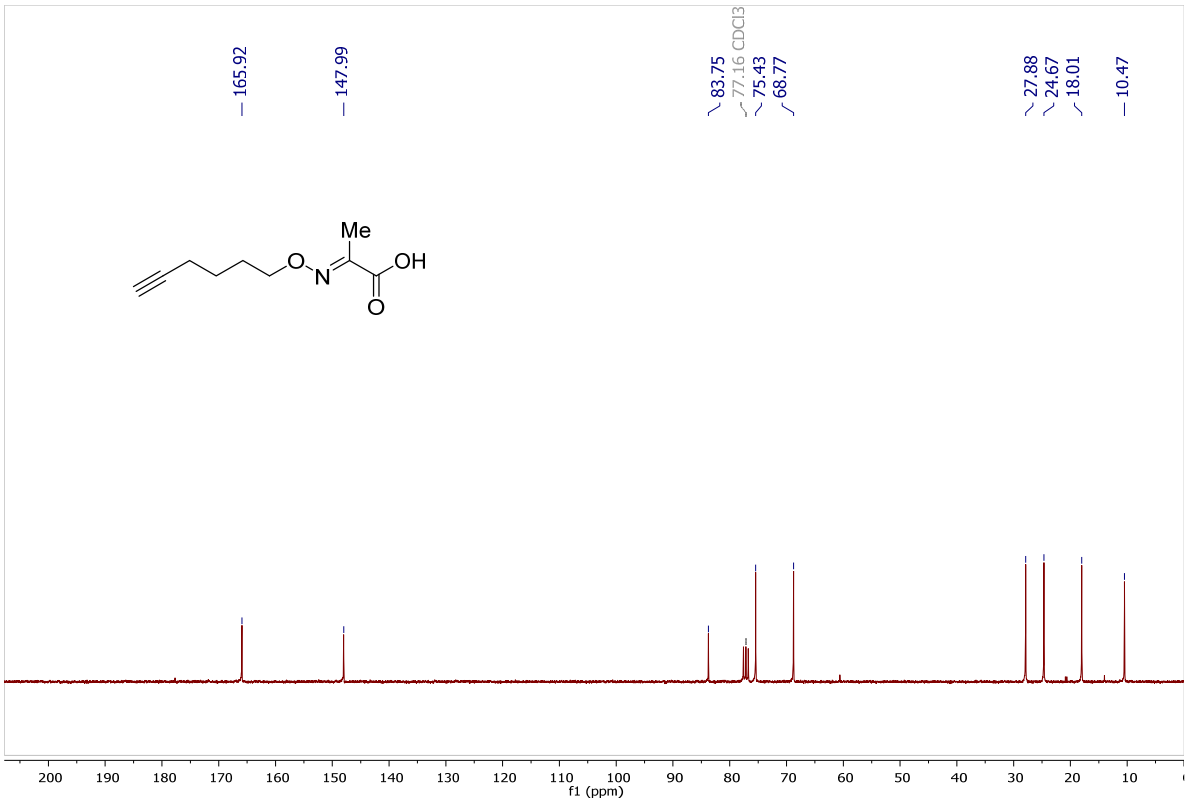
Proposed mechanism supported by computational studies to transformed **1a** in **2a**. Calculated free Gibbs energy (G) values at 298 K (Kcalmol^{-1}) [CPCM(acetone) UB3LYP-D3/def2-svp].



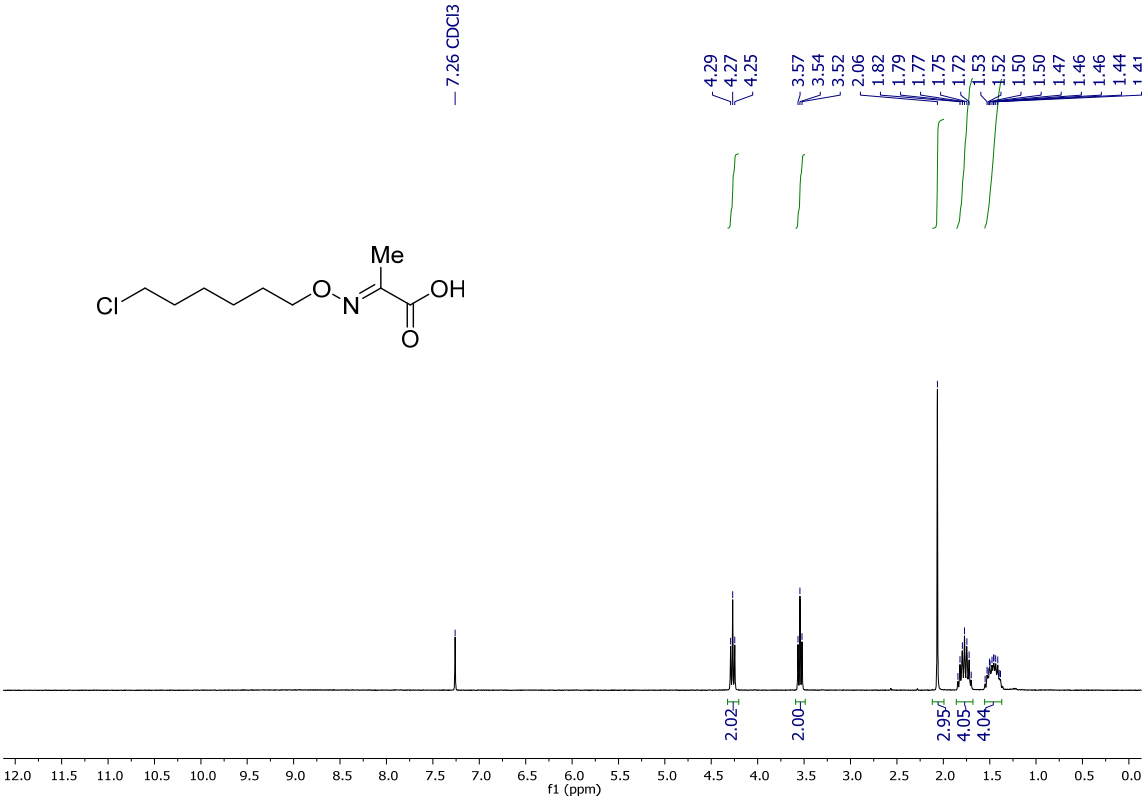
6 NMR spectra



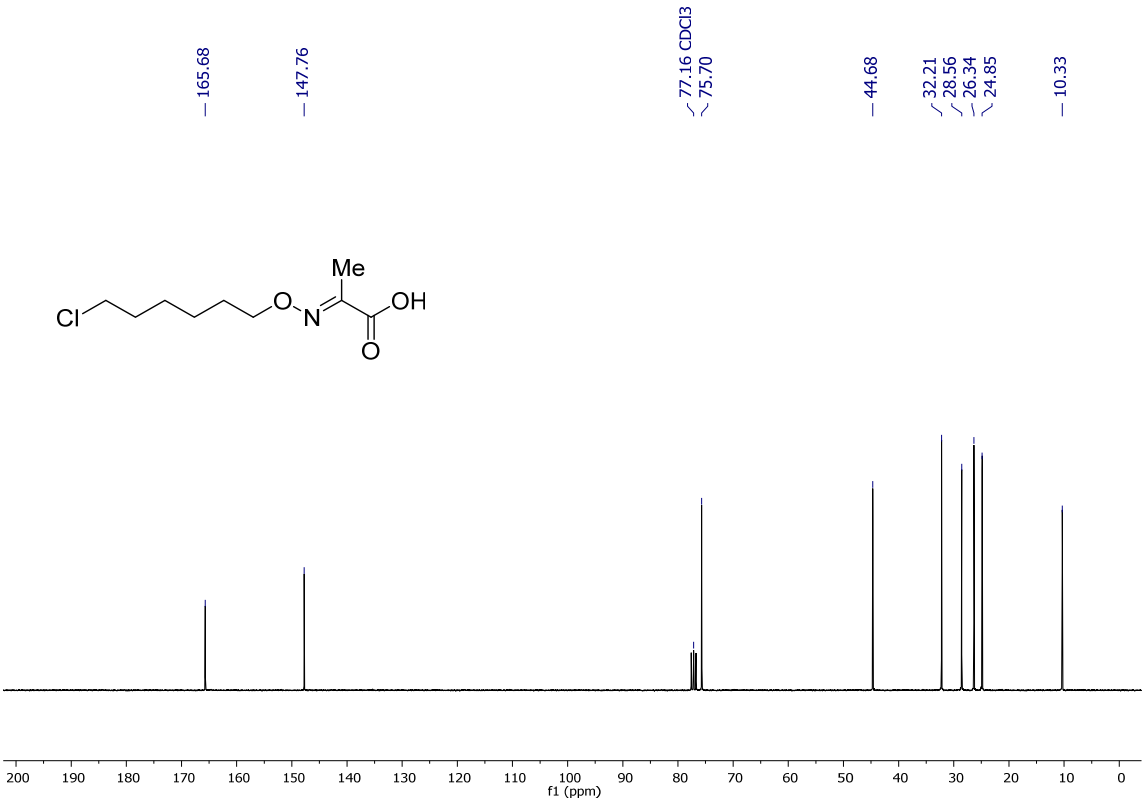
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2f**.



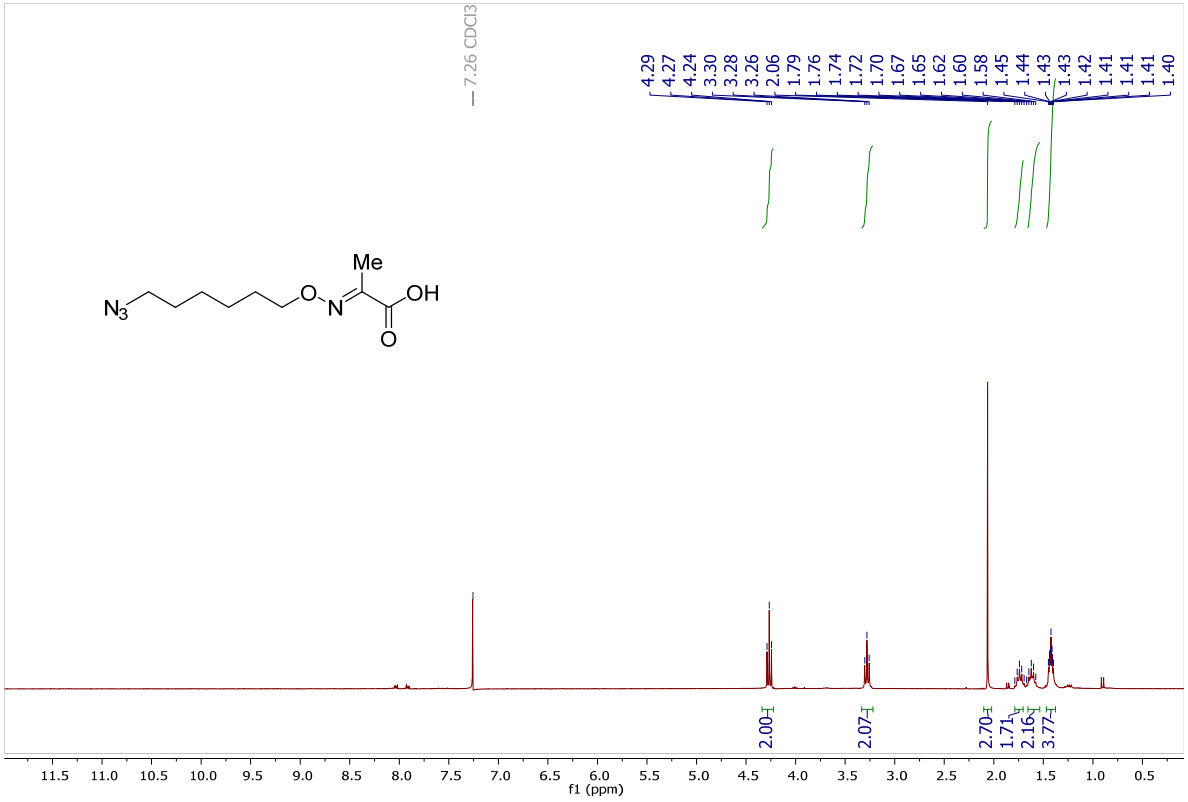
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2f.**



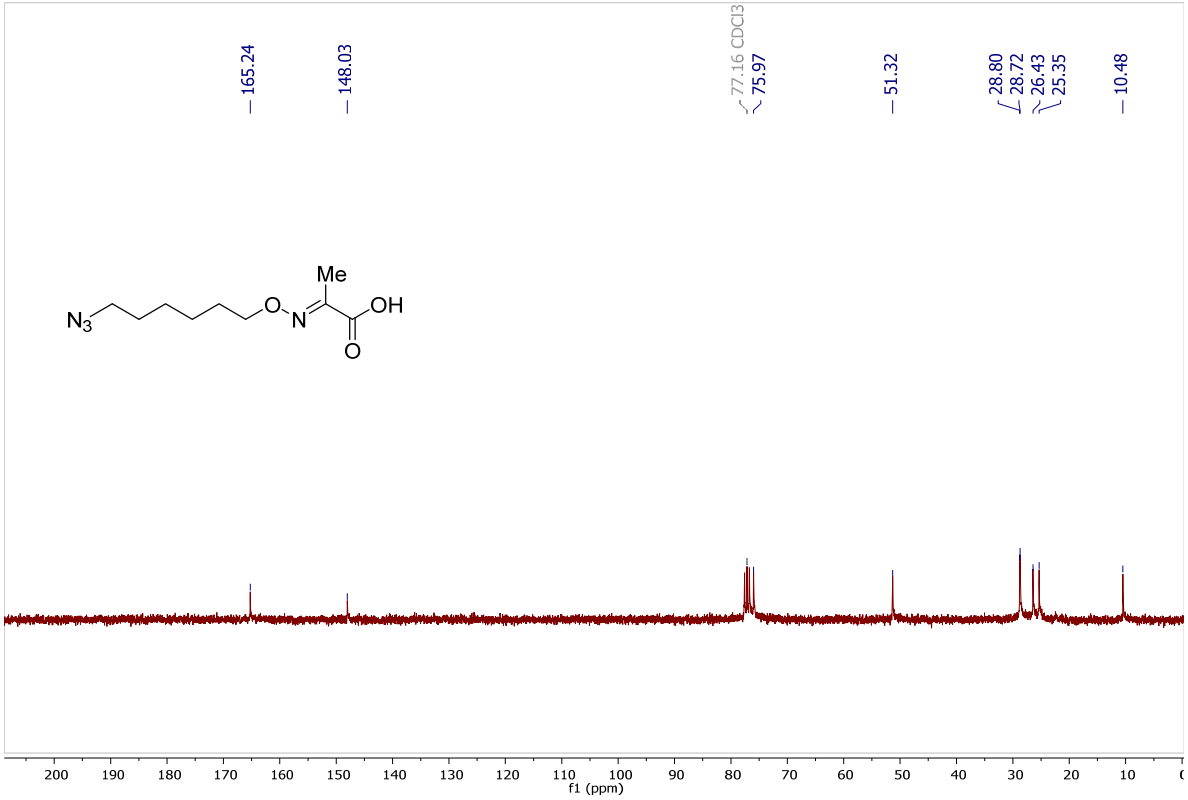
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2i**.



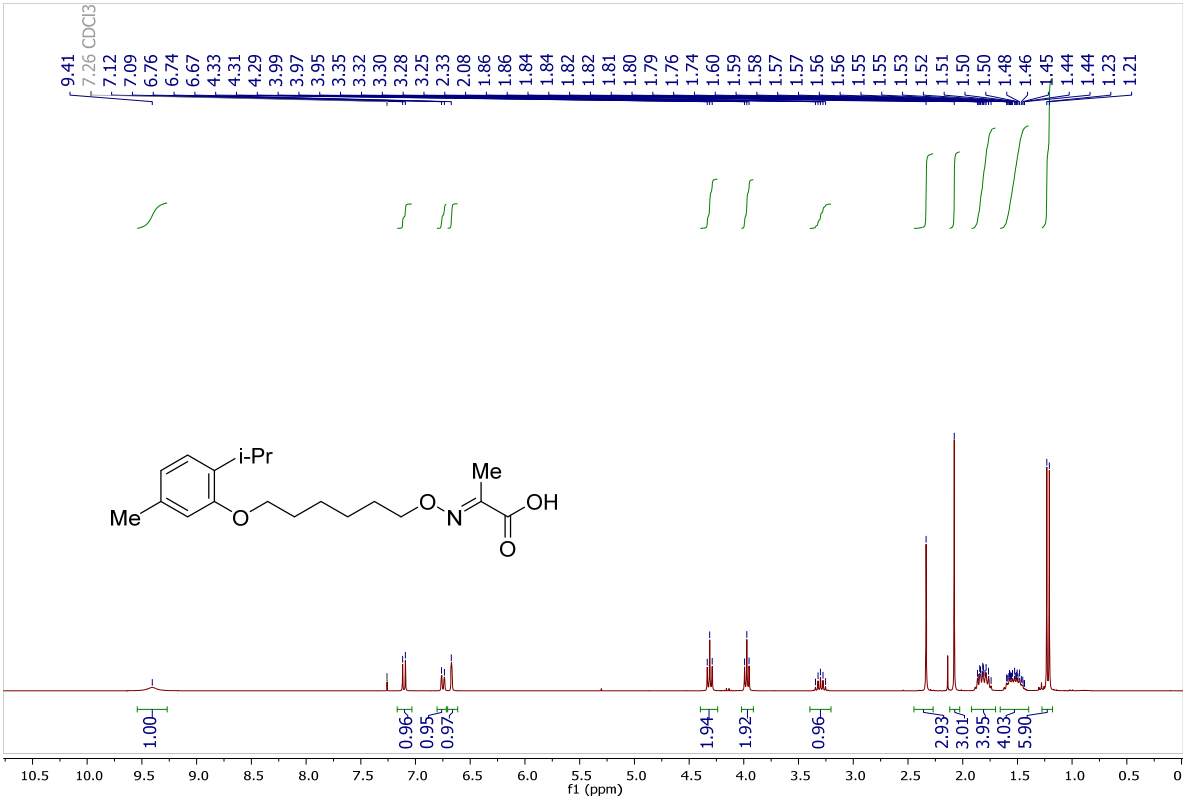
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2i.**



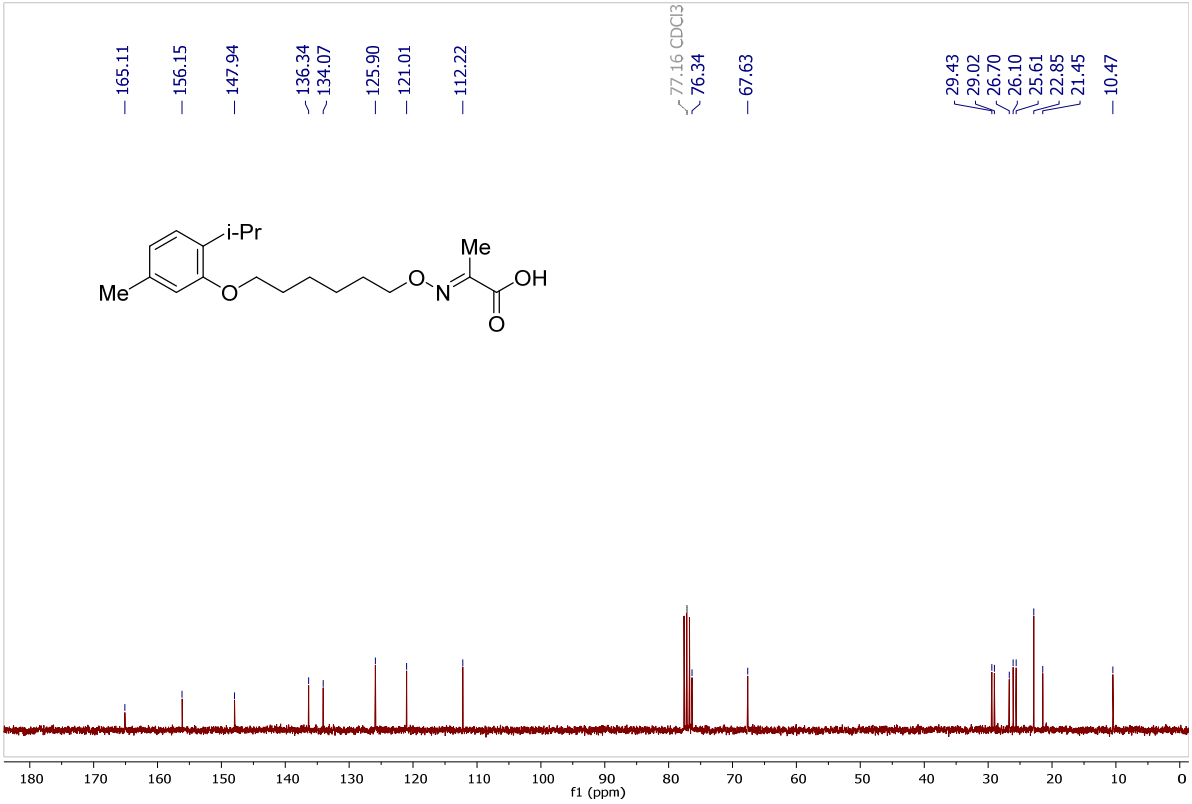
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2j**.



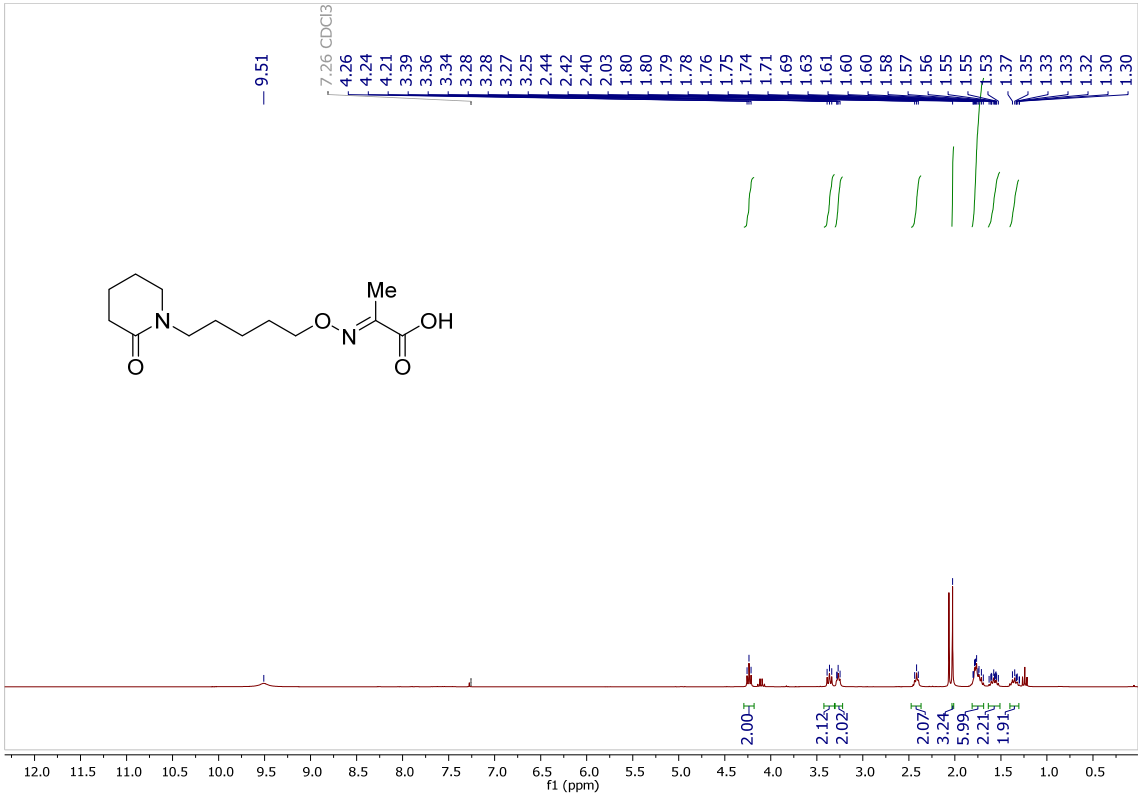
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2j.**



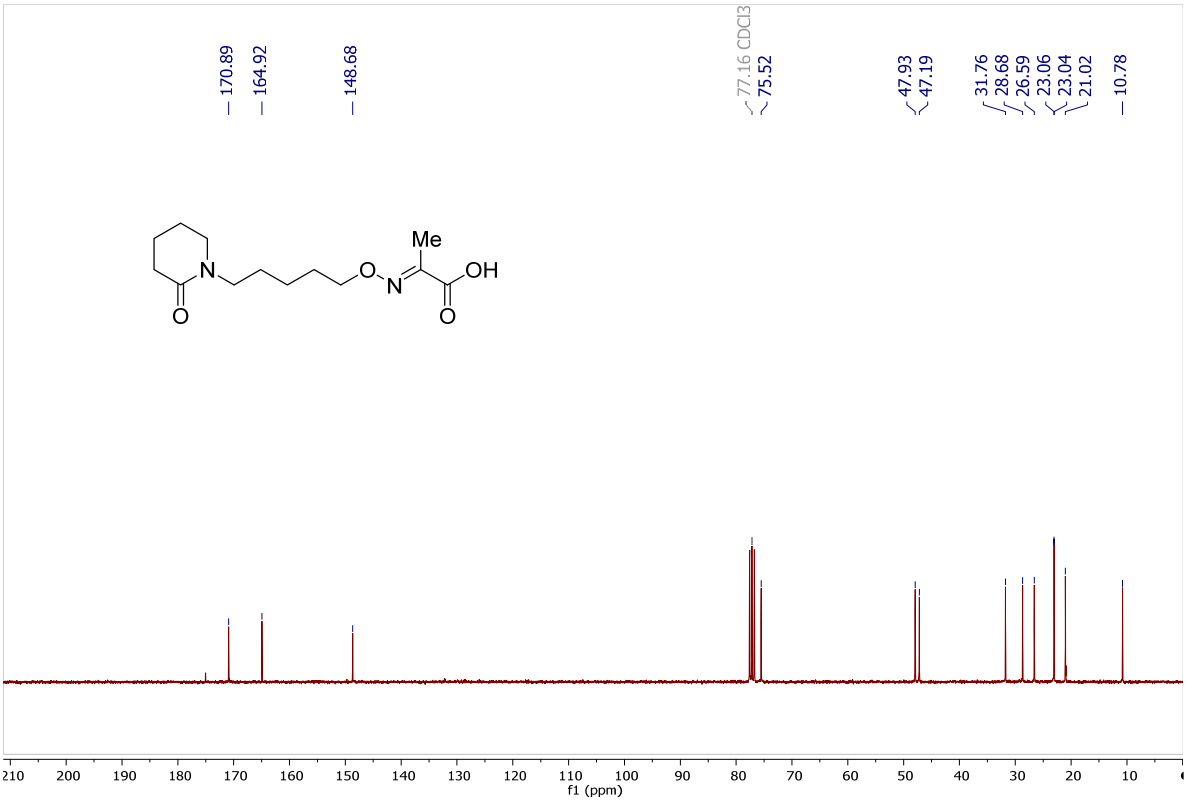
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2k**.



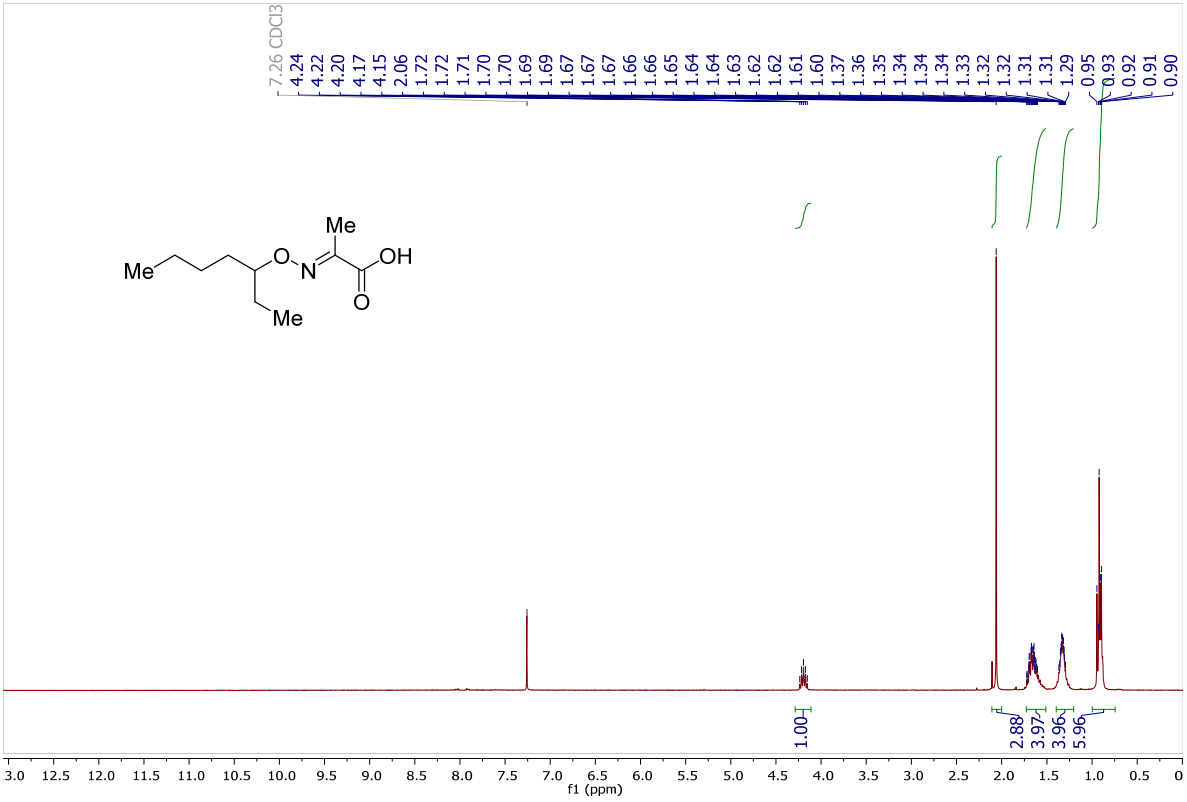
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2k**



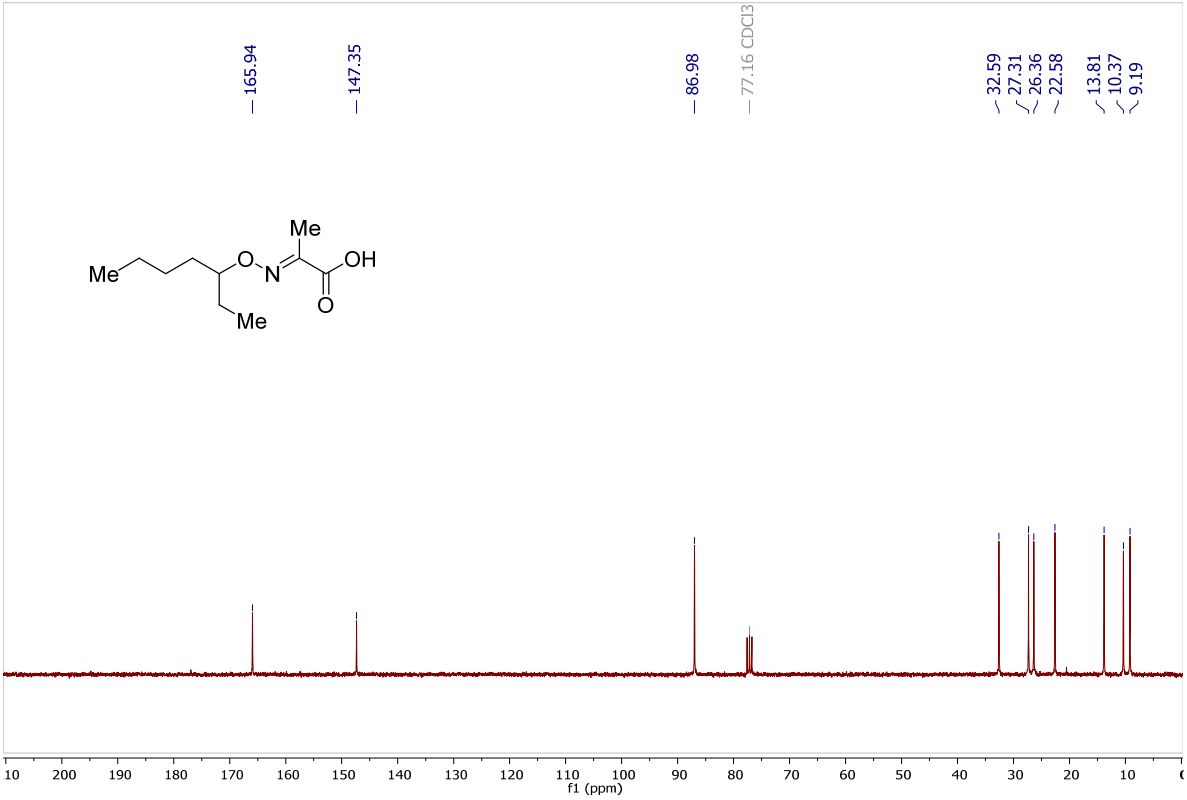
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2n**.



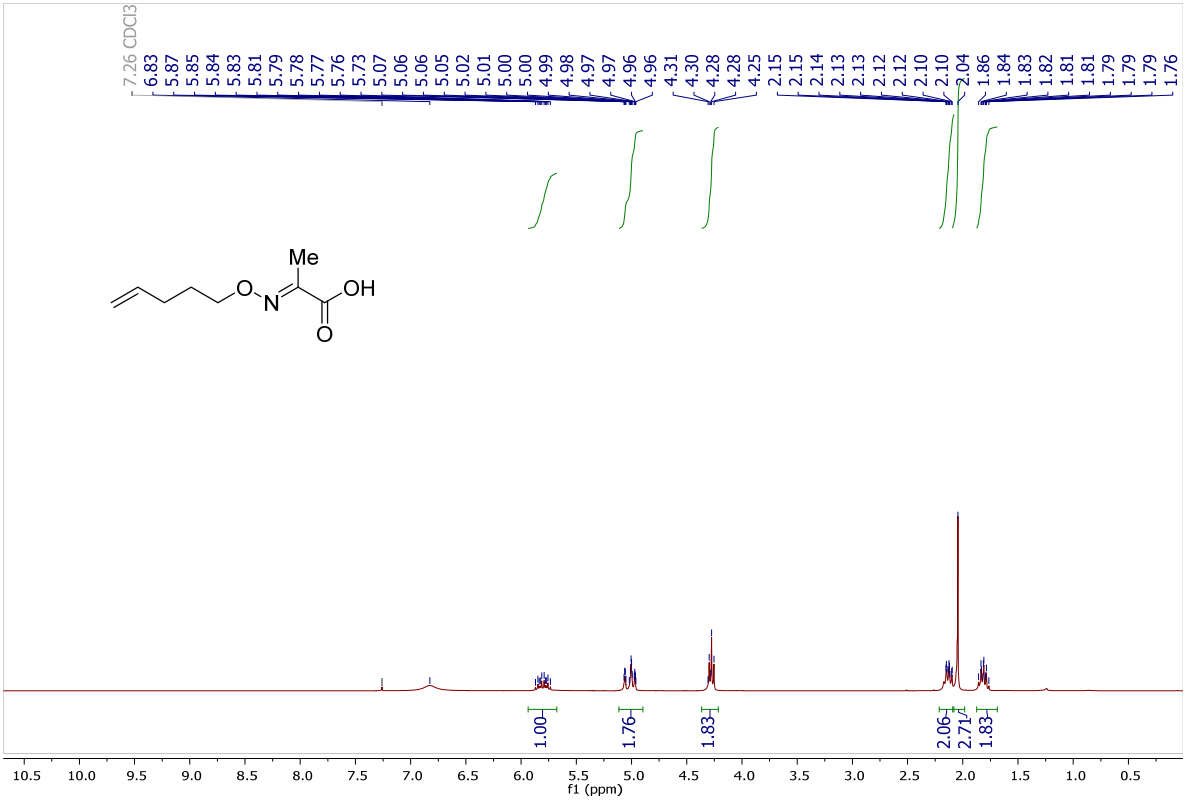
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2n.**



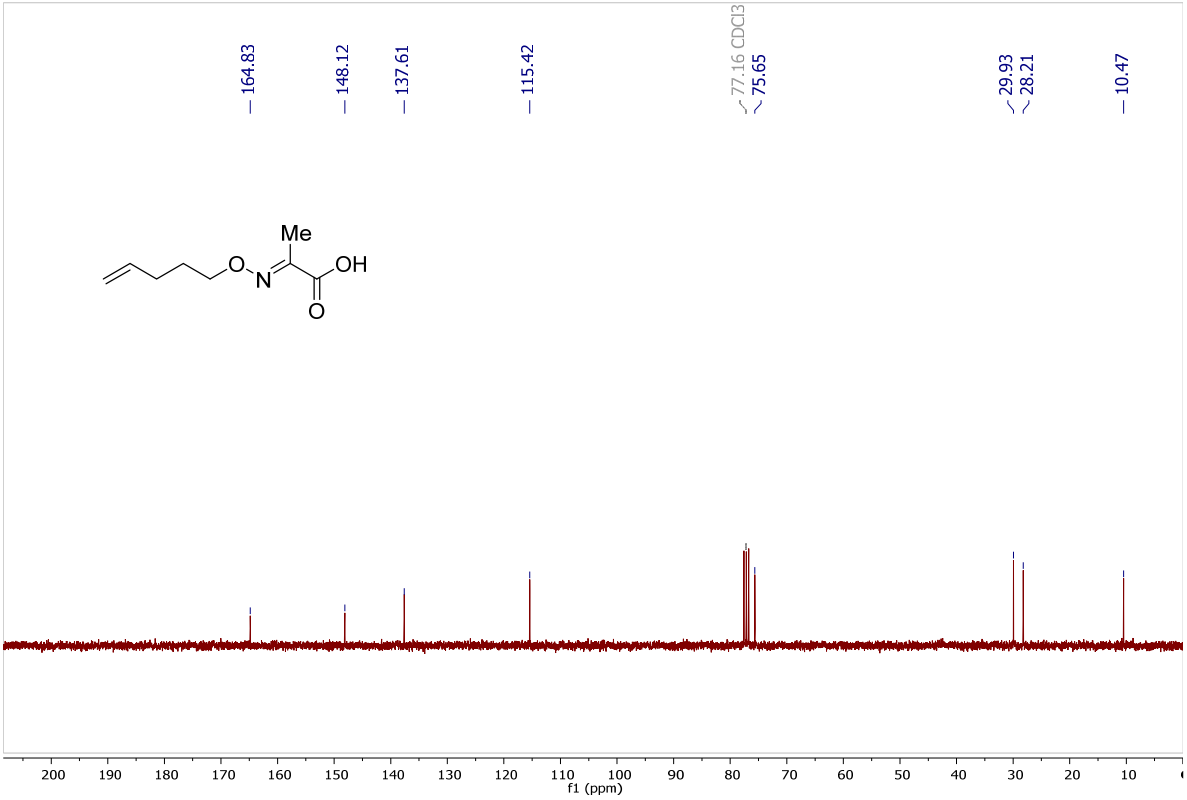
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2p**.



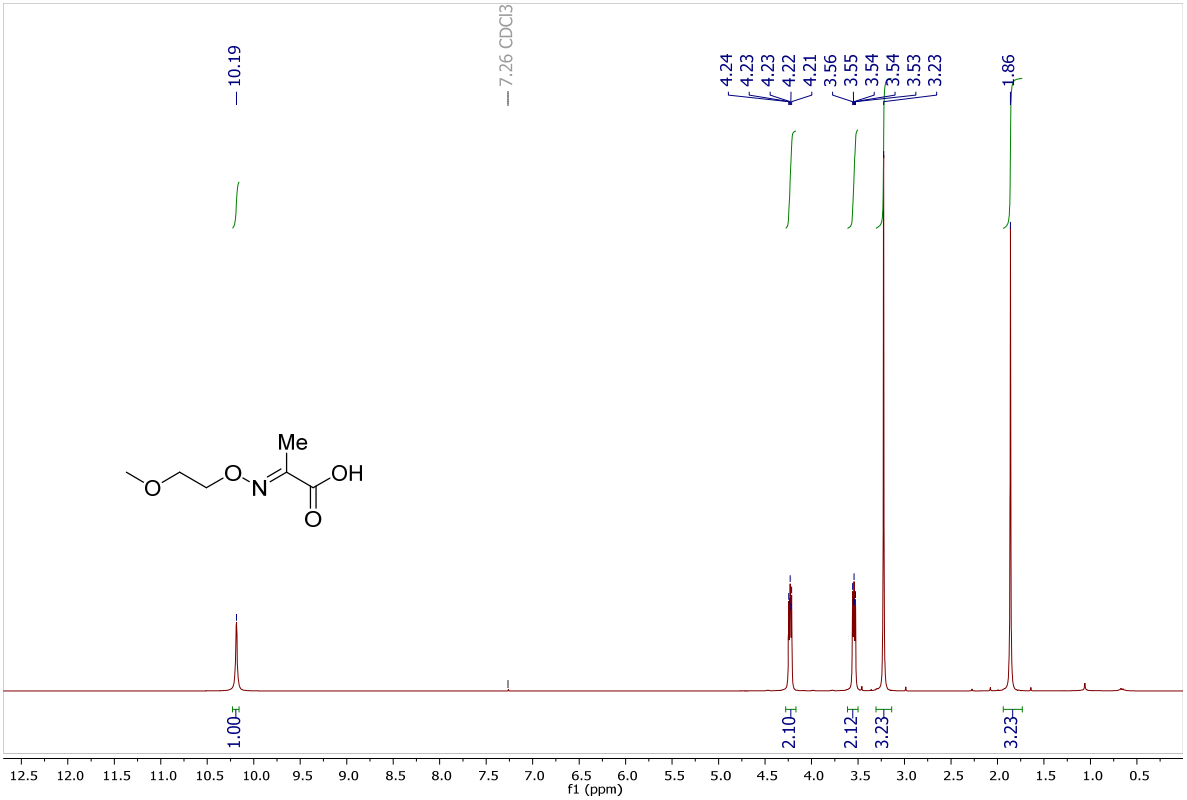
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2p.**



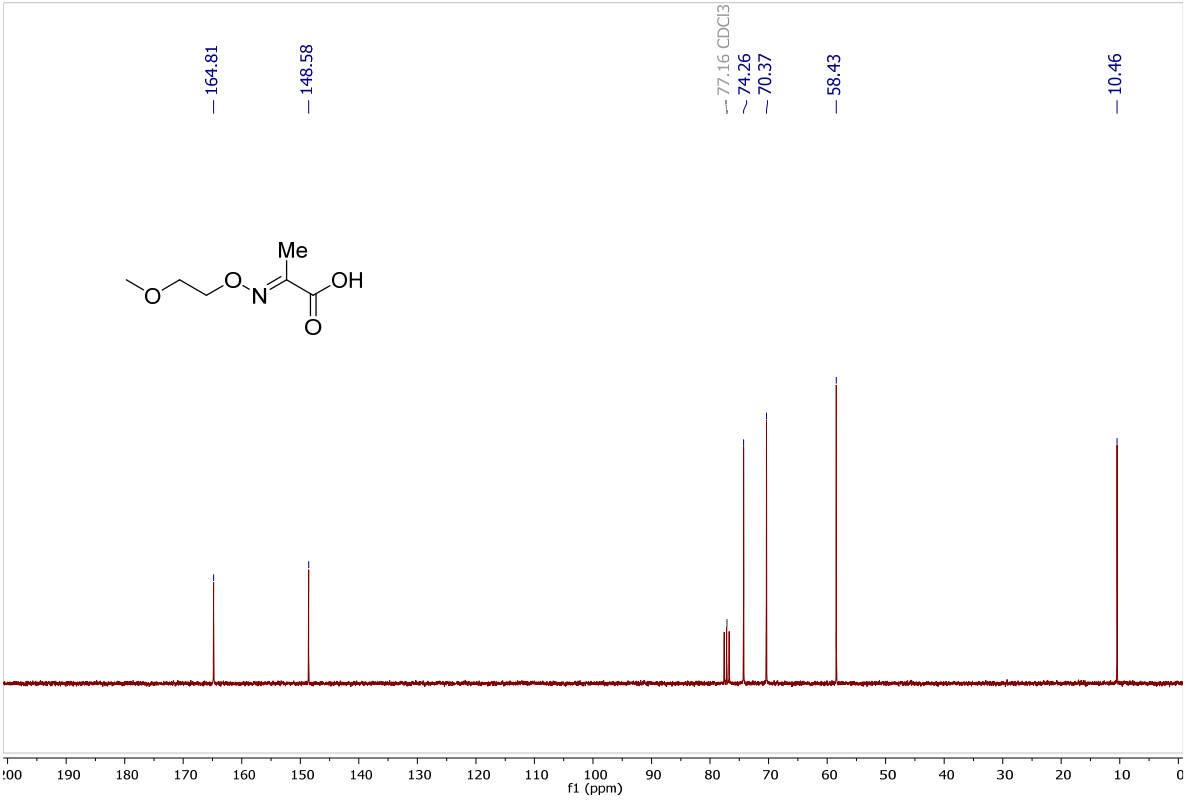
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2r**.



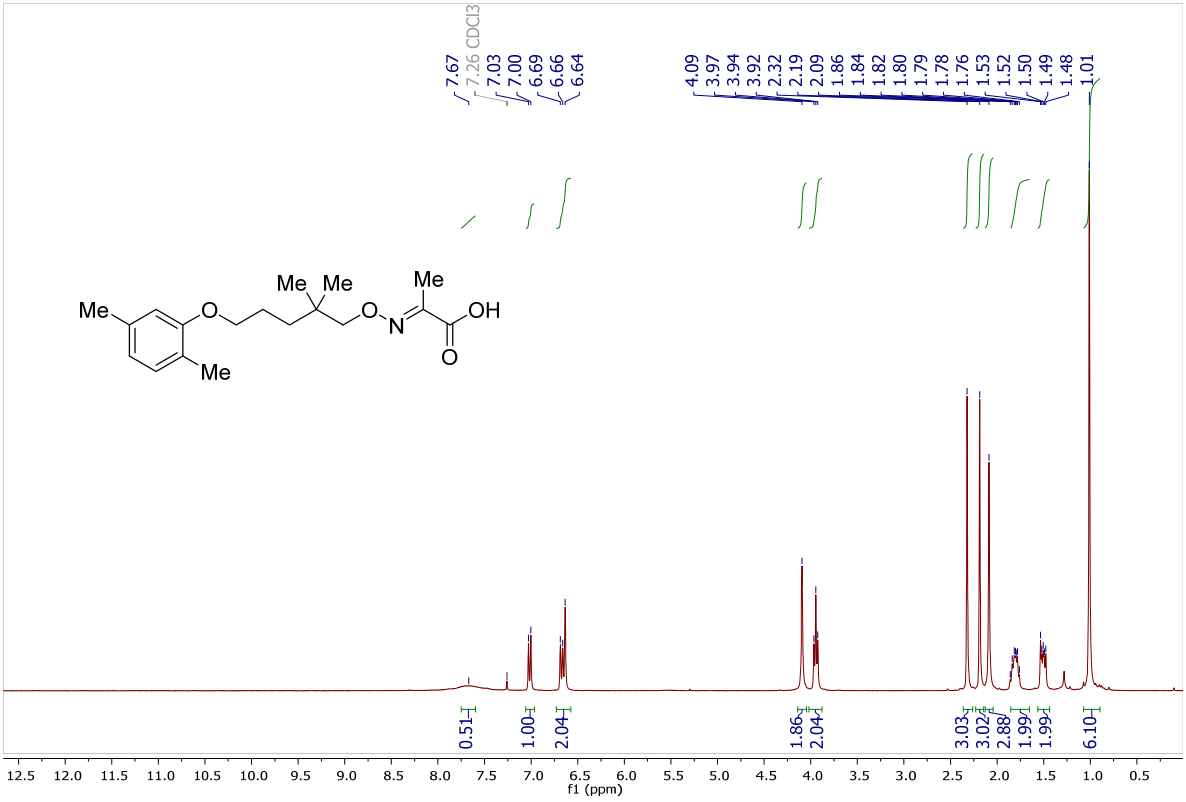
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2r.**



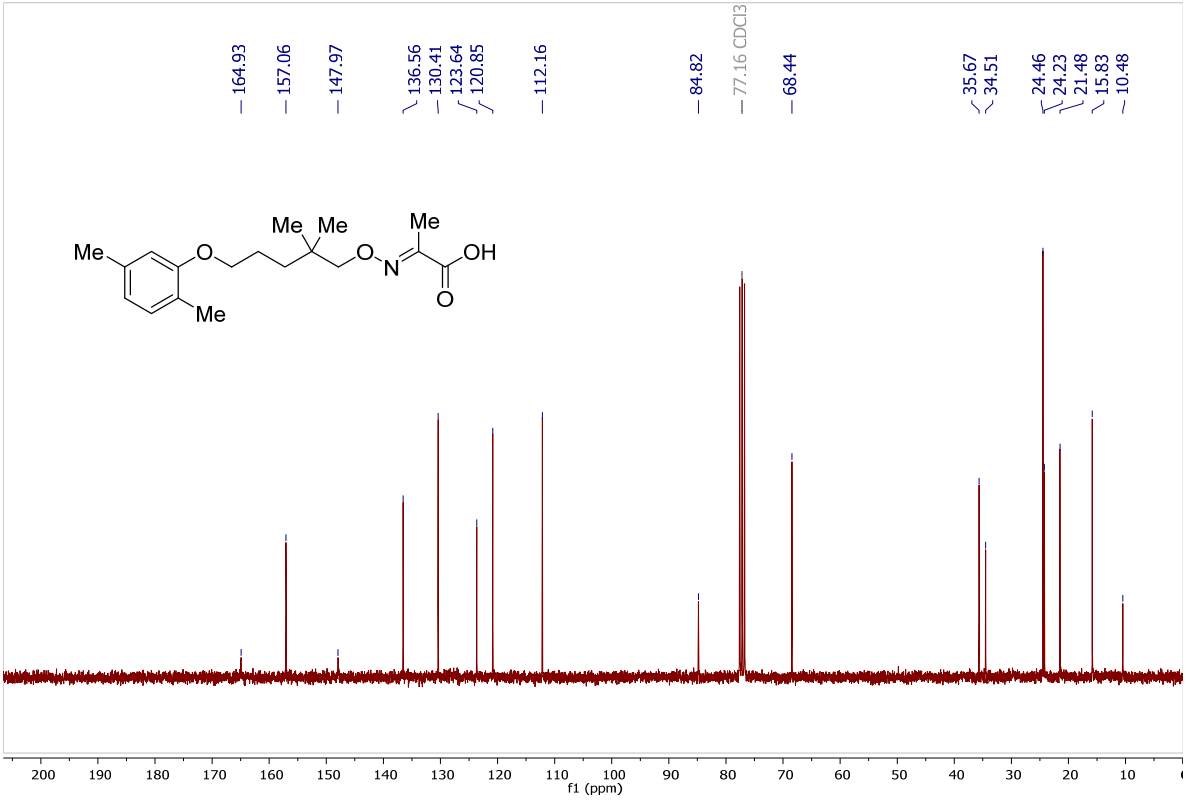
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2y**.



