# Homologative Alkene Difunctionalization

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## Supplementary Information

## Table of Contents

## I. General Information

**General experimental procedure** Unless otherwise indicated, all reagents were purchased from commercial vendors, including Sigma-Aldrich (Merck), Thermo-Fisher Scientific (for Acros Organics and Alfa Aesar), TCI, BLD pharm, Combi-blocks, Strem, Daejung, and Samchun and used without further purification. Dichloromethane (DCM), diethyl ether ($Et_2O$), *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) were purified and collected under argon using a Glass Contour Solvent Purification System. All other solvents were ACS grade or better and degassed prior to use or purchased anhydrous and sealed under argon. Manipulations for reaction setup were conducted under an argon atmosphere in oven-dried (100 °C) or flame-dried apparatus using standard Schlenk techniques, unless otherwise noted. Air-sensitive liquids and solutions were transferred via syringe. Reactions that require heating were performed in pre-heated aluminum heating blocks. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 $F_{254}$ plates, basic alumina 60 $F_{254}$ plates, or amino-bonded high-performance silica gel $UV_{254}$ plates. Visualization on TLC was achieved by the use of UV light (254 nm), iodine staining, or treatment with potassium permanganate or phosphomolybdic acid followed by heating. Flash column chromatography was performed using a Teledyne Isco Combiflash® NextGen 300+ or Biotage® Isolera™ One with silica columns (60 Å porosity, 20-40 μm) or amino-functionalized silica columns (60 Å porosity, 40 μm, purchased from Yamazen). After isolation, all products were further dried under reduced pressure for removal of residual solvents.

**Product characterization.** $^1H$ NMR spectra were collected with an Agilent 400-MR DD2 Magnetic Resonance System, Varian/Oxford AS-500 instrument, or Bruker 500MHz NMR spectrometer. $^1H$ NMR chemical shifts are given in ppm with respect to solvent residual peak ($CDCl_3$, δ 7.26 ppm; $D_2O$, δ 4.79 ppm; MeCN-*d*$_3$, δ 1.94 ppm). $^{19}F$ NMR were recorded on a Bruker 500 MHz spectrometer (471 MHz). $^{13}C$ NMR spectra were recorded on an Agilent 400-MR DD2 Magnetic Resonance System, Varian/Oxford AS-500 instrument, or Bruker 500 MHz NMR spectrometer, and were fully decoupled by broadband decoupling. $^{13}C$ NMR shifts are given in ppm with respect to ($CDCl_3$, δ 77.16 ppm; MeCN-*d*$_3$, 118.26 ppm). All NMR spectra were processed using MestReNova software. Multiplicities are described as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants are reported in Hertz (Hz). High-resolution mass spectrometry (HRMS) were conducted on SFC-QTOF-MS (Xevo G2-XS-UPC, Waters corporation) from the Chiral Material Core Facility Center of Sungkyunkwan University for ESI methods and HRMS (JMS-700, Jeol) from the Korea Basic Science Institute Daegu center for EI/FAB methods. Time-resolved photoluminescence (PL) decay measurements were performed via Time-Correlated Single Photon Counting (TCSPC) technique using Edinburgh FS5-TCSPC with a 450 nm diode laser (EPL-450). The data collection for X-ray single crystal structure analysis was performed at room temperature on a Bruker D8 QUEST diffractometer equipped with Iμs 3.0 Mo x-ray tube ($\lambda$ = 0.71073 Å) and Photon II detector. Crystals coated with Parabar oil were mounted on goniometer for diffraction experiment. The diffraction data were integrated, scaled, and reduced using the Bruker APEX3 software. The crystal structures were solved by the SHELX structure solution program and refined by full-matrix least-squares calculations with the SHELXL.

**Setup for photocatalytic reactions.** A custom-made, double-layer cooling bath connected to a Compact Low Temperature Circulator (Eyela CCA-1111 or CCA-1112A) was used for photocatalytic reactions at low temperatures (Fig. S1). The cooling bath, filled with isopropanol (IPA), was placed on a stir plate. To maintain the desired temperature (5 ± 2 °C), the coolant circulated through the space between the outer and inner layers of the bath using the chiller during the reaction. The temperature was monitored with a thermometer placed directly in front of an active LED lamp within the bath. Two blue Kessil™ LED lamps (PR160L-456 nm) were positioned above the cooling bath using clamps. Reaction vials (4 mL capacity, up to three per LED lamp) were arranged in a white plastic rack.