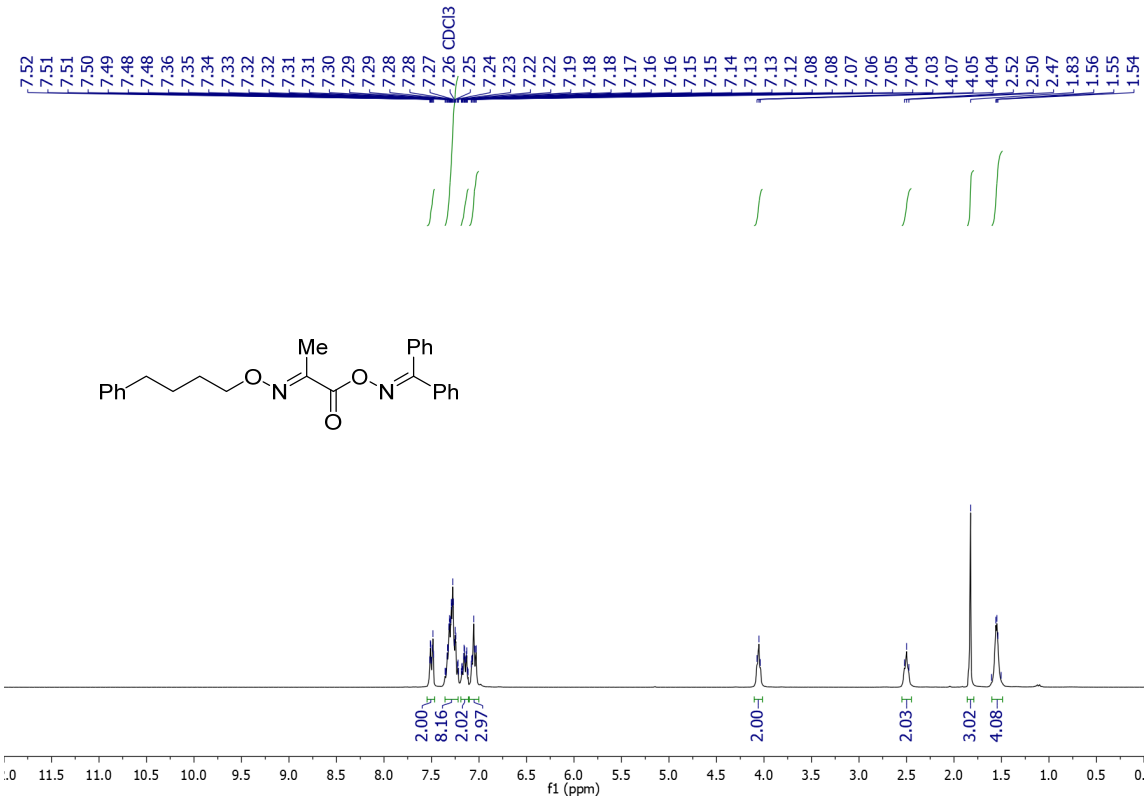
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2y.**



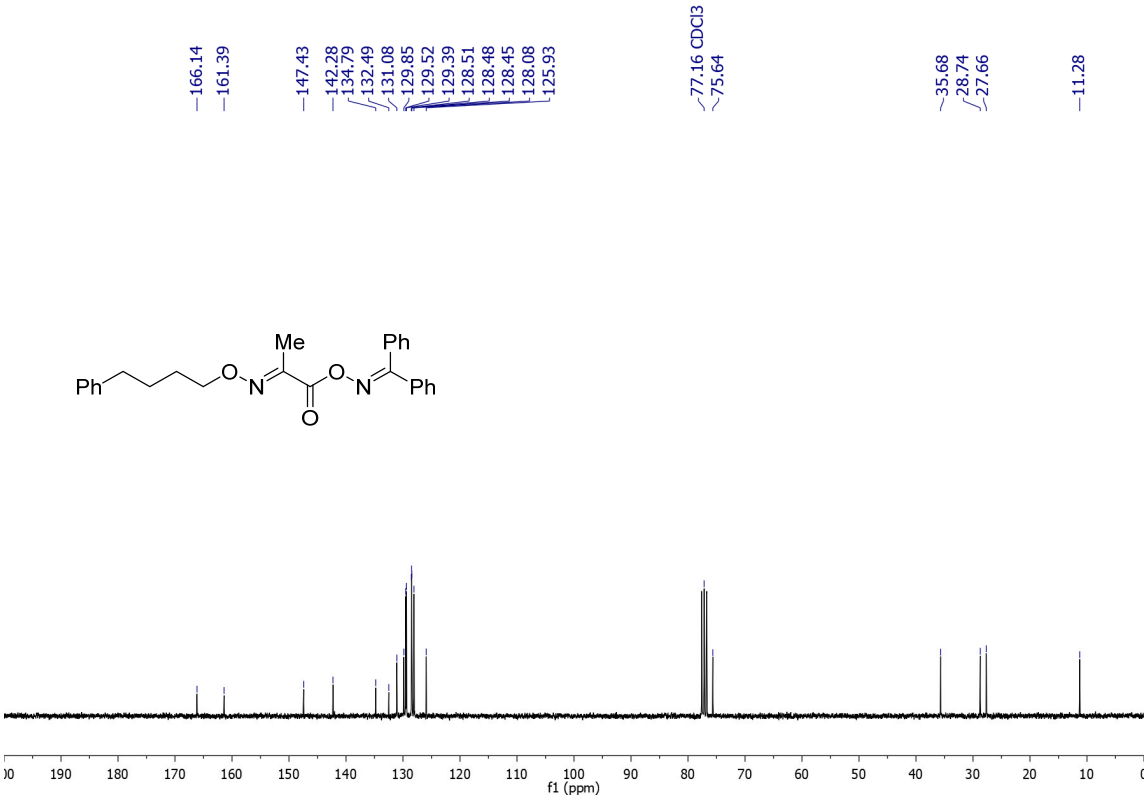
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S2z**.



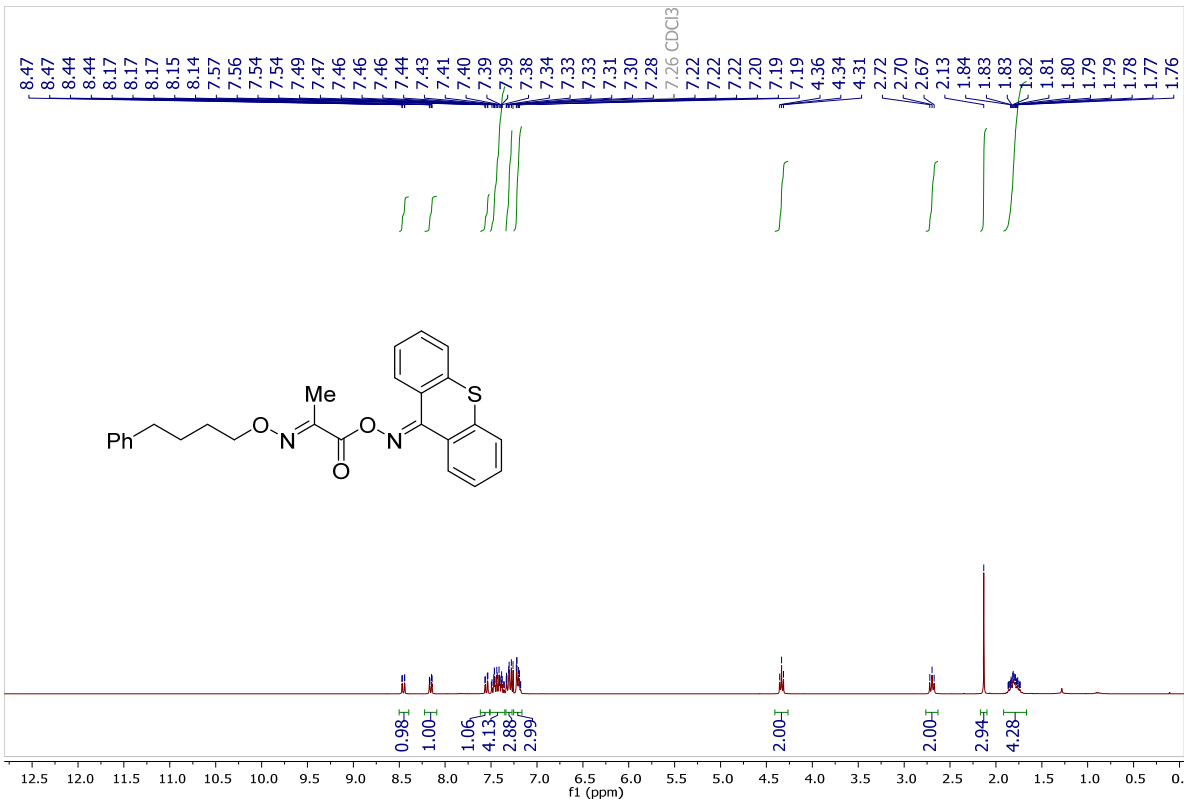
^{13}C NMR (75 MHz, $CDCl_3$) of compound **S2z.**



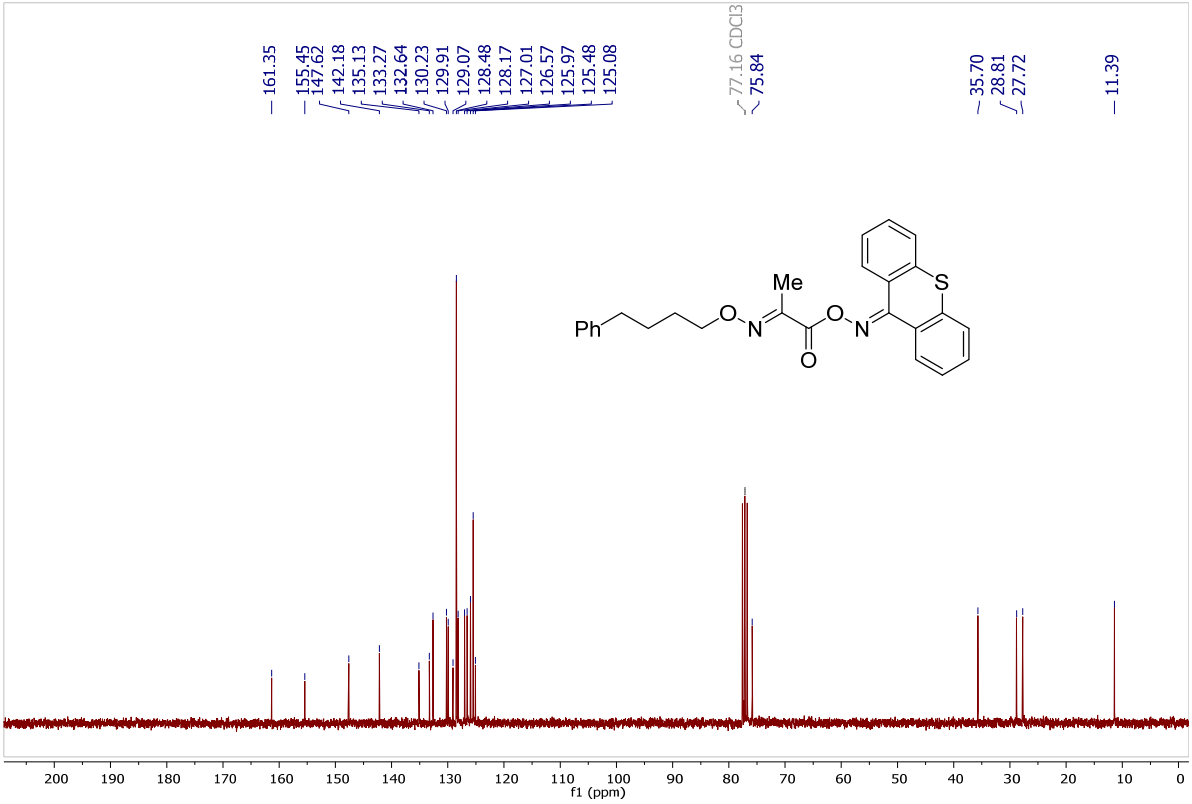
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1a**.



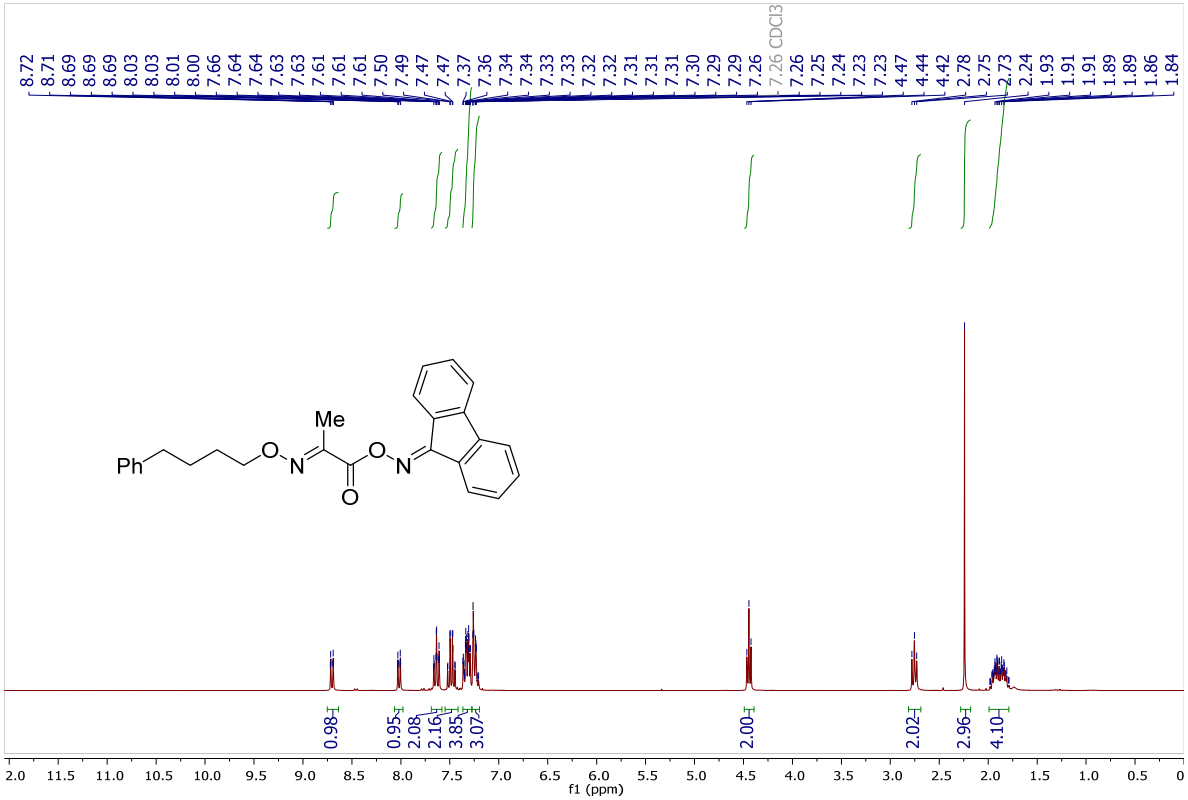
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1a.**



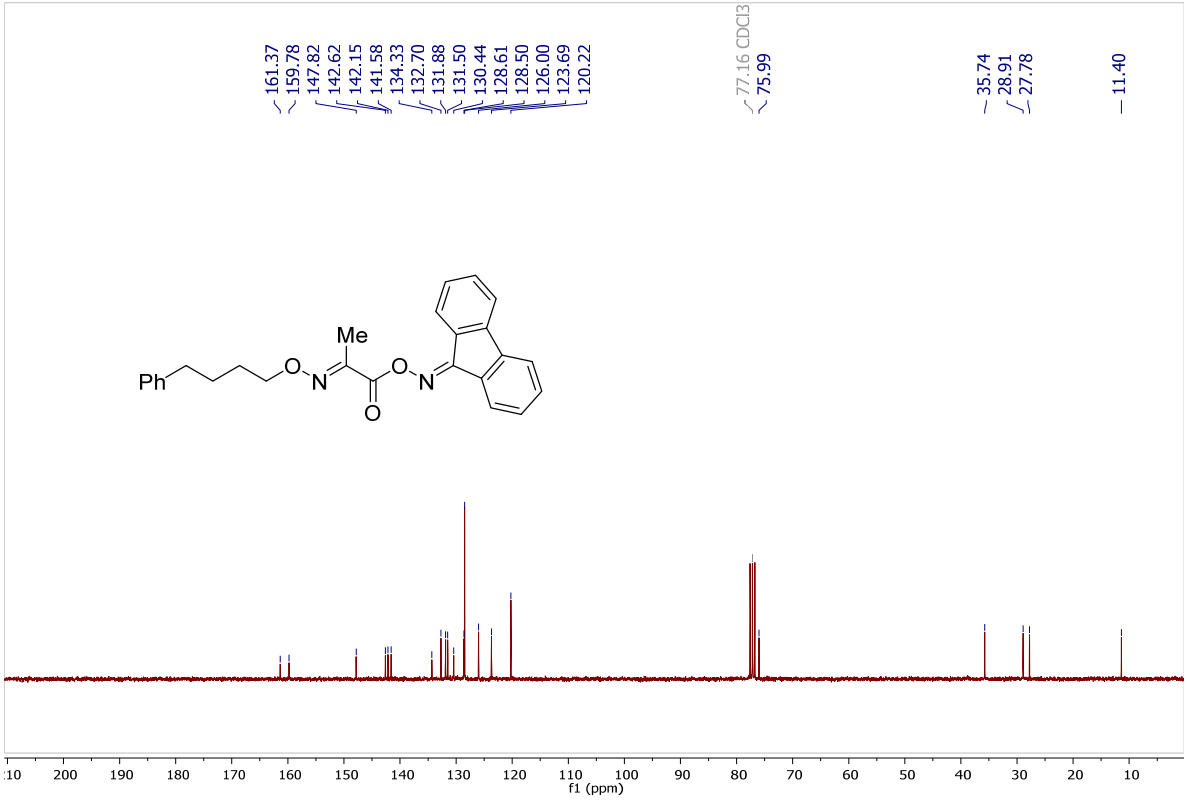
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1b**.



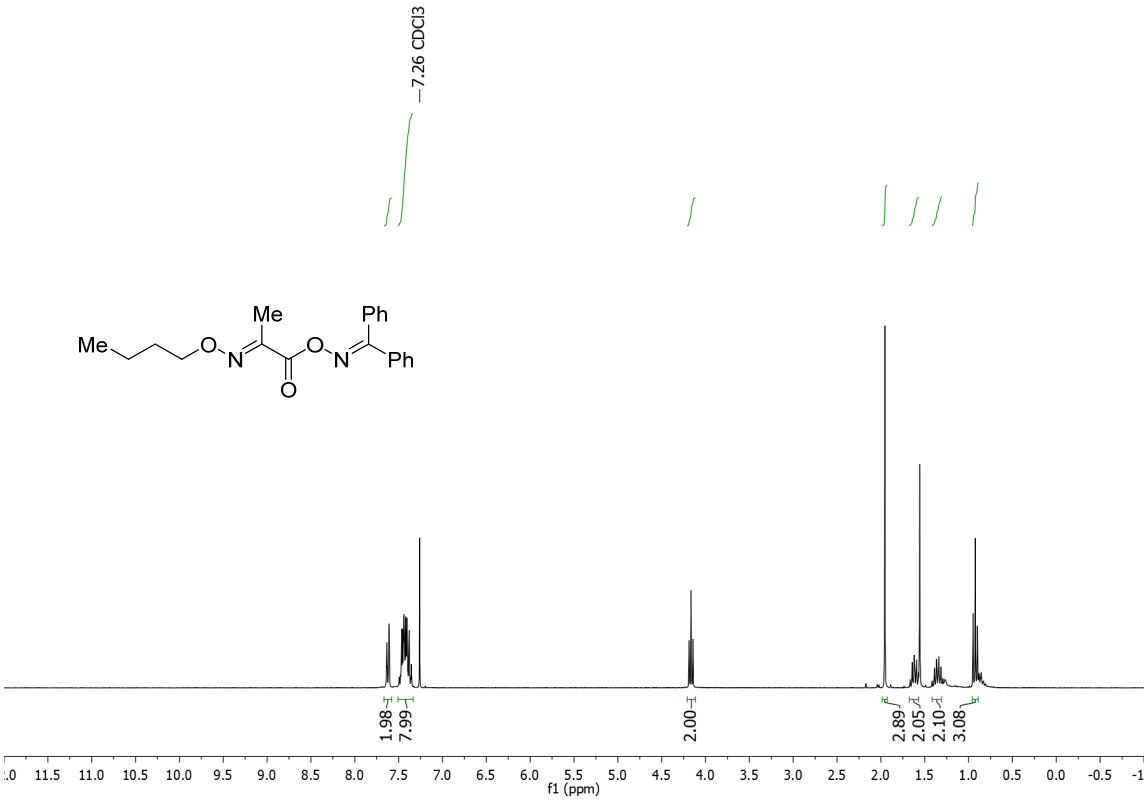
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1b.**



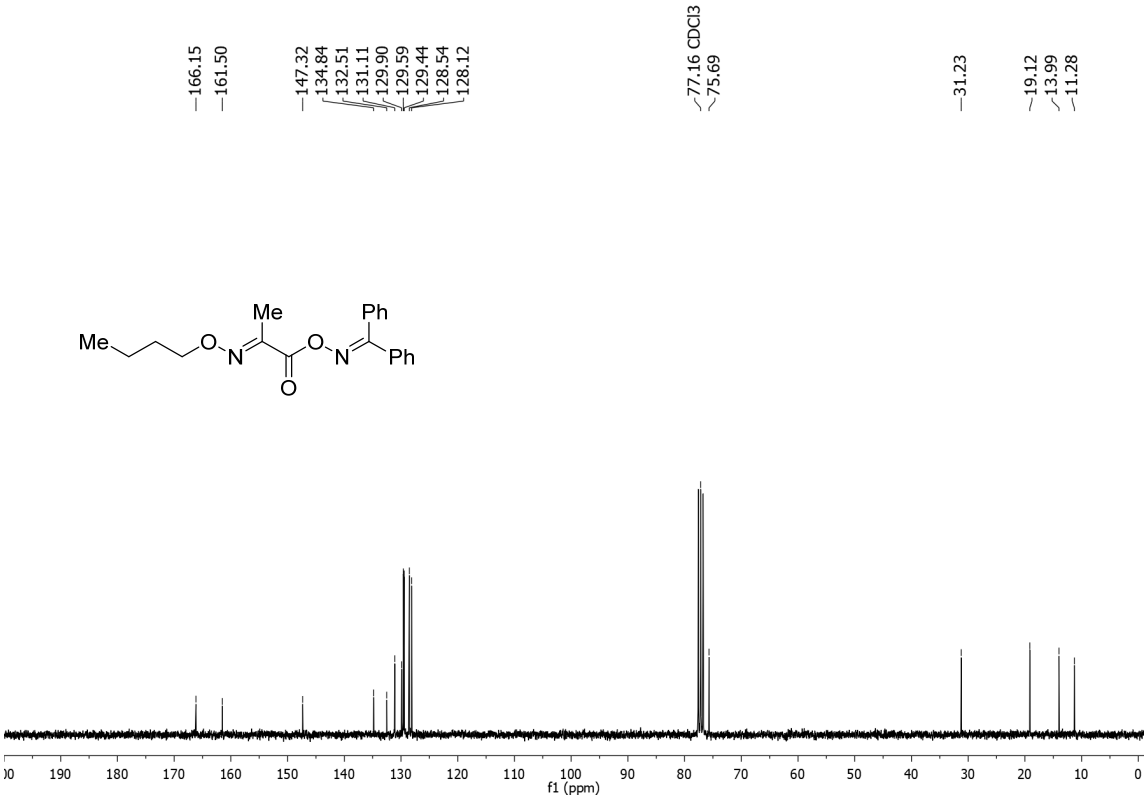
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1c**.



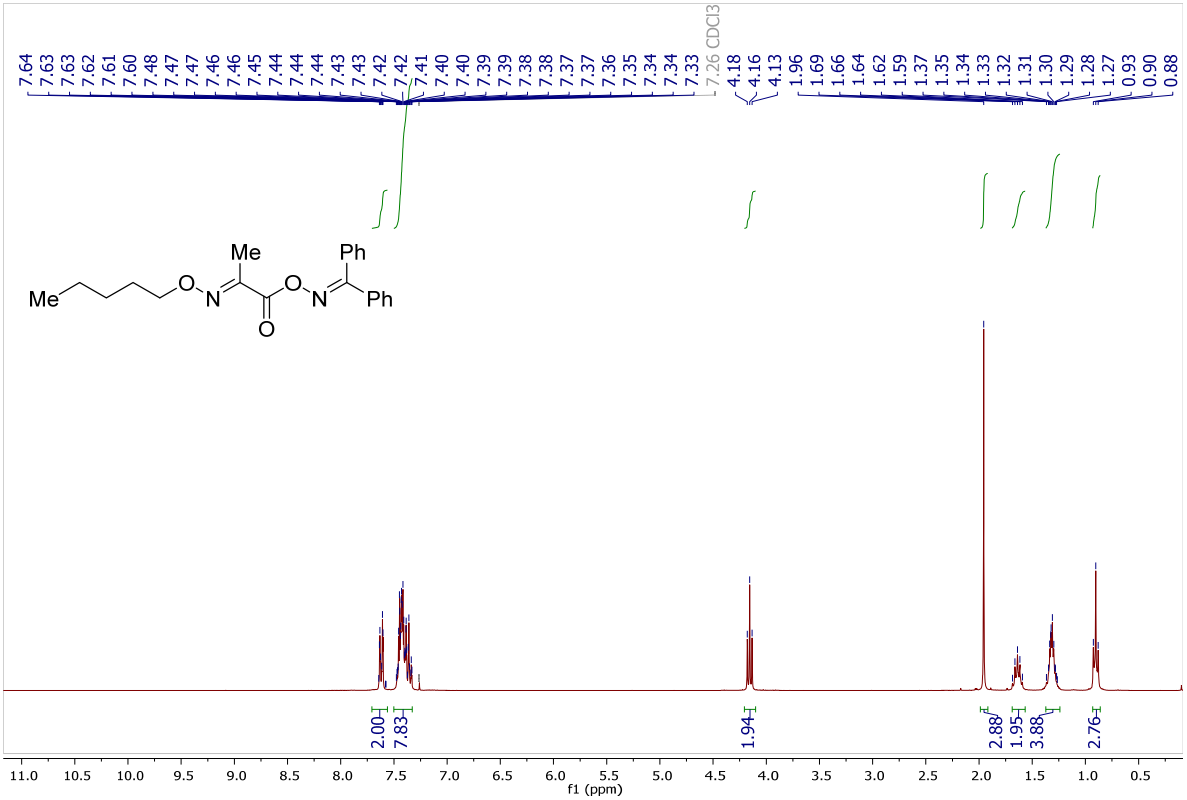
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1c.**



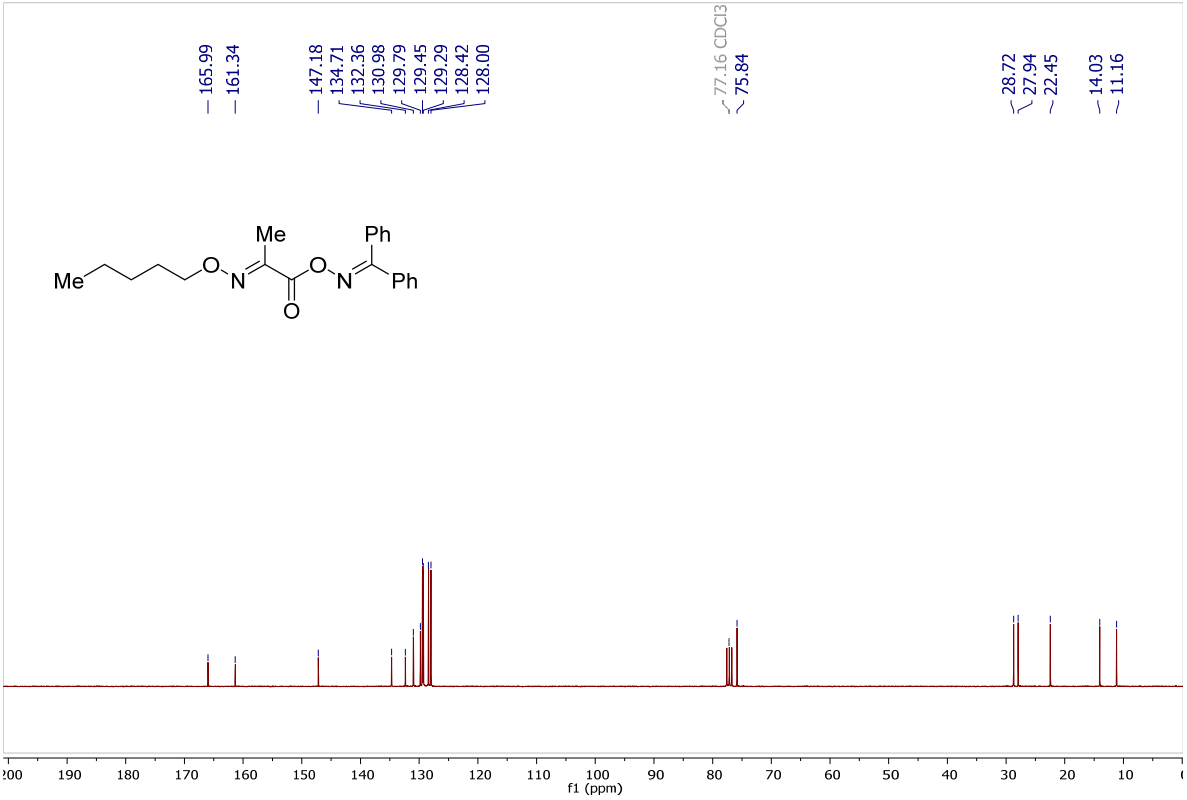
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1d**.



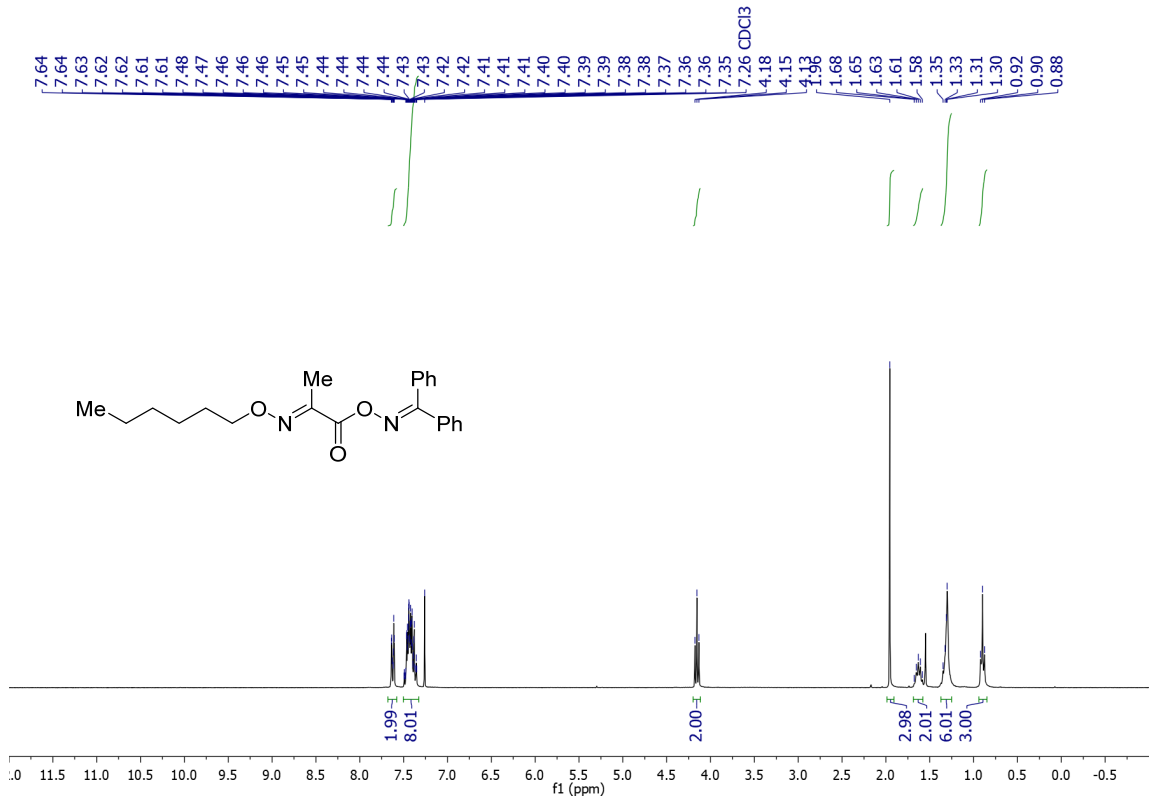
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1d.**



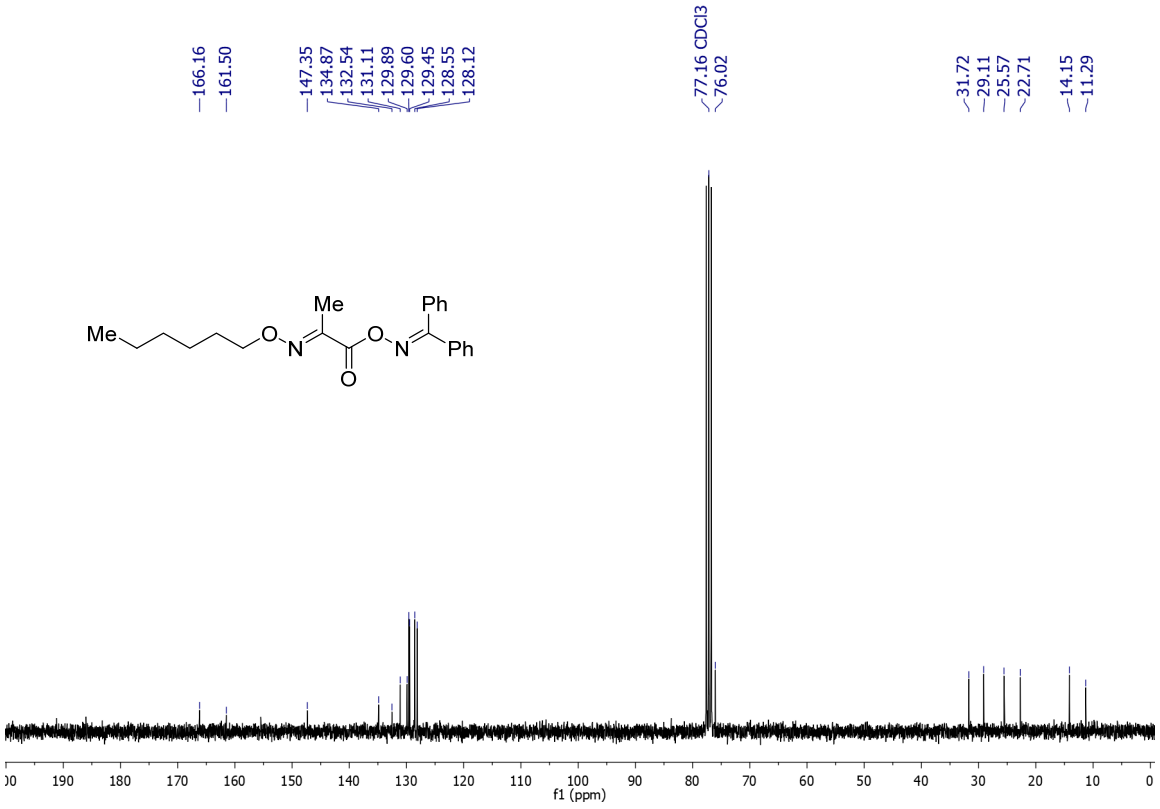
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1e**



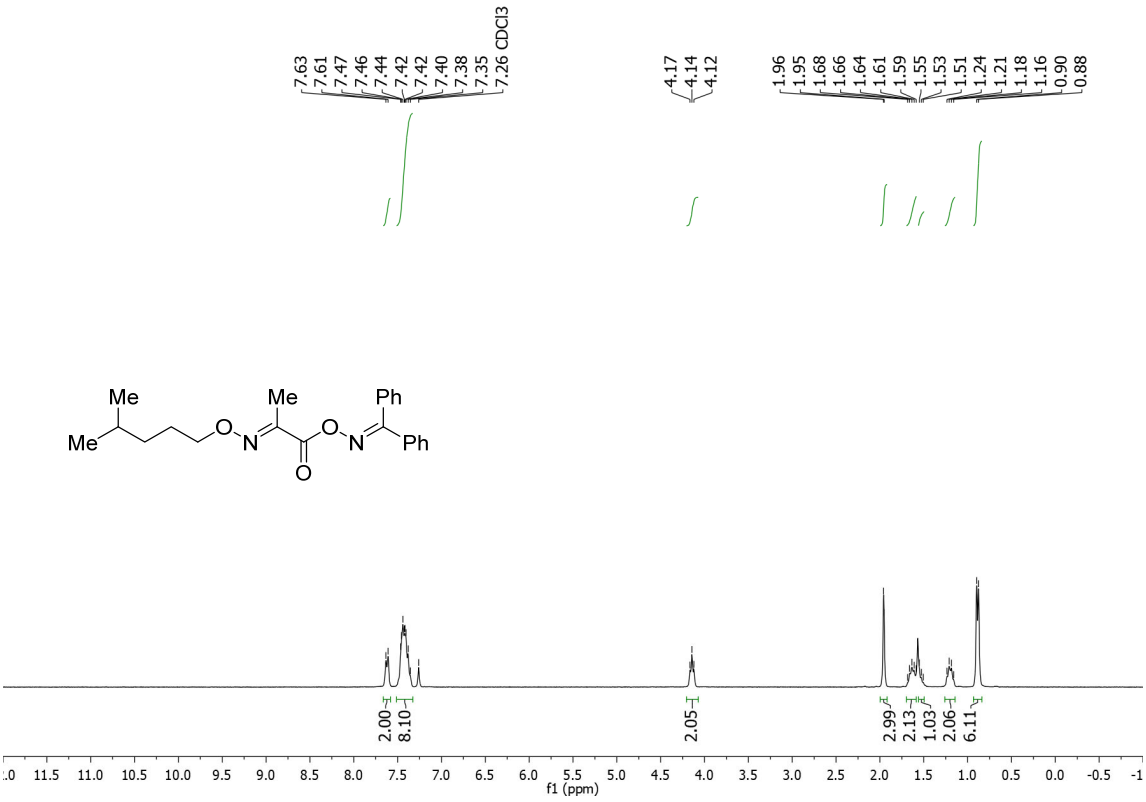
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1e.**



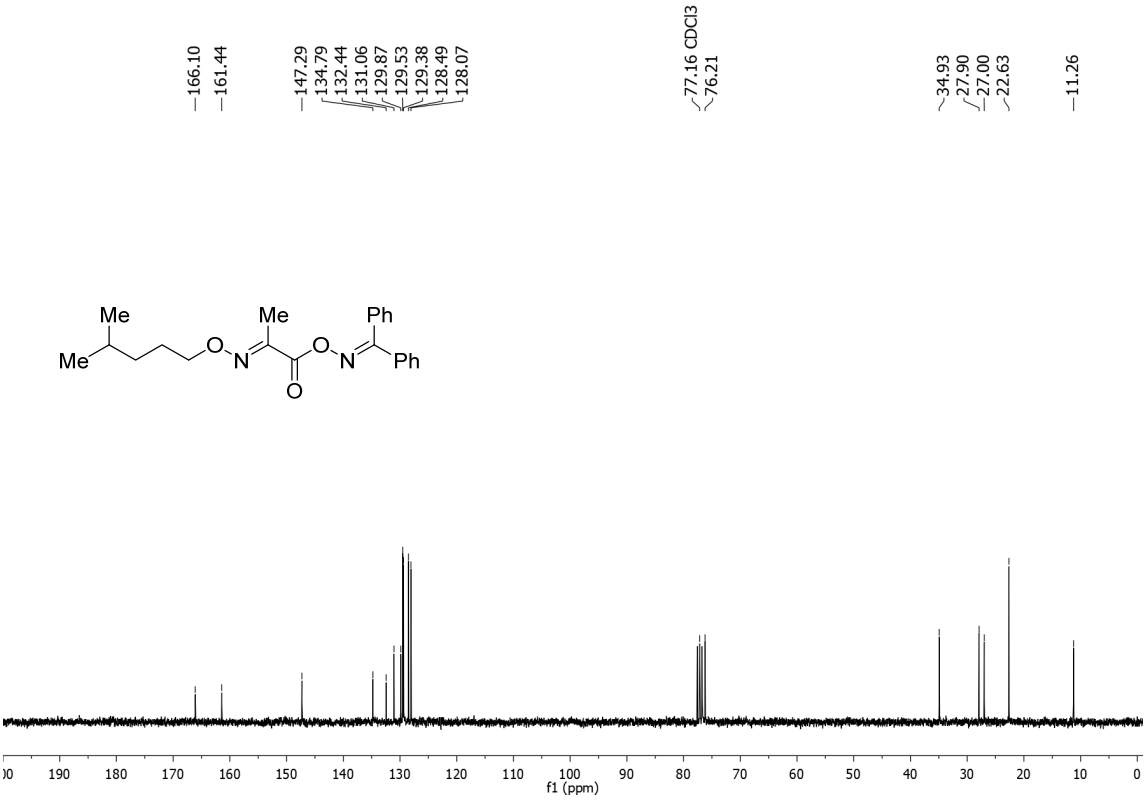
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1f**.



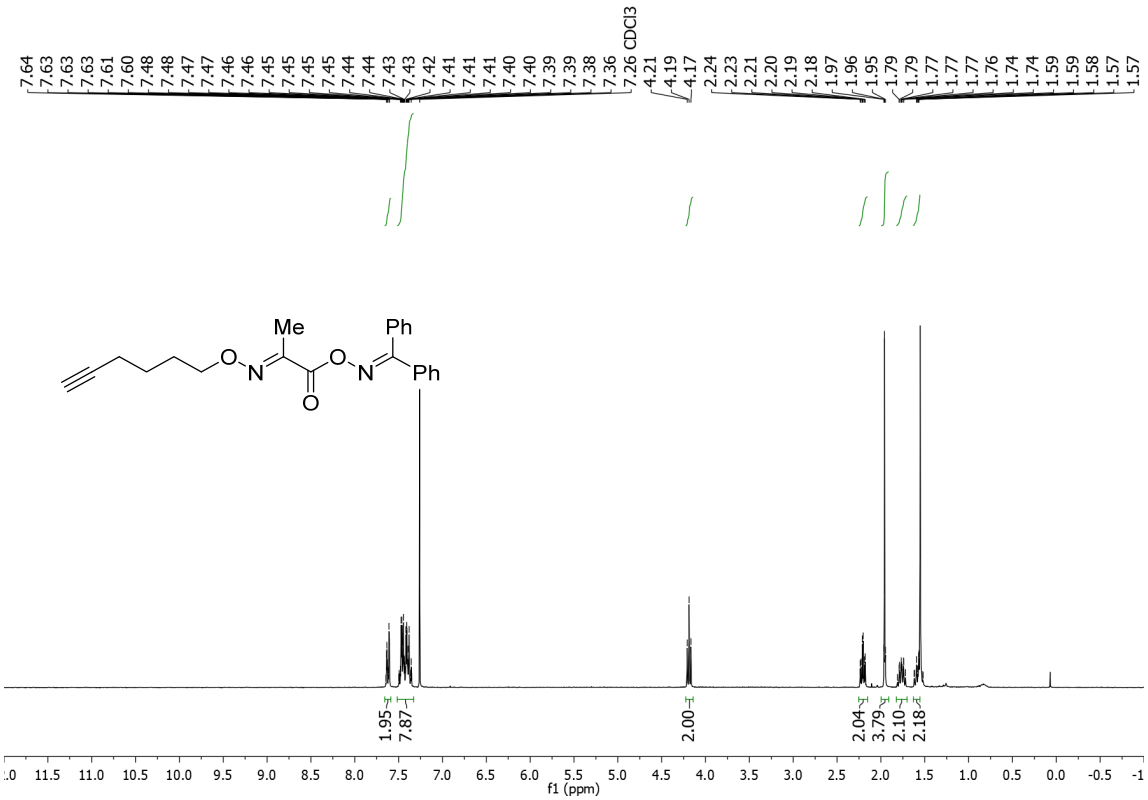
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1f.**



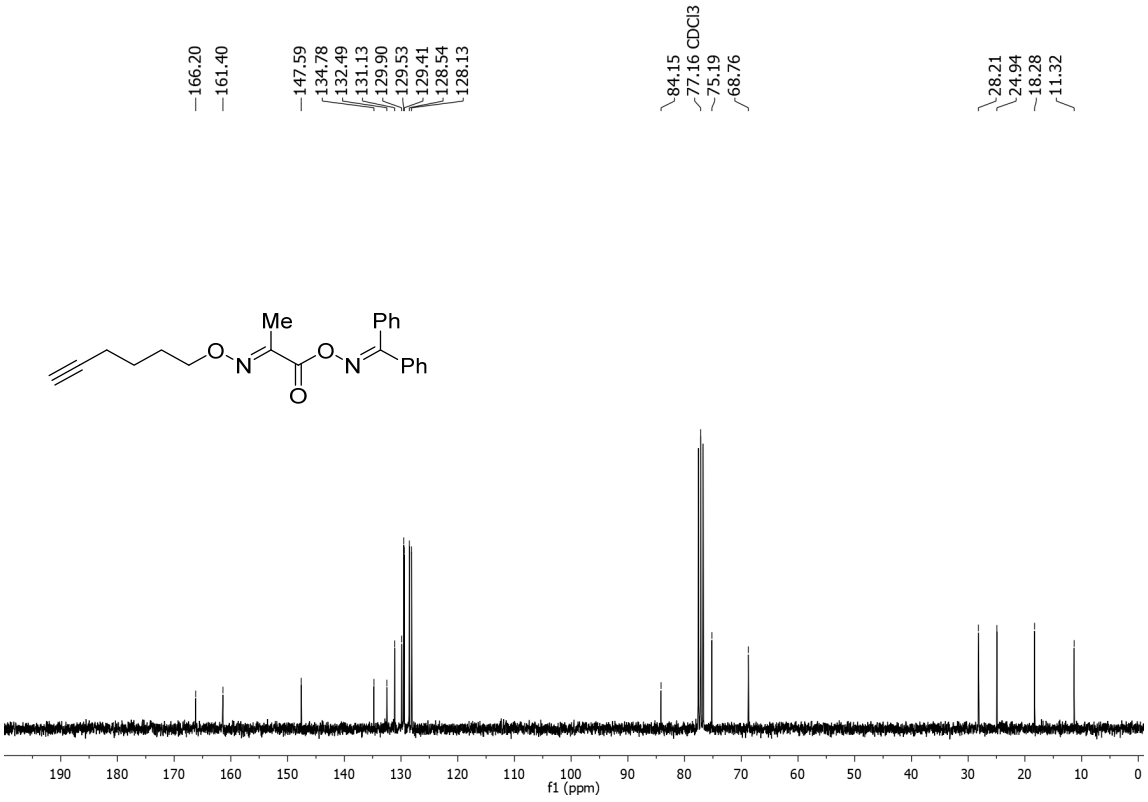
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1g**.



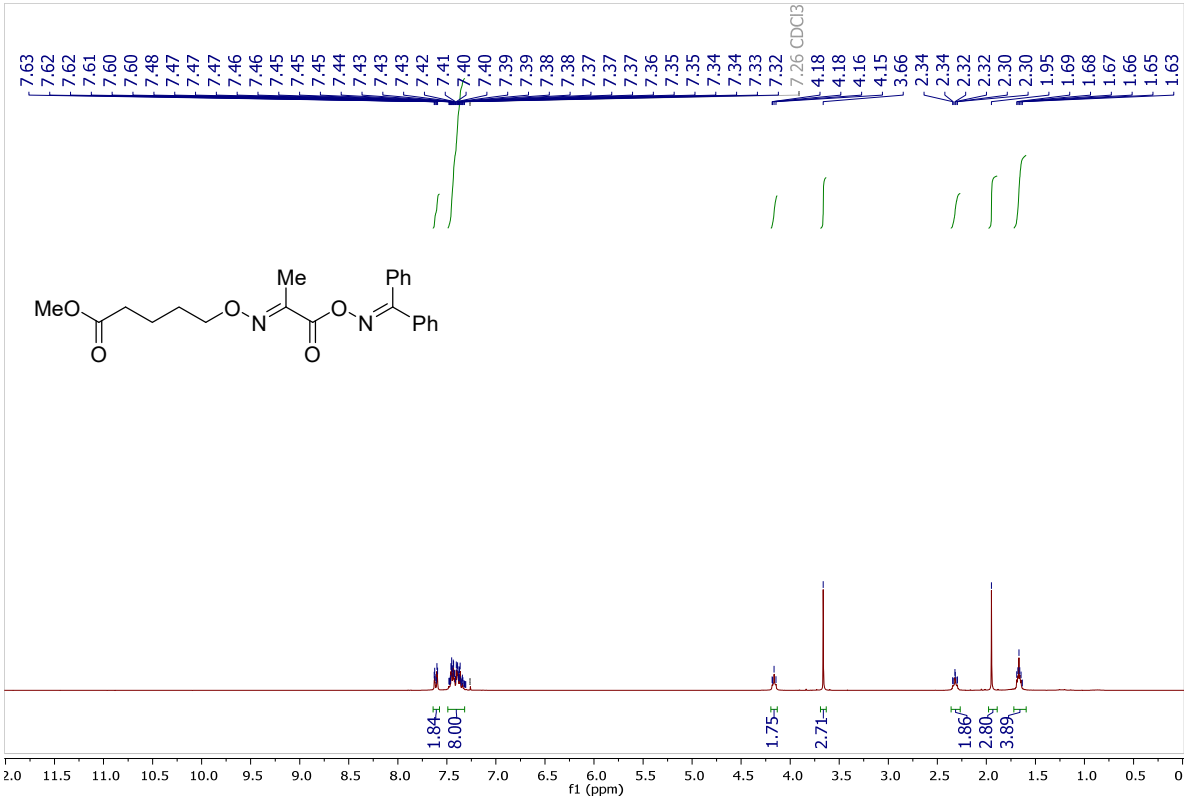
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1g.**



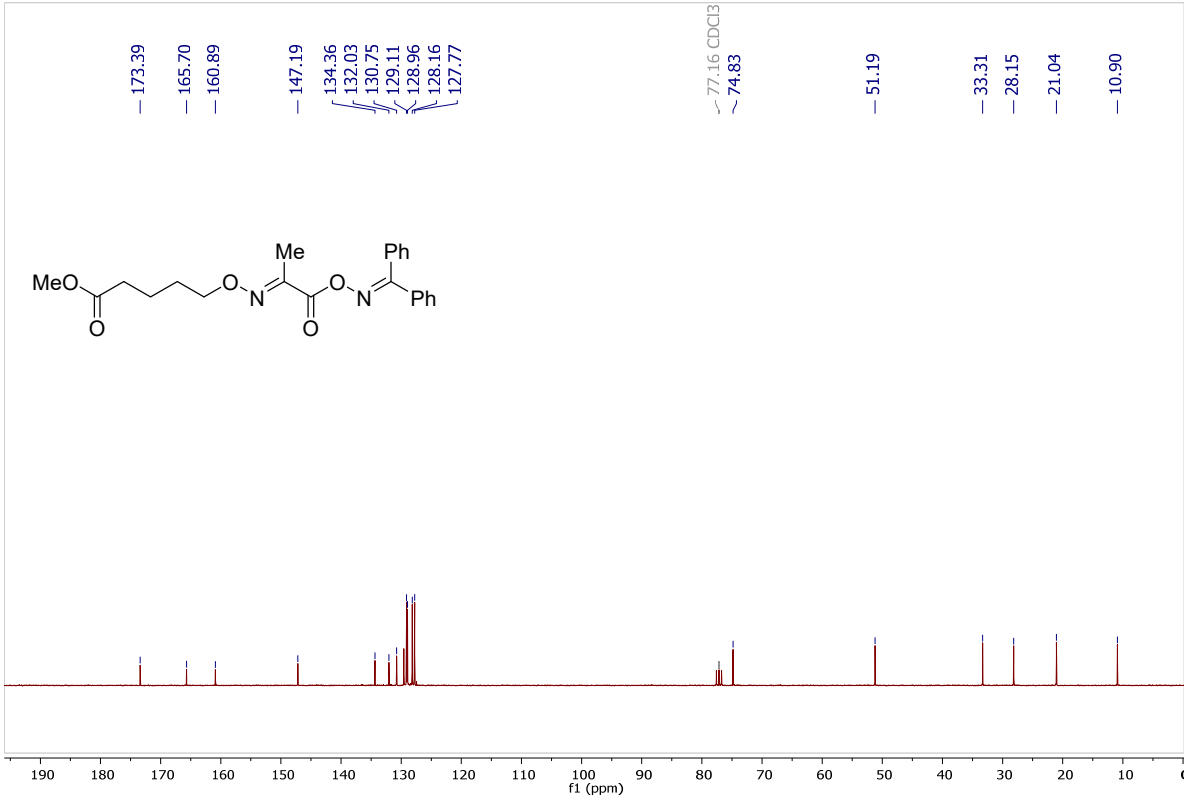
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1h**.



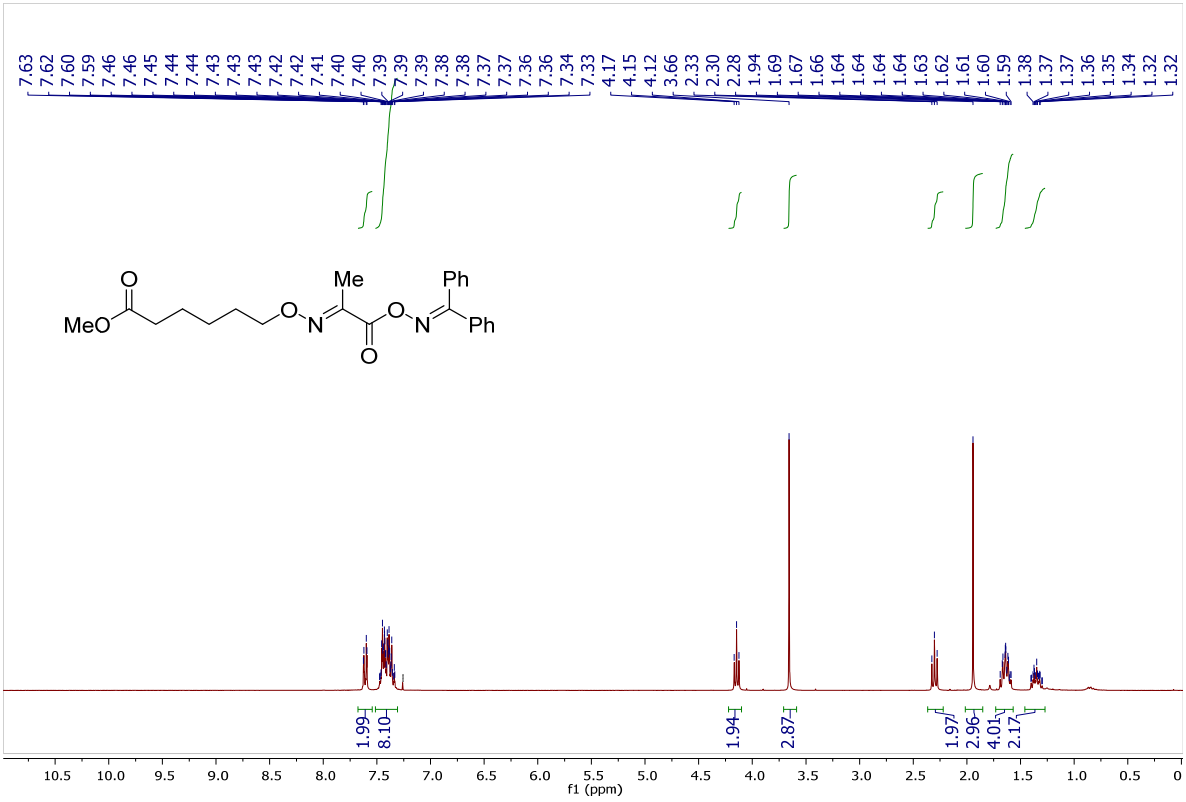
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1h.**



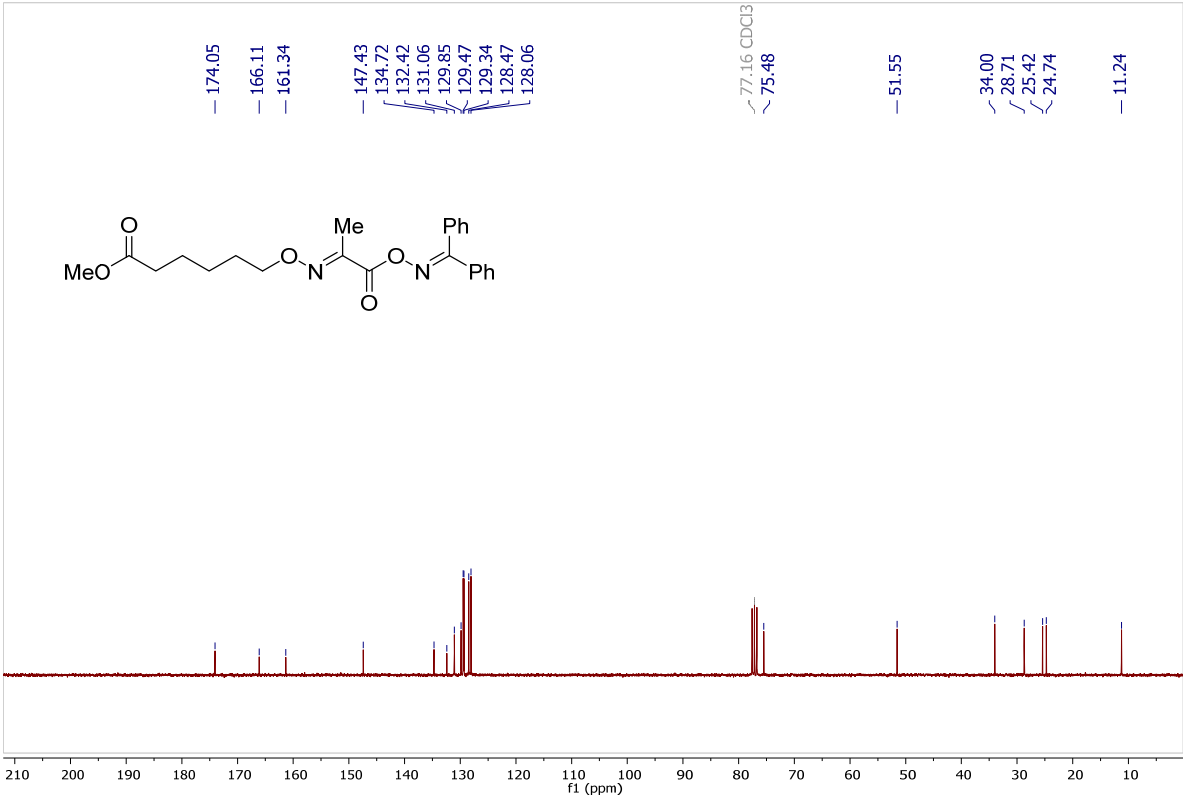
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1i**.



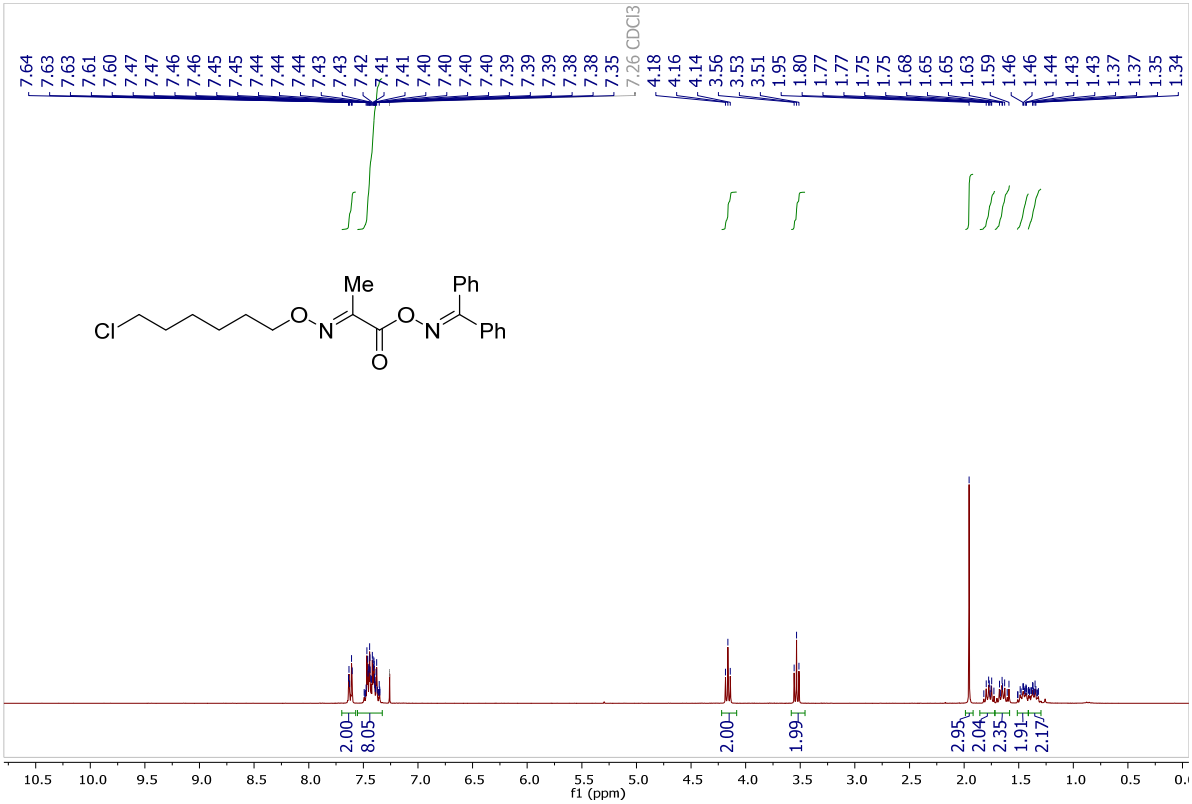
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1i.**



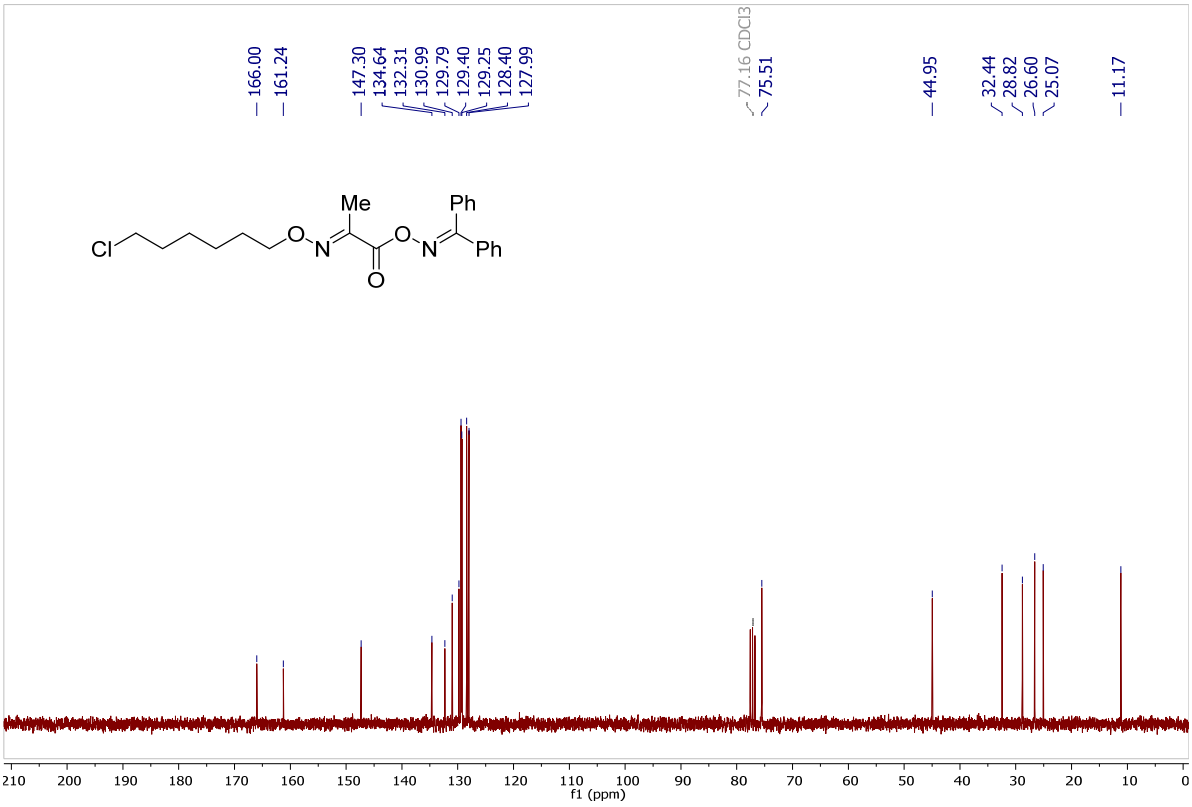
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1j**.



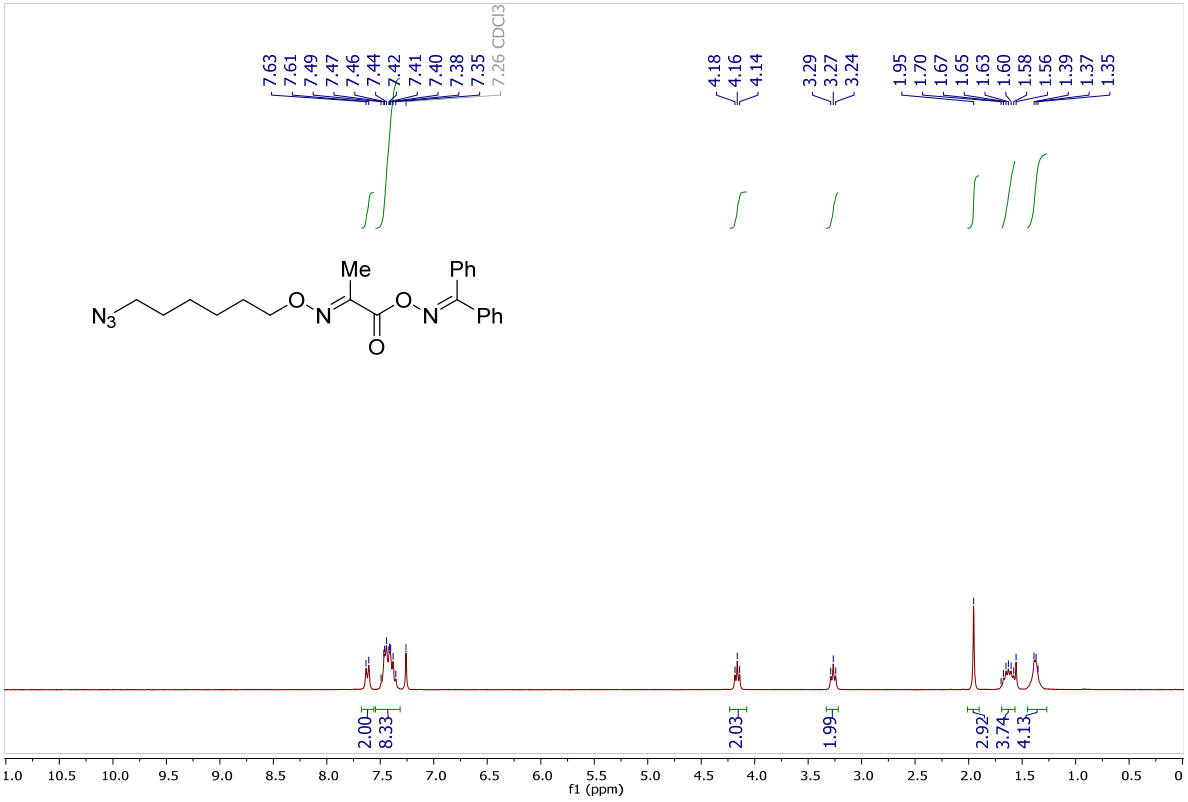
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1j.**



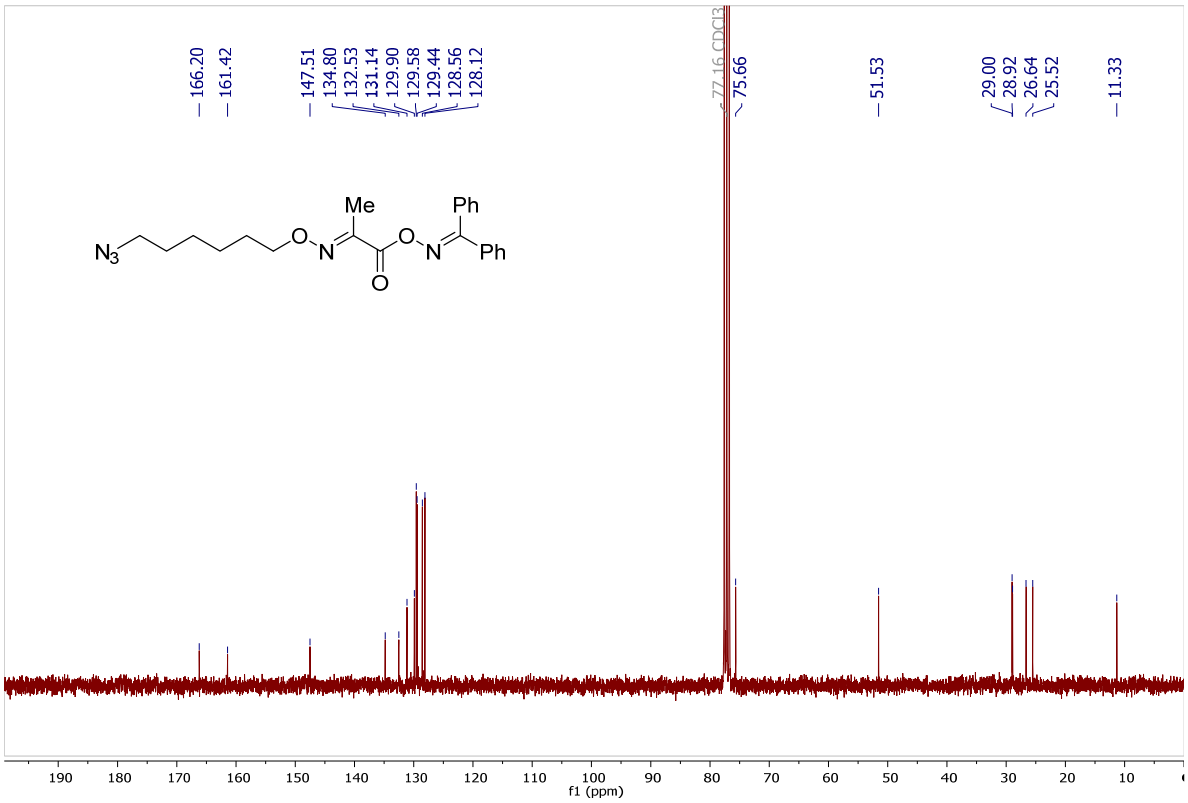
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1k**.



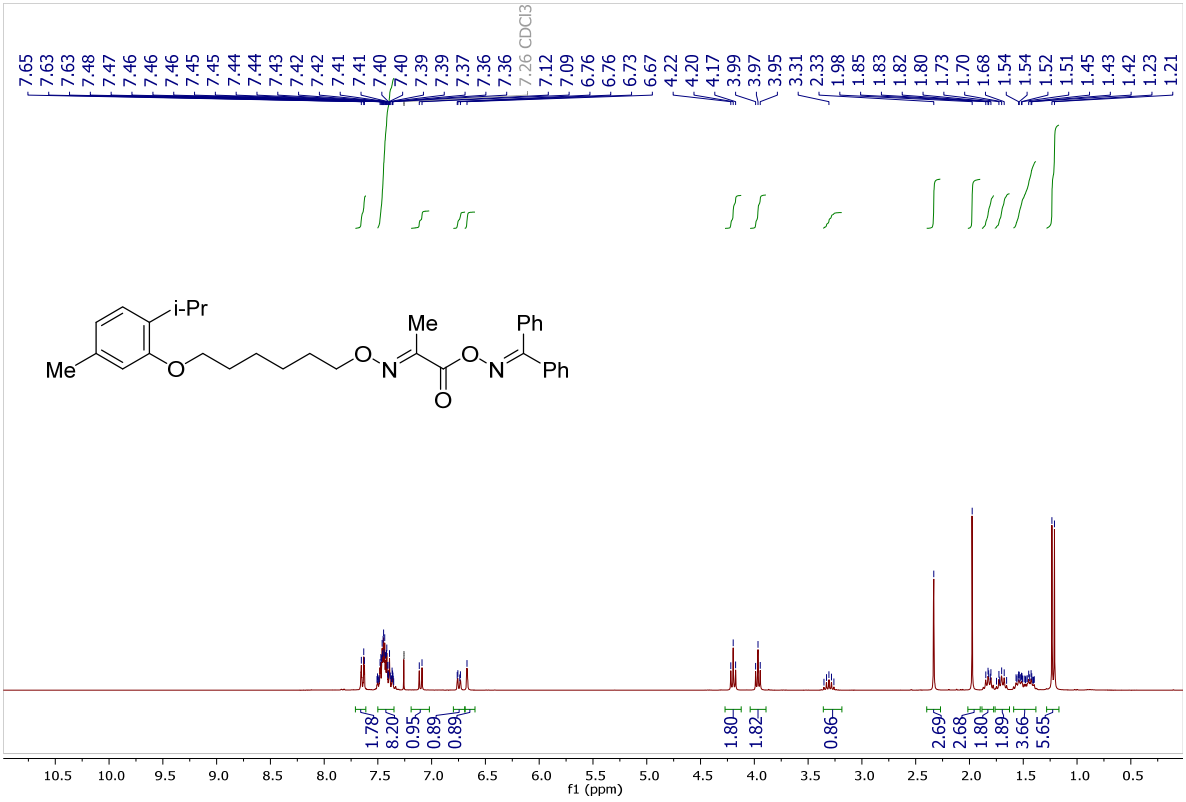
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1k.**



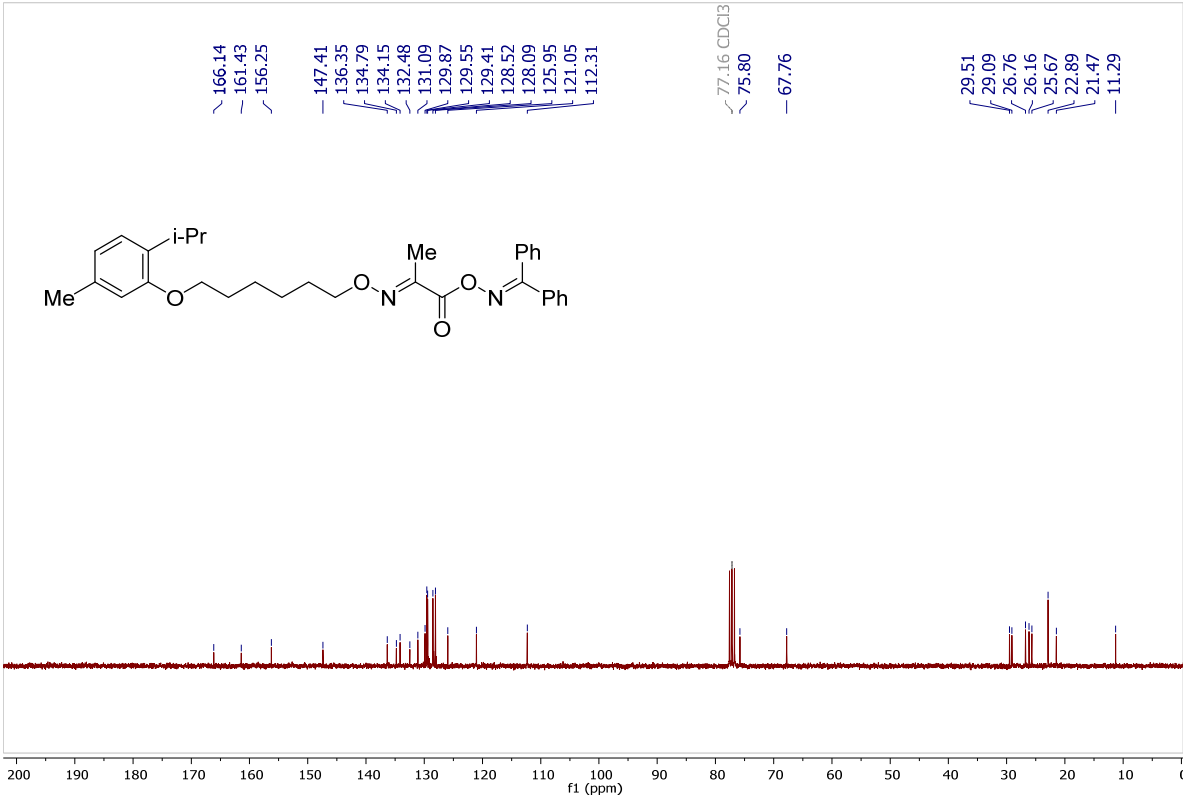
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1l**.



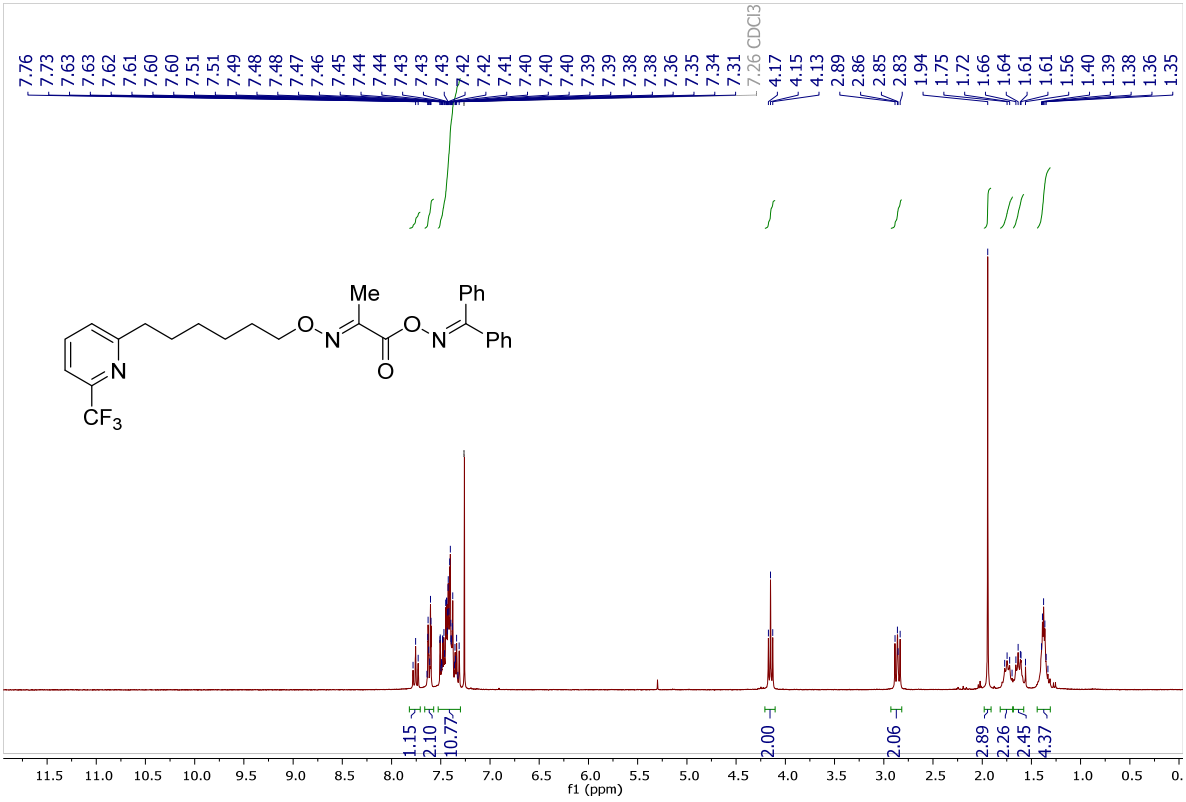
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1l.**



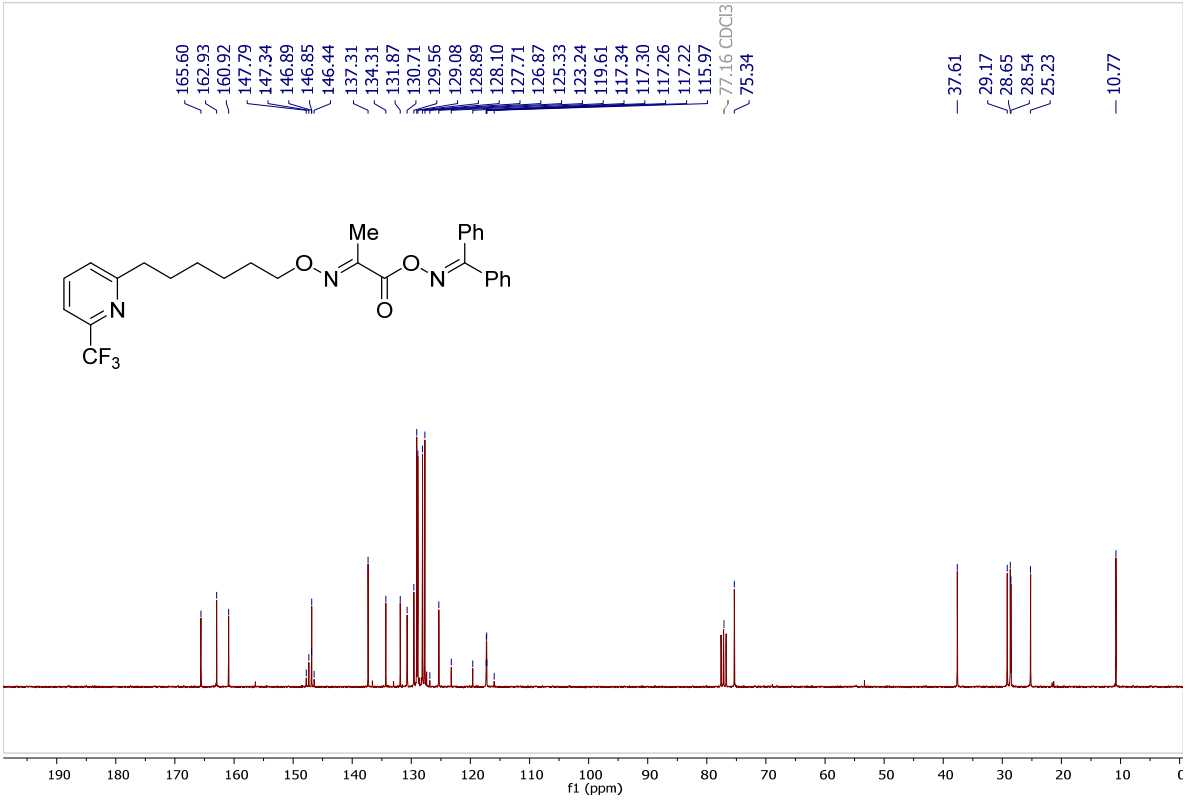
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1m**.



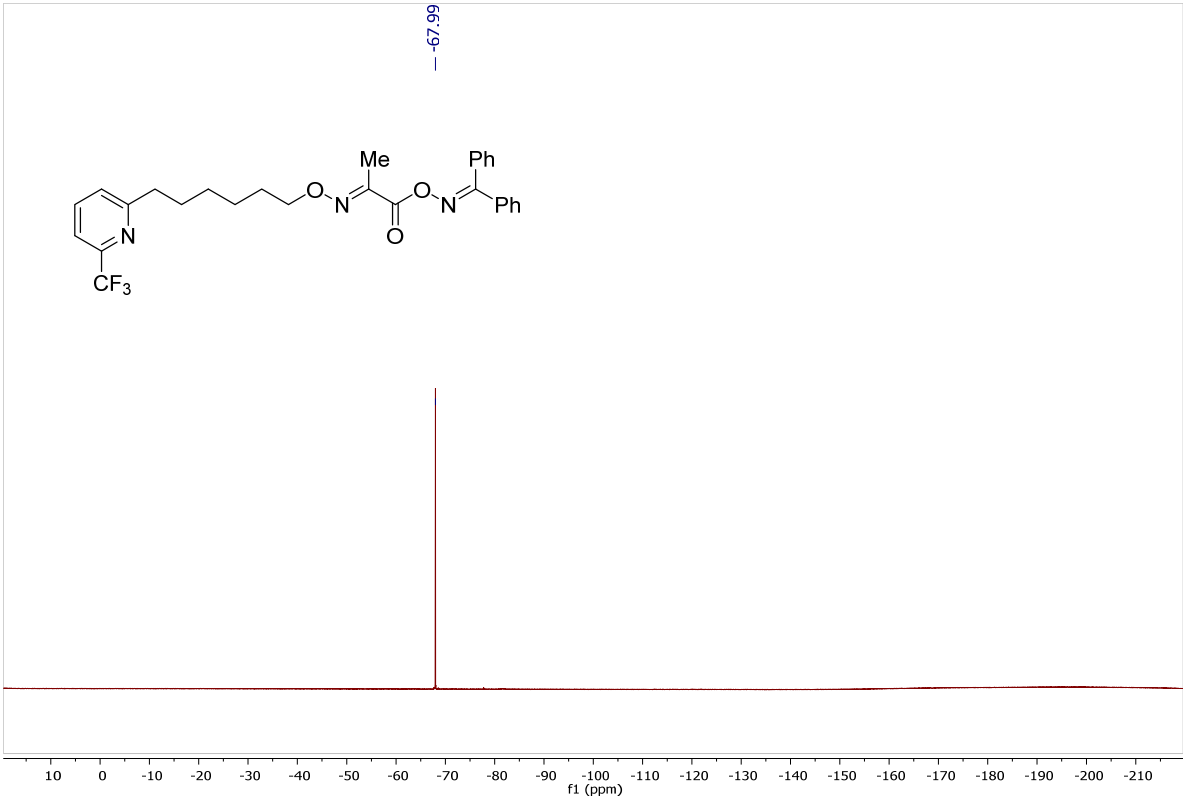
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1m.**



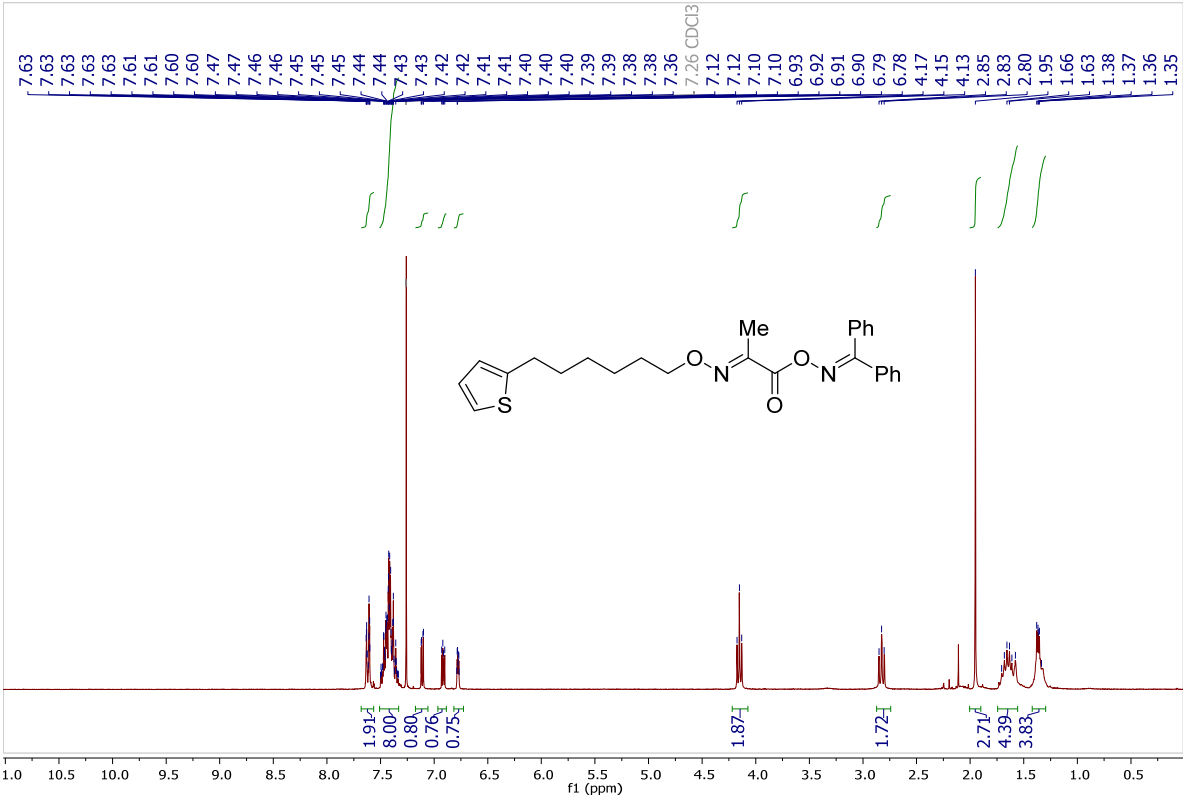
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1n**.



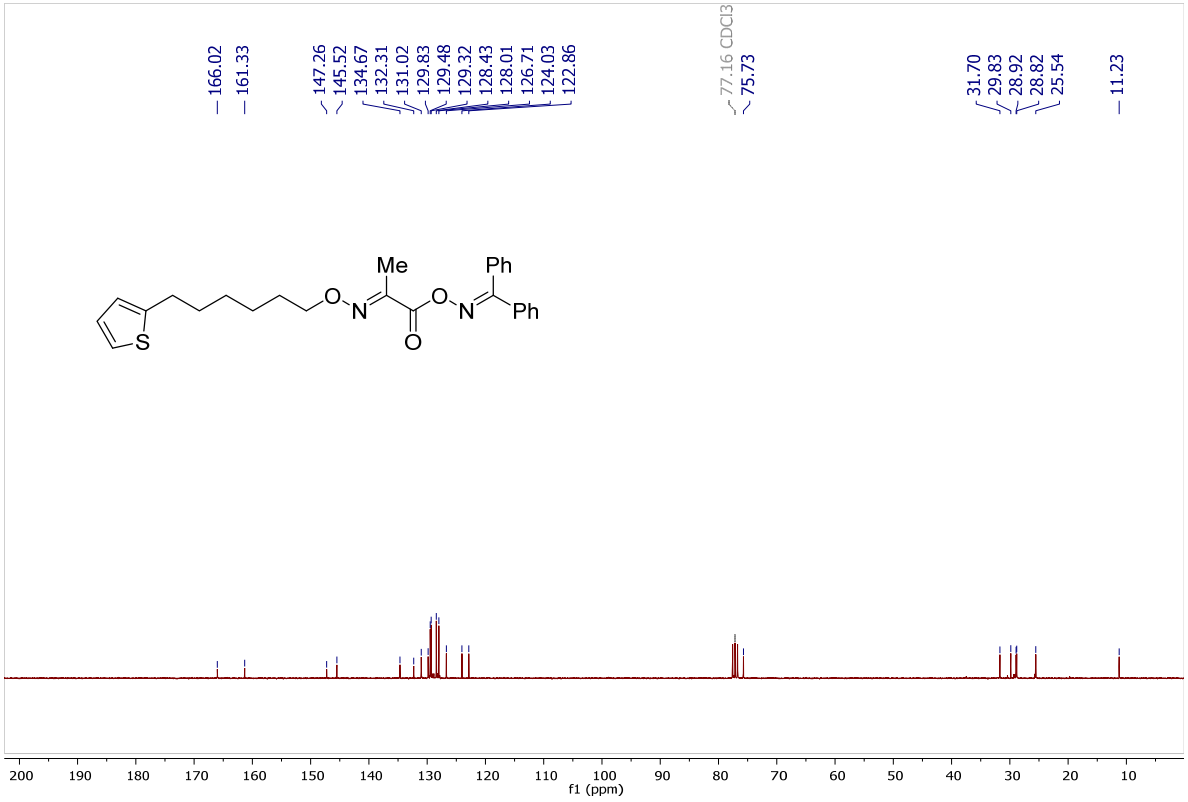
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1n.**



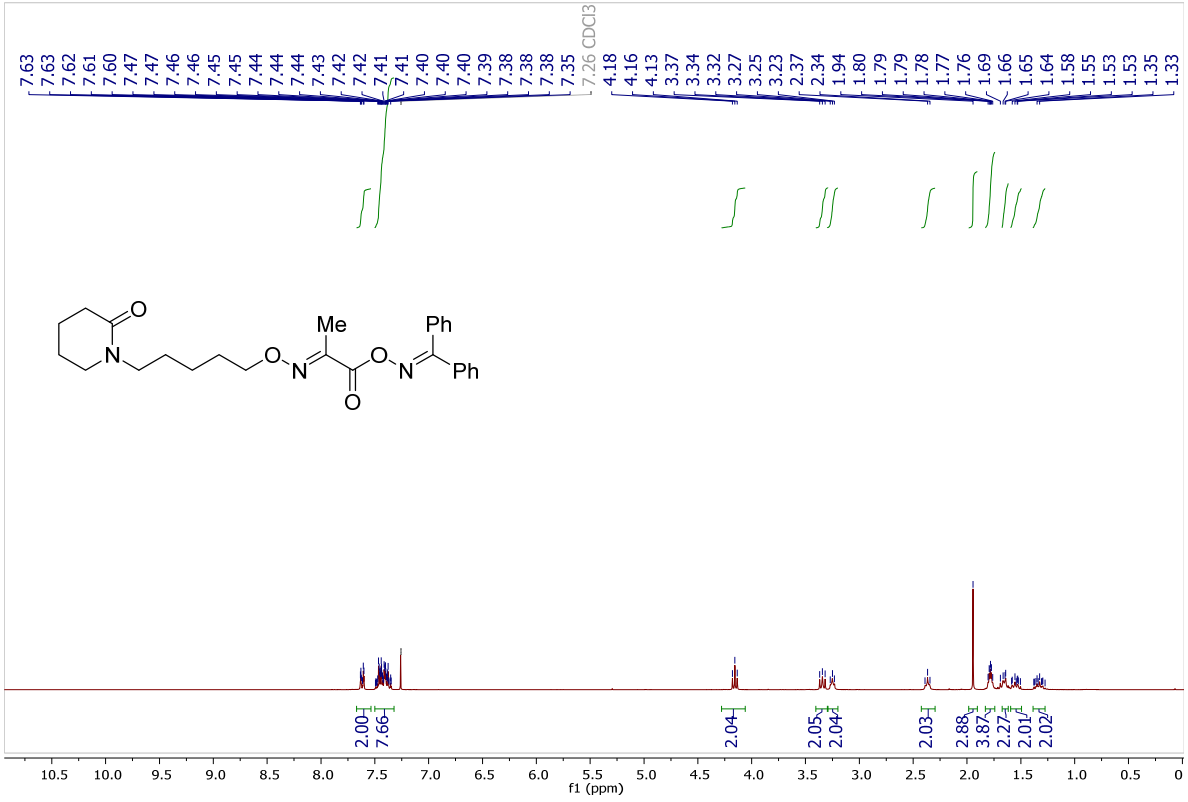
^{19}F NMR (282 MHz, $CDCl_3$) of compound **1n.**



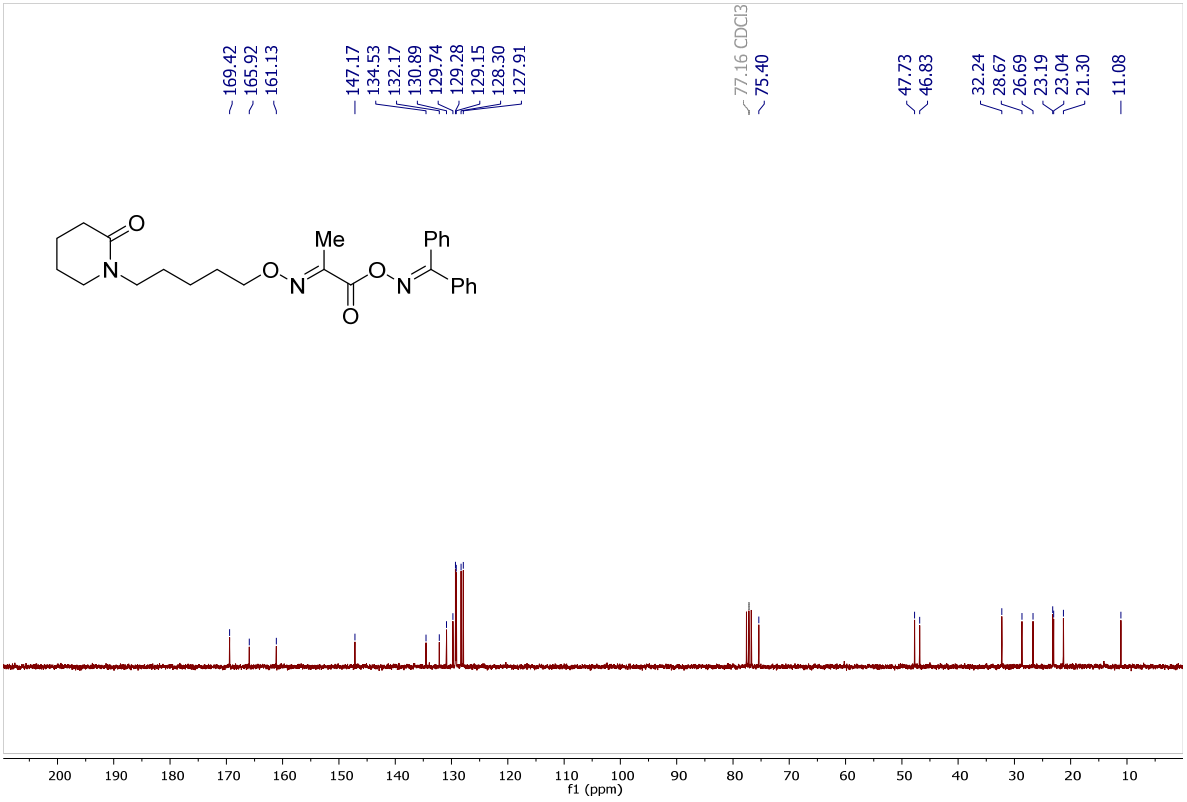
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1o**.