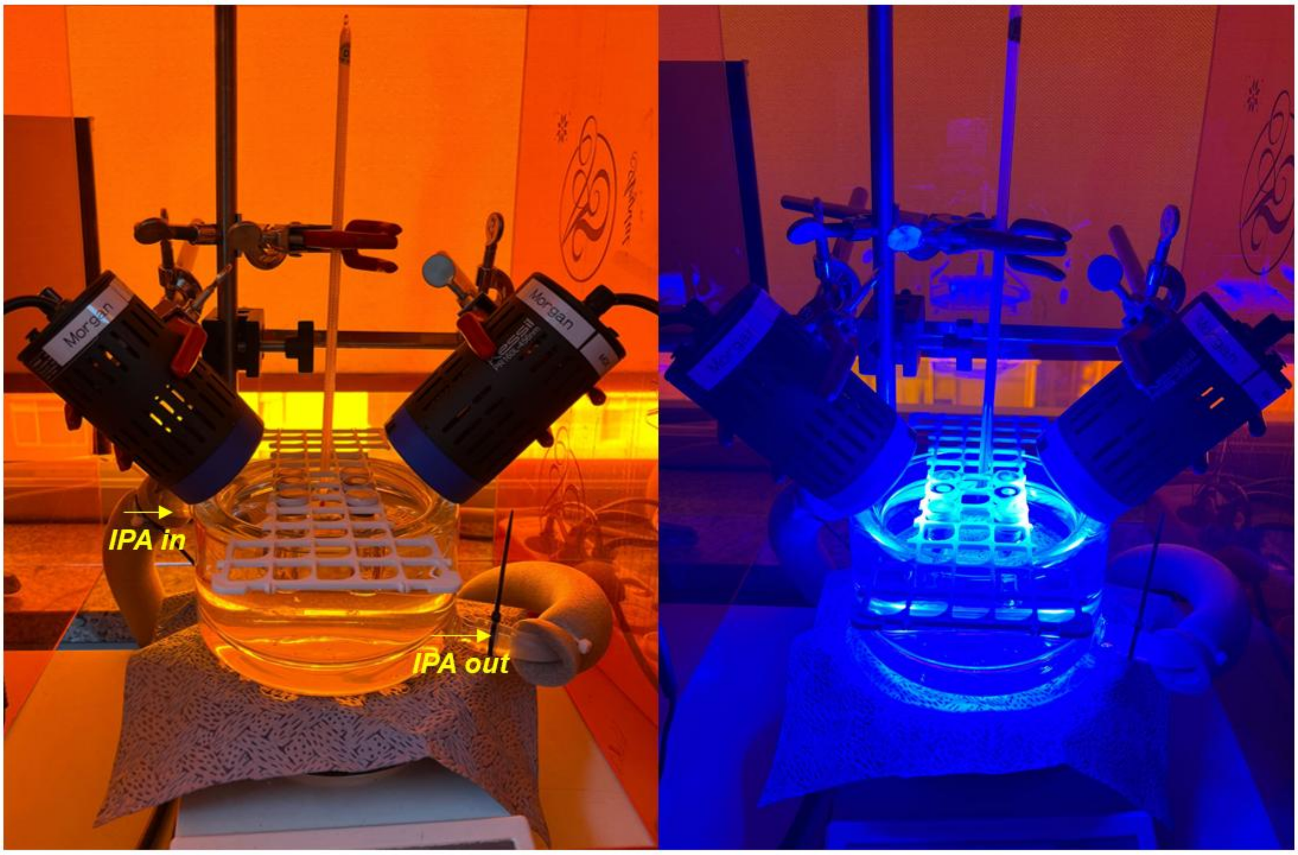
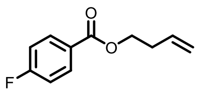


**Fig. S1.** Photographs of the photochemical reaction setup with controlled cooling, taken without (left) and with (right) light irradiation.

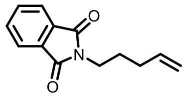
## II. Procedures for the Preparation of Starting Materials

### A. Preparation of alkene substrates

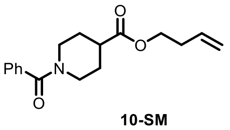
**S3**



**7-SM**



**9-SM**



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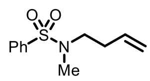

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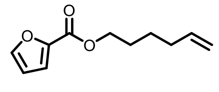
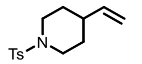
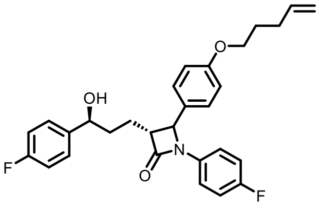


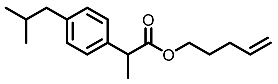
**43-SM**



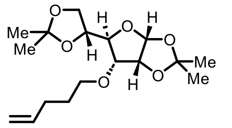
**44-SM**



**58-SM**



**73**



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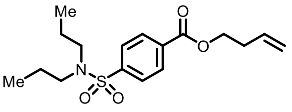
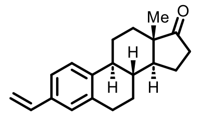
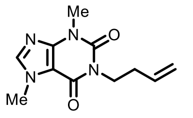