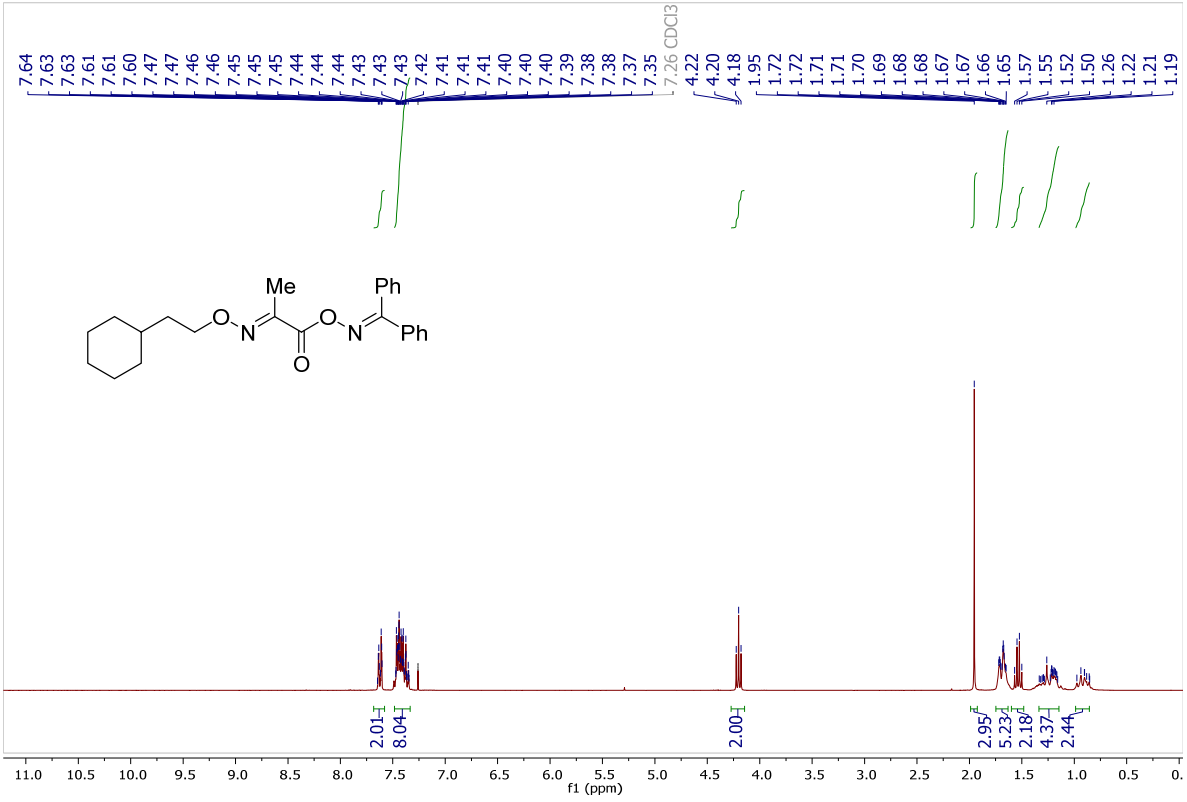
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1o.**



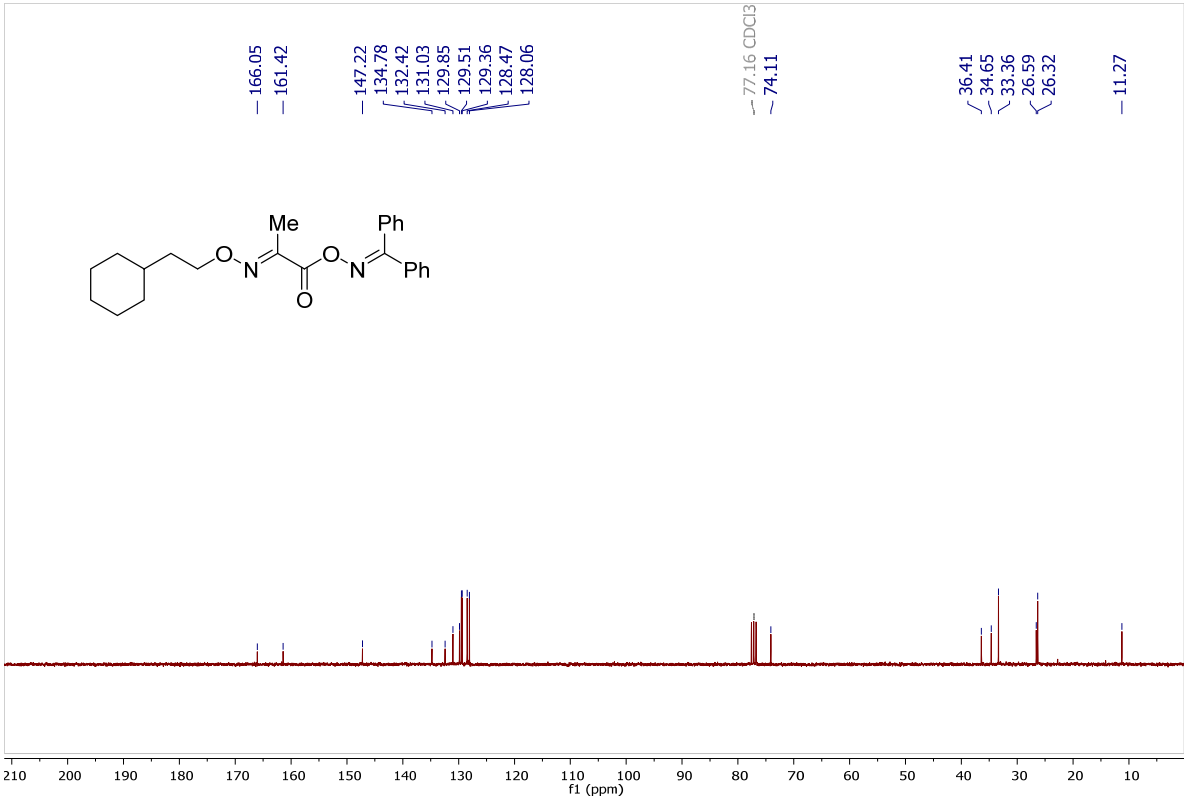
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1p**.



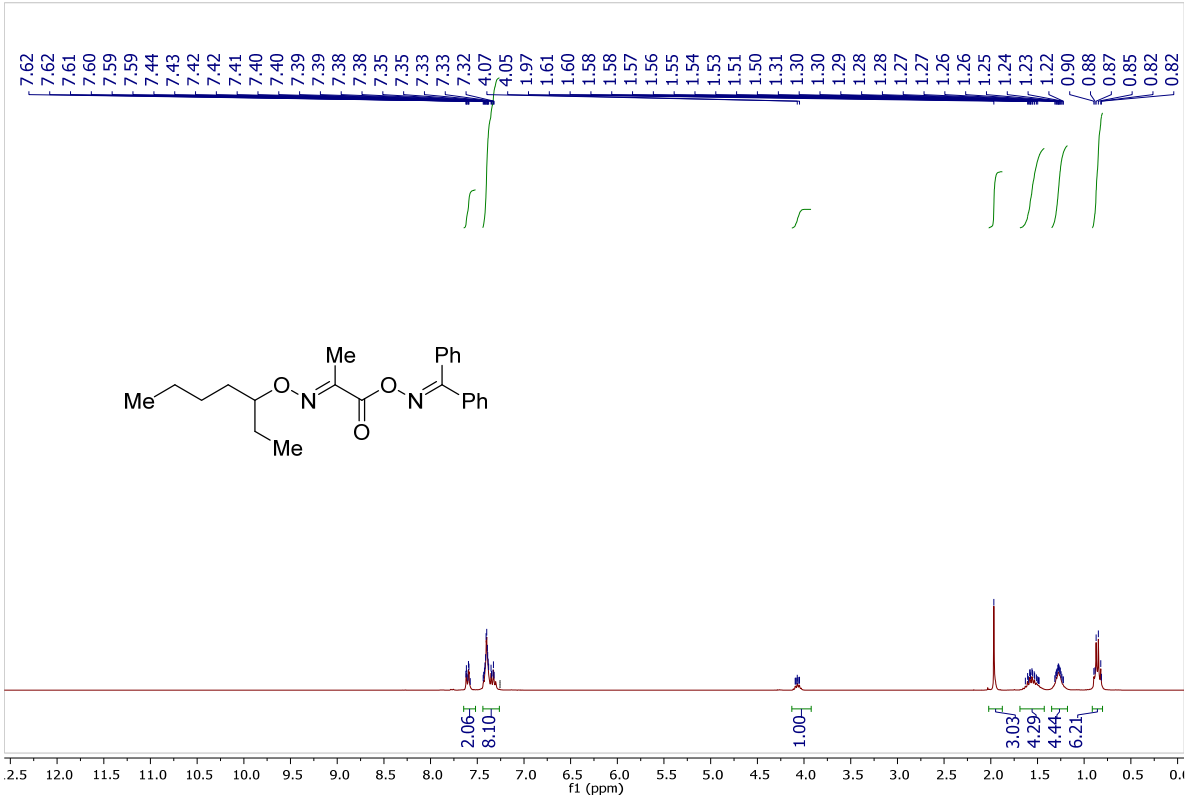
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1p.**



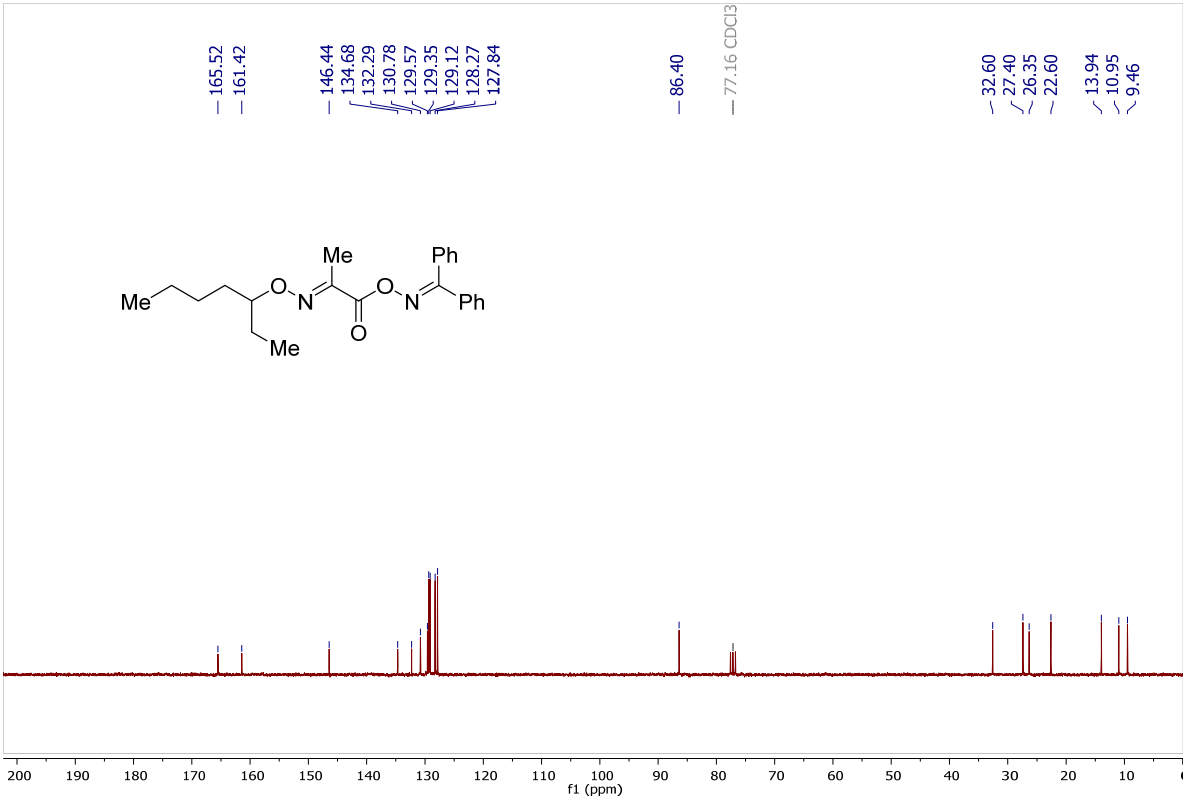
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1q**.



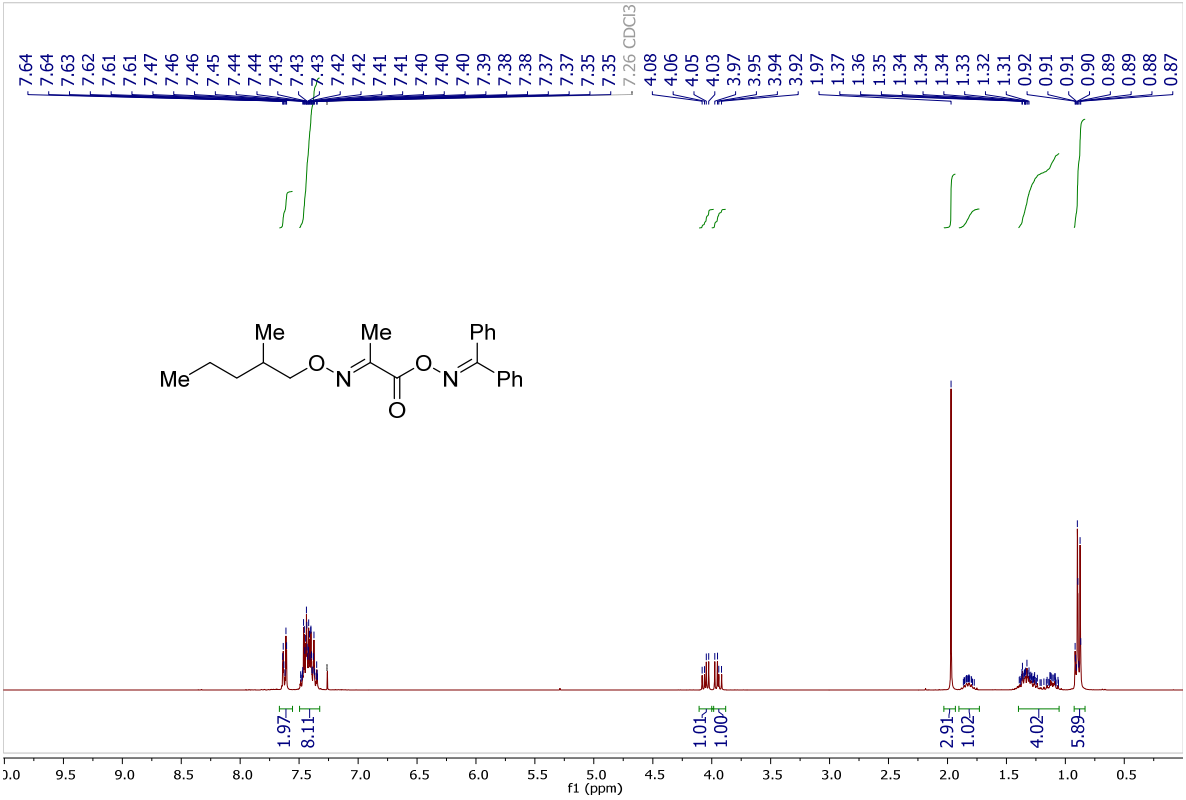
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1q.**



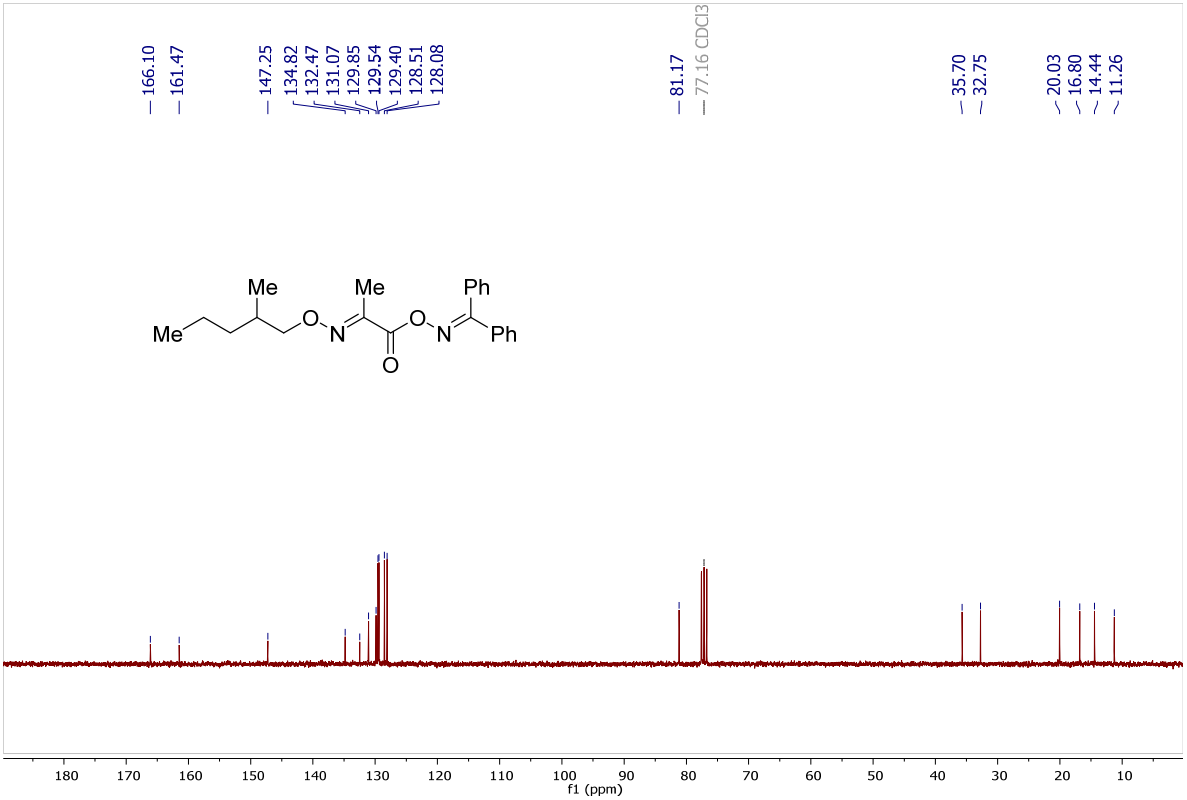
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1r**.



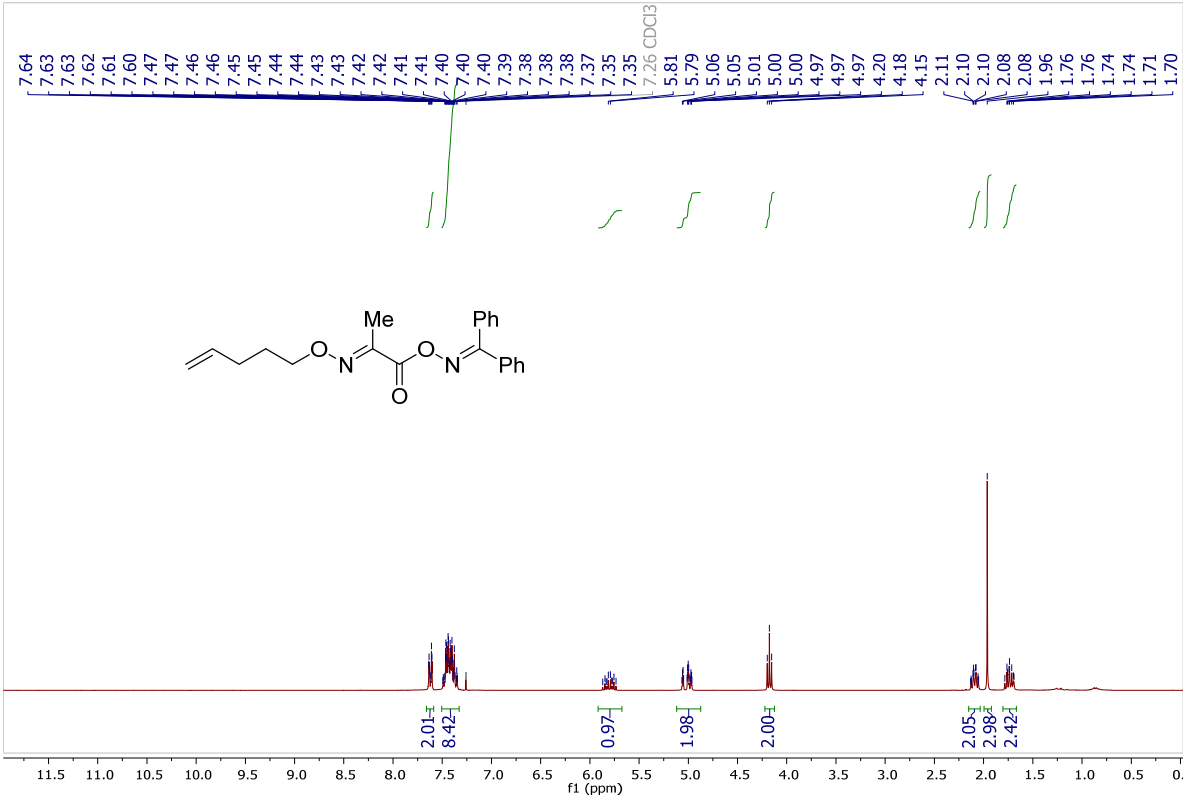
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1r.**



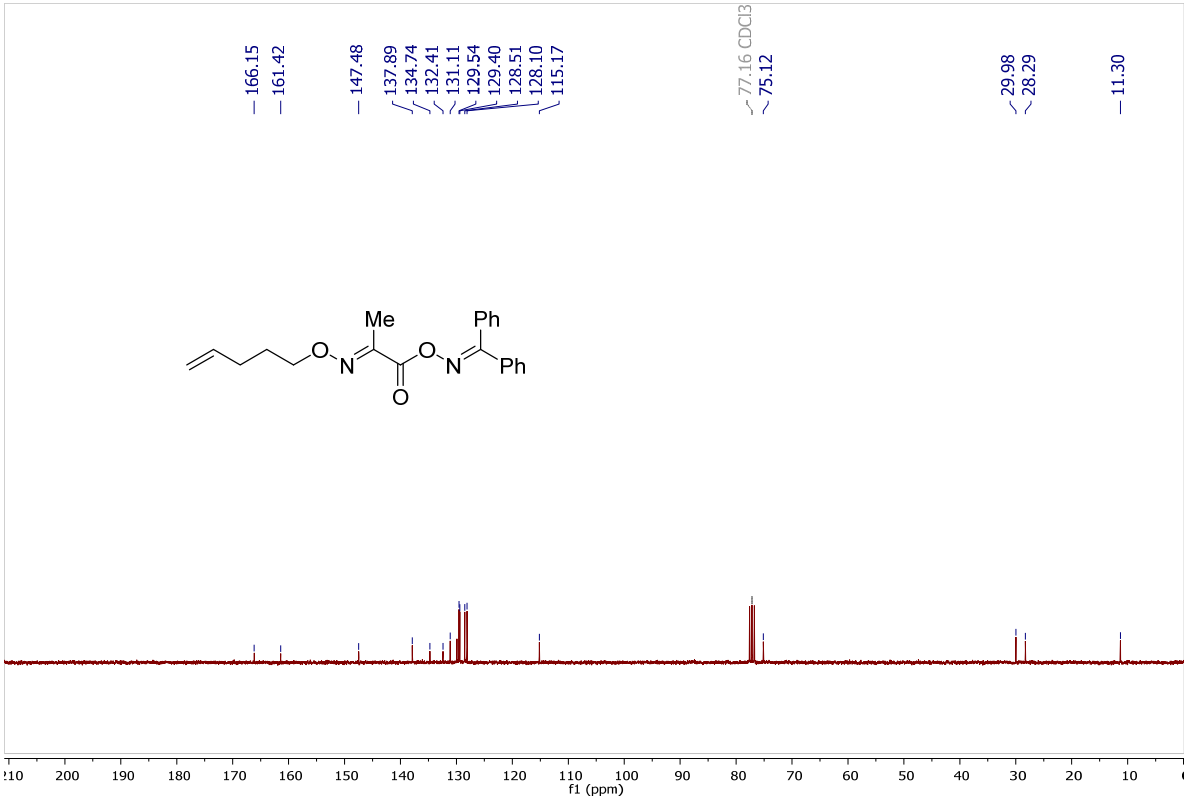
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1s**.



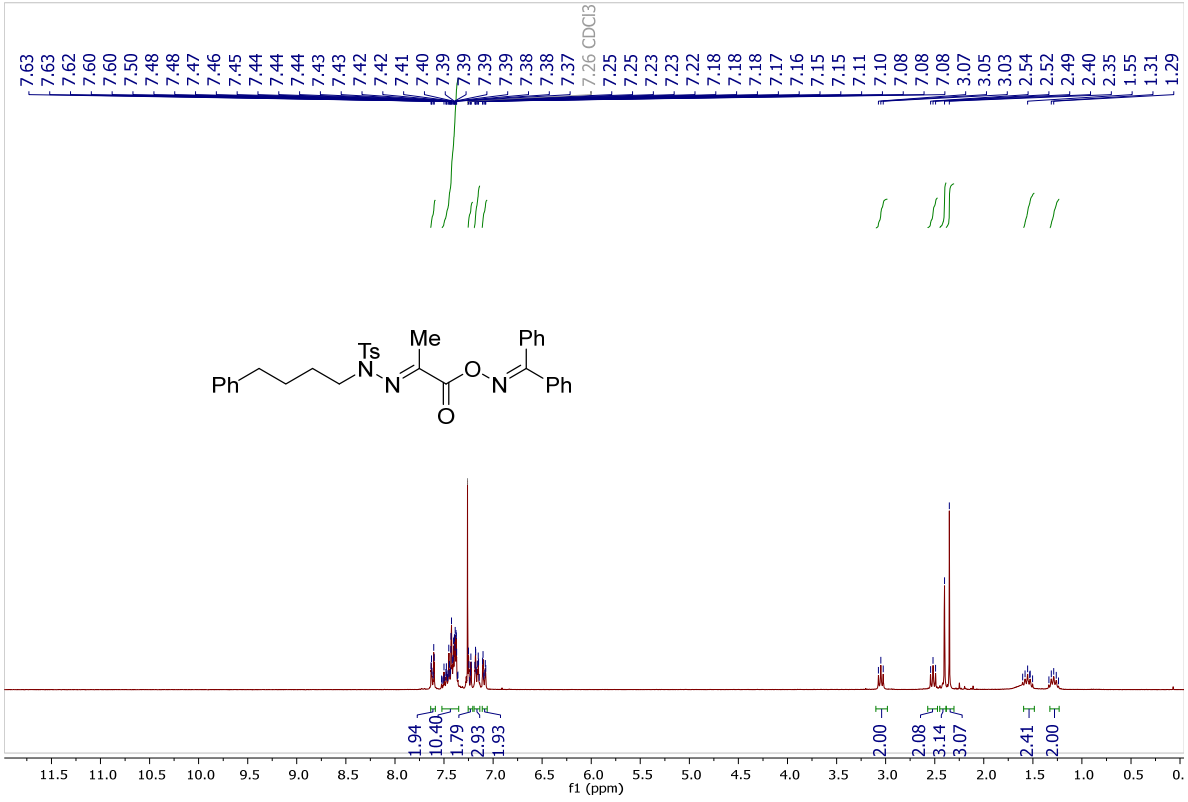
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1s.**



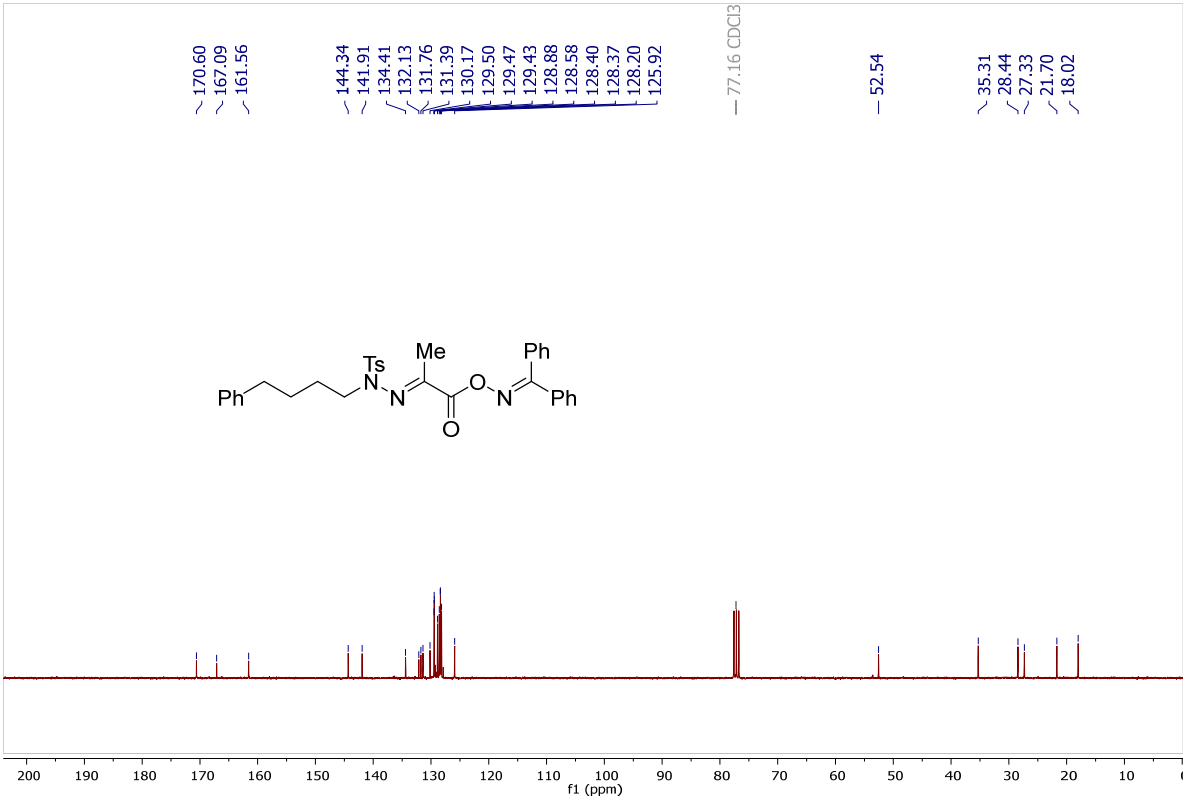
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1t**.



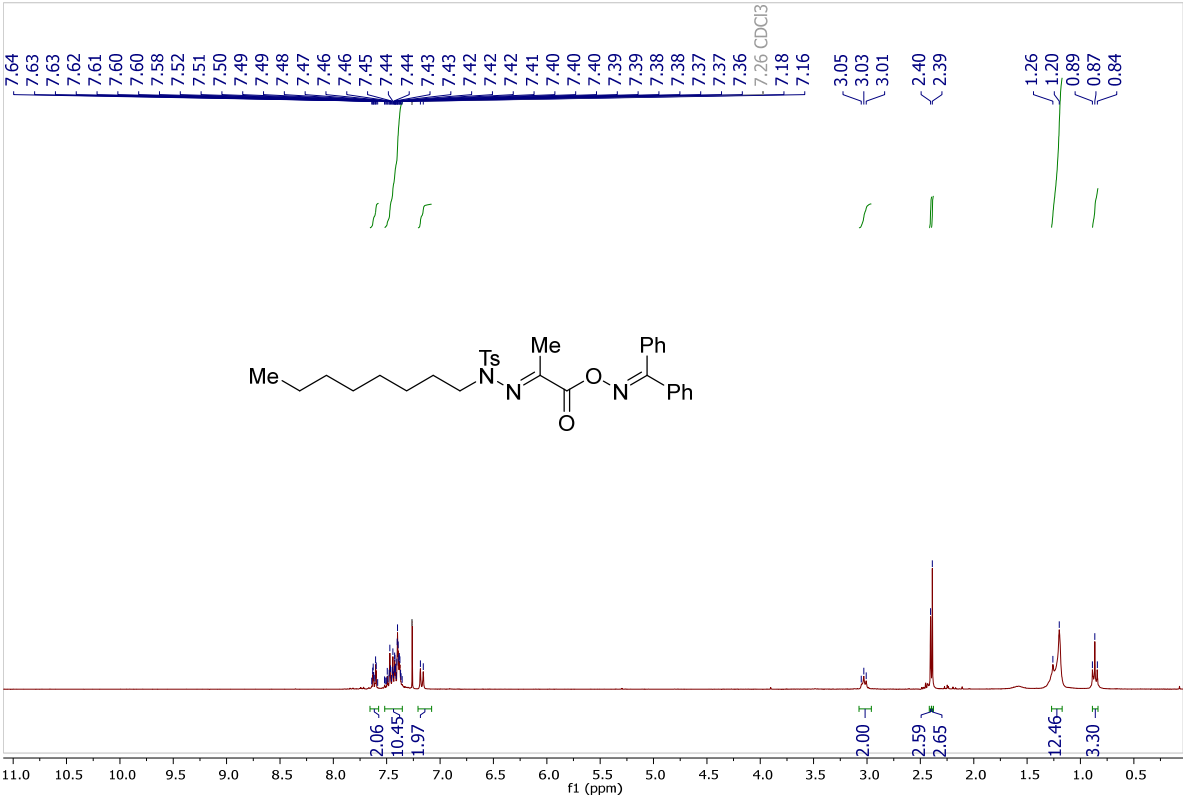
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1t.**



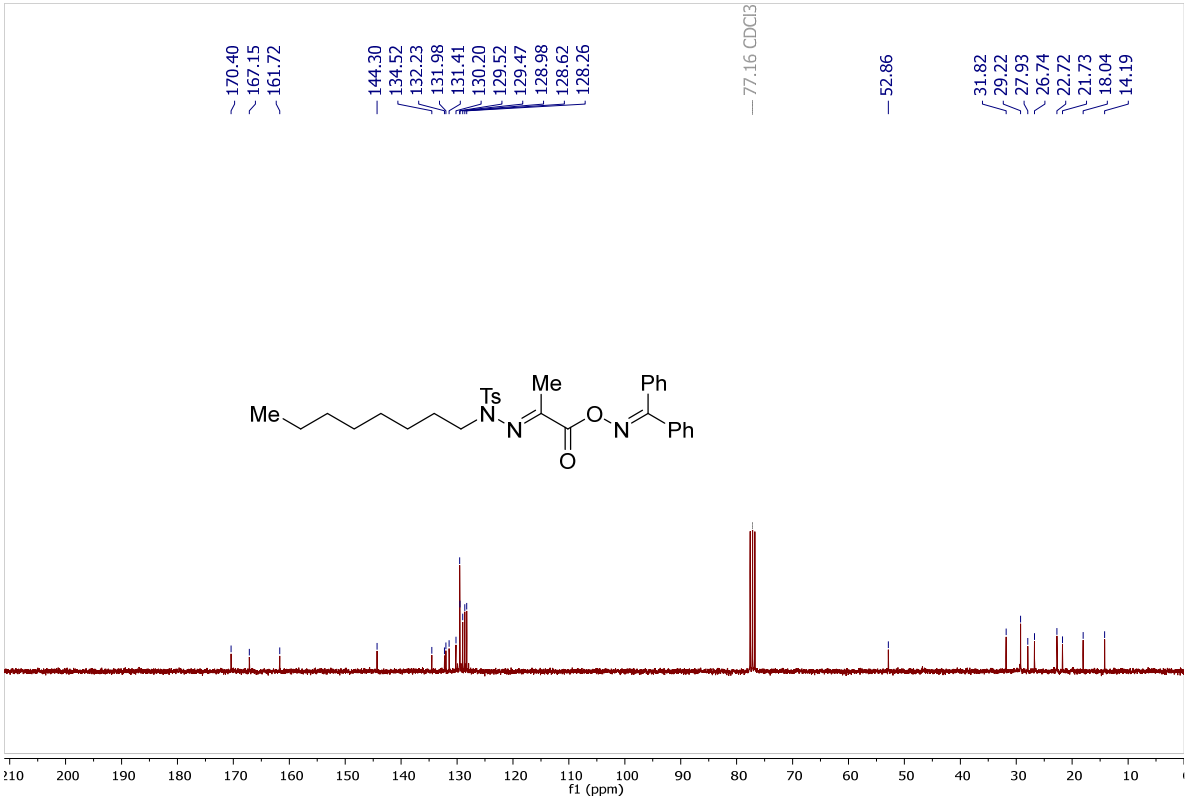
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1u**.



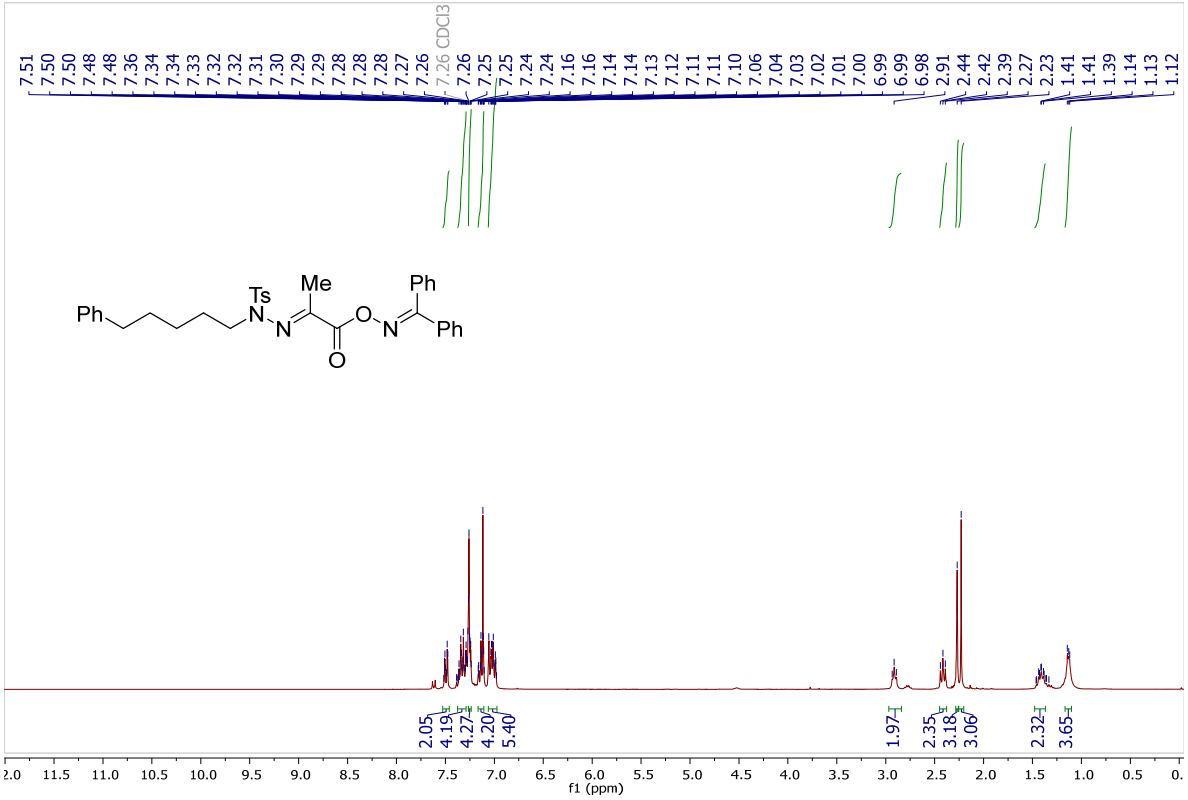
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1u.**



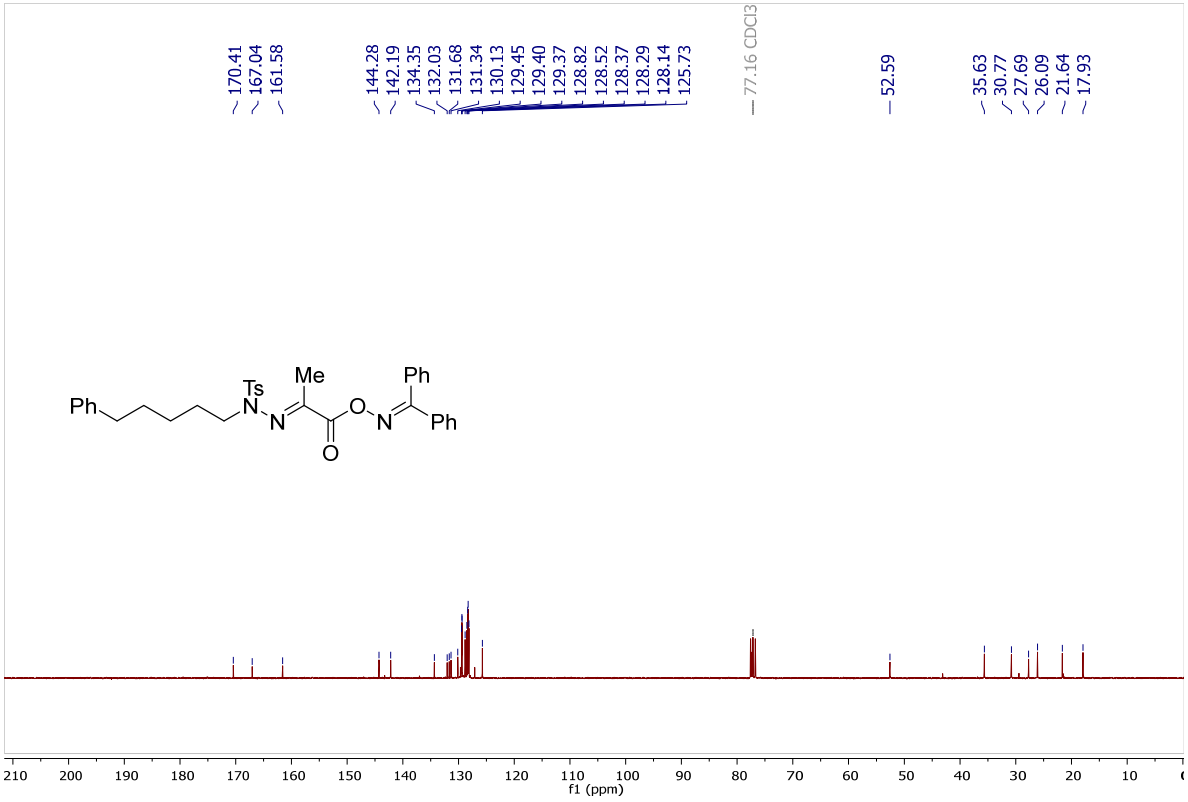
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1v**.



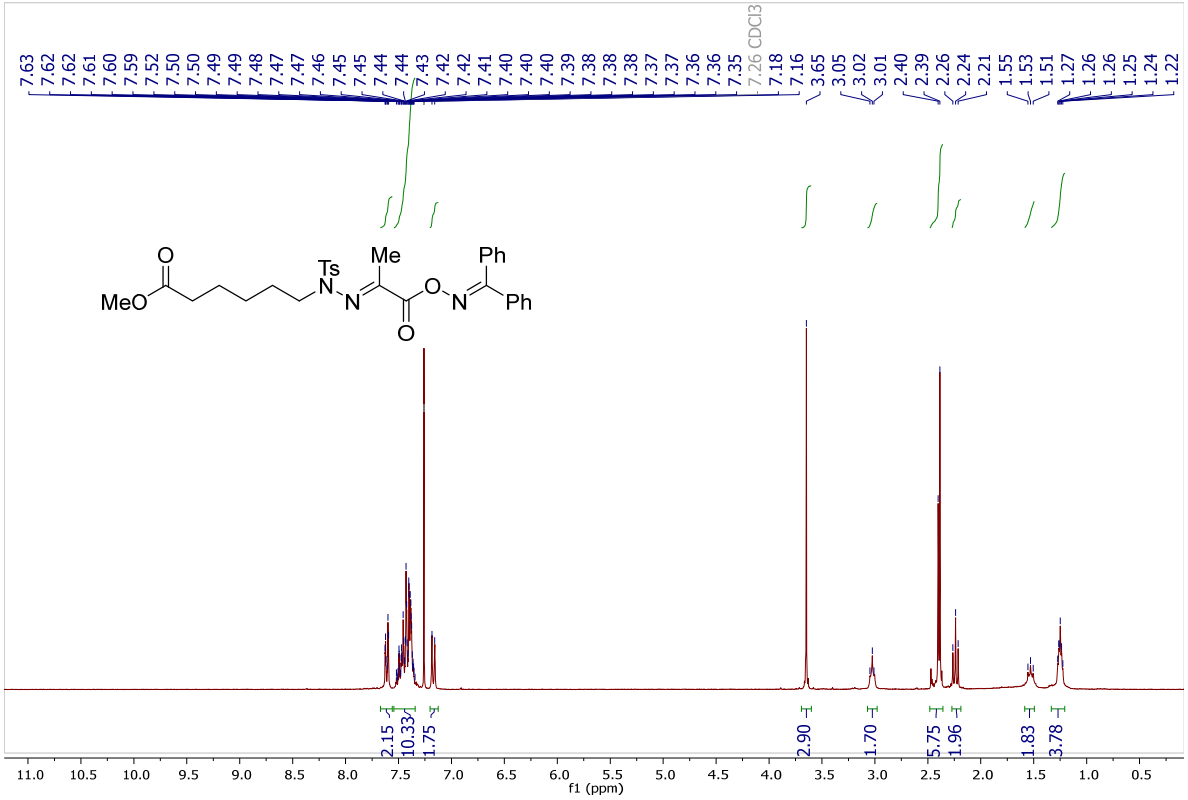
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1v.**



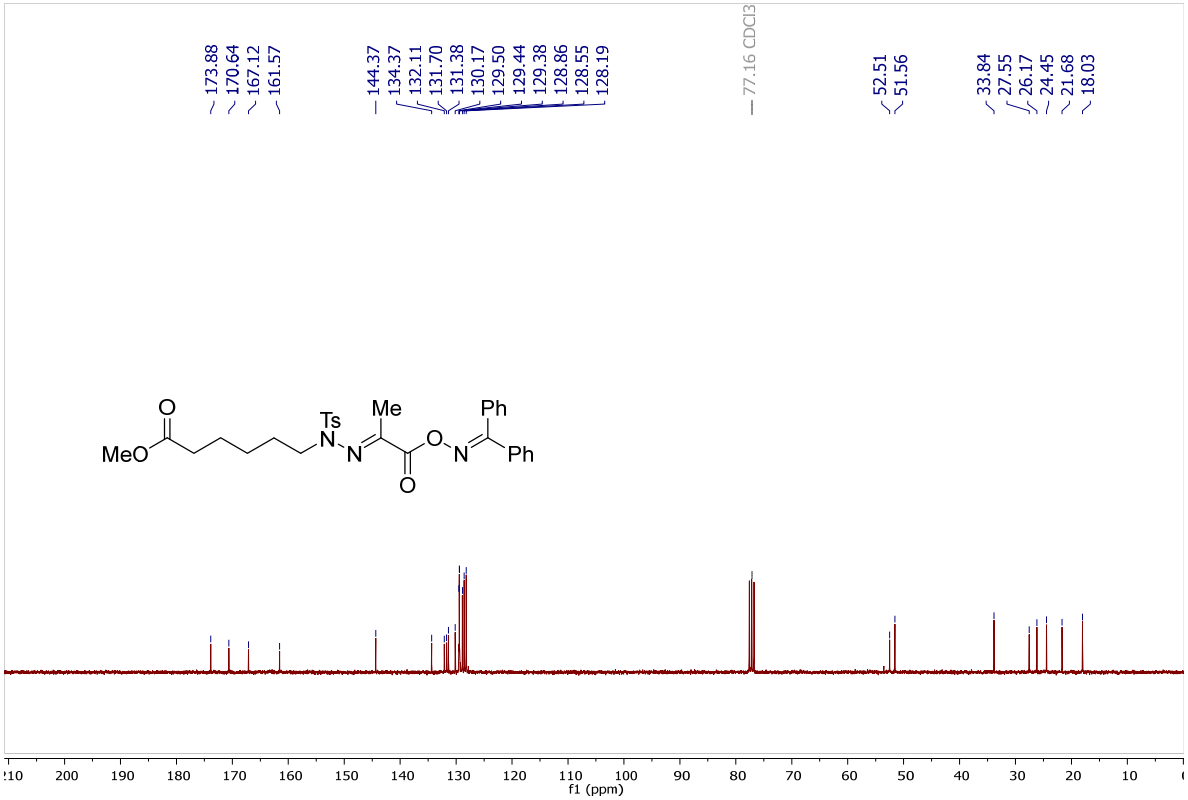
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1w**.



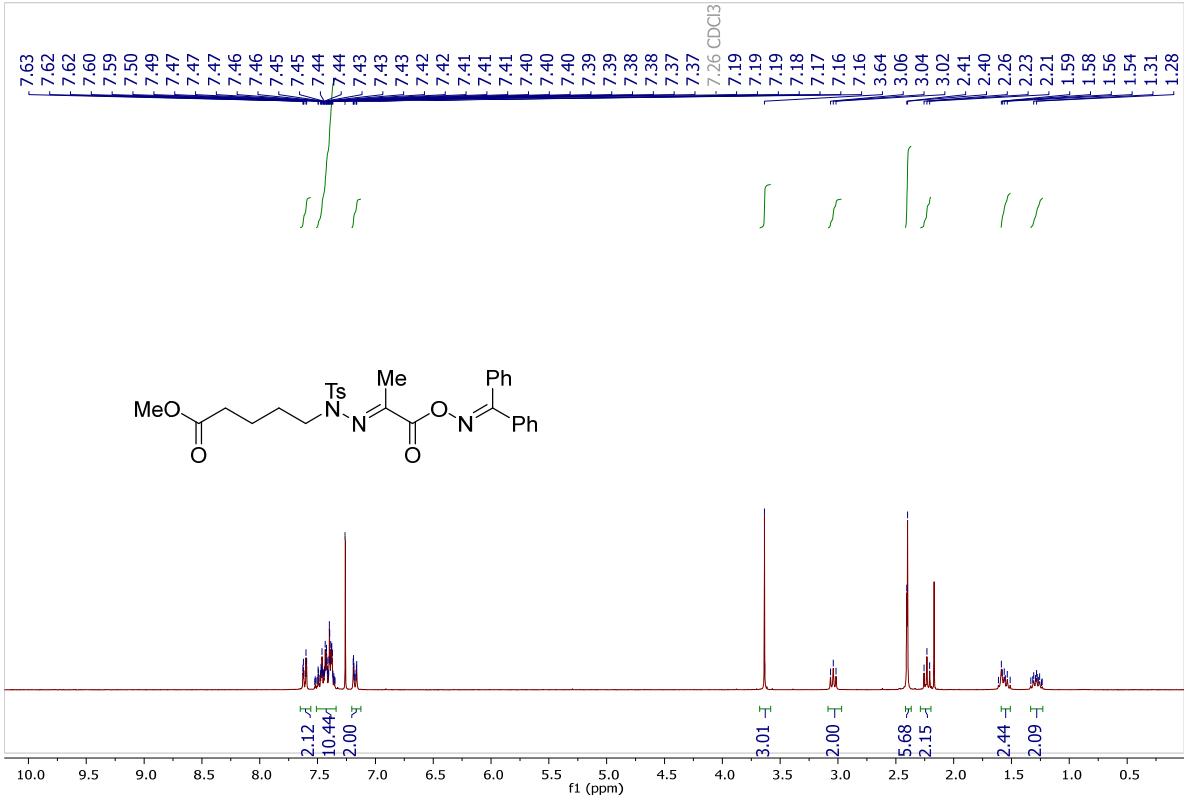
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1w.**



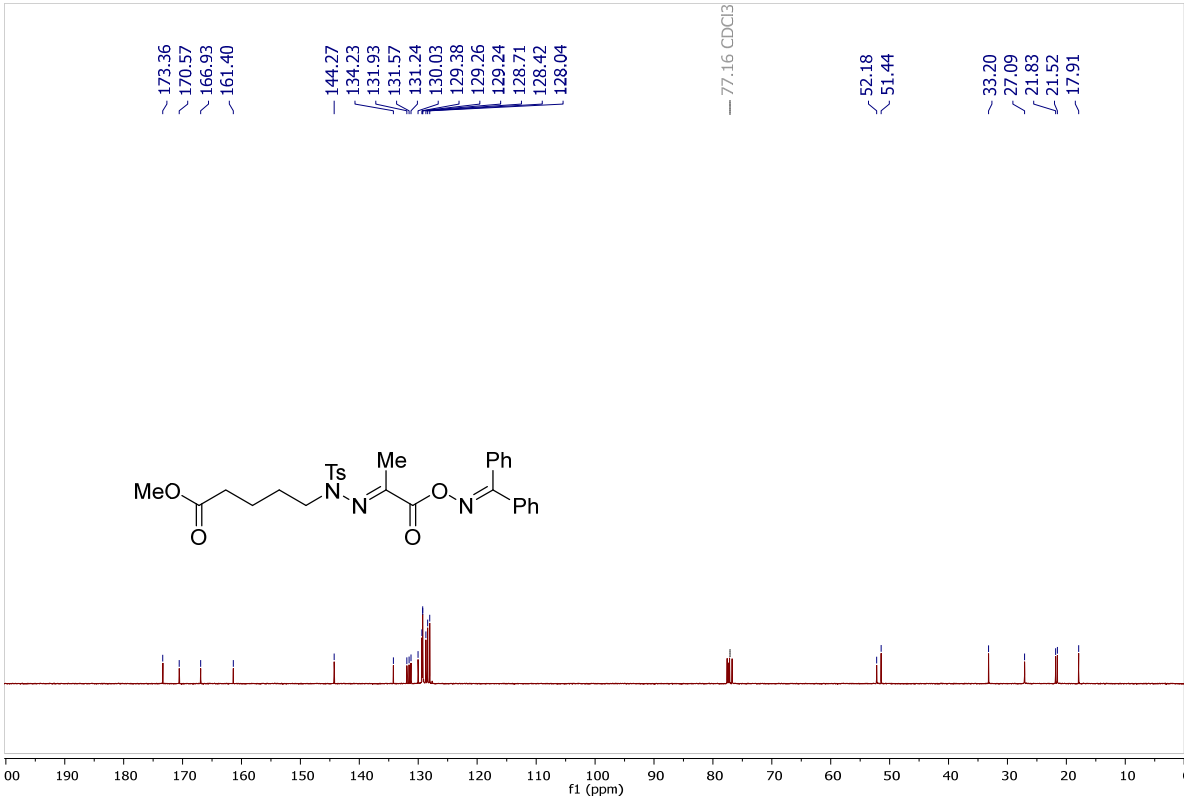
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1x**.



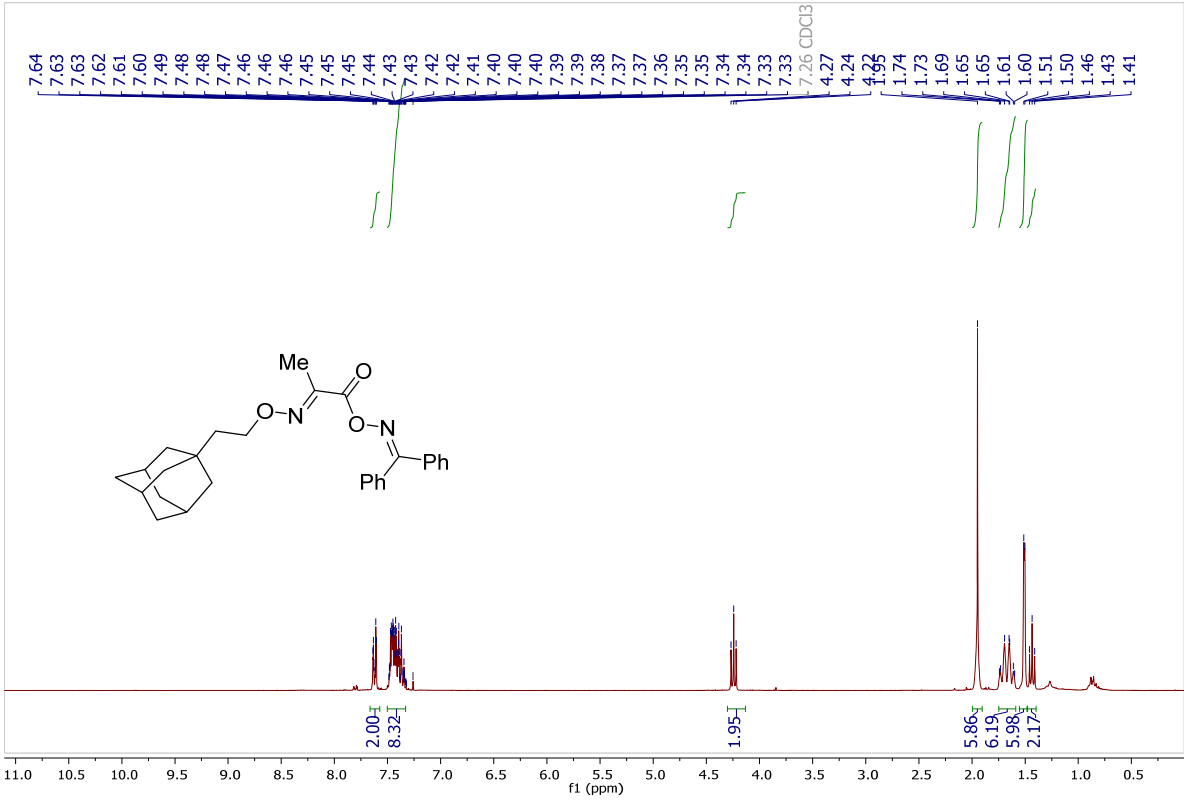
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1x.**



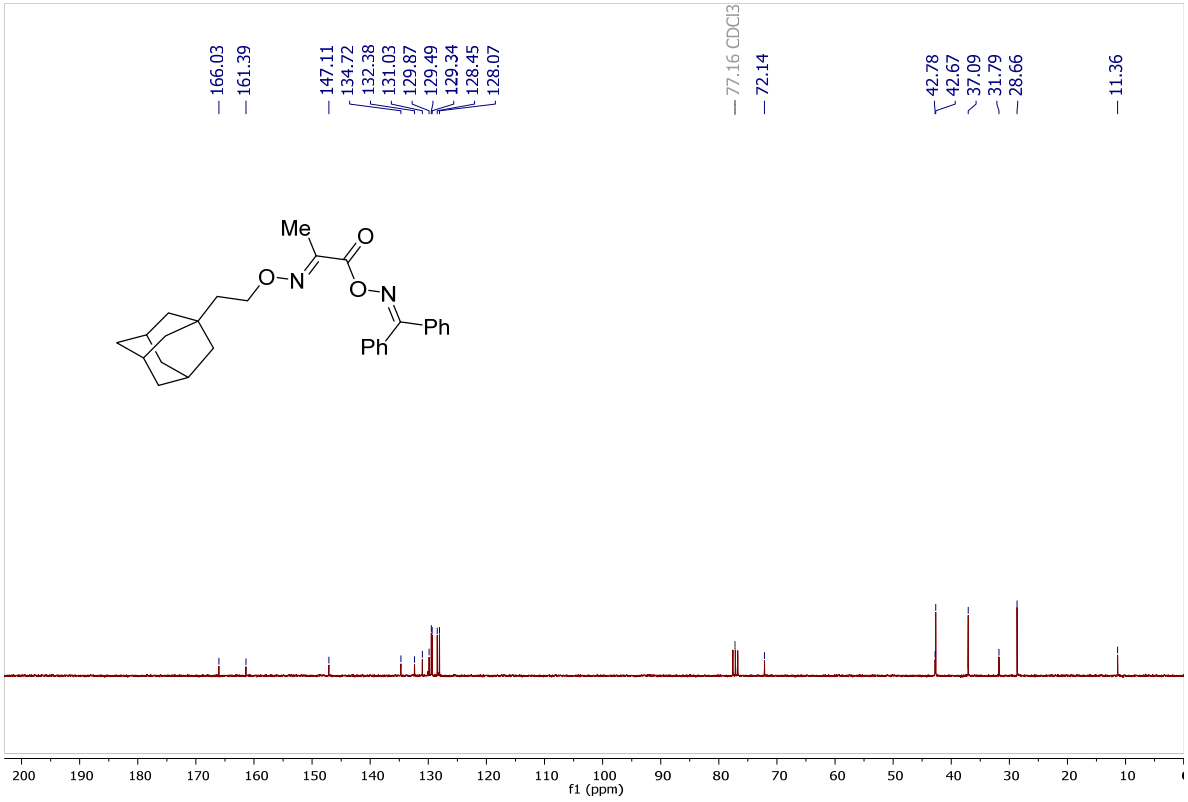
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1y**.



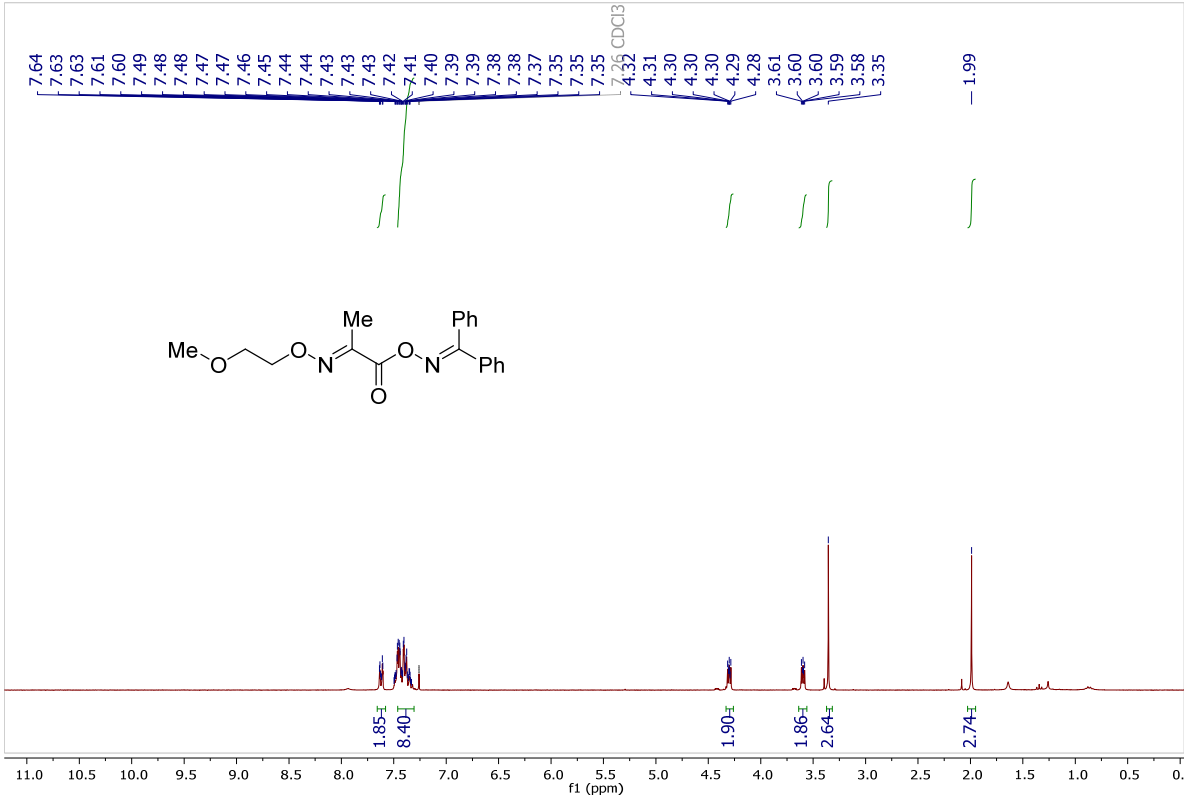
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1y.**



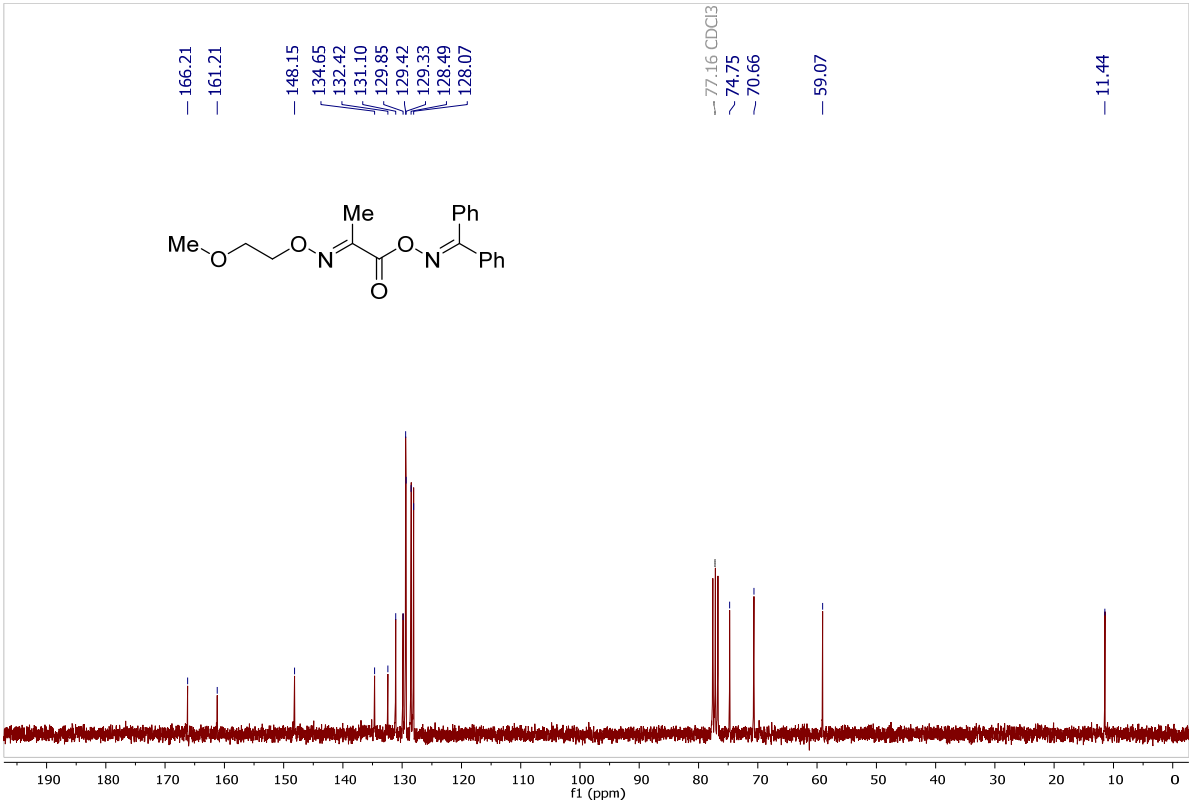
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1z**.



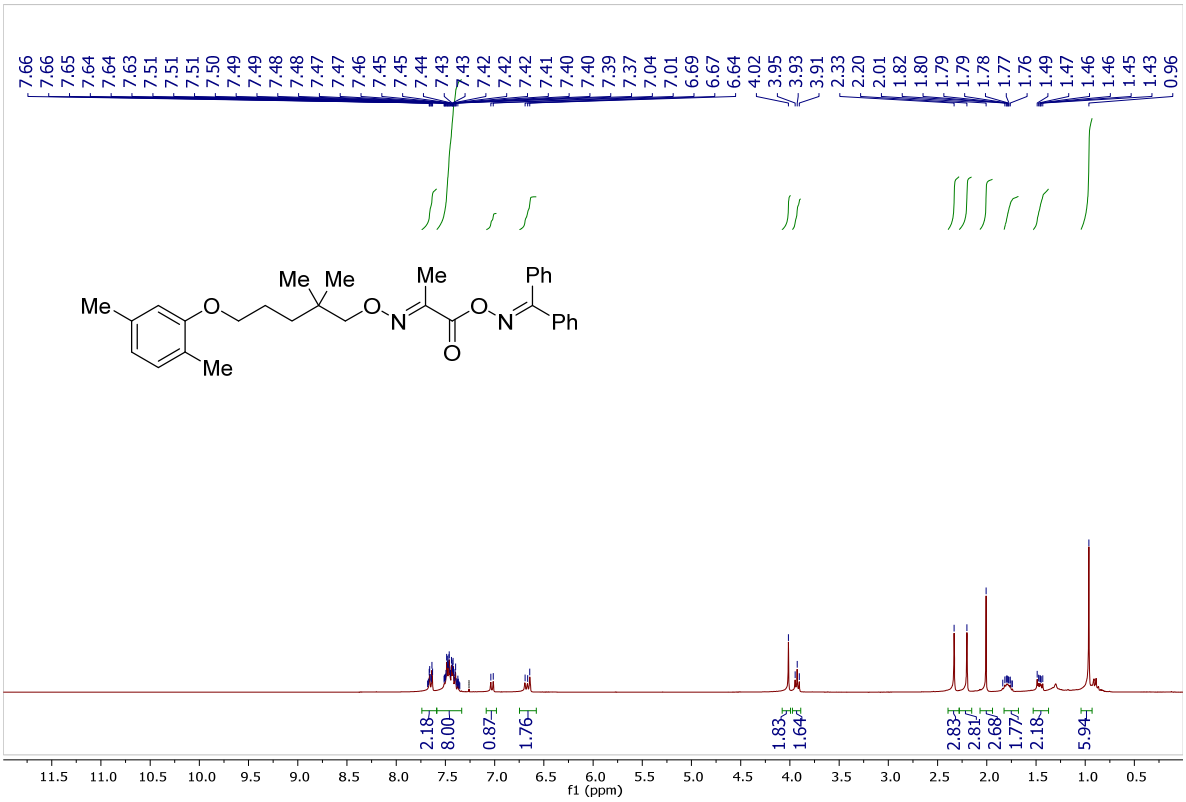
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1z.**



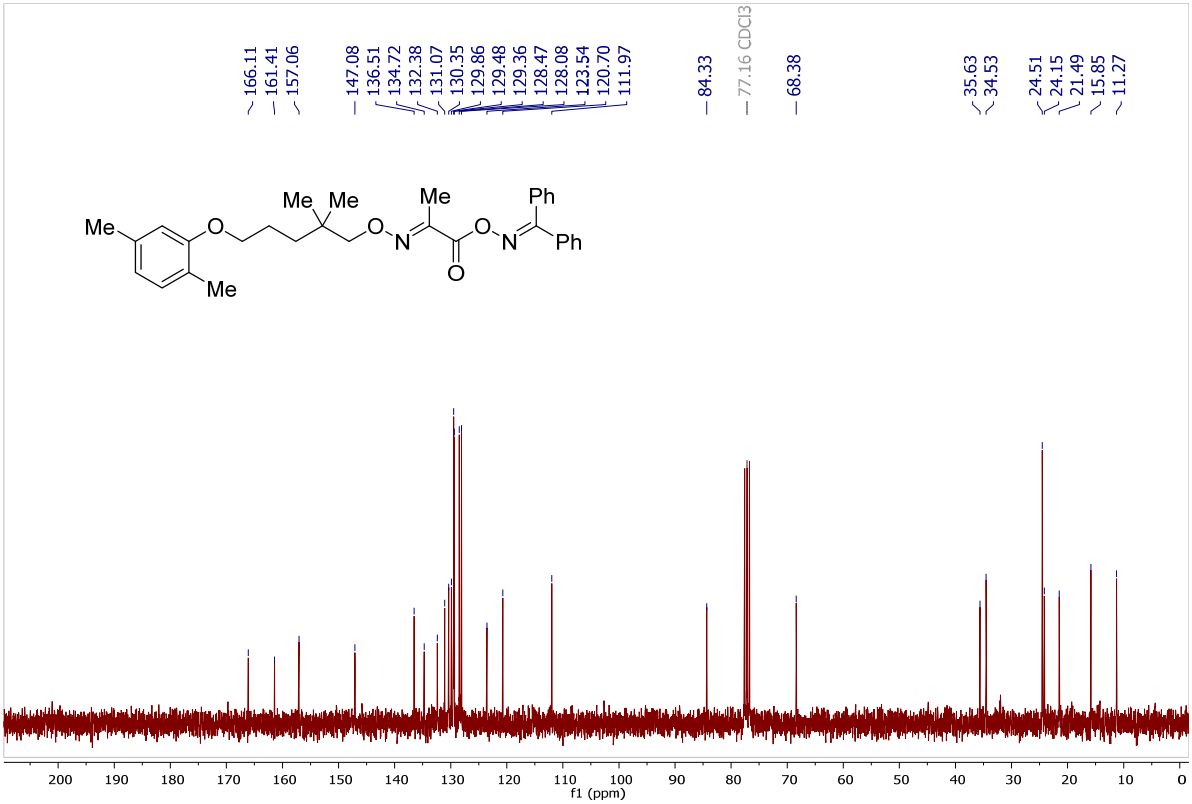
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1aa**.



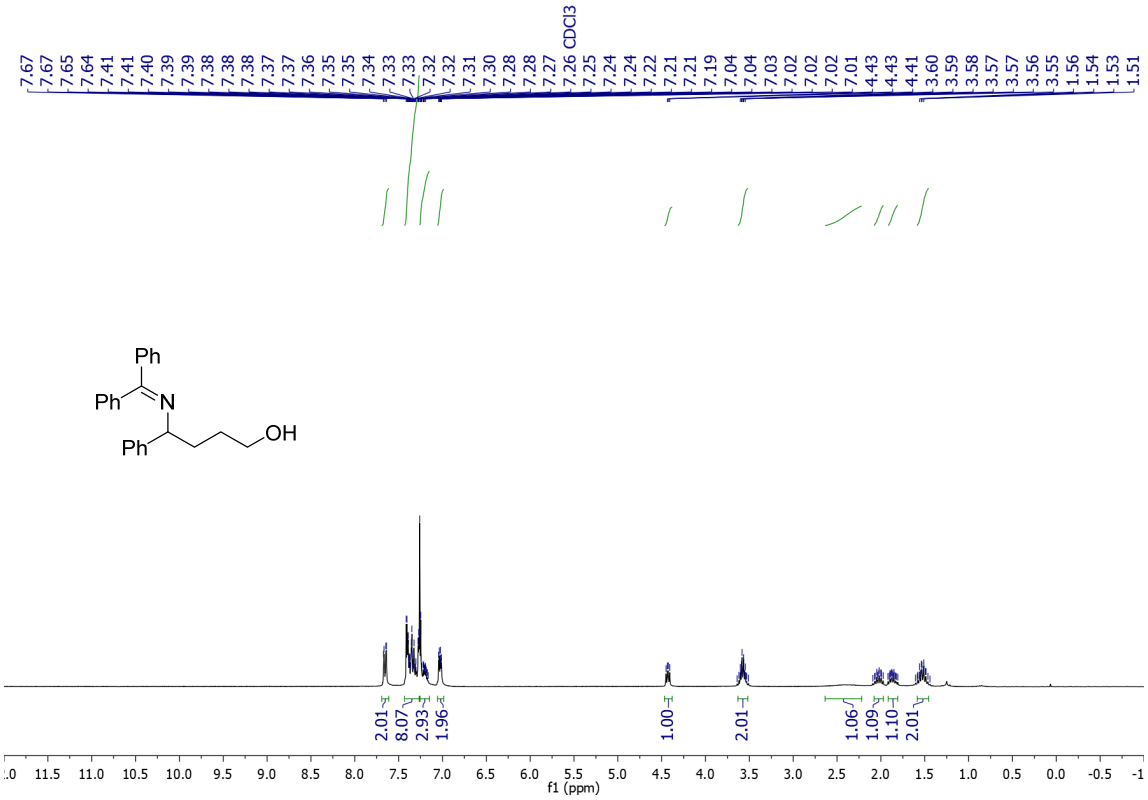
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1aa.**



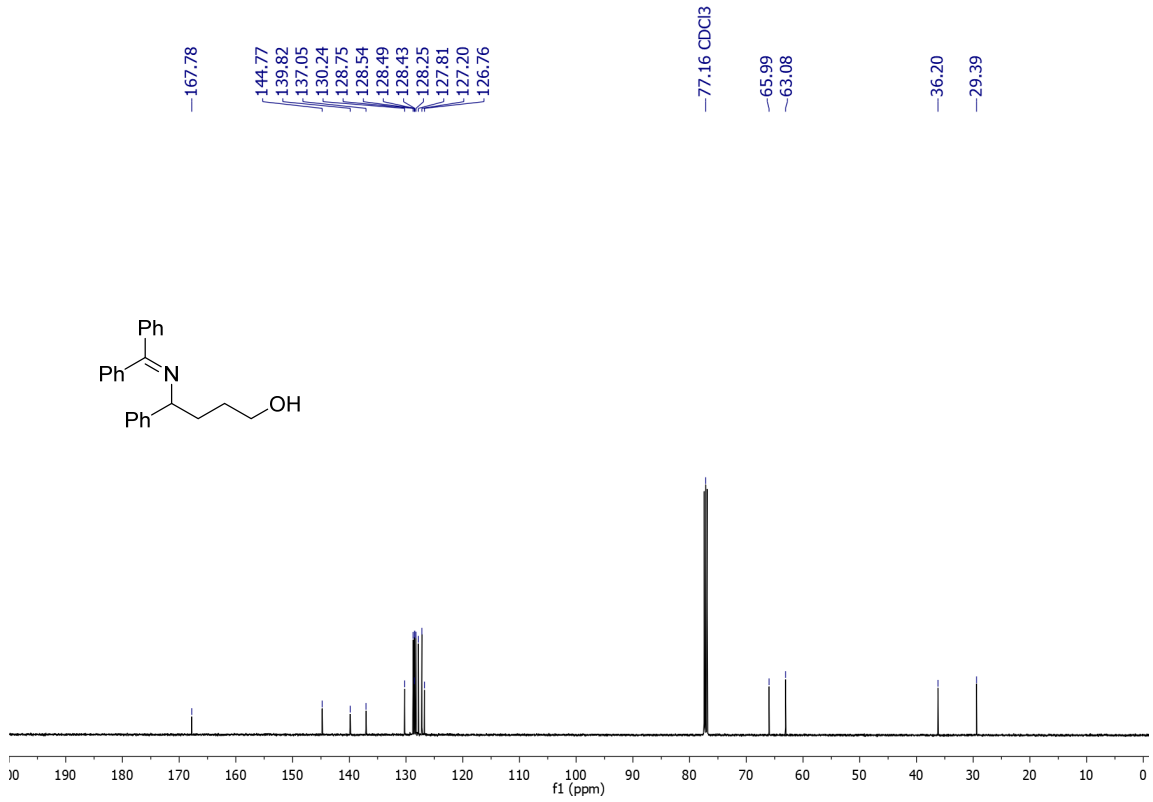
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1ab**.



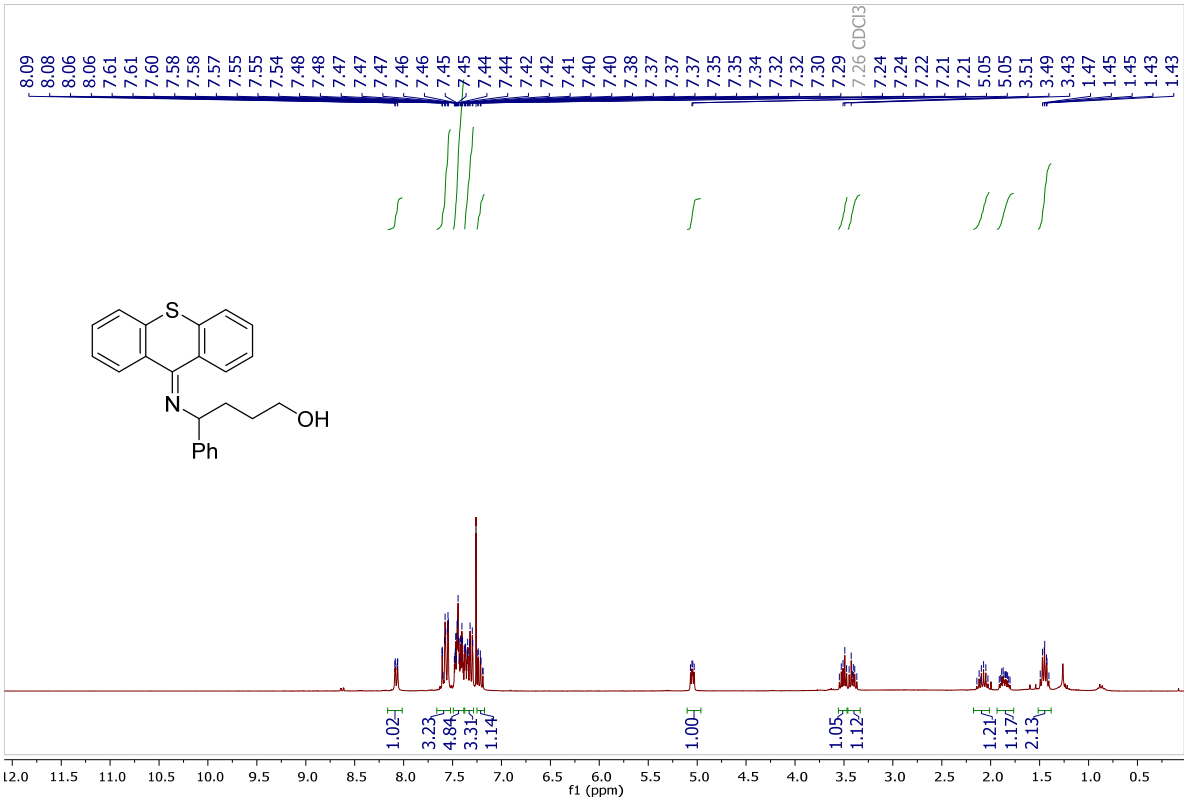
^{13}C NMR (75 MHz, $CDCl_3$) of compound **1ab.**



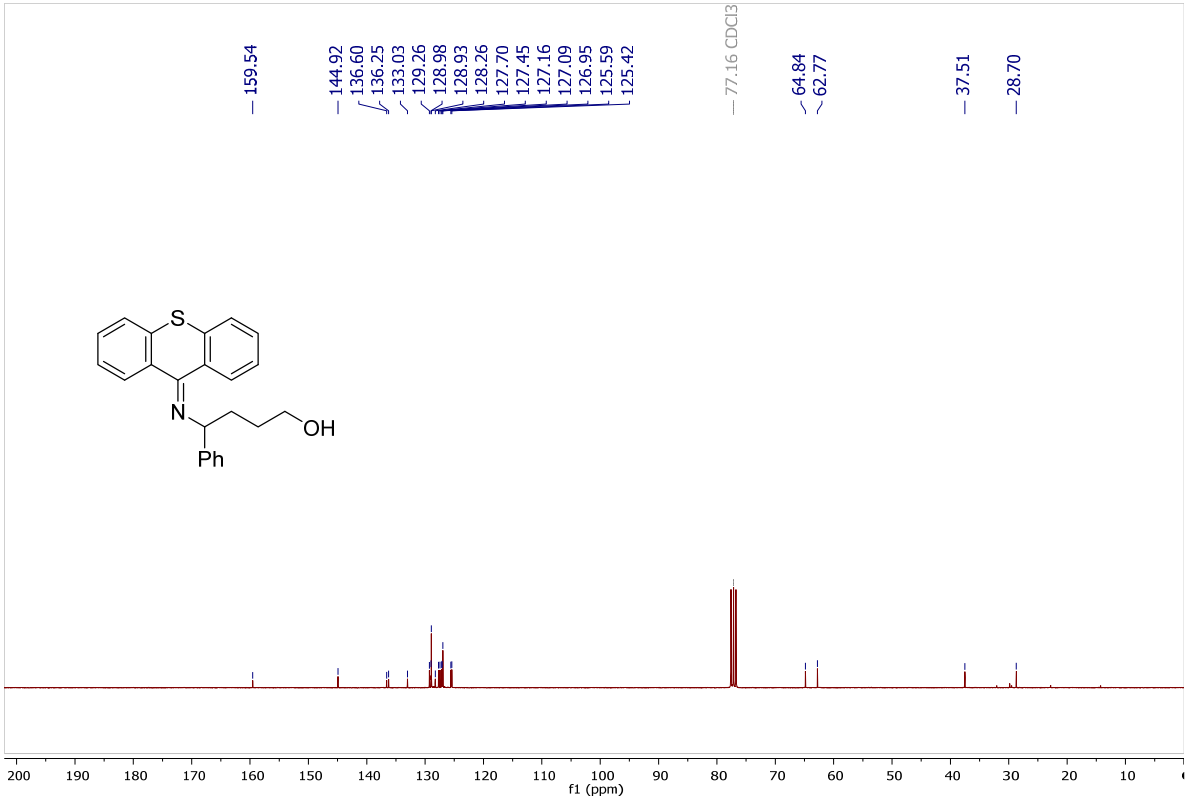
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2a**.



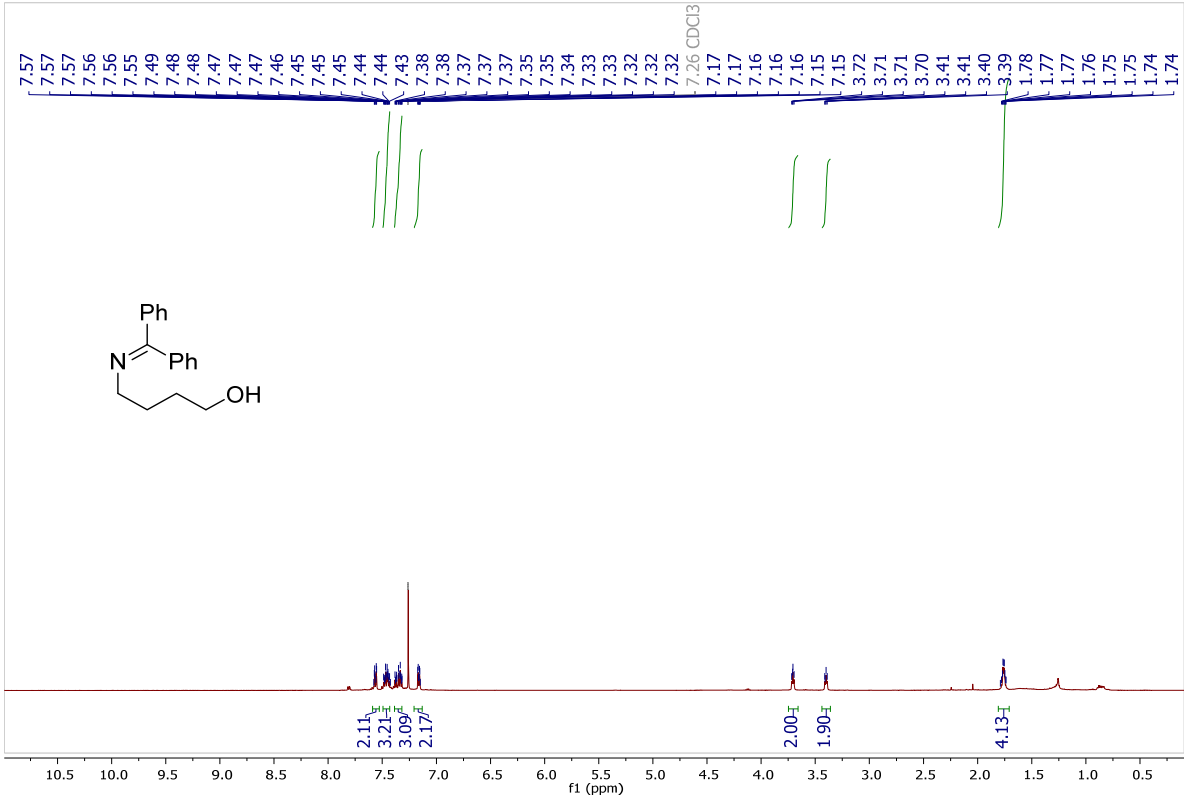
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2a.**



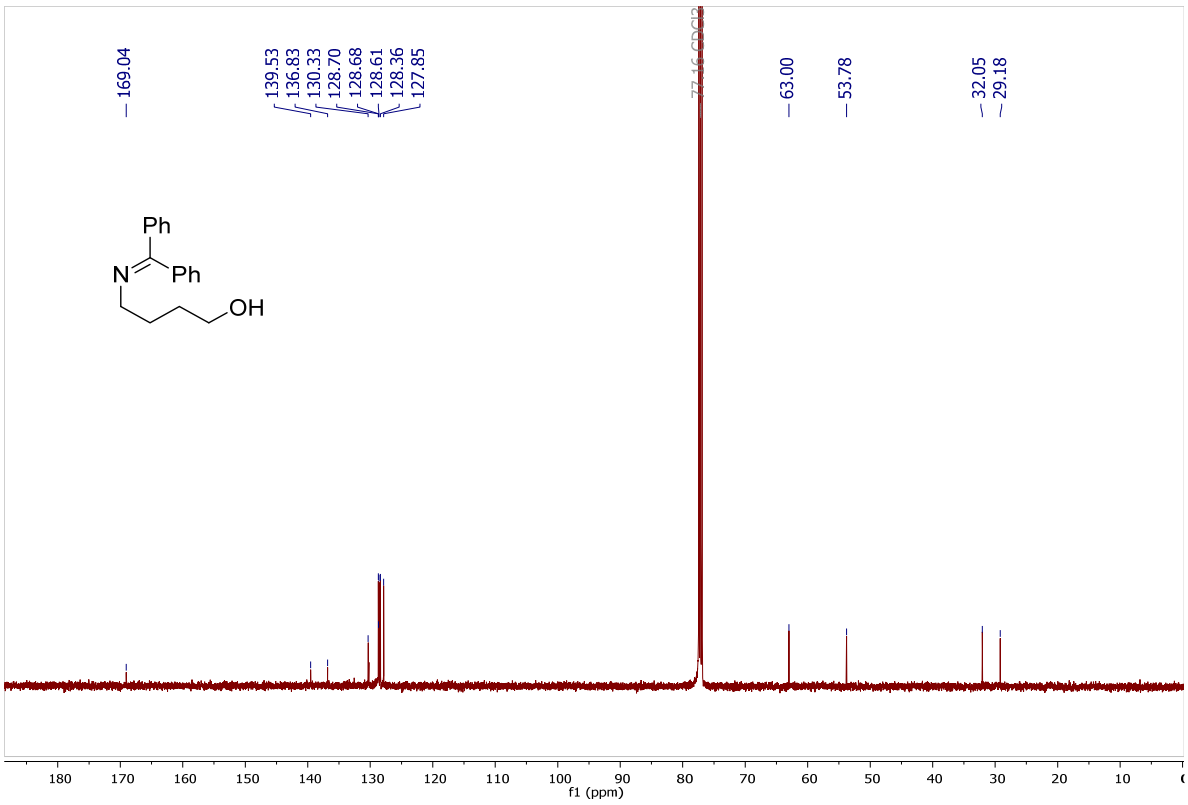
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2b**.



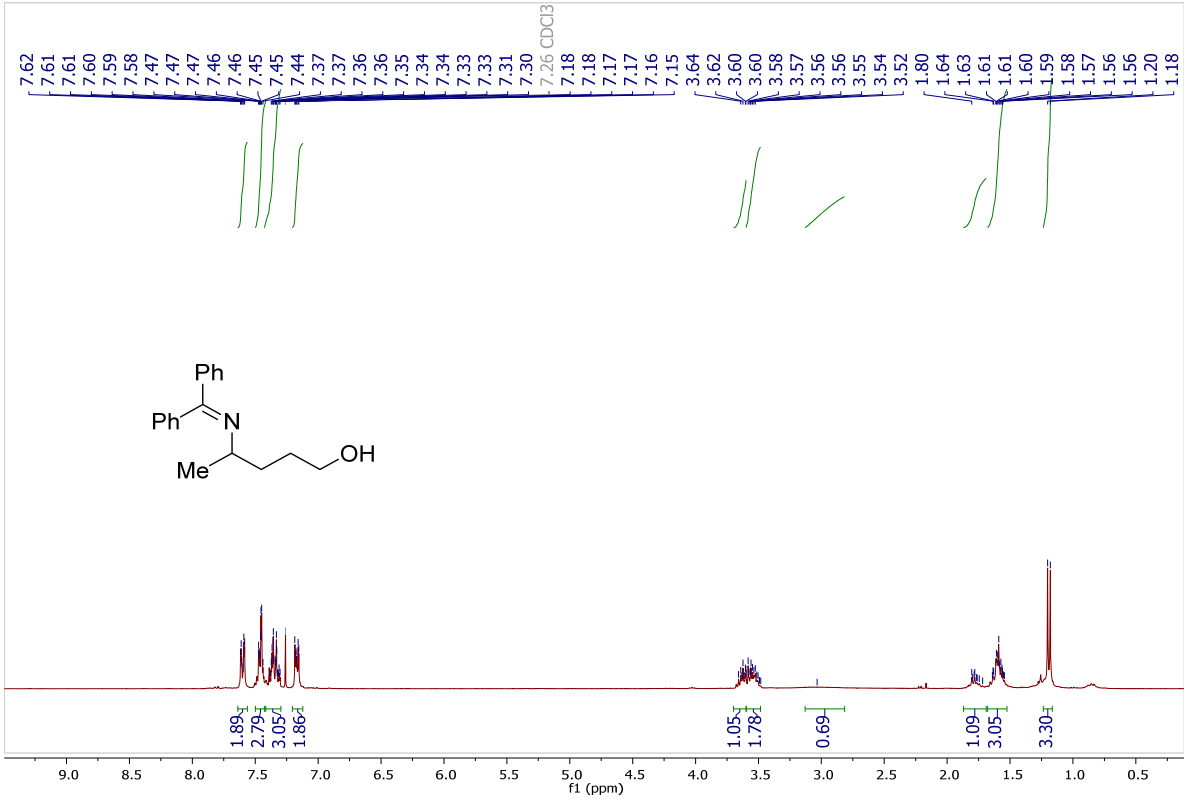
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2b.**



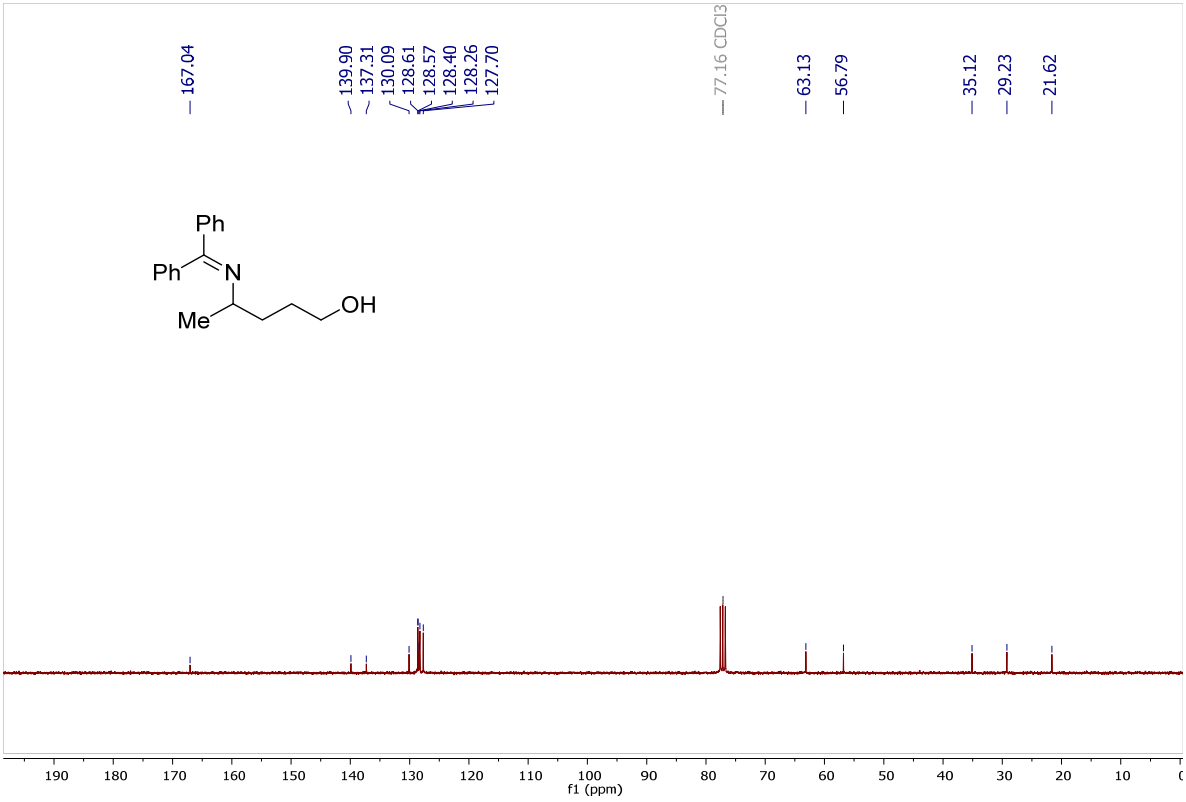
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2d**.



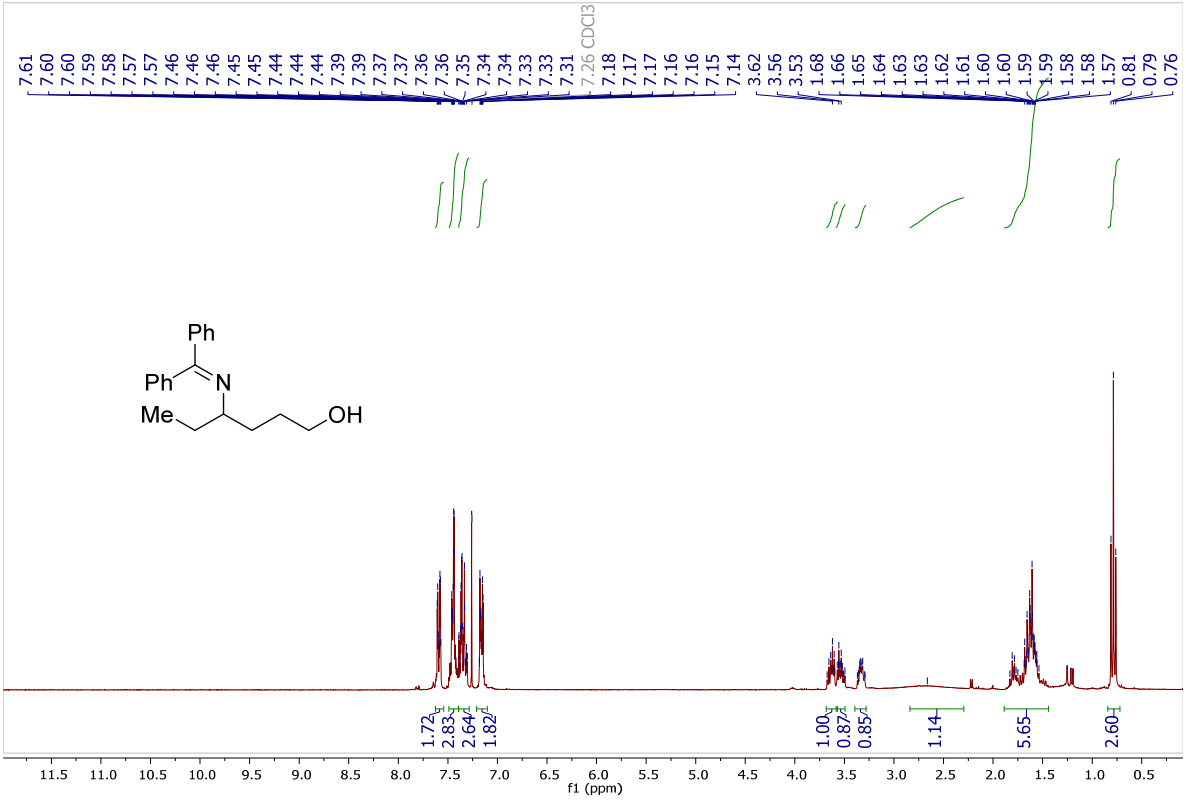
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2d.**



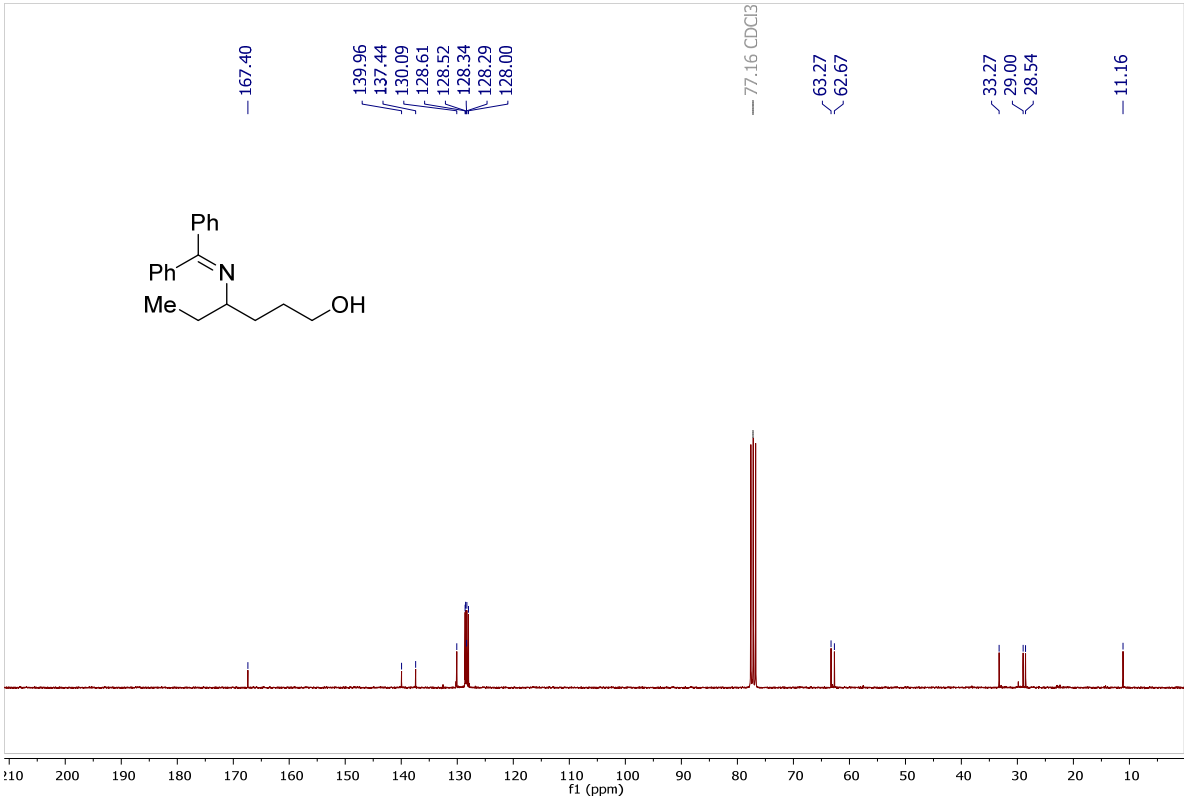
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2e**.