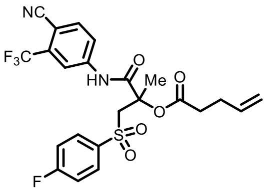
**61-SM**



**62-SM**



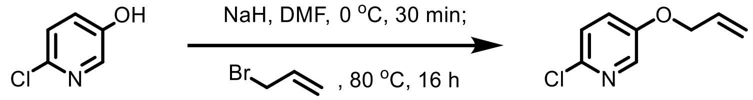
**63-SM**



**64-SM**

*trans*-(2-Vinylcyclopropyl)benzene (**S3**)[1], but-3-en-1-yl 4-fluorobenzoate (**7-SM**)[2], 2-(pent-4-en-1-yl)isoindoline-1,3-dione (**9-SM**)[3], but-3-en-1-yl 1-benzoylpiperidine-4-carboxylate (**10-SM**)[4], *N*-(but-3-en-1-yl)-*N*-methylbenzenesulfonamide (**11-SM**)[5], hex-5-en-1-yl furan-2-carboxylate (**43-SM**)[6], 1-tosyl-4-vinylpiperidine (**44-SM**)[7], (3*R*)-1-(4-fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-(pent-4-en-1-yloxy)phenyl)azetidin-2-one (**58-SM**)[8], pent-4-en-1-yl 2-(4-isobutylphenyl)propanoate (**73**)[3], (3*aR*,5*R*,6*R*,6*aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(pent-4-en-1-yloxy)tetrahydrofuro[2,3-*d*][1,3]dioxole (**60-SM**)[9], but-3-en-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (**61-SM**)[4], (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**62-SM**)[1], 1-(but-3-en-1-yl)-3,7-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (**63-SM**)[10], 1-((4-cyano-3-(trifluoromethyl)phenyl)amino)-3-((4-fluorophenyl)sulfonyl)-2-methyl-1-oxopropan-2-yl pent-4-enoate (**64-SM**)[4] were prepared according to literature methods. All other alkenes of which procedures are not described in Supplementary Information were purchased from commercial vendors, and used without further purification.

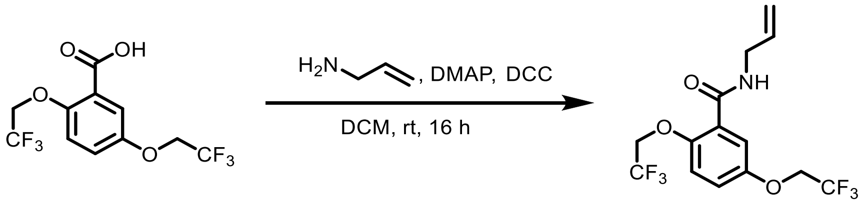
### Preparation of 5-(Allyloxy)-2-chloropyridine (65):



65

To a flame-dried 250 mL two-neck round-bottom flask equipped with a magnetic stir bar were added 2-chloro-5-hydroxypyridine (2.67 g, 20.0 mmol, 1.0 equiv., 97%) and sodium hydride (1.20 g, 30.0 mmol, 1.5 equiv., 60% in mineral oil). The flask was cooled down to 0 °C in an ice bath, and anhydrous DMF (54 mL) was added via syringe slowly. The reaction mixture was stirred for 30 min at 0 °C. Subsequently, allyl bromide (3.5 mL, 40.0 mmol, 2.0 equiv., 99%) was added to the flask via syringe. The mixture was warmed up to 80 °C and stirred for 16 hours. Upon completion, the mixture was cooled down to room temperature and quenched with water. Reaction mixture was diluted with EA and washed with brine five times. Combined organic layers were dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 19:1 on silica gel (91%, 3.1 g, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.02 (ddt, *J* = 17.5, 10.6, 5.3 Hz, 1H), 5.42 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.33 (dq, *J* = 10.6, 1.5 Hz, 1H), 4.57 (dt, *J* = 5.4, 1.6 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 154.05, 142.68, 137.06, 132.15, 125.24, 124.43, 118.63, 69.57. *NMR spectroscopic signatures are matched with previously reported ones*[11].

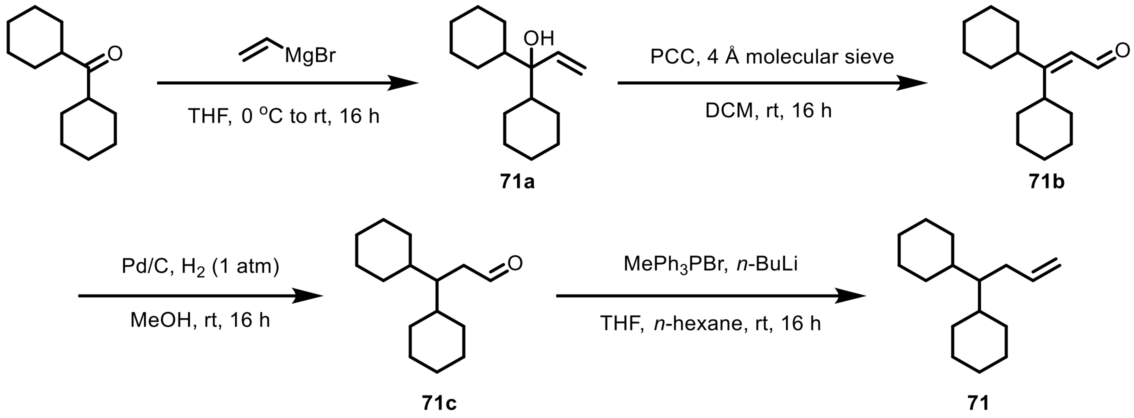
### Preparation of *N*-Allyl-2,5-bis(2,2,2-trifluoroethoxy)benzamide (69):