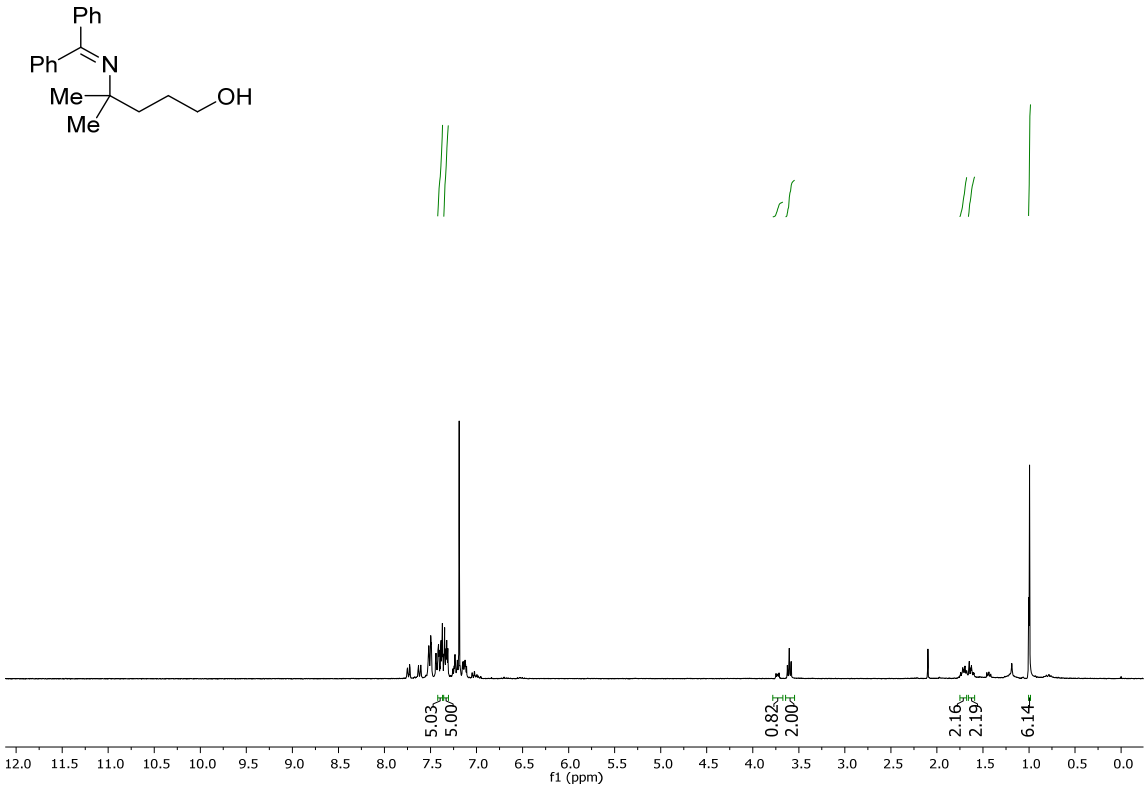
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2e.**



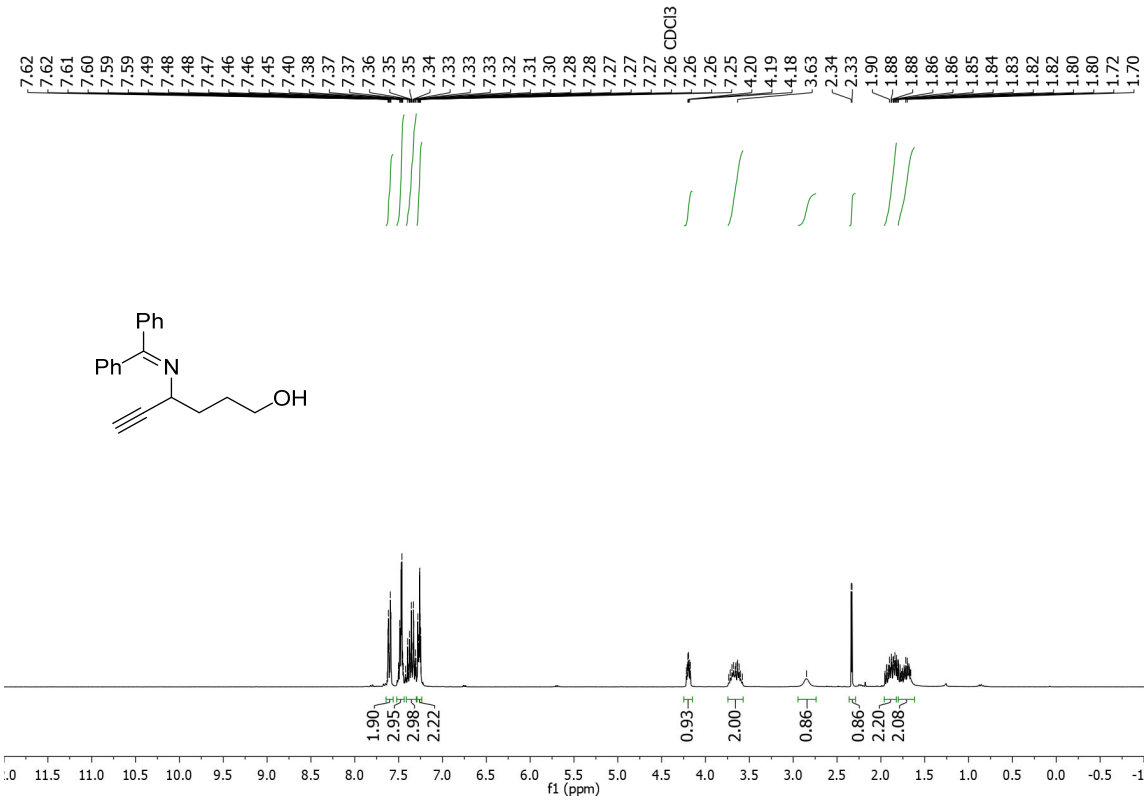
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2f**.



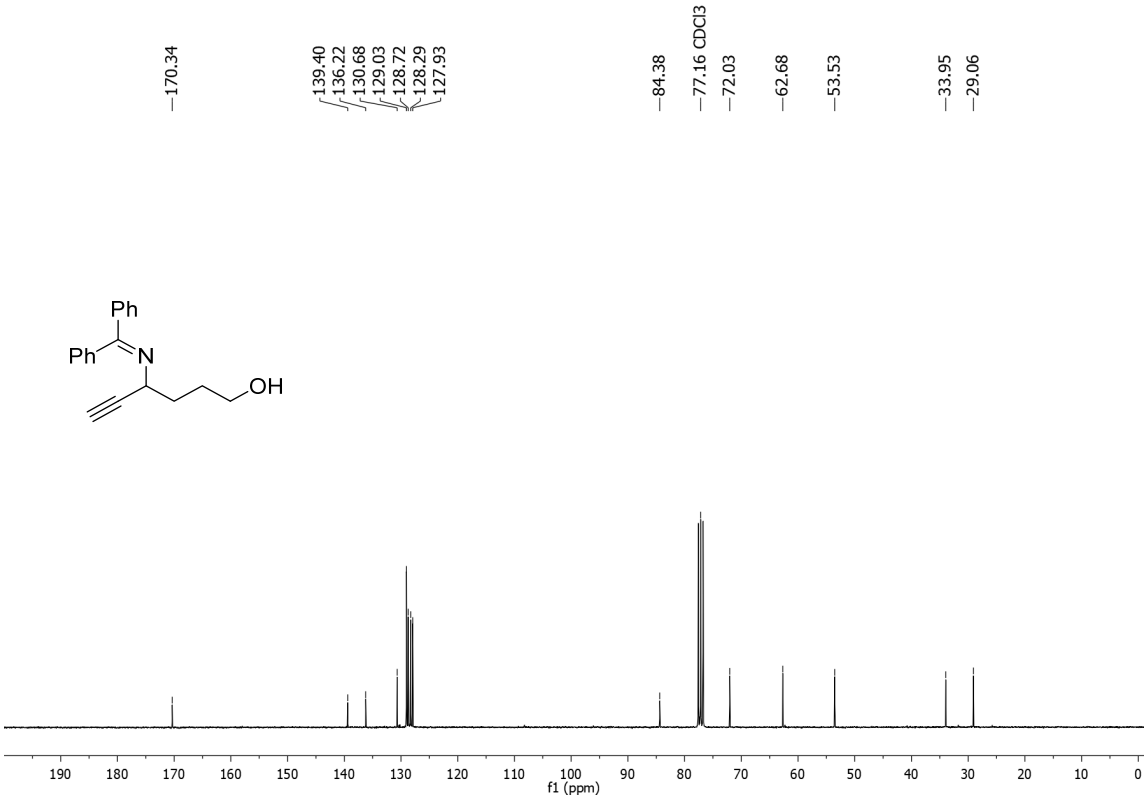
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2f.**



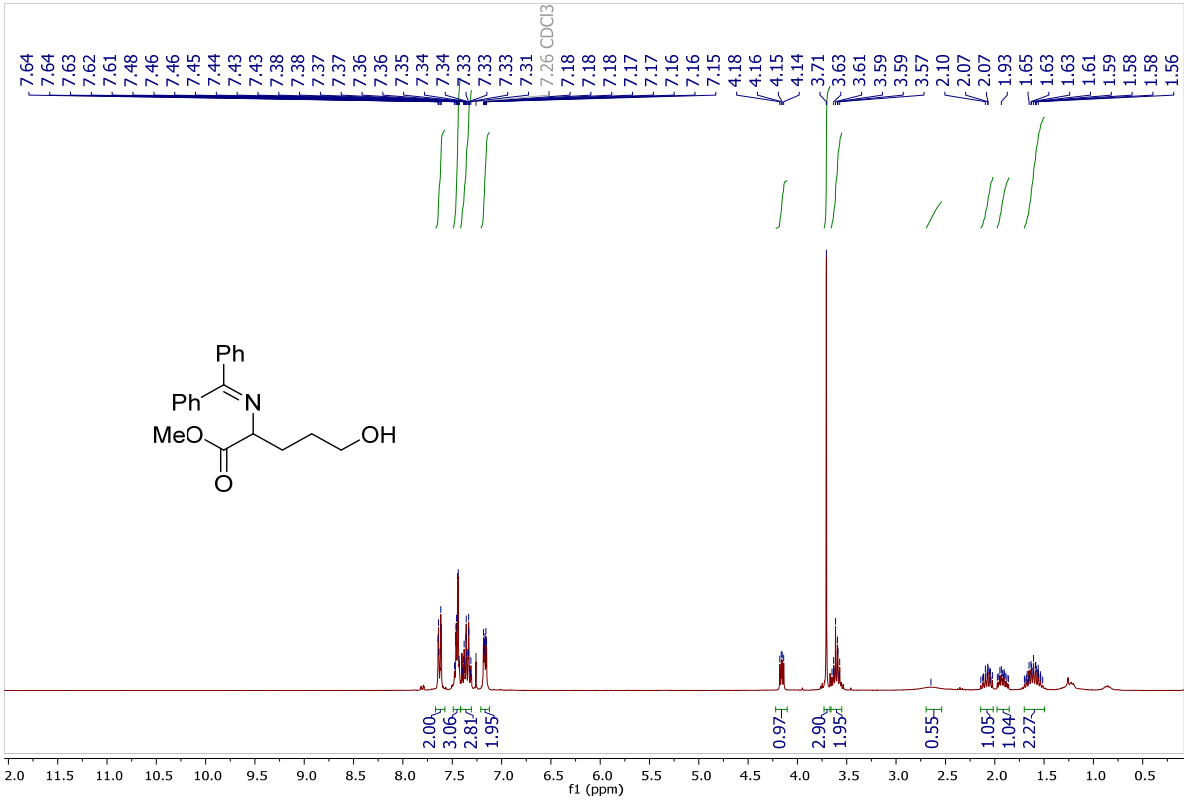
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2g**.



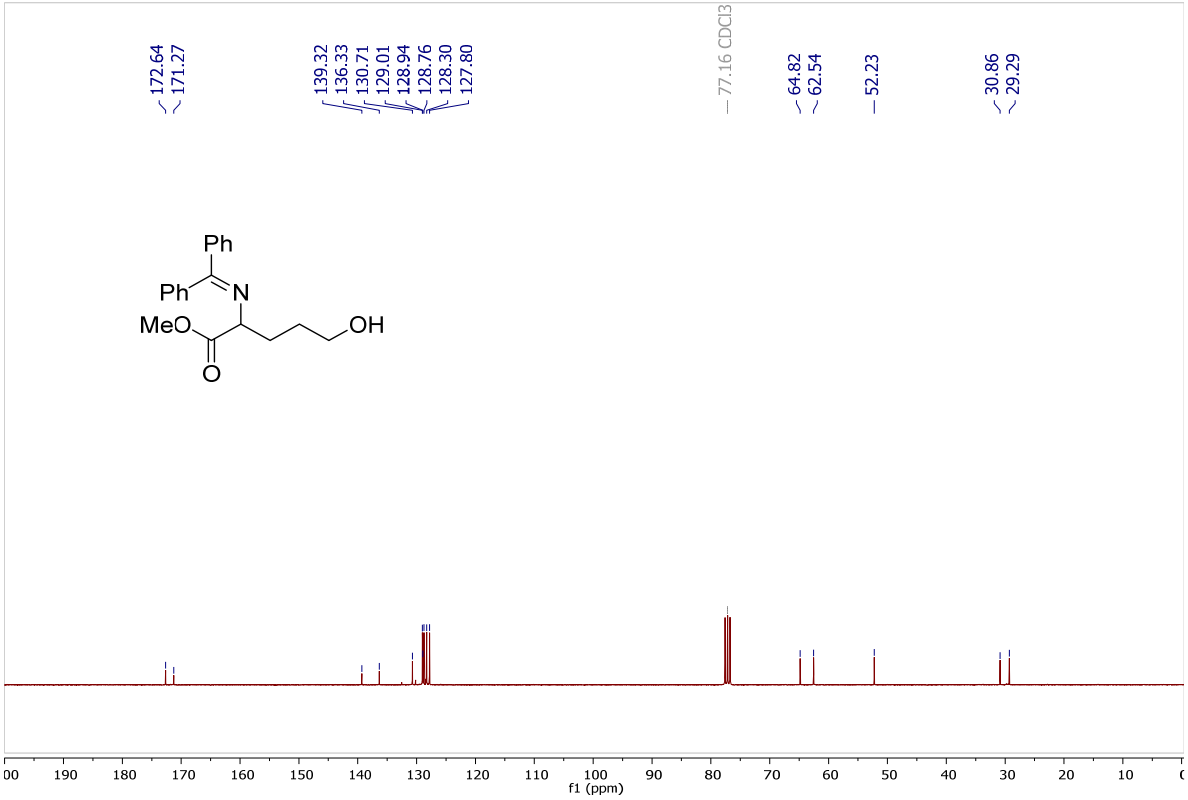
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2g**.



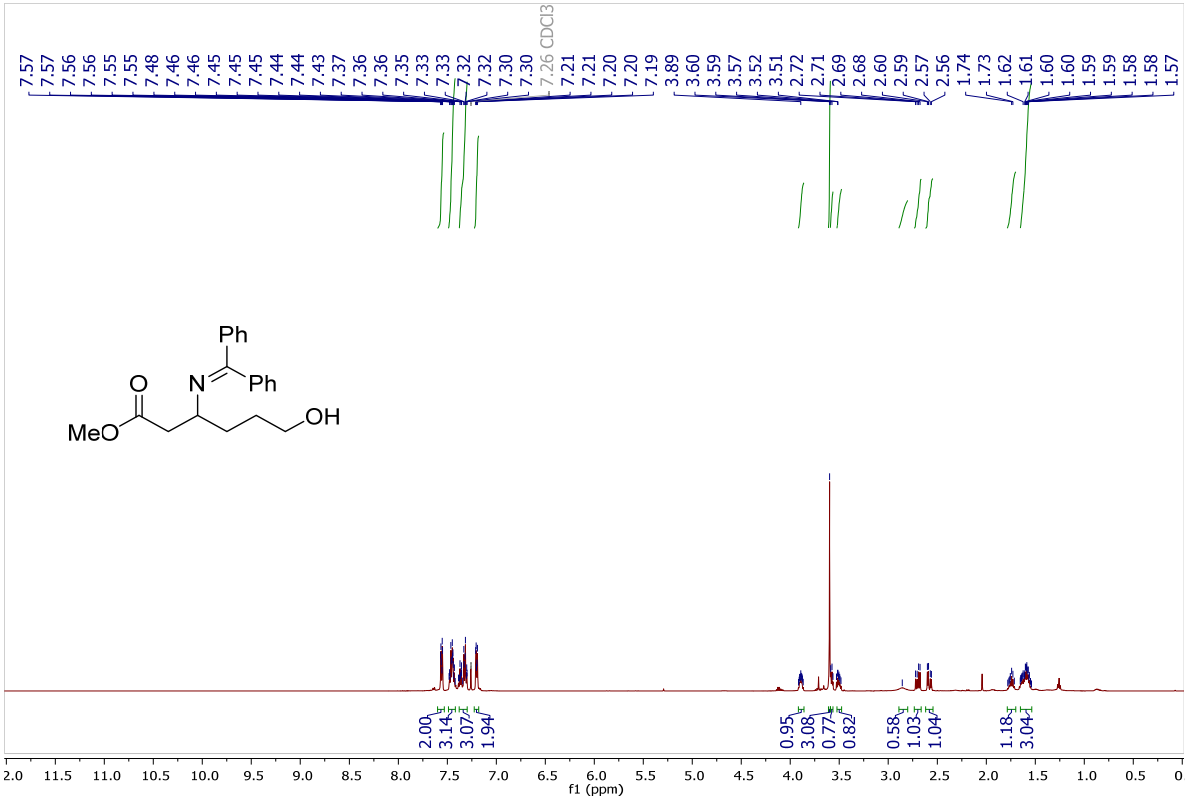
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2h.**



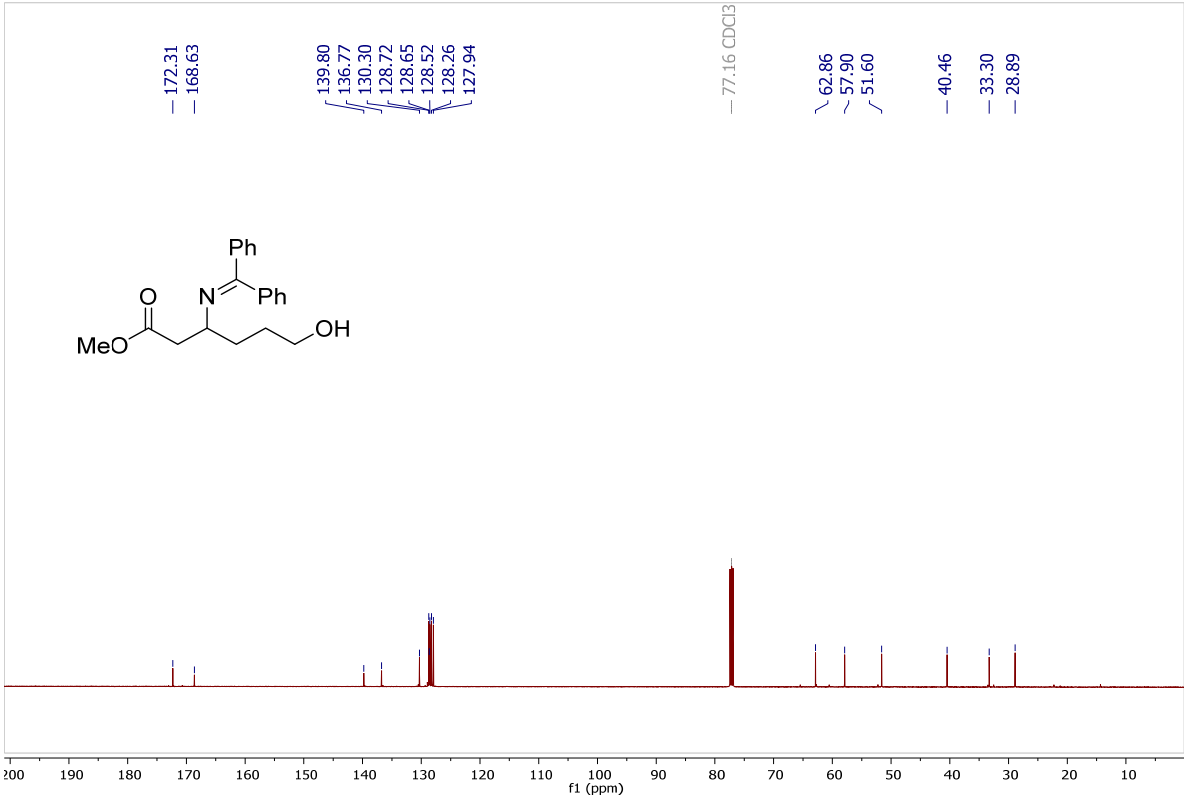
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2i**.



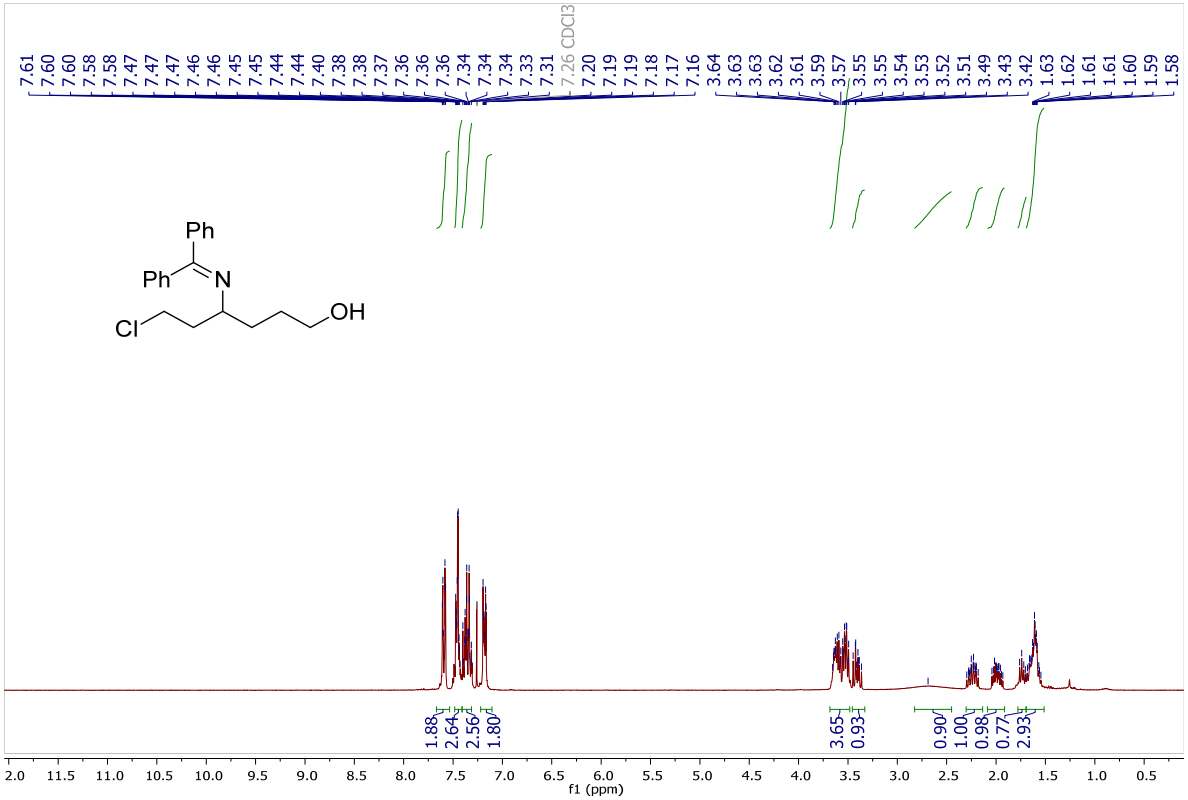
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2i.**



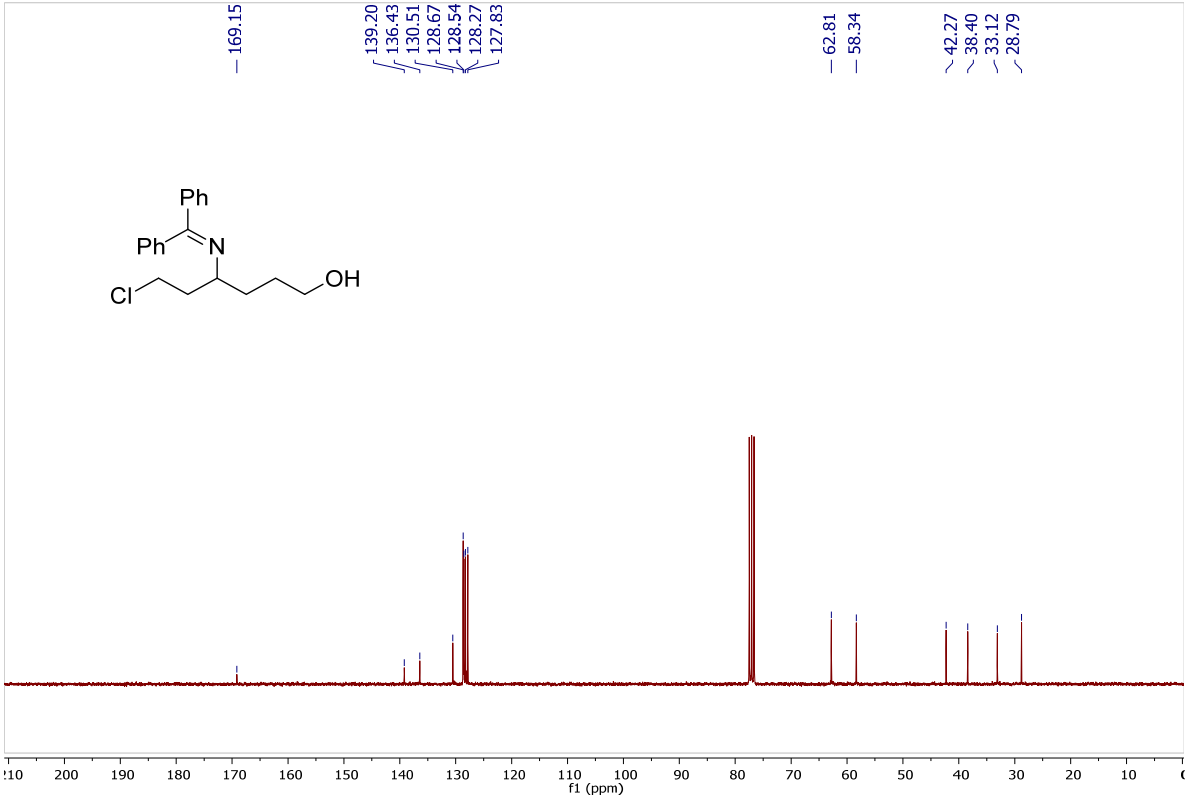
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2j**.



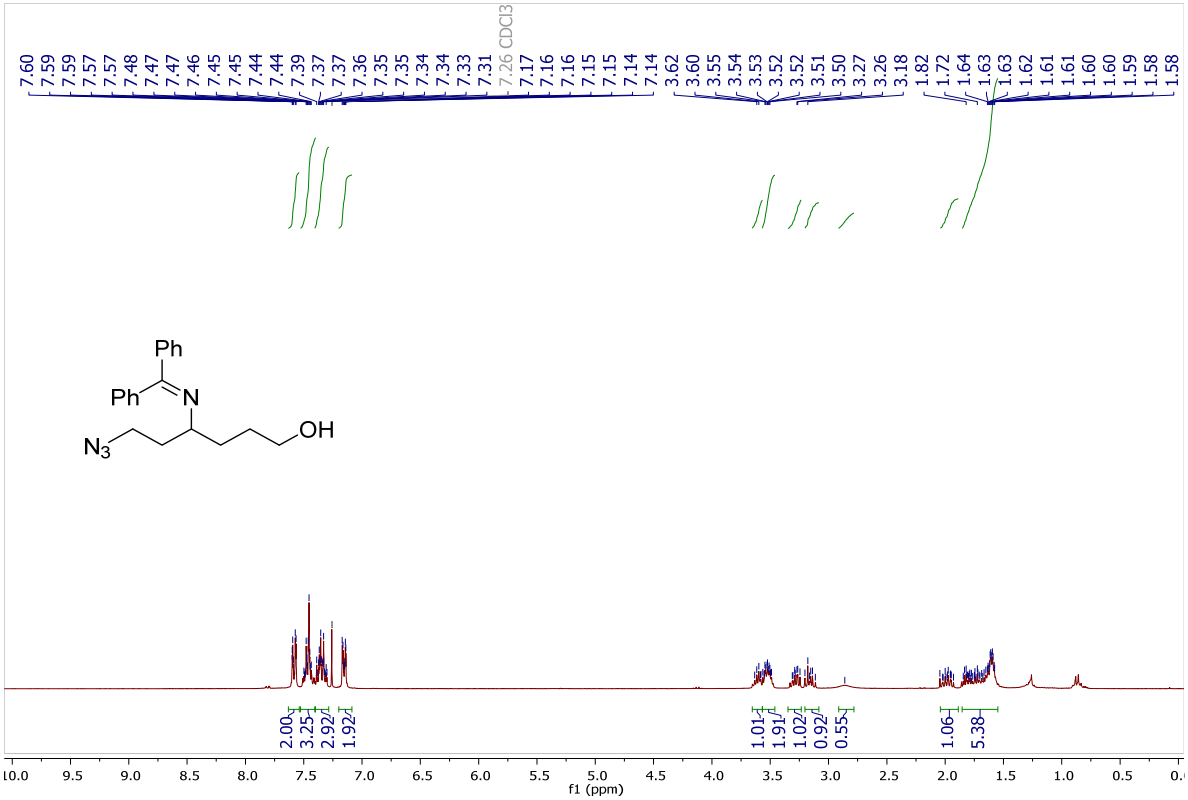
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2j.**



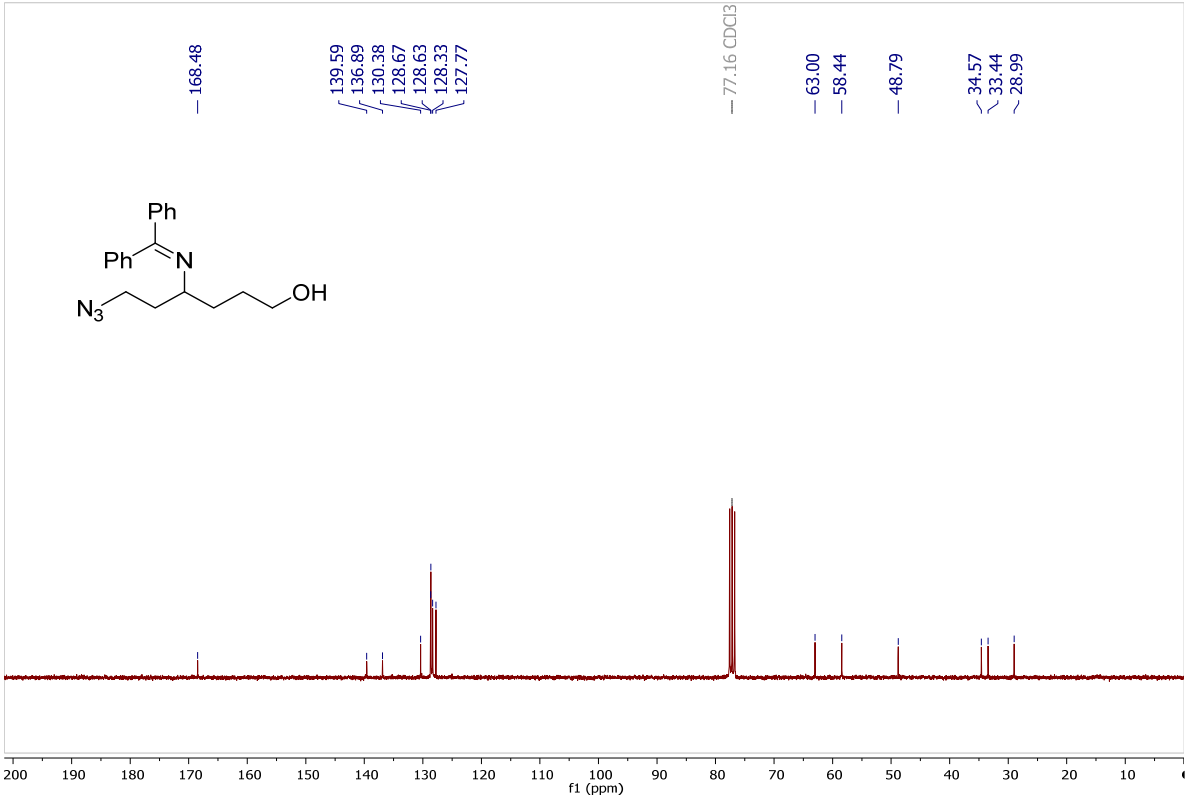
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2k**.



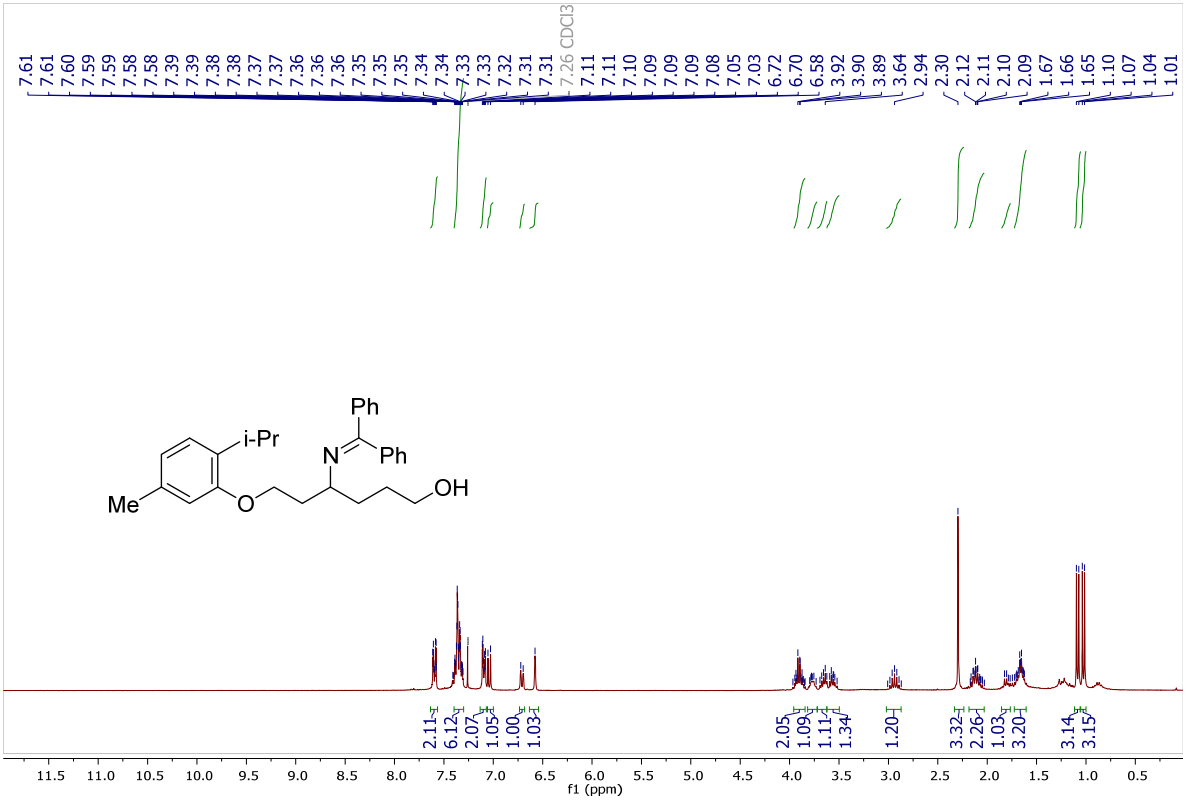
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2k.**



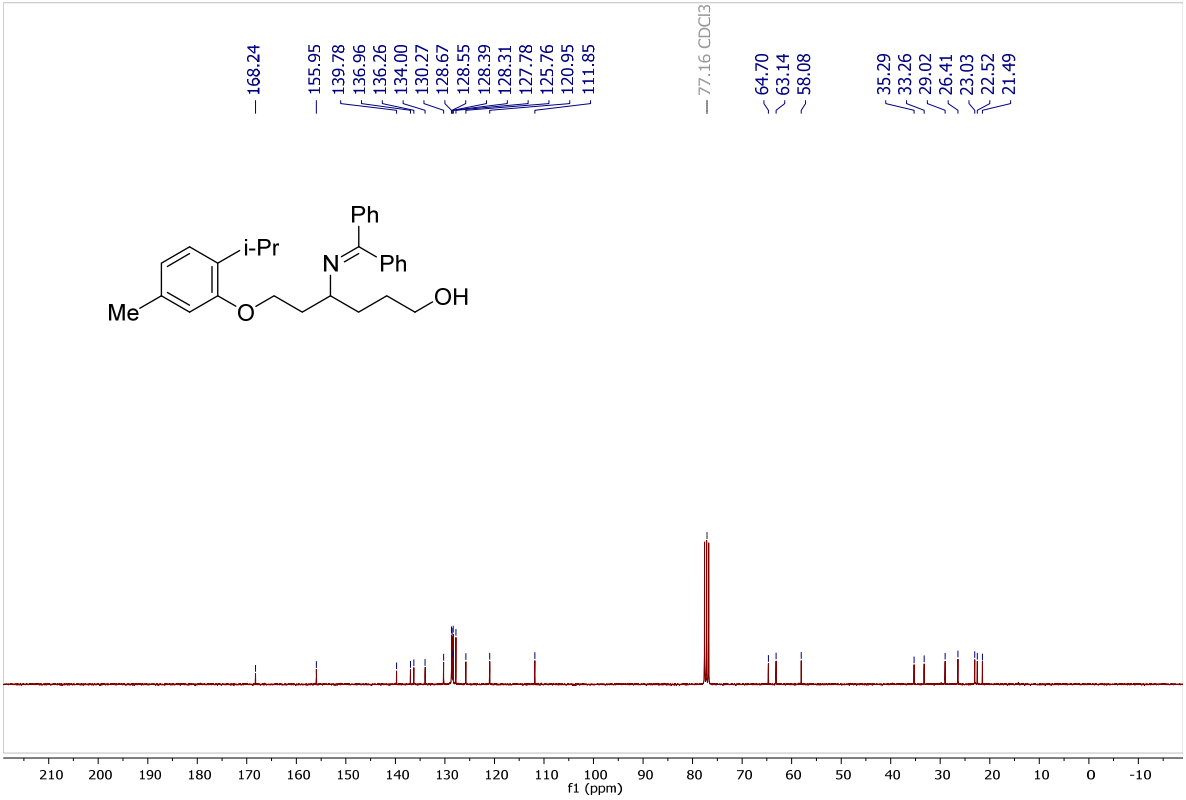
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2l**.



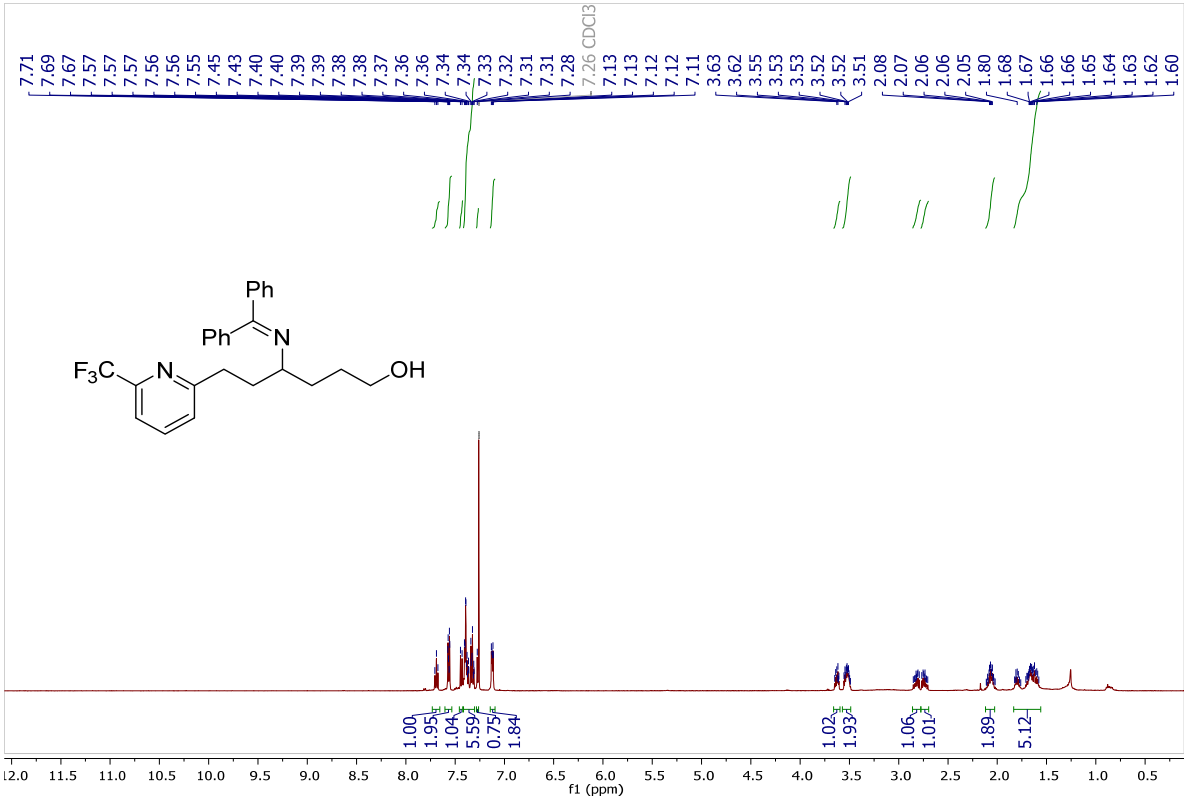
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2l.**



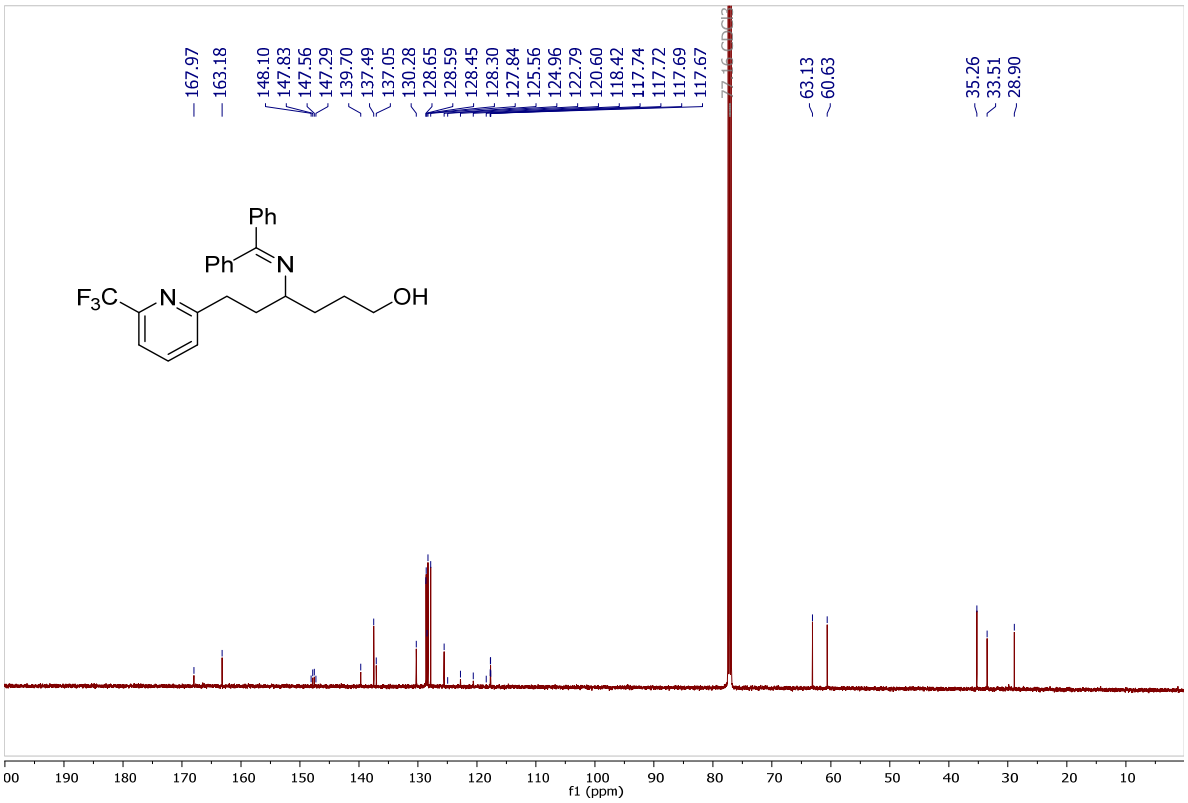
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2m**.



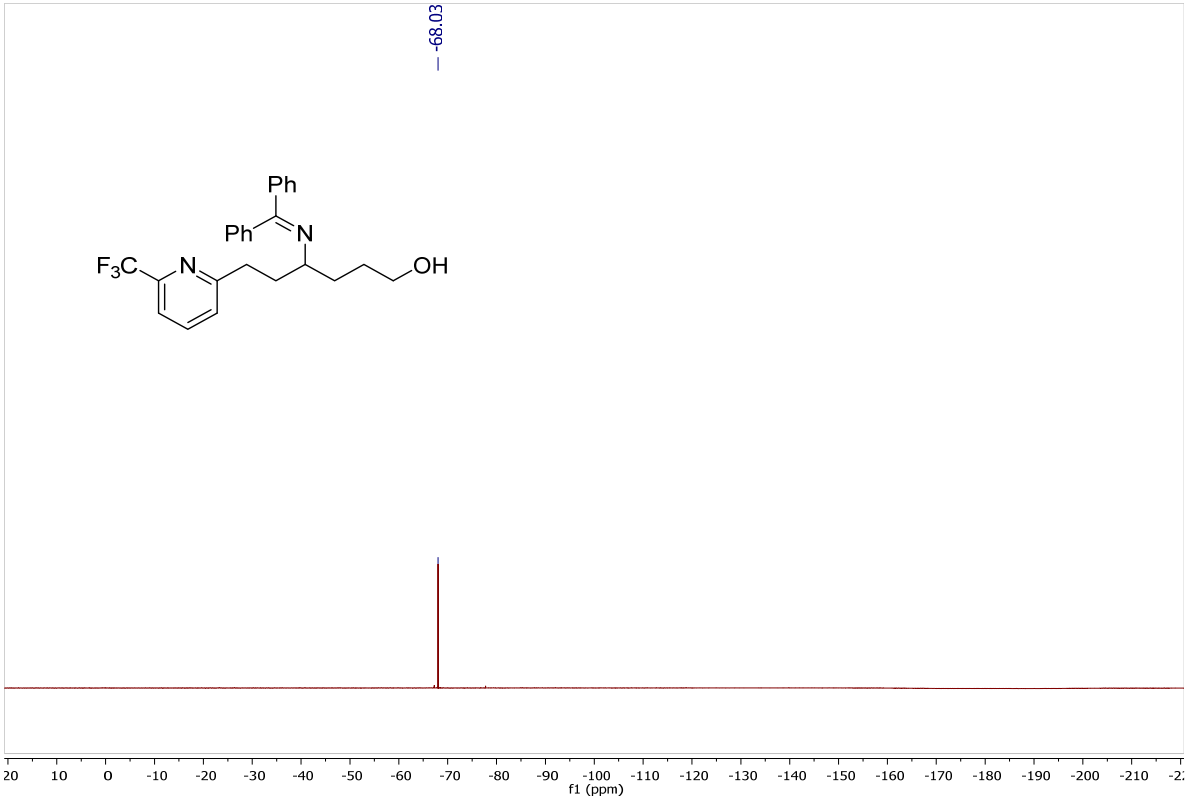
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2m.**



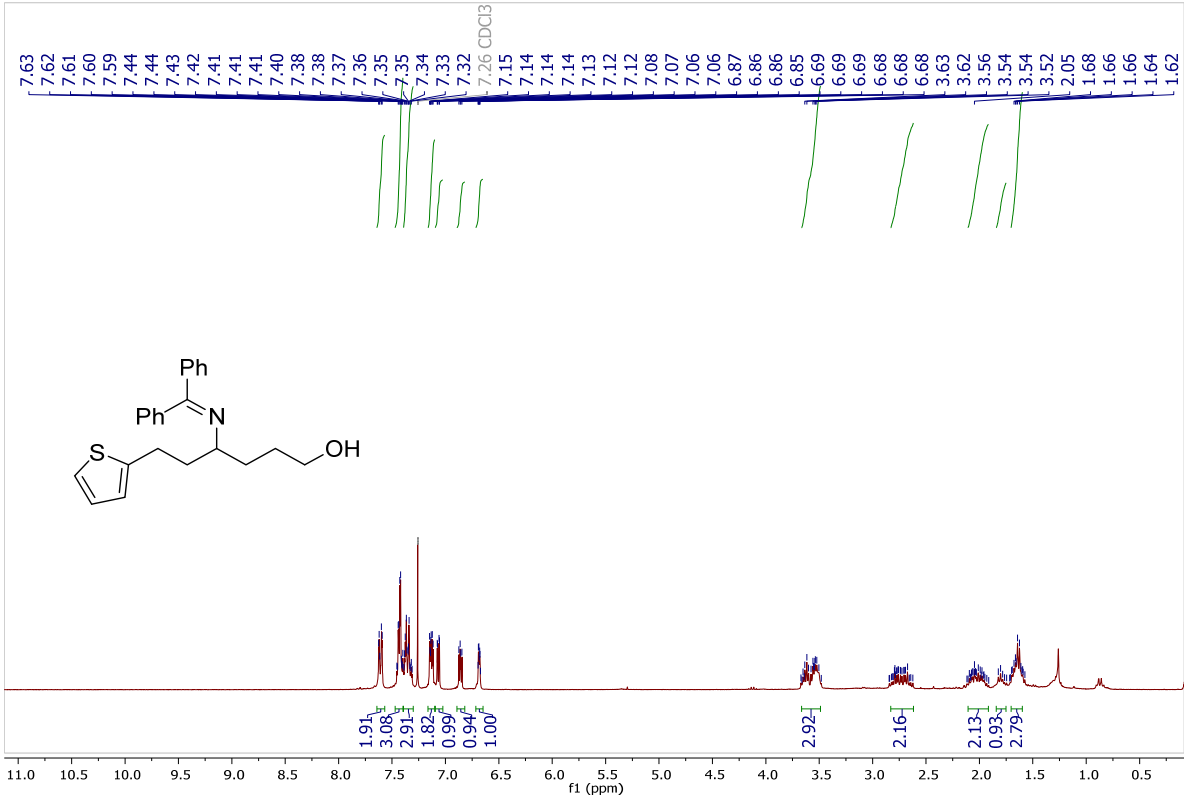
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2n**.



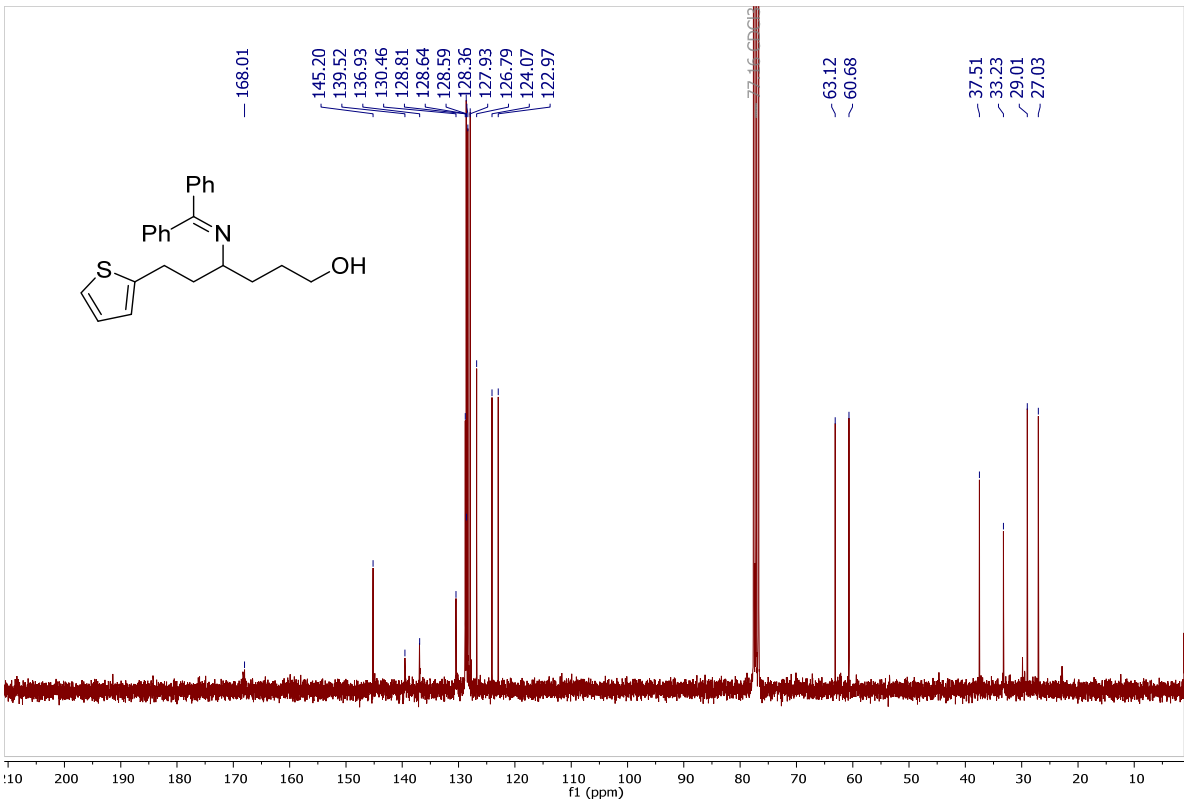
^{13}C NMR (125 MHz, $CDCl_3$) of compound **2n.**



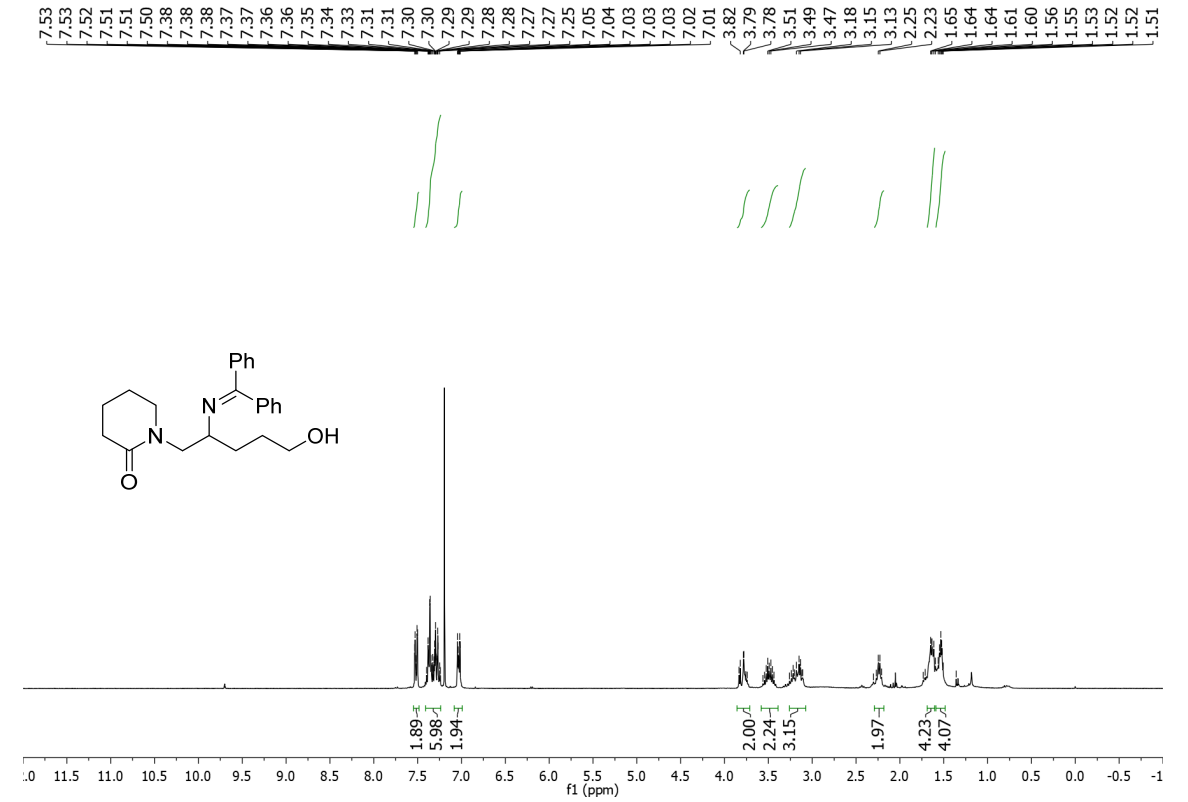
^{19}F NMR (282 MHz, $CDCl_3$) of compound **2n.**



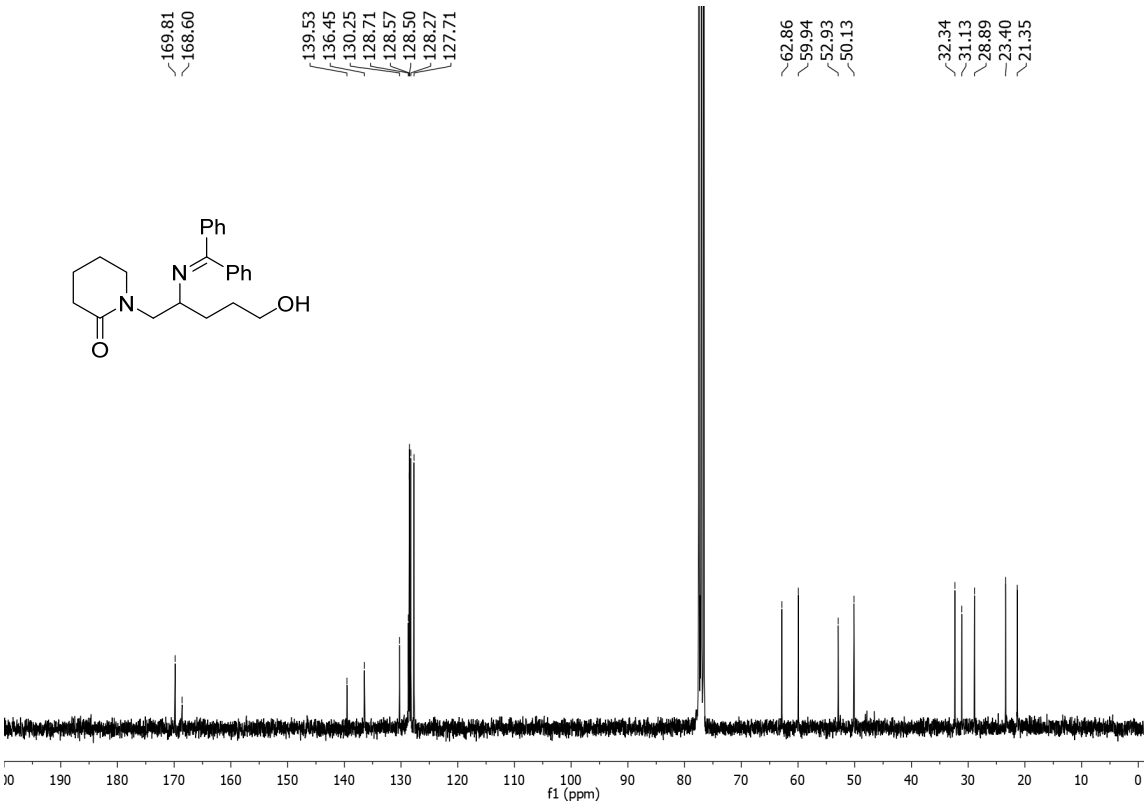
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2o**.



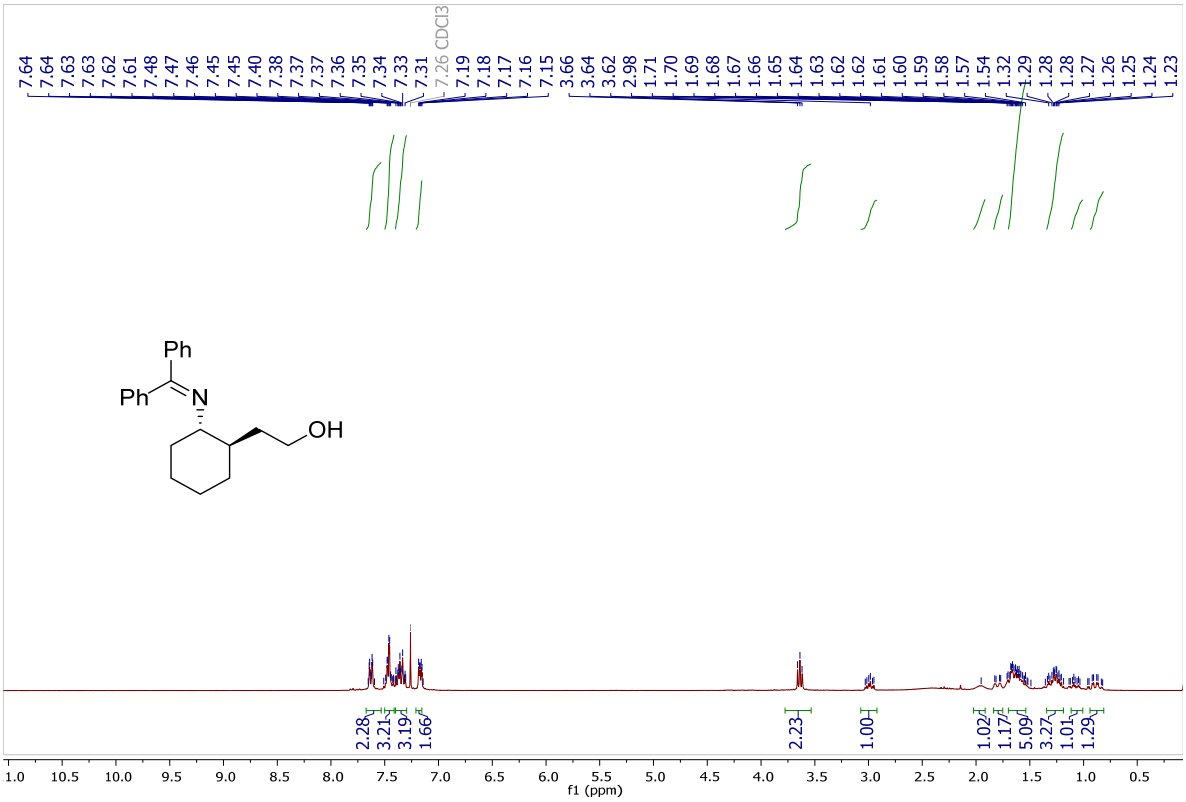
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2o.**



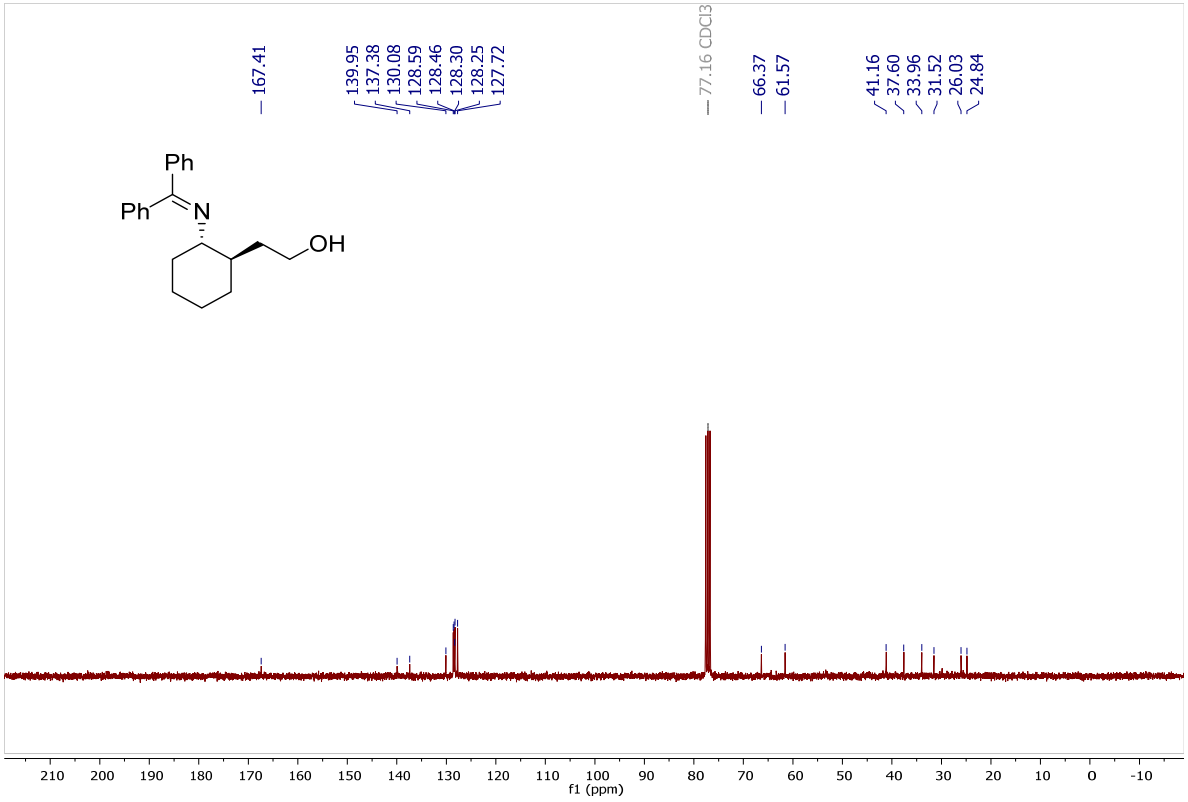
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2p**.



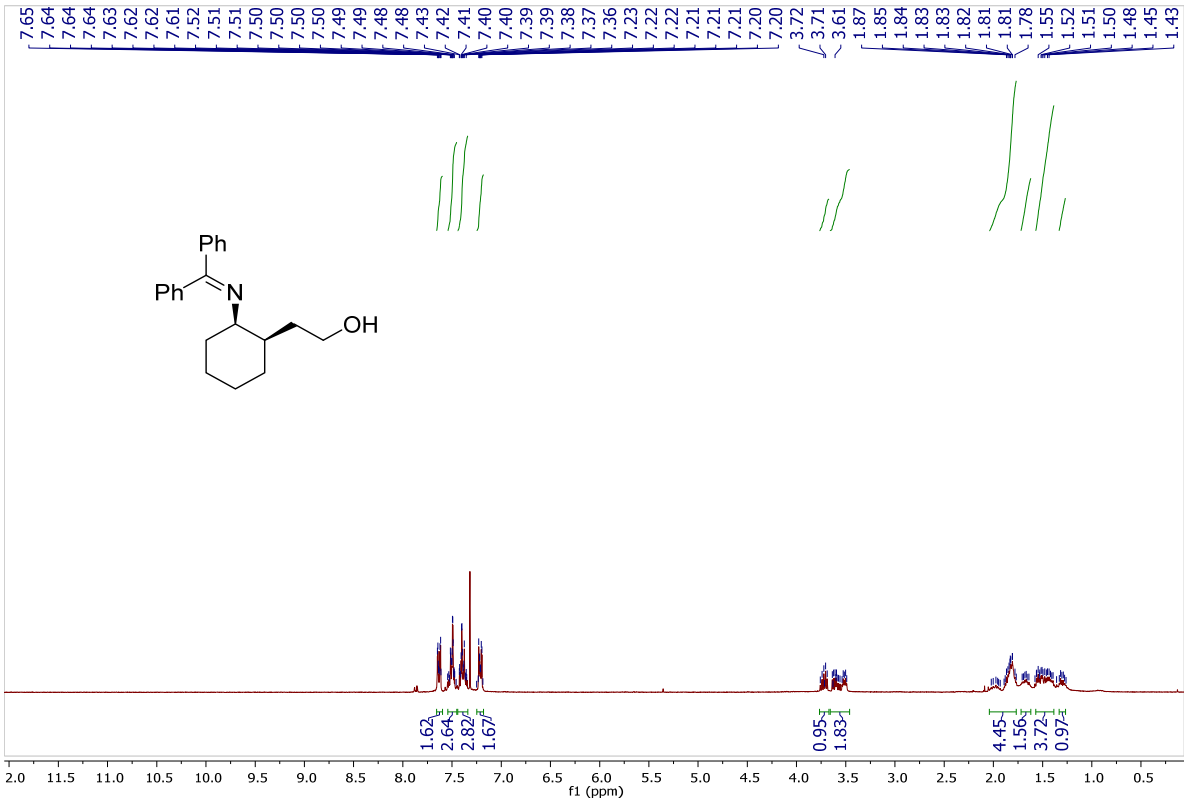
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2p.**



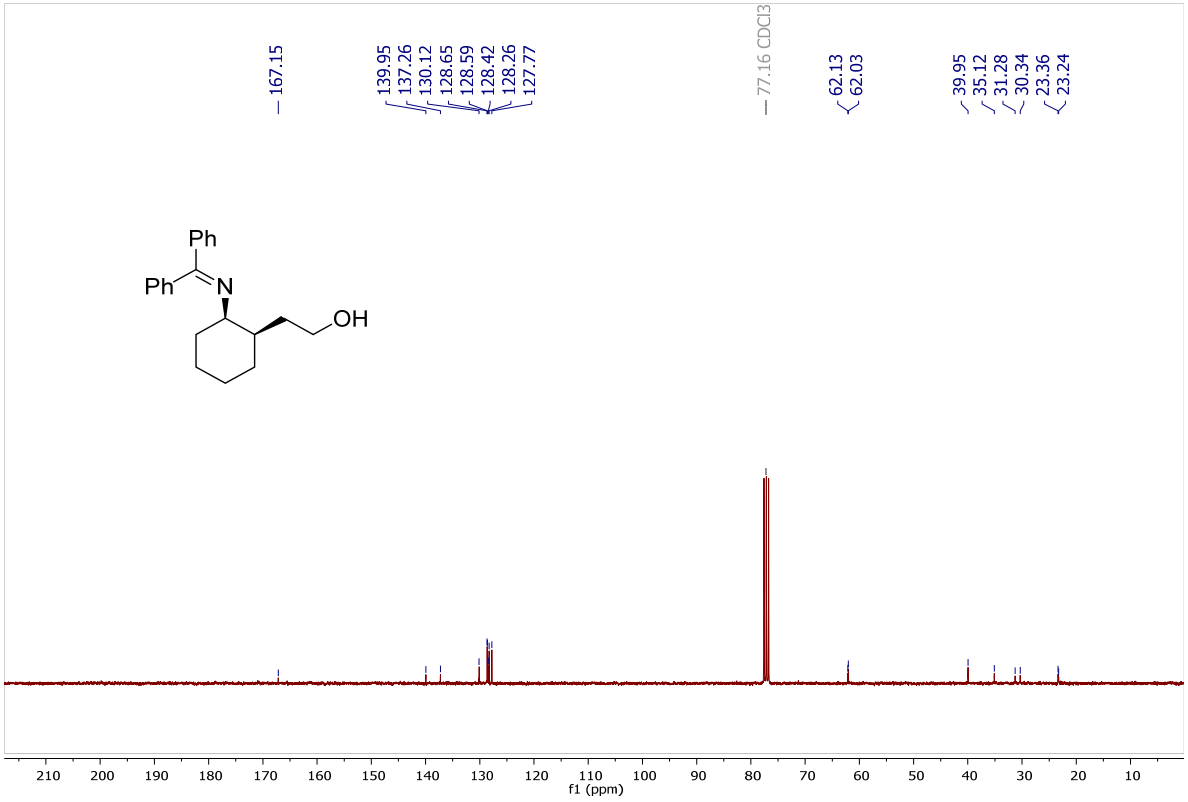
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2q**.



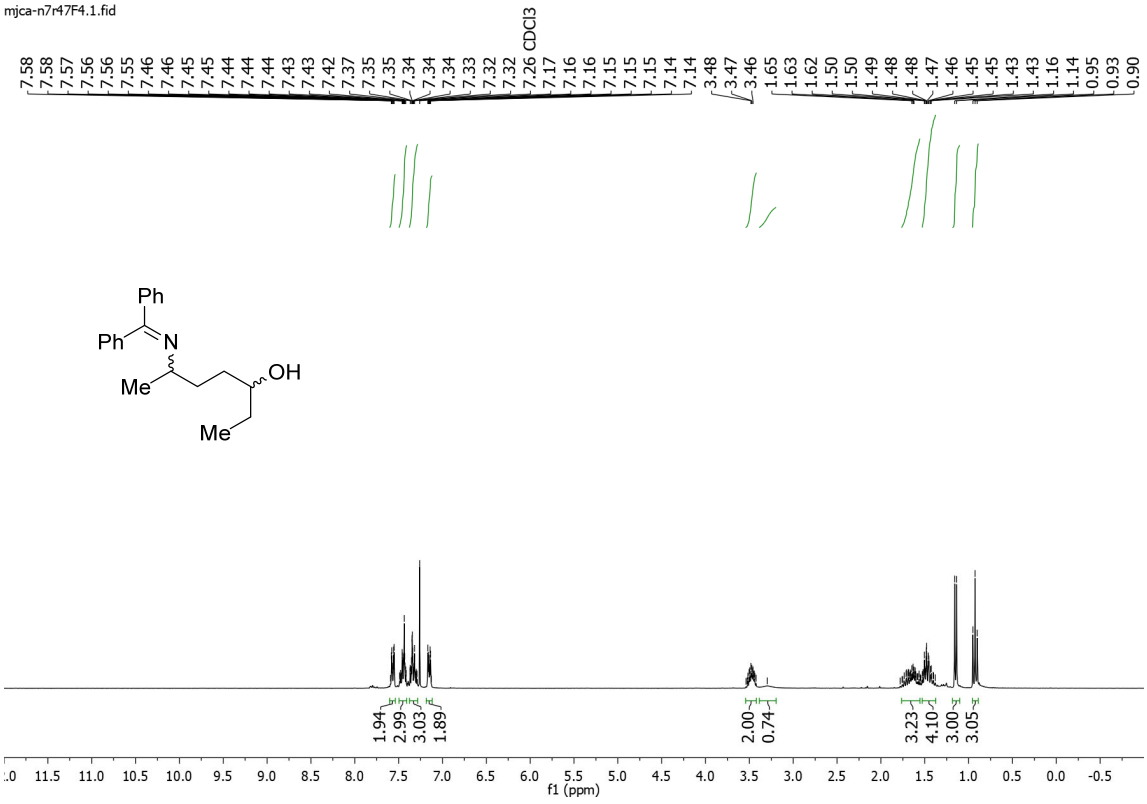
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2q.**



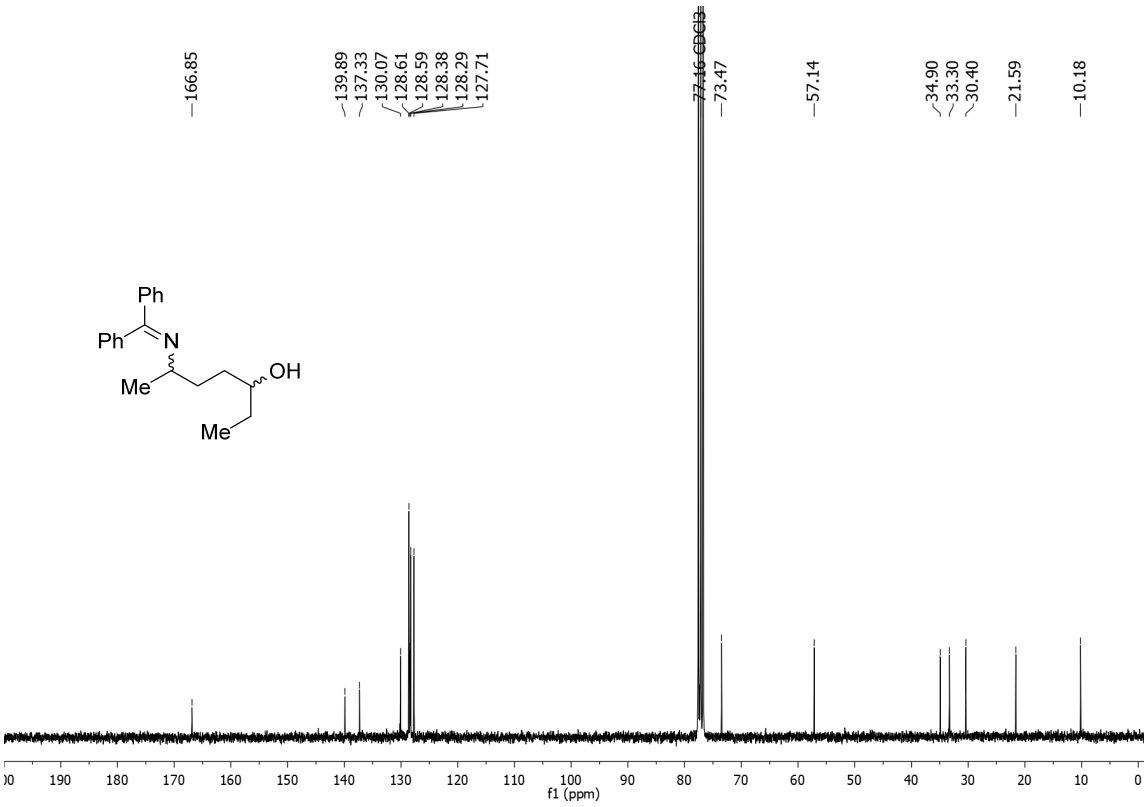
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2q'**.



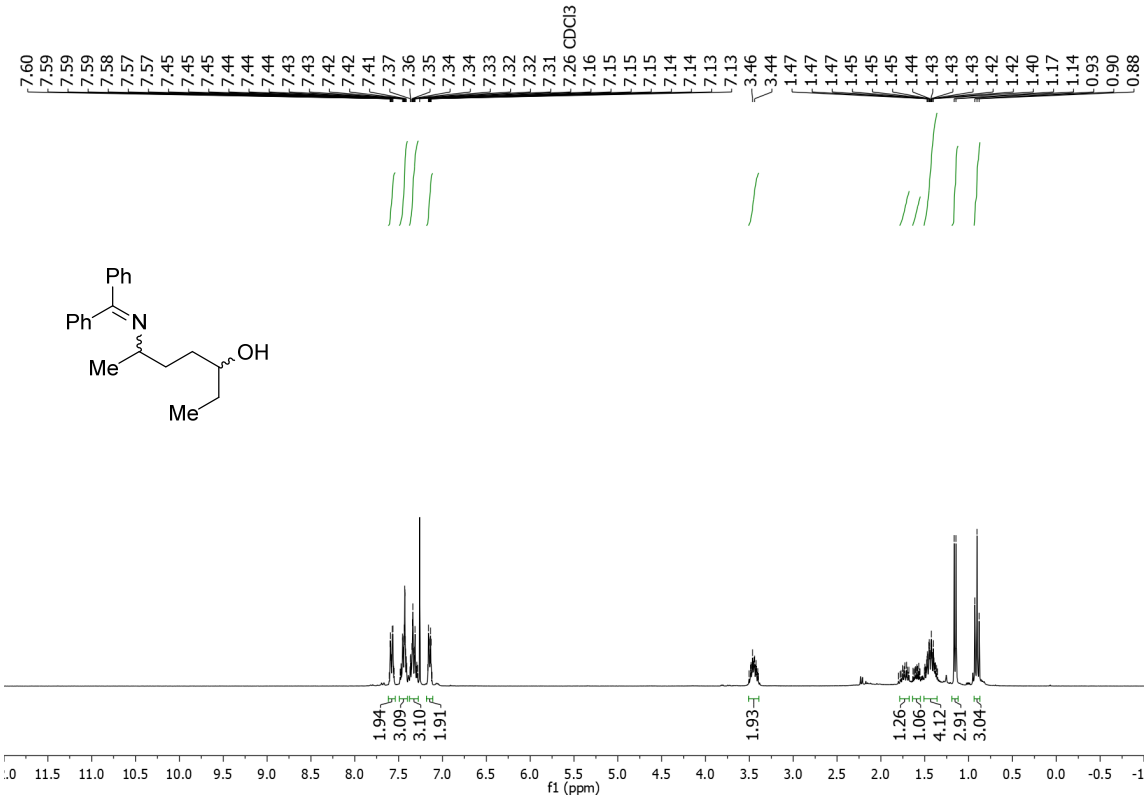
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2q'.**



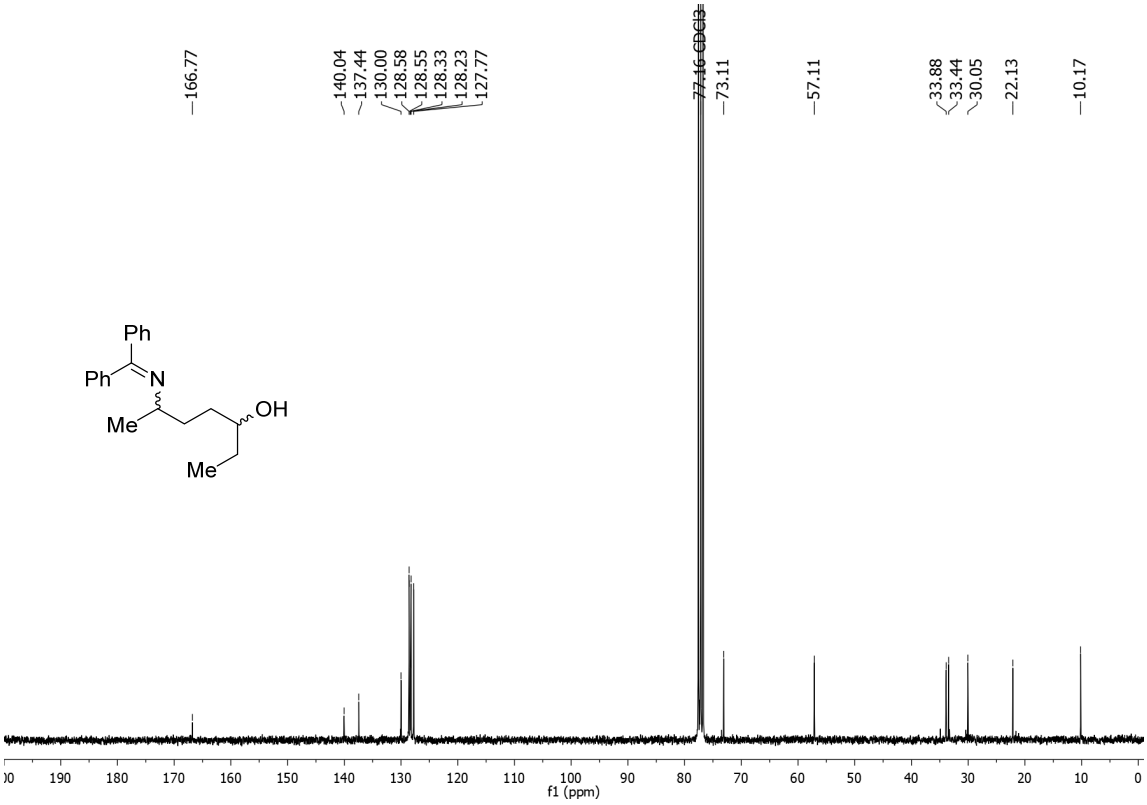
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2r**.



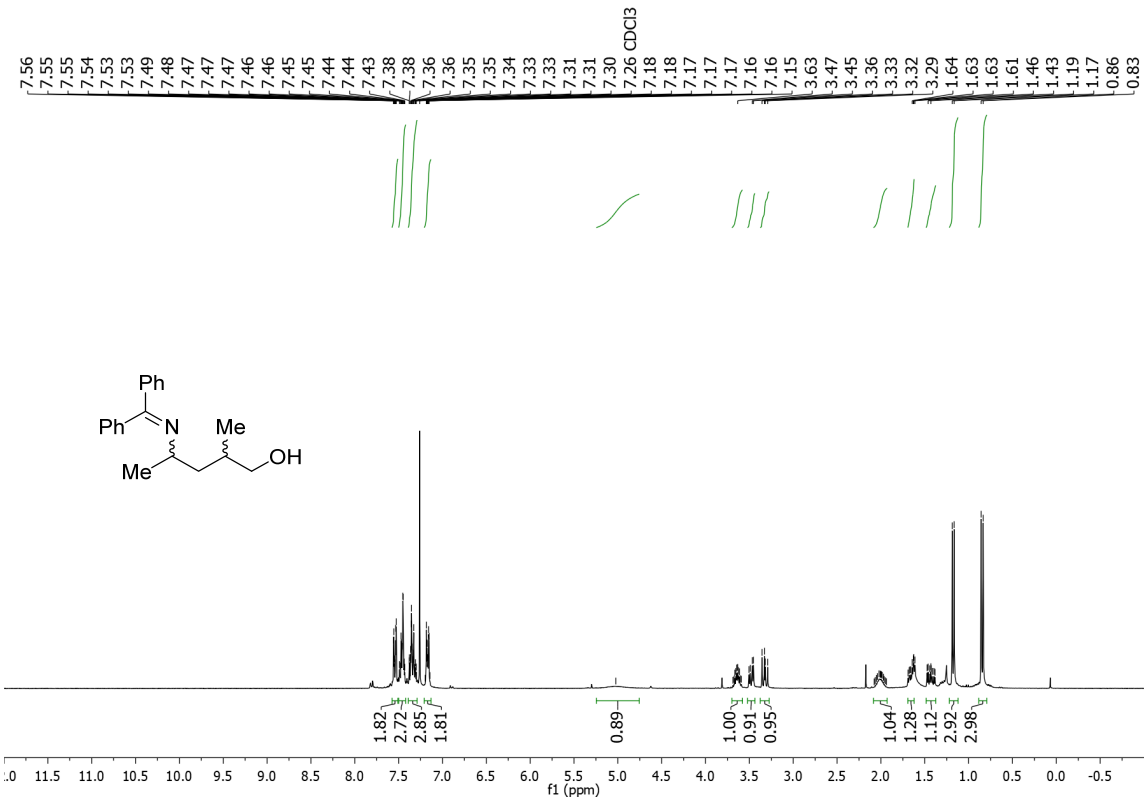
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2r.**



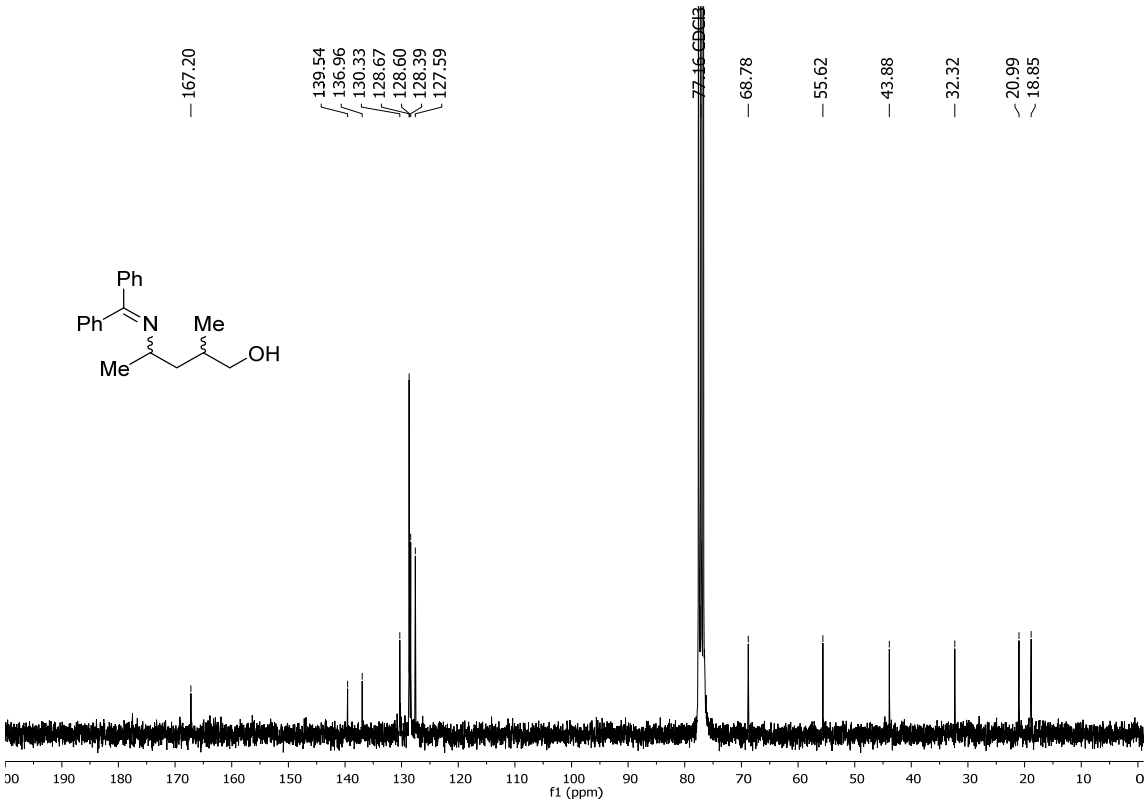
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2r'**.



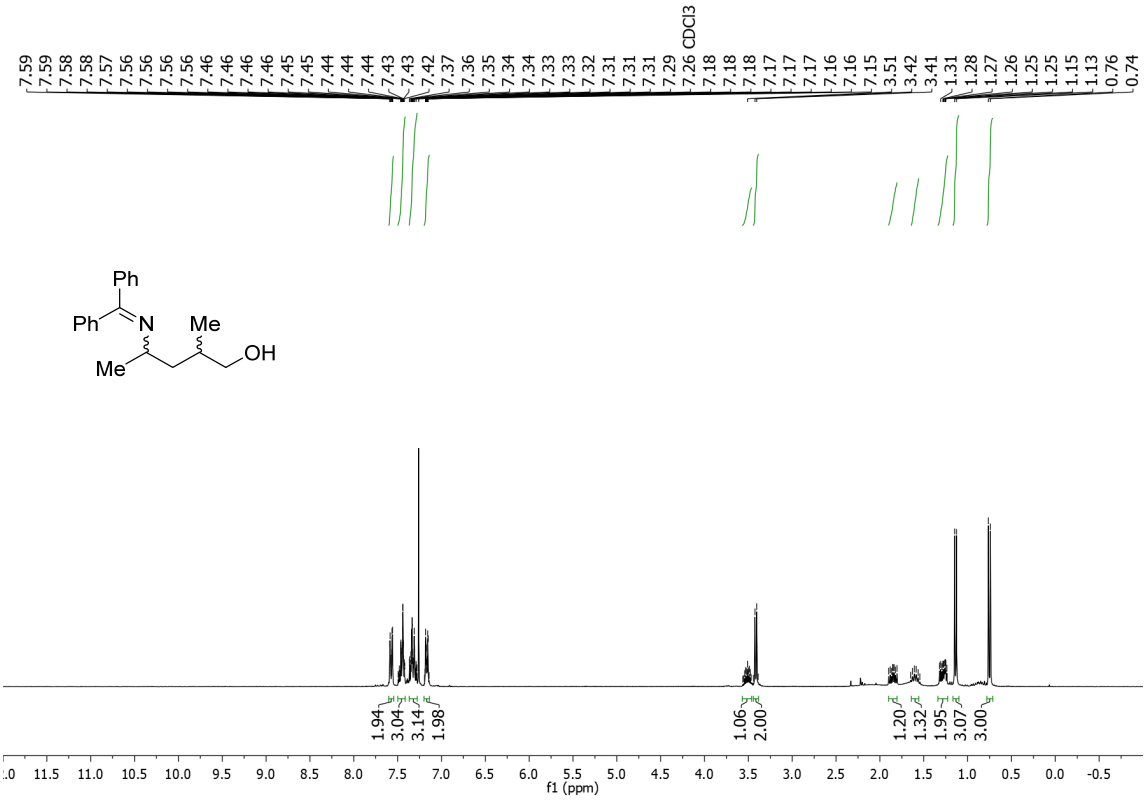
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2r'.**



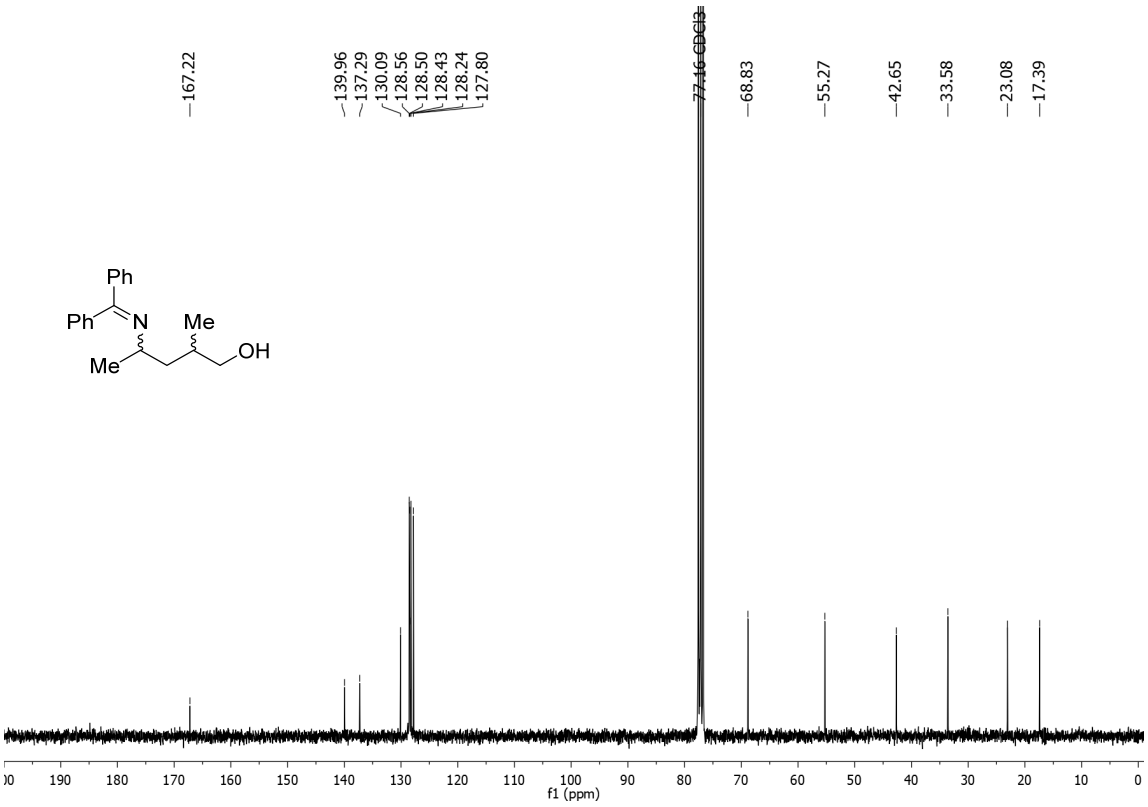
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2s**.



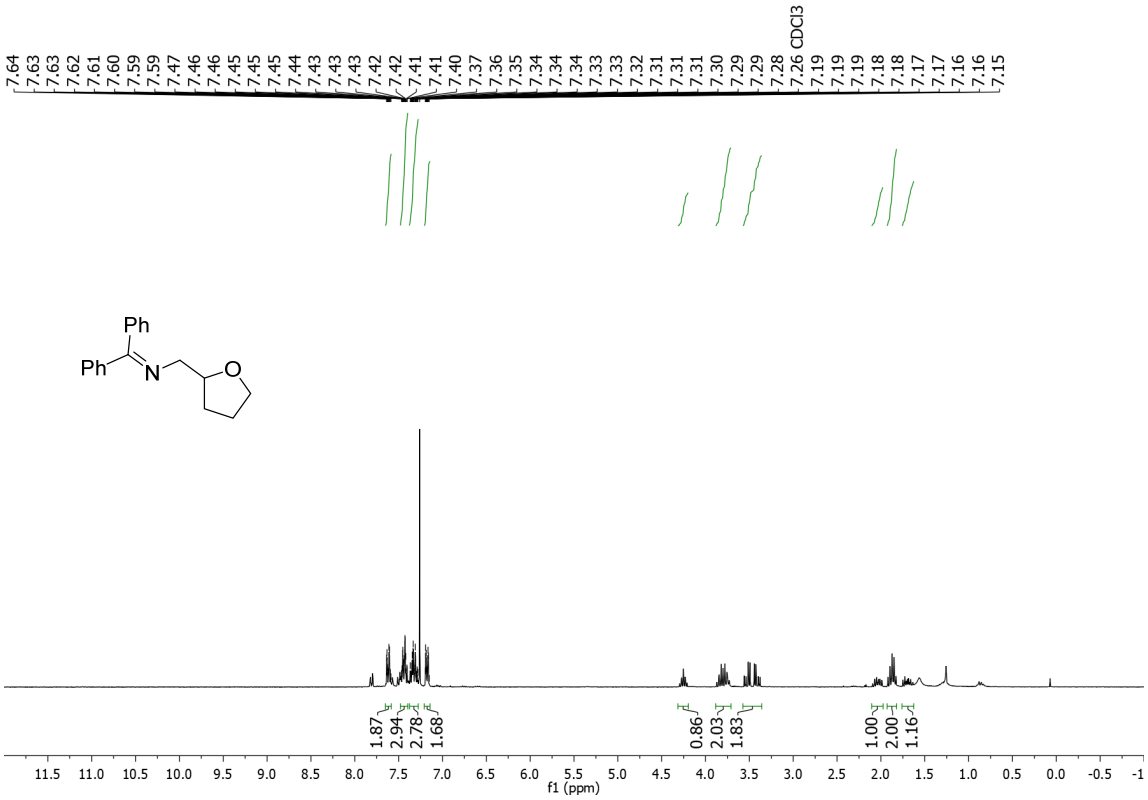
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2s.**



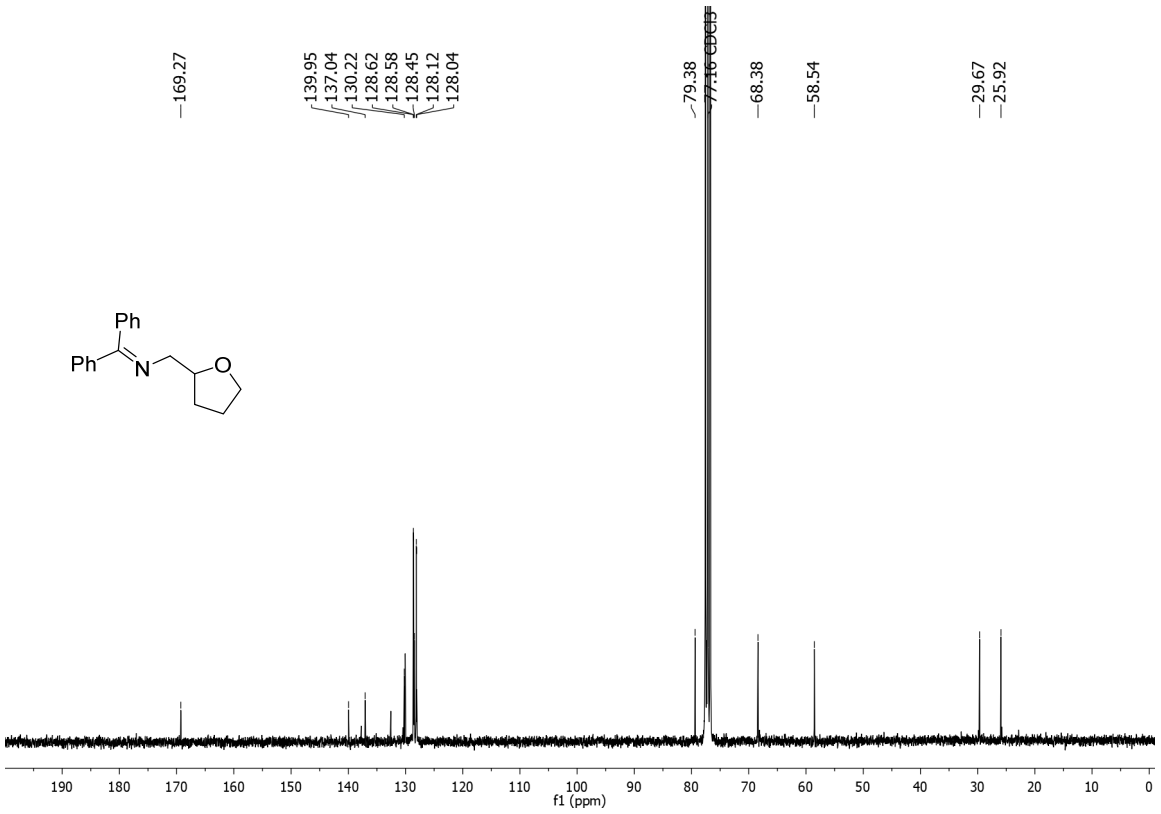
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2s'**.