69

To a flame-dried two-neck round-bottom flask equipped with a magnetic stir bar were added 2,5-bis(2,2,2-trifluoroethoxy)benzoic acid (3.25 g, 10.0 mmol, 1.0 equiv., 98%), DCC (2.06 g, 10.0 mmol, 1.0 equiv., 99%), and DMAP (0.123 g, 1.0 mmol, 0.1 equiv., 99%) and the flask was sealed with rubber septa. After evacuation and back-filling with argon three times, DCM (100 mL) was added, and allylamine (0.83 mL, 11.0 mmol, 1.1 equiv., 99%) was added via syringe over a period of 10 min. The reaction mixture was stirred at room temperature for 16 hours. Upon completion, the mixture was filtrated using DCM to remove the precipitate and the filtrate was concentrated under reduced pressure. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 7:3 on silica gel (83%, 2.97 g, white solid). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 3.3 Hz, 1H), 7.58 (s, 1H), 7.11 (ddd, *J* = 9.0, 3.4, 1.3 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 5.92 (ddt, *J* = 17.0, 10.1, 5.7 Hz, 1H), 5.27 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.19 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.45 (q, *J* = 7.9 Hz, 2H), 4.38 (qd, *J* = 8.1, 1.2 Hz, 2H), 4.09 (tt, *J* = 5.7, 1.5 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 163.65, 153.14, 150.30, 133.75, 124.05, 123.32 (q, J = 278.1 Hz), 123.06 (q, J = 278.0 Hz), 120.76, 117.41, 116.87, 114.96, 67.29 (q, J = 35.9 Hz), 66.55 (q, J = 35.8 Hz), 42.68. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -73.72 (t, *J* = 7.9 Hz), -74.00 (t, *J* = 7.9 Hz). **HRMS** (ESI) calculated for $C_{14}H_{13}F_6NO_3$ $[M+H]^+$: 358.0873; Found: 358.710872.

### Preparation of but-3-ene-1,1-diyldicyclohexane (71):



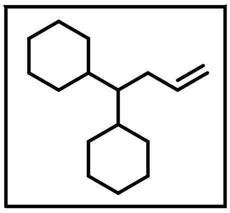
*1,1-Dicyclohexylprop-2-en-1-ol* (**71a**) *was prepared using the modified procedure reported in literature*[12]: A flame-dried 100 mL two-neck round-bottom flask equipped with a magnetic stir bar was sealed, and filled with argon via Schlenk technique. To the flask, dicyclohexyl ketone (4.0 mL, 20.0 mmol, 1.0 equiv., 98%) and anhydrous THF (40 mL) were added via syringes. The reaction mixture was cooled down to 0 °C, and 1.0 M vinylmagnesium bromide THF solution (26 mL, 26.0 mmol, 1.3 equiv.) was added dropwise to the mixture. The reaction mixture was warmed up to room temperature and stirred overnight. After the reaction, the crude mixture was quenched with saturated $NH_4Cl$ solution and diluted with EA. The desired product was extracted with EA three times. The combined organic layers were dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 19:1 on silica gel (85%, 3.8 g, colorless oil).

*3,3-Dicyclohexylacrylaldehyde* (**71b**) *was prepared from 1,1-dicyclohexylprop-2-en-1-ol* (**71a**) *using the modified procedure reported in literature*[13]: To a flame-dried 250 mL two-neck round-bottom flask equipped with a magnetic stir bar was added PCC (11.0 g, 51.0 mmol, 3.0 equiv., 98%). The flask was sealed and put into an argon-filled glovebox. To the round-bottom flask were added 4 Å molecular sieve (11.0 g) and anhydrous DCM (81 mL). Then the mixture was taken out from the glovebox, and 1,1-dicyclohexylprop-2-en-1-ol (3.79 g, 17.0 mmol, 1.0 equiv.) was added. The reaction mixture was stirred overnight at room temperature. After the reaction, the crude mixture was diluted with $Et_2O$, filtrated through a pad of Celite, and concentrated under reduced pressure. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 19:1 on silica gel (33%, 1.2 g, colorless oil).

*But-3-ene-1,1-diyldicyclohexane* (**71**) *was prepared from 3,3-dicyclohexylacrylaldehyde* (**71b**) *using the modified procedure reported in the literatures*[14,15]: To a flame-dried 100 mL two-neck round-bottom flask equipped with a magnetic stir bar was added 10 wt% Pd/C (246 mg, 20 wt% of substrate). The flask was sealed, evacuated and filled with argon by Schlenk technique for three times. Subsequently, anhydrous MeOH (28 mL) and 3,3-dicyclohexylacrylaldehyde (1.23 g, 5.60 mmol, 1.0 equiv.) were added. The mixture was $H_2$-purged using a balloon filled with $H_2$, and stirred under 1 atm $H_2$ atmosphere for 16 hours at room temperature. After the reaction, the crude mixture was filtrated through a pad of Celite and concentrated under reduced pressure. The crude product of **71c** was used for the next reaction without further purification.

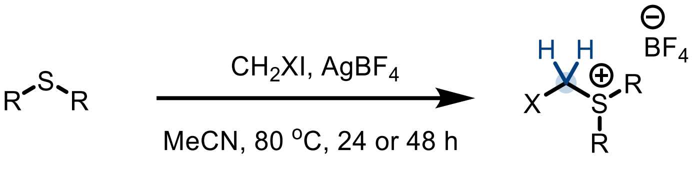
Methyltriphenylphosphonium bromide (2.11 g, 5.80 mmol, 1.1 equiv., 98%) was added to a flame-dried 50 mL two-neck round-bottom flask equipped with a magnetic stir bar under an argon atmosphere. To the flask were added anhydrous THF (5.3 mL) and 2.0 M *n*-butyllithium cyclohexane solution (2.9 mL, 5.80 mmol, 1.1 equiv.) slowly at 0 °C in sequence. The mixture was warmed up to room temperature and stirred for 2 hours. Then, crude 3,3-dicyclohexylpropanal (1.19 g, 5.30 mmol, 1.1 equiv.) was added slowly and the mixture was stirred for 16 hours at room temperature. After completion, *n*-hexane was added to the mixture, and the precipitated triphenylphosphine oxide was removed by filtration. The filtrate was concentrated under reduced pressure. The product was purified by flash column chromatography with 100% *n*-hexane on silica gel.

**But-3-ene-1,1-diyldicyclohexane (71):**



Colorless oil (63% over two steps, 790 mg). **$^1$H NMR** δ 5.79 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H), 4.97 (dd, J = 17.2, 2.1 Hz, 1H), 4.91 (d, J = 10.0 Hz, 1H), 2.05 (t, J = 6.5 Hz, 2H), 1.74 – 1.57 (m, 10H), 1.40 (tq, J = 11.4, 3.6 Hz, 2H), 1.24 – 1.02 (m, 11H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.79, 114.34, 49.14, 39.70, 32.93, 31.96, 30.37, 27.29, 27.08, 26.98. **HRMS** (ESI) calculated for $C_{16}H_{28}$ $[M]^+$: 220.2191; Found: 220.2192.

## B. Preparation of halomethylsulfonium reagents

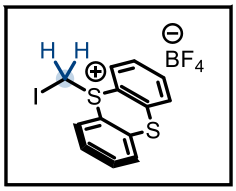


**1a-e**

**Fig. S2**. General schematic description of the preparation of **1a-e**

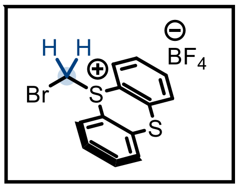
To a flame-dried two-neck round-bottom flask equipped with a reflux condenser and a stir bar were added corresponding sulfide (1.0 equiv.) and silver tetrafluoroborate (1.05 equiv.). The flask was sealed with rubber septa. Following evacuation and introduction of argon (three cycles) on a Schlenk line, dry MeCN (0.67 M) and corresponding $CH_2XI$ (1.0 equiv.) were added sequentially via syringe, and the mixture was stirred at 80 °C in the dark (48 hours for **1a-c** and 24 hours for **1d**-**e**). Upon completion, the reaction mixture was allowed to cool to room temperature and filtered through a pad of Celite. The resulting filtrate was concentrated under reduced pressure and suspended in 1:9 mixture of MeCN and $Et_2O$ (~150 mL) and filtered. The filter cake was further washed with $Et_2O$, THF and DCM, then collected and dried under reduced pressure to afford the desired product.

**5-(Iodomethyl)-5*H*-thianthren-5-ium tetrafluoroborate (1a):**



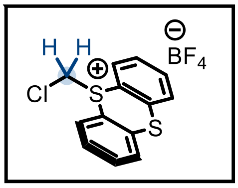
Prepared according to the above procedure using thianthrene (10.9 g, 50.0 mmol, 1.0 equiv., 99%), diiodomethane (4.1 mL, 50.0 mmol, 1.0 equiv., 98%) and silver tetrafluoroborate (10.3 g, 52.5 mmol, 1.05 equiv., 99%). White crystalline solid (56%, 12.3 g). **$^1$H NMR** (500 MHz, MeCN-*d*$_3$) δ 8.15 (dd, J = 8.0, 1.4 Hz, 2H), 7.98 (dd, J = 8.0, 1.3 Hz, 2H), 7.87 (td, J = 7.7, 1.4 Hz, 2H), 7.74 (td, J = 7.7, 1.3 Hz, 2H), 4.86 (s, 2H). **$^{13}$C NMR** (126 MHz, MeCN-*d*$_3$) δ 136.37, 136.14, 135.90, 131.06, 130.38, 118.45, 0.15. **$^{19}$F NMR** (471 MHz, MeCN-*d*$_3$) δ -151.38, -151.43. **HRMS** (ESI) calculated for $C_{13}H_{10}IS_2^+$ $[M]^+$: 356.9263; Found: 356.9264.

**5-(Bromomethyl)-5*H*-thianthren-5-ium tetrafluoroborate (1b):**



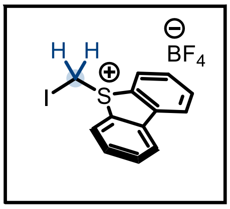
Prepared according to the above procedure using thianthrene (1.53 g, 7.00 mmol, 1.0 equiv., 99%), bromoiodomethane (0.54 mL, 7.0 mmol, 1.0 equiv., 97%), and silver tetrafluoroborate (1.45 g, 7.35 mmol, 1.05 equiv., 99%). White solid (66%, 1.83 g). **$^1$H NMR** (500 MHz, MeCN-*d*$_3$) δ 8.17 (dd, J = 8.0, 1.4 Hz, 2H), 7.98 (dd, J = 8.0, 1.3 Hz, 2H), 7.88 (td, J = 7.7, 1.4 Hz, 2H), 7.75 (td, J = 7.7, 1.3 Hz, 2H), 5.10 (s, 2H). **$^{13}$C NMR** (126 MHz, MeCN-*d*$_3$) δ 136.87, 136.50, 136.28, 131.16, 130.62, 116.76, 33.05. **$^{19}$F NMR** (471 MHz, MeCN-*d*$_3$) δ -151.84, -151.89. **HRMS** (ESI) calculated for $C_{13}H_{10}BrS_2^+$ $[M]^+$: 308.9402; Found: 308.9400.

**5-(Chloromethyl)-5*H*-thianthren-5-ium tetrafluoroborate (1c):**



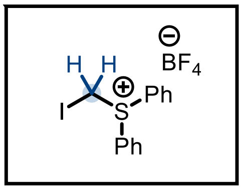
Prepared according to the above procedure using thianthrene (1.53 g, 7.00 mmol, 1.0 equiv., 99%), chloroiodomethane (0.52 mL, 7.00 mmol, 1.0 equiv., 97%), and silver tetrafluoroborate (1.45 g, 7.35 mmol, 1.05 equiv., 99%). White solid (75%, 1.85 g). **$^1$H NMR** (500 MHz, MeCN-*d*$_3$) δ 8.19 (dd, J = 8.0, 1.4 Hz, 2H), 7.98 (dd, J = 7.9, 1.3 Hz, 2H), 7.89 (td, J = 7.7, 1.4 Hz, 2H), 7.75 (td, J = 8.0, 1.3 Hz, 2H), 5.32 (s, 2H). **$^{13}$C NMR** (126 MHz, MeCN-*d*$_3$) δ 137.09, 136.62, 136.45, 131.15, 130.73, 115.74, 49.22. **$^{19}$F NMR** (471 MHz, MeCN-*d*$_3$) δ -151.77, -151.83. **HRMS** (ESI) calculated for $C_{13}H_{10}ClS_2^+$ [M]$^+$: 264.9907; Found: 264.9907.

**5-(Iodomethyl)-5*H*-dibenzo[*b,d*]thiophen-5-ium tetrafluoroborate (1d):**



Prepared according to the above procedure using dibenzothiophene (1.31 g, 7.00 mmol, 1.0 equiv., 98%), diiodomethane (0.58 mL, 7.00 mmol, 1.0 equiv., 98%), and silver tetrafluoroborate (1.45 g, 7.35 mmol, 1.05 equiv., 99%). White solid (61%, 1.76 g) **$^1$H NMR** (500 MHz, MeCN-*d*$_3$) δ 8.25 (d, J = 7.8 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H), 7.97 – 7.90 (m, 2H), 7.78 – 7.72 (m, 2H), 5.33 (s, 2H). **$^{13}$C NMR** (126 MHz, MeCN-*d*$_3$) δ 141.78, 136.07, 132.36, 129.91, 129.38, 125.21, 12.93. **$^{19}$F NMR** (471 MHz, MeCN-*d*$_3$) δ -151.64, -151.69. **HRMS** (ESI) calculated for $C_{13}H_{12}IS^+$ [M]$^+$: 324.9542; Found: 324.9540.

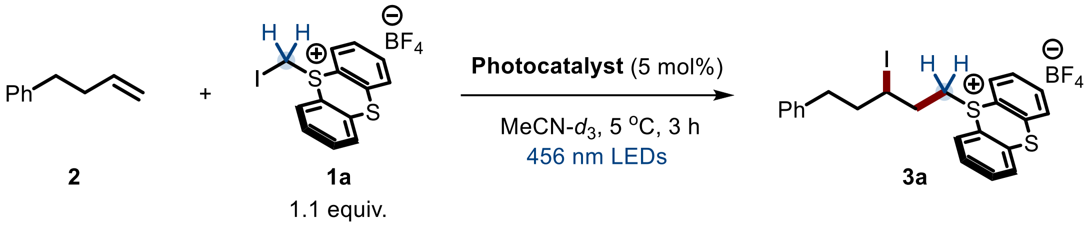
**(Iodomethyl)diphenylsulfonium tetrafluoroborate (1e):**



Prepared according to the above procedure using phenyl sulfide (1.16 mL, 7.00 mmol, 1.0 equiv., 98%), diiodomethane (0.58 mL, 7.00 mmol, 1.0 equiv., 98%), and silver tetrafluoroborate (1.45 g, 7.35 mmol, 1.05 equiv., 99%). White solid (65%, 1.88 g) **$^1$H NMR** (500 MHz, MeCN-*d*$_3$) δ 7.90 – 7.83 (m, 6H), 7.75 (t, J = 7.9 Hz, 4H), 5.23 (s, 2H). **$^{13}$C NMR** (126 MHz, MeCN-*d*$_3$) δ 136.28, 132.46, 131.59, 126.09, 2.42. **$^{19}$F NMR** (471 MHz, MeCN-*d*$_3$) δ -151.87, -151.92. **HRMS** (ESI) calculated for $C_{13}H_{12}IS^+$ [M]$^+$: 326.9699; Found: 326.9698.

## III. Optimization of Reaction Conditions

### A. Investigation of photocatalysts



To a flame-dried 4 mL vial with a magnetic stir bar were added photocatalyst (5 mol%) and **1a** (12.2 mg, 0.0275 mmol, 1.1 equiv). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon three times via Schlenk line. MeCN-$d_3$ (0.2 mL) and 4-phenyl-1-butene **2** (3.8 µL, 0.025 mmol, 1.0 equiv., 98%) were added via syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred in an isopropanol cooling bath maintained at 5 (± 2) °C for 3 hours under irradiation by two blue LED Kessil$^{TM}$ lamps (PR160L-456 nm, 37.5 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. The reaction mixture was diluted with MeCN-$d_3$ (~0.2 mL) to a total volume of ~0.4 mL, transferred to an NMR tube, and analyzed via $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane (δ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **3a** (δ = 3.92 ppm, tt, 1H).

**Table S1.** Investigation of Photocatalysts

| Entry | Photocatalyst | Yield of **3** (%) | Conversion (%) |
|---|---|---|---|
| 1 | 4CzIPN (standard conditions) | 95 | 99 |
| 2 | Ru(bpy)$_3$(PF$_6$)$_2$ | 5 | 6 |
| 3 | Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$ | 33 | 38 |
| 4 | Ir(dtbbpy)(ppy)$_2$PF$_6$ | 76 | 94 |
| 5 | Ir(dFppy)$_3$ | 32 | 52 |
| 6 | Ir(ppy)$_3$ | 5 | 5 |
| 7 | Thioxanthone | 21 | 27 |

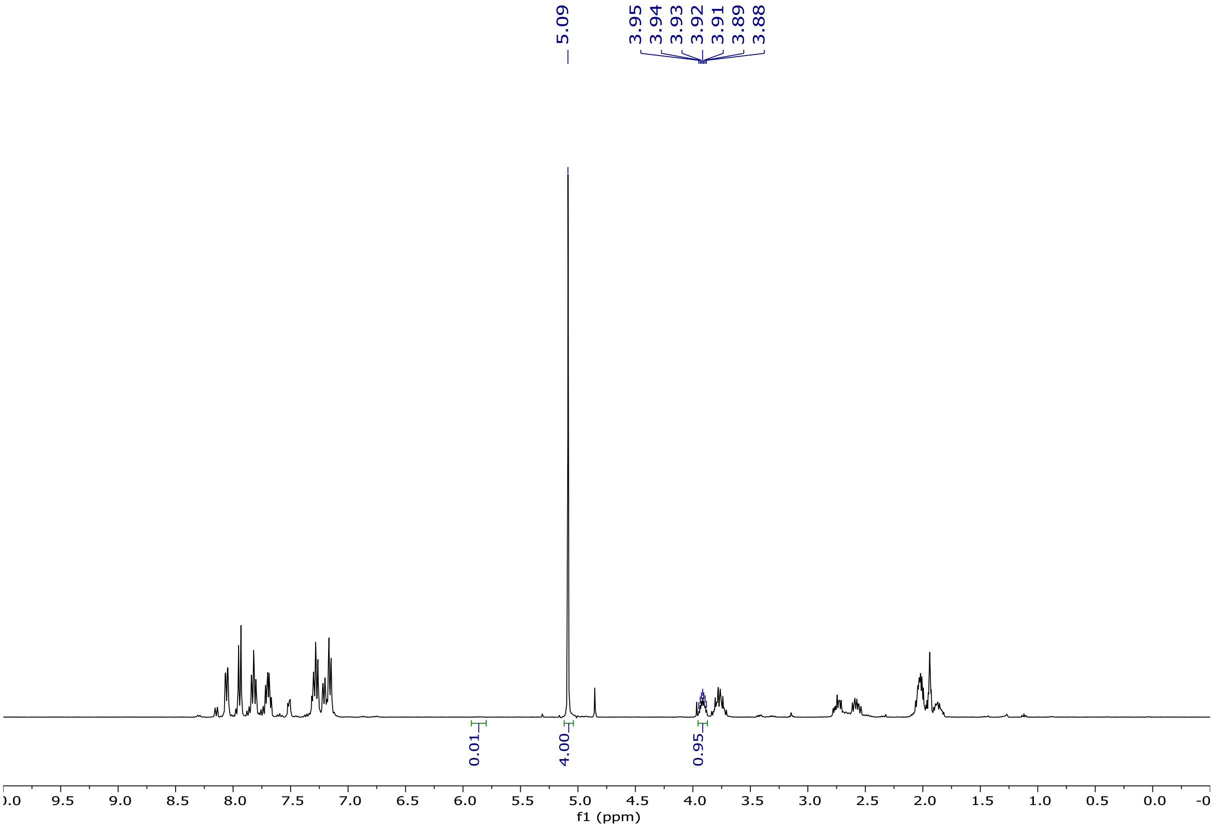
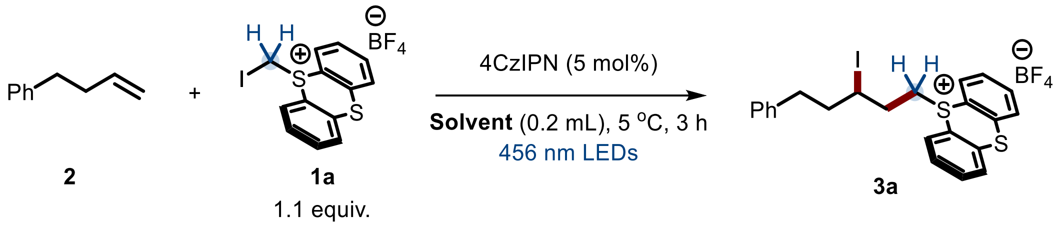


**Fig. S3.** Representative $^1$H NMR spectrum for yield determination in optimization of homologative alkene difunctionalization using **1a** (optimal conditions, 95% **3a**).

## B. Investigation of various solvents

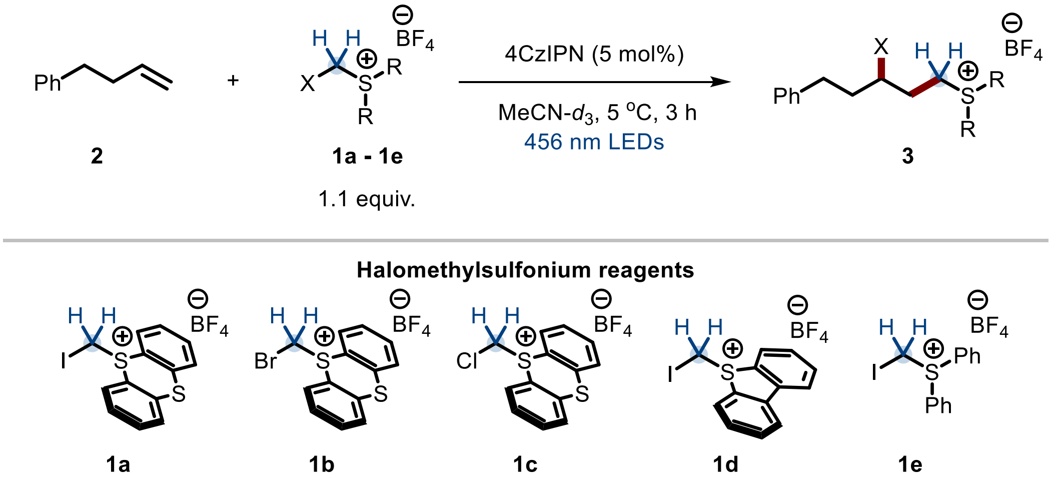


To a flame-dried 4 mL vial with a magnetic stir bar were added 4CzIPN (0.99 mg, 5 mol%) and **1a** (12.2 mg, 0.0275 mmol, 1.1 equiv). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon via Schlenk line. The indicated solvent (0.2 mL) and 4-phenyl-1-butene **2** (3.8 µL, 0.025 mmol, 1.0 equiv., 98%) were added via syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred in an isopropanol cooling bath maintained at 5 (± 2) °C for 3 hours under irradiation by two blue LED Kessil$^{TM}$ lamps (PR160L-456 nm, 37.5 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. An aliquot (~0.05 mL) of the reaction mixture was diluted with MeCN-*d*$_3$ (~0.35 mL) to a total volume of ~0.4 mL, transferred to an NMR tube, and analyzed via $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane (δ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **3a** (δ = 3.92 ppm, tt, 1H).

**Table S2**. Investigation of solvents

| Entry | Solvent | Yield of **3** (%) | Conversion (%) |
|---|---|---|---|
| 1 | MeCN (standard conditions) | 95 | 99 |
| 2 | Acetone | 75 | 99 |
| 3 | DMF | 73 | 75 |
| 4 | MeOH | Trace | < 1 |
| 5 | DCM | 35 | 99 |
| 6 | Toluene | Trace | 6 |

## C. Investigation of halomethylsulfonium reagents (1a-1e)



To a flame-dried 4 mL vial with a magnetic stir bar were added 4CzIPN (0.99 mg, 5 mol%) and the indicated halomethylsulfonium reagent (0.0275 mmol, 1.1 equiv). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon via Schlenk line. MeCN-*d*$_3$ (0.2 mL) and 4-phenyl-1-butene **2** (3.8 µL, 0.025 mmol, 1.0 equiv., 98%) were added via syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred in an isopropanol cooling bath maintained at 5 (± 2) °C for 3 hours under irradiation by two blue LED Kessil$^{TM}$ lamps (PR160L-456 nm, 37.5 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. The reaction mixture was diluted with MeCN-*d*$_3$ (~0.2 mL) to a total volume of ~0.4 mL, transferred to an NMR tube, and analyzed