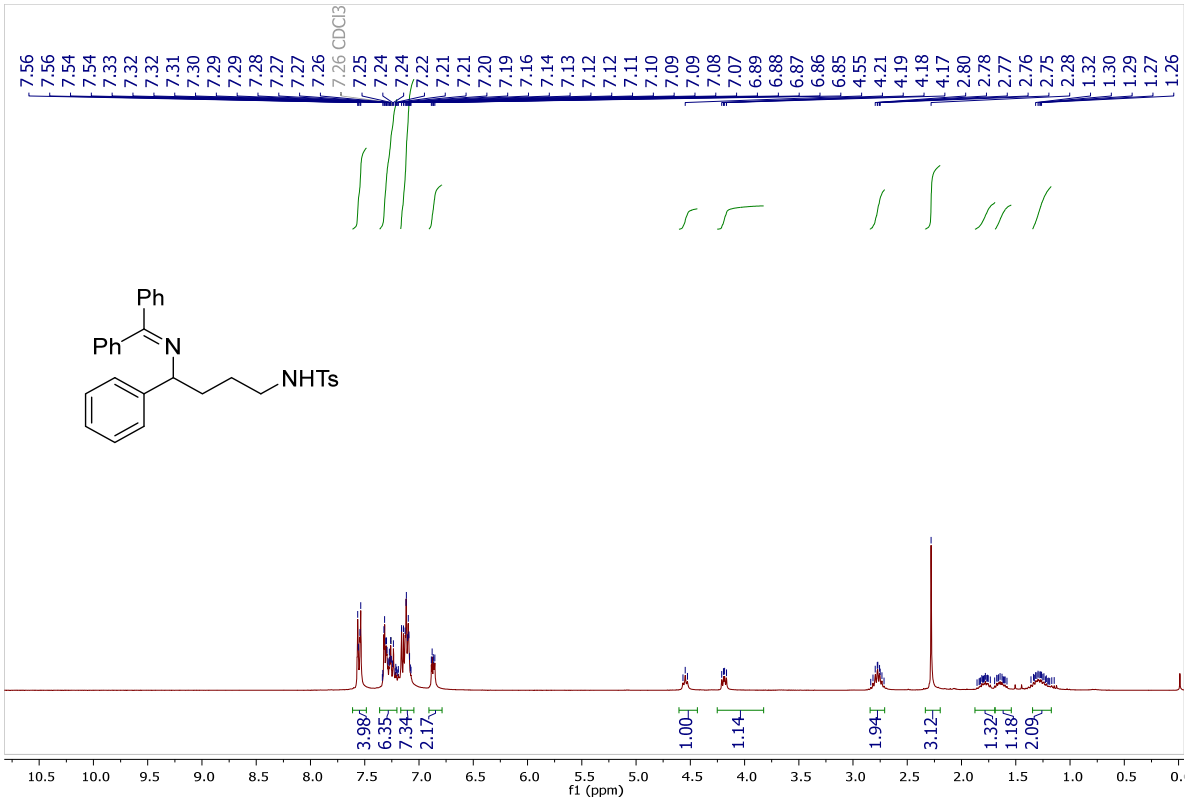
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2s'.**



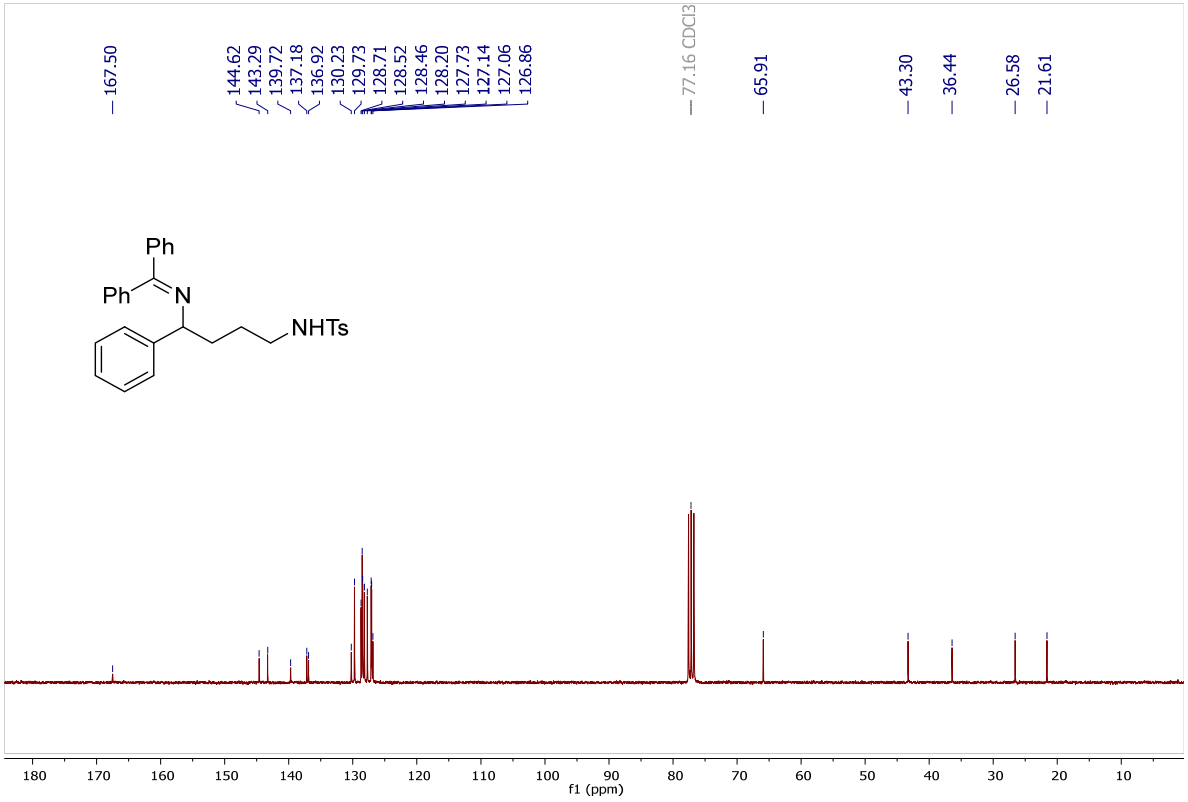
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2t**.



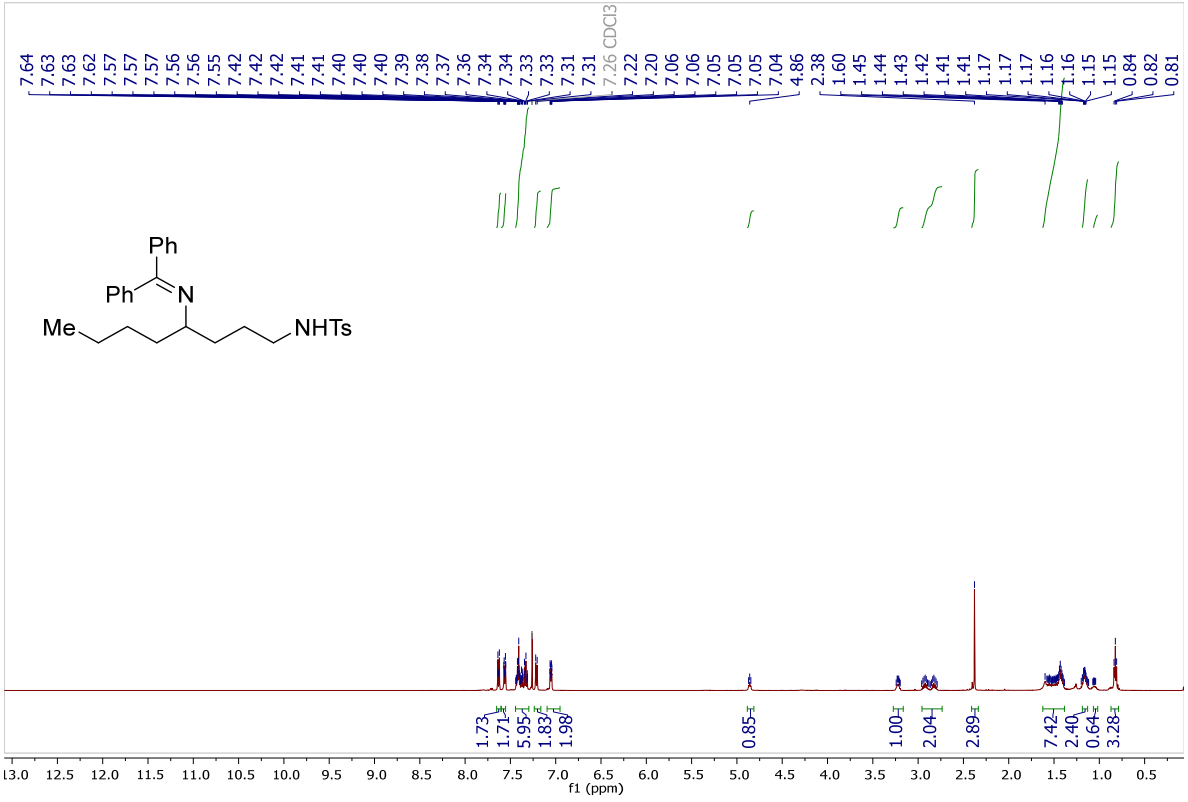
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2t.**



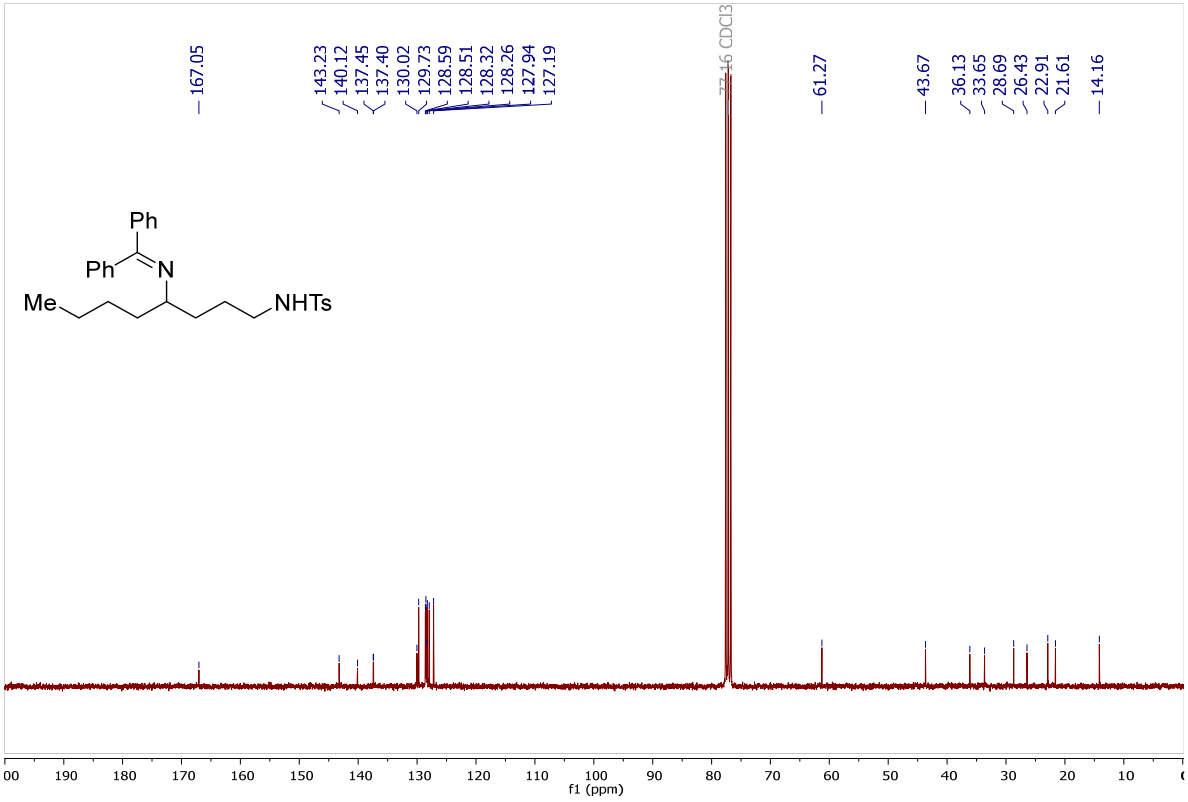
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2u**.



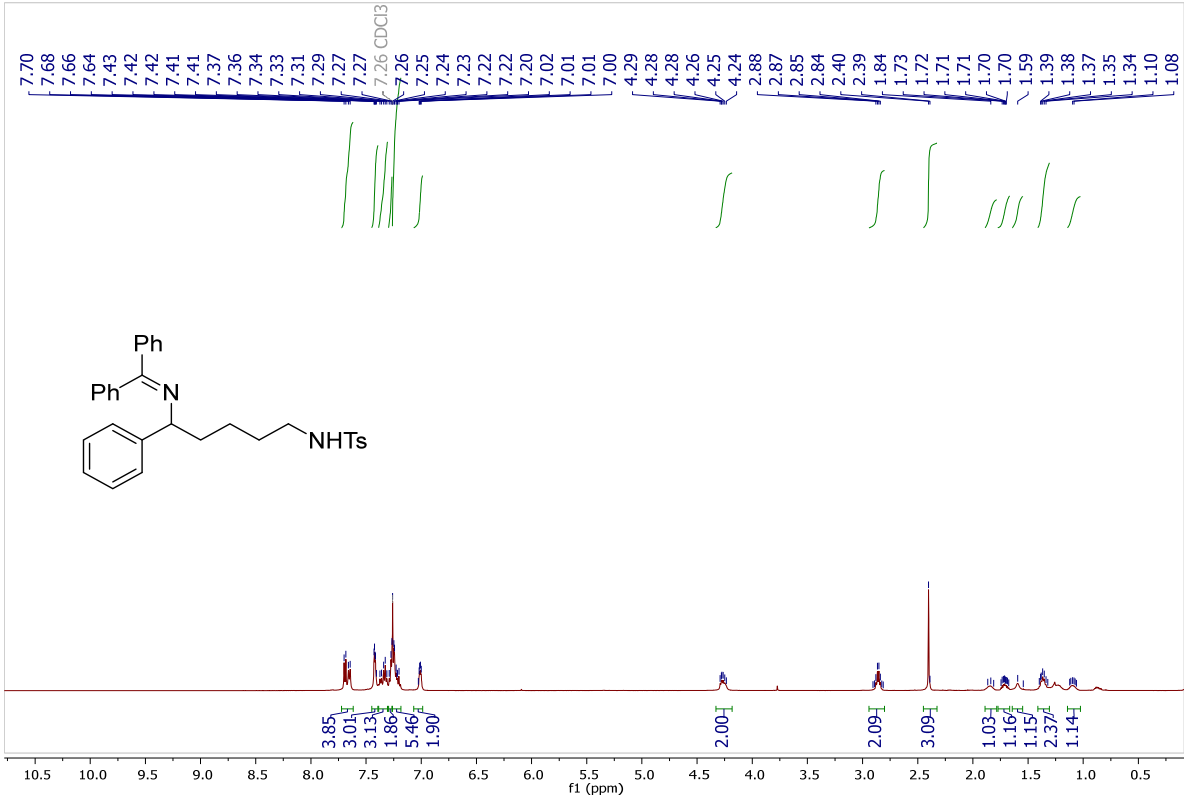
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2u.**



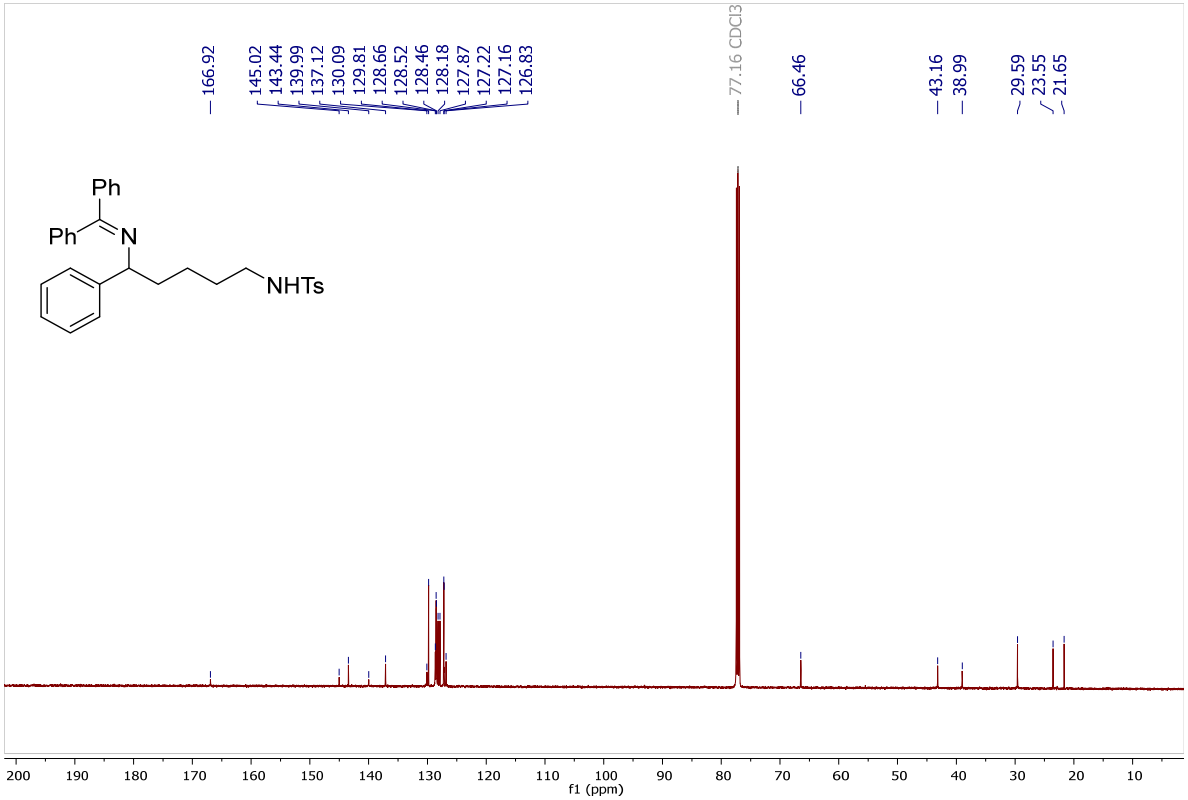
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2v**.



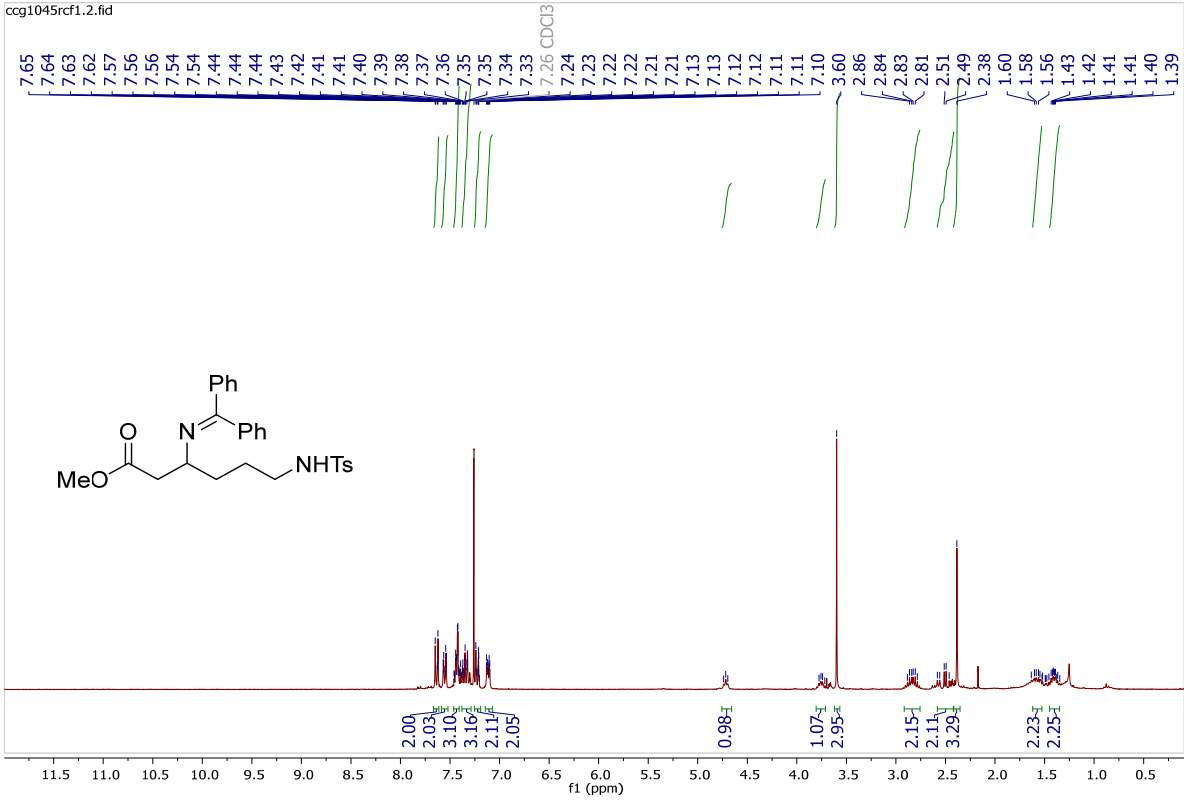
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2v.**



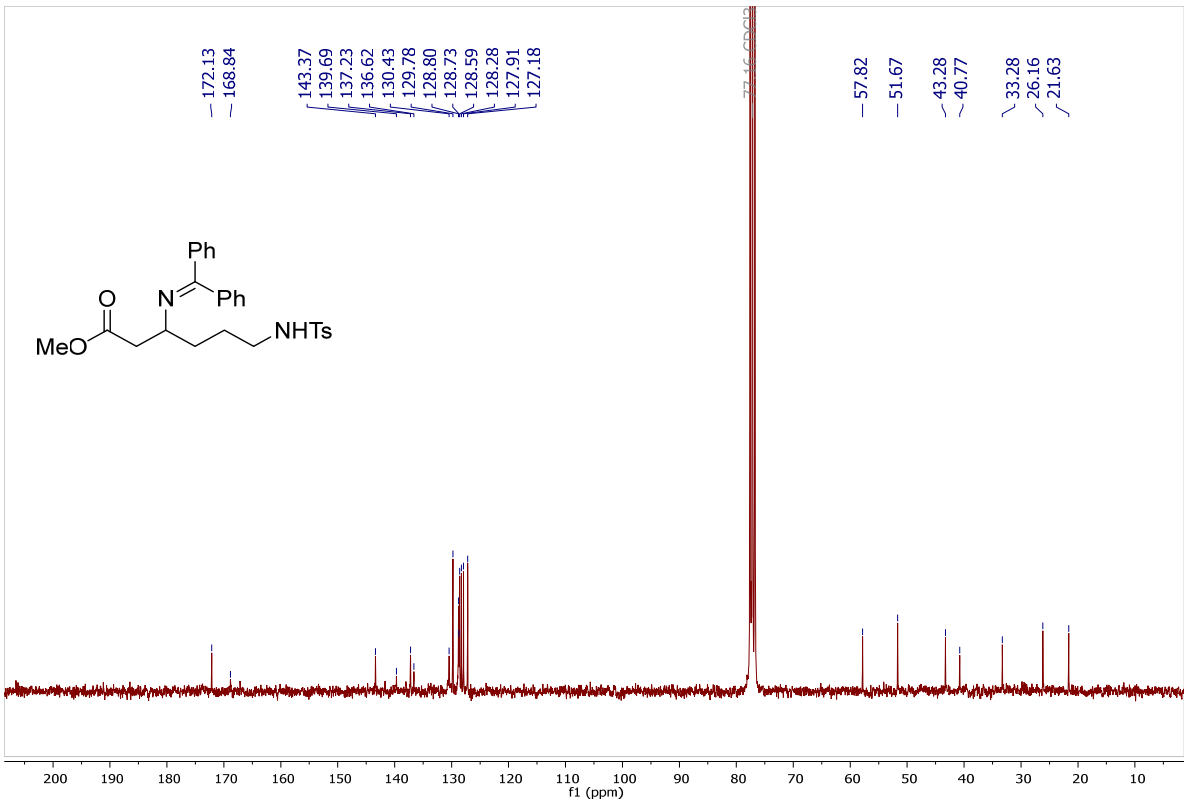
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2w**.



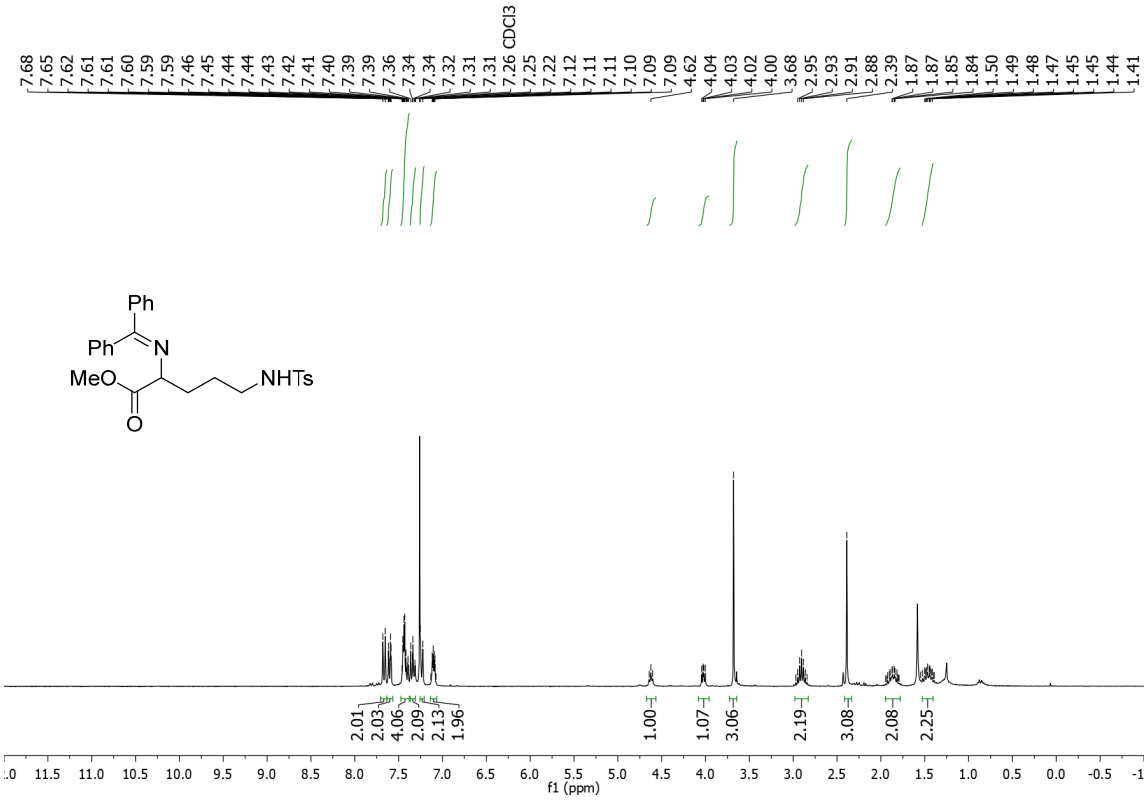
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2w.**



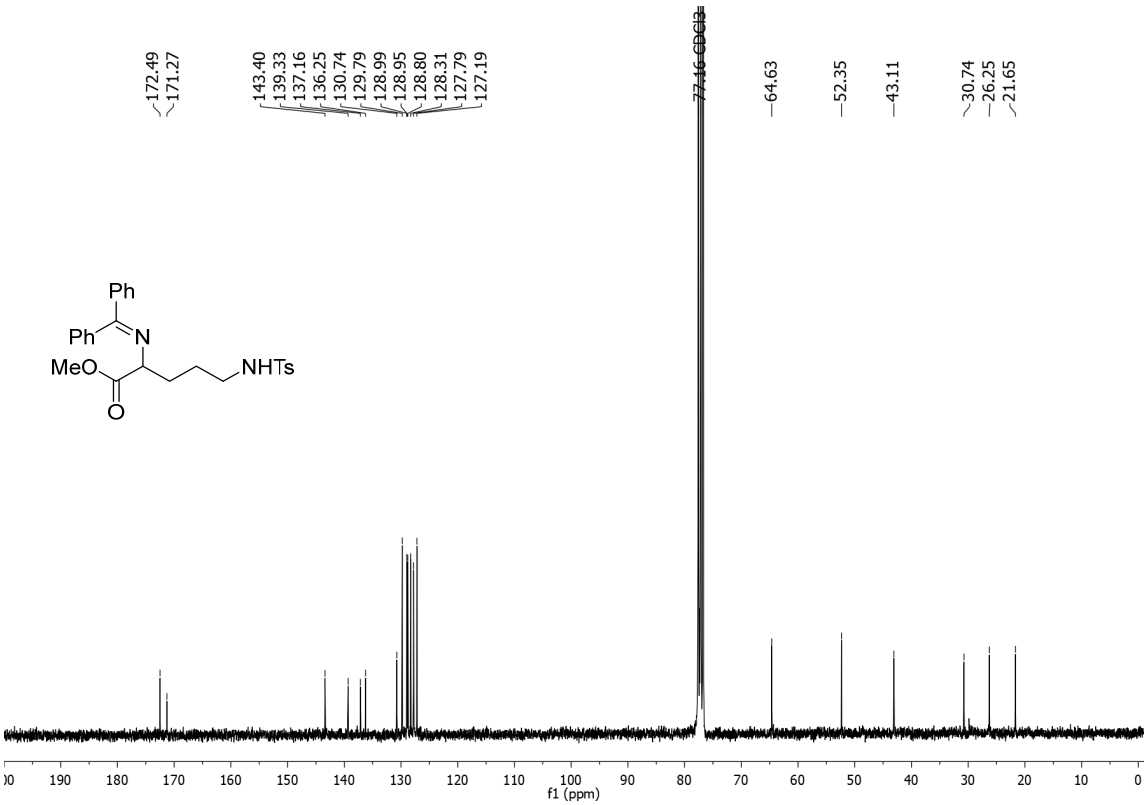
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2x**.



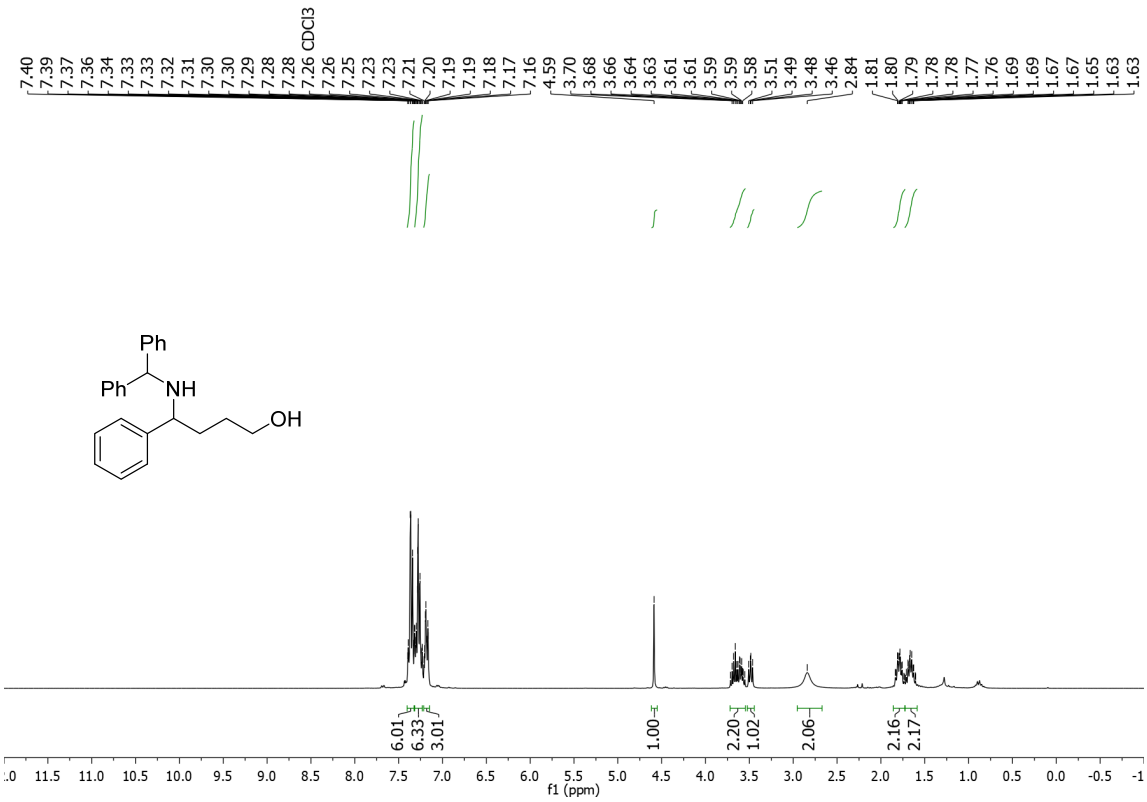
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2x.**



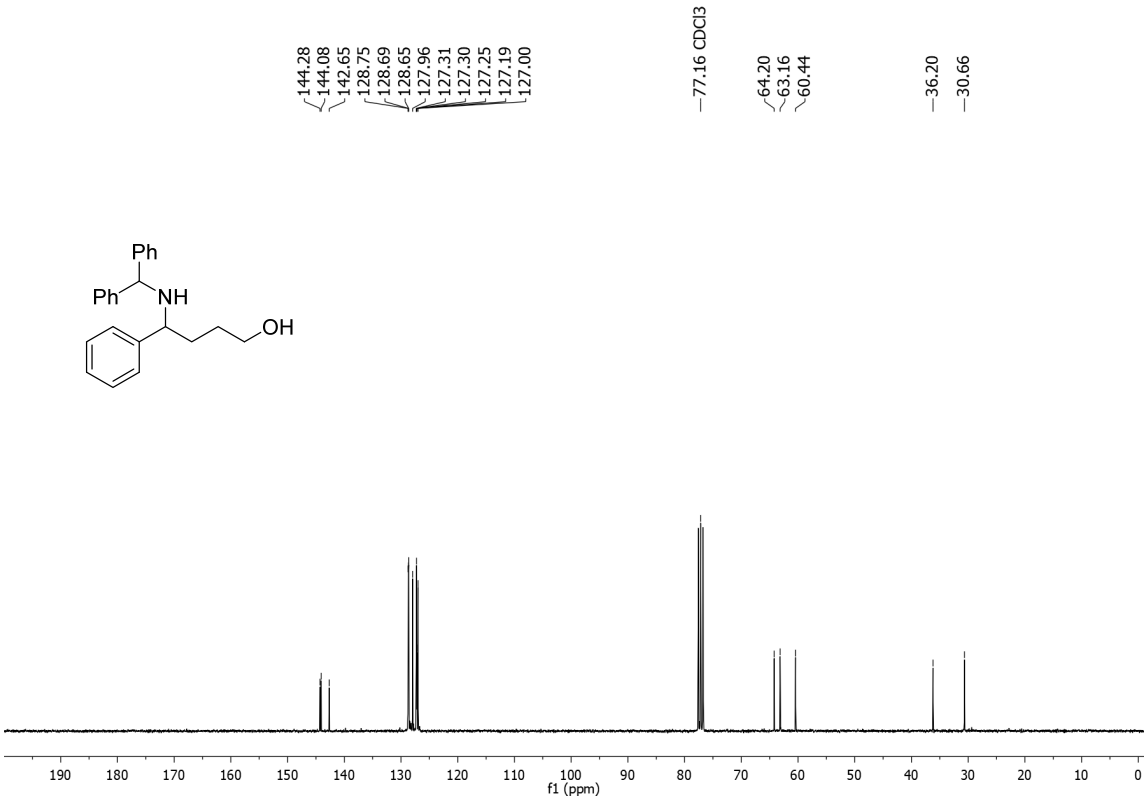
^{1}H NMR (300 MHz, $CDCl_3$) of compound **2y**.



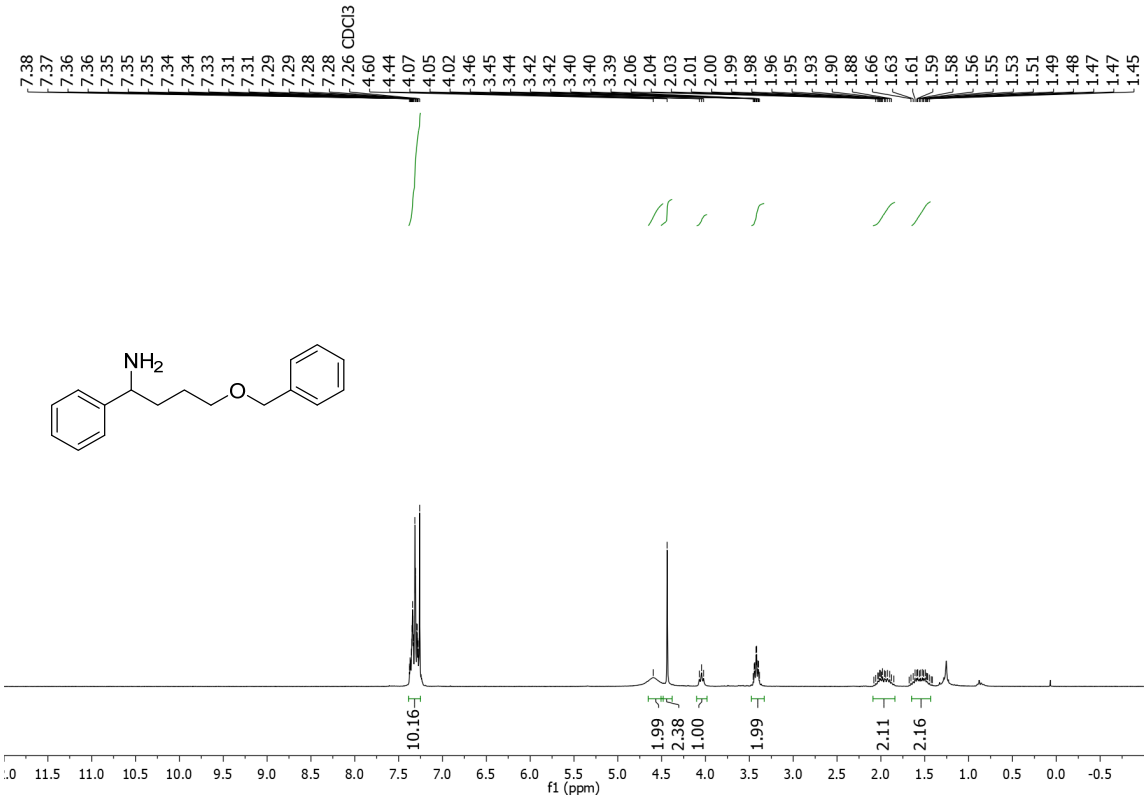
^{13}C NMR (75 MHz, $CDCl_3$) of compound **2y.**



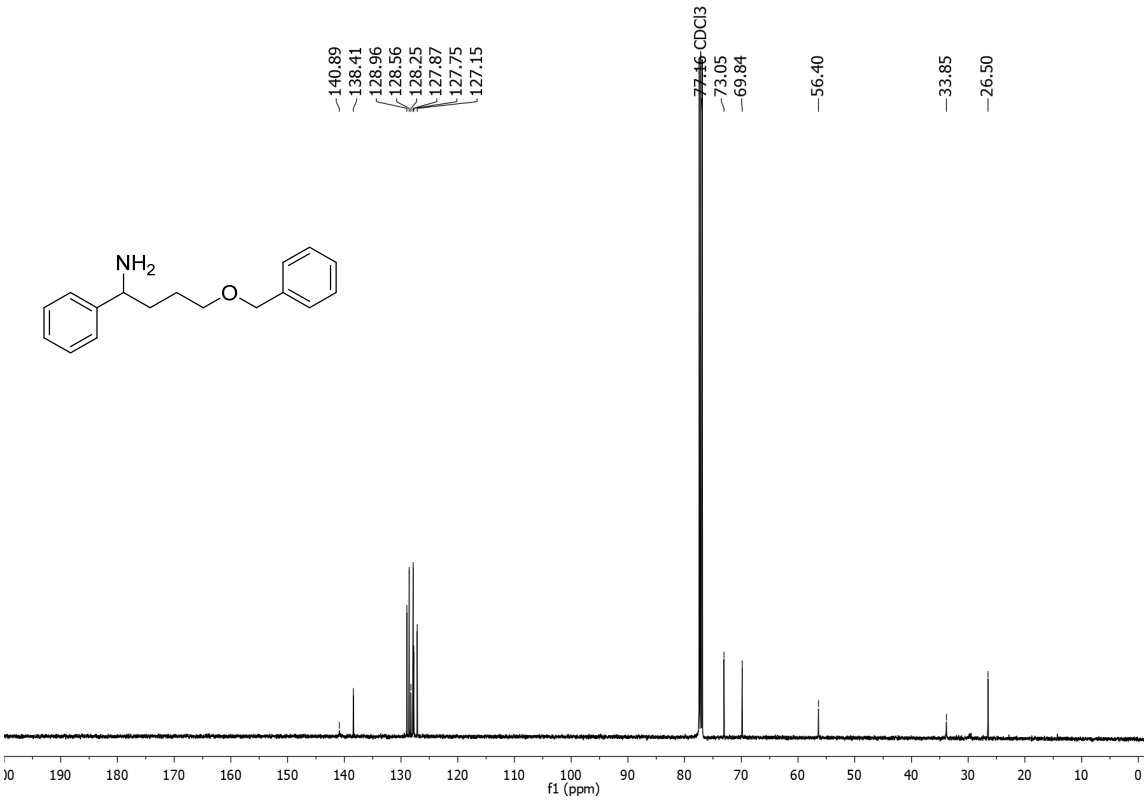
^{1}H NMR (300 MHz, $CDCl_3$) of compound **3**.



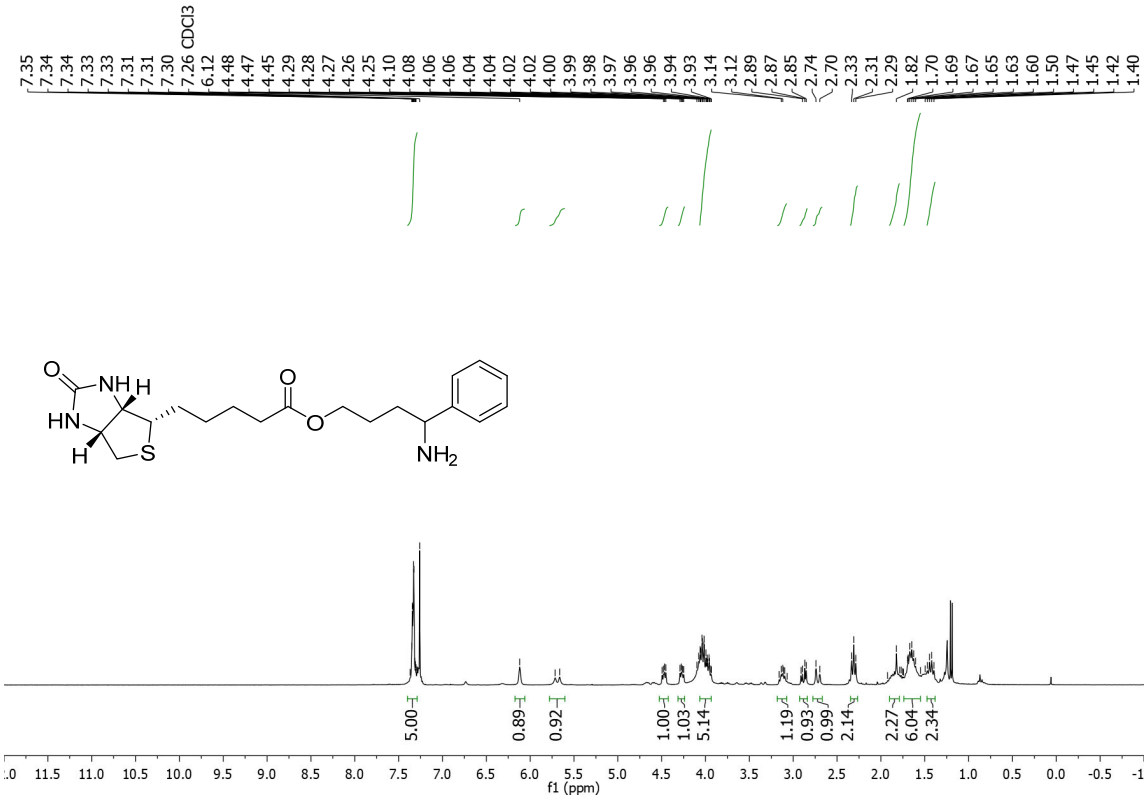
^{13}C NMR (75 MHz, $CDCl_3$) of compound **3.**



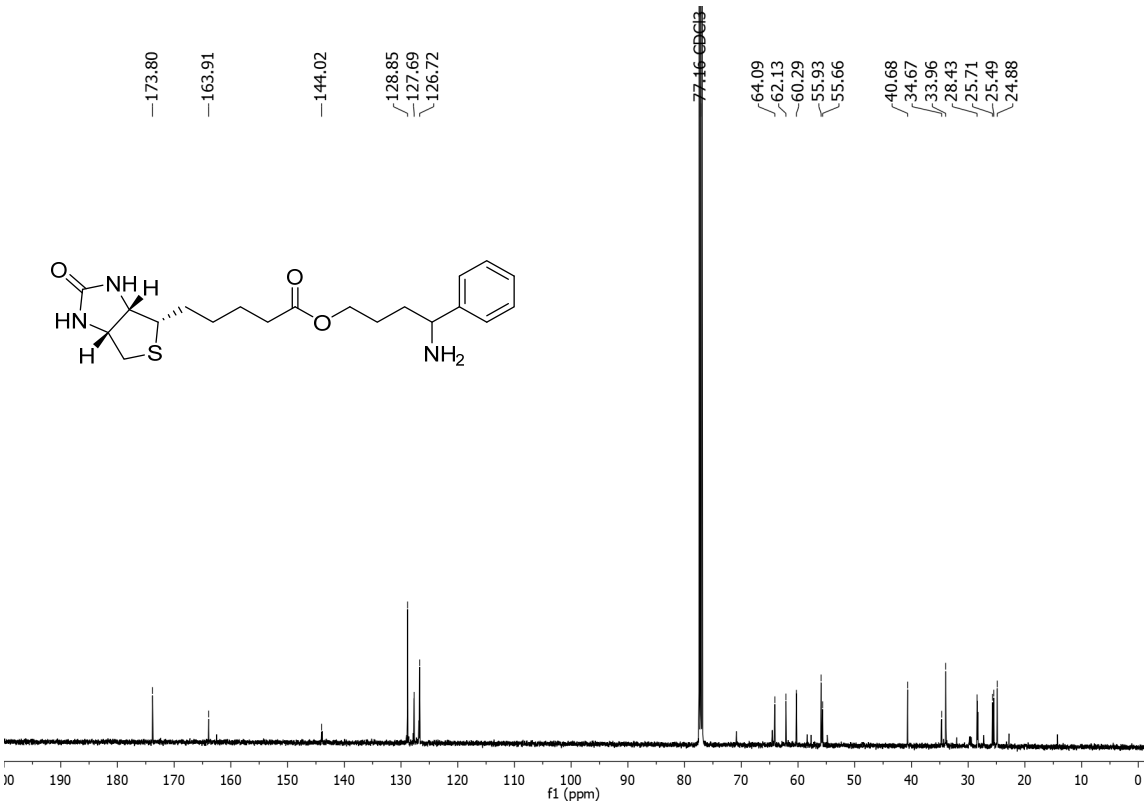
^{1}H NMR (300 MHz, $CDCl_3$) of compound **4**.



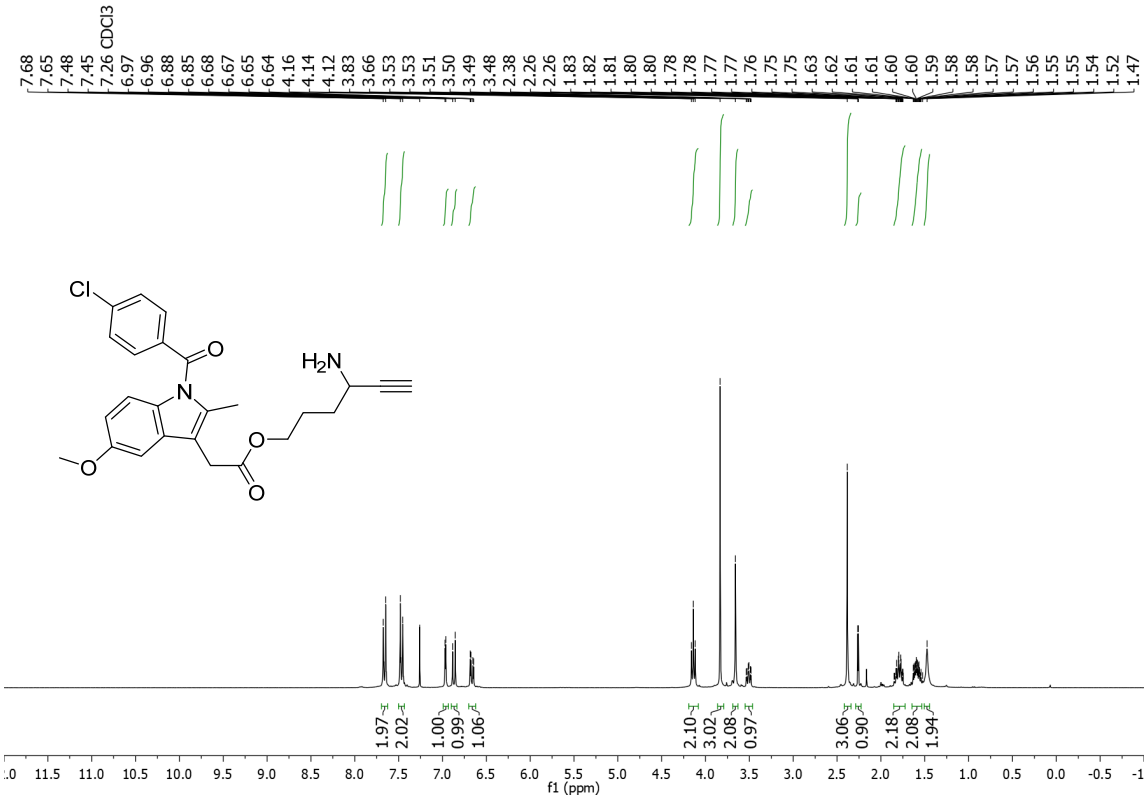
^{13}C NMR (125 MHz, $CDCl_3$) of compound **4.**



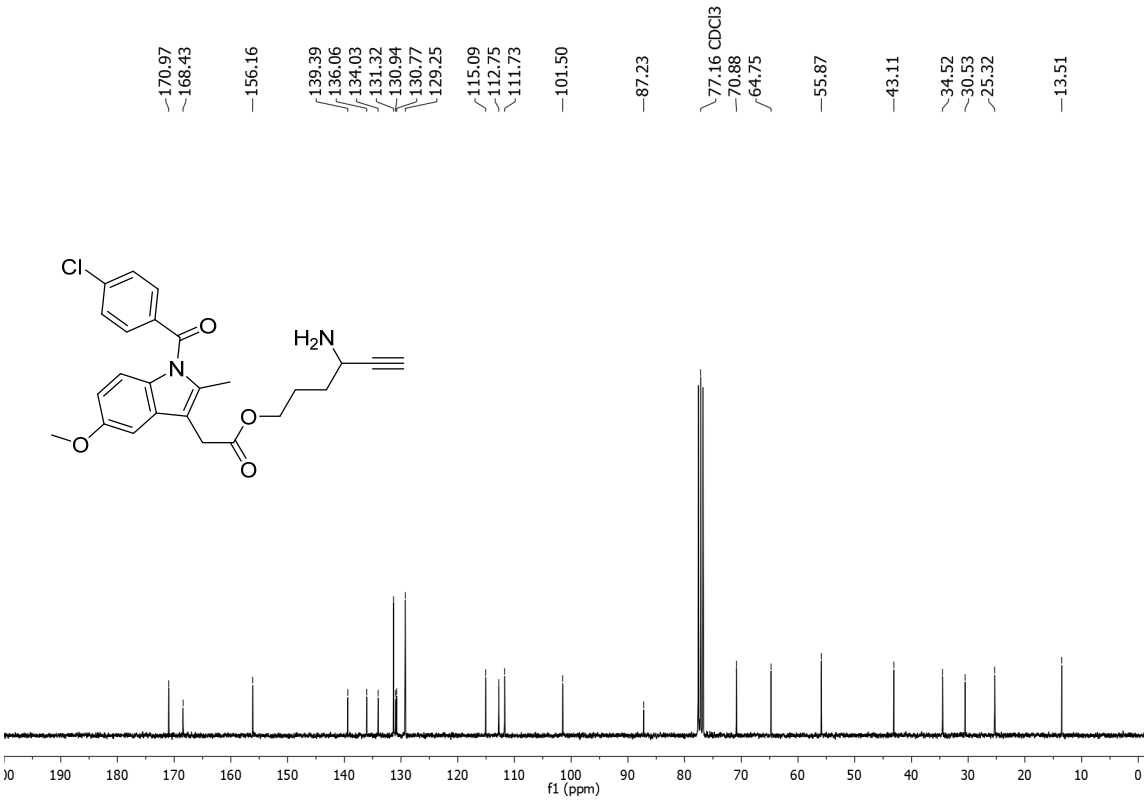
^{1}H NMR (300 MHz, $CDCl_3$) of compound **5**.



^{13}C NMR (75 MHz, $CDCl_3$) of compound **5.**



^{1}H NMR (300 MHz, $CDCl_3$) of compound **6**.



^{13}C NMR (75 MHz, $CDCl_3$) of compound **6.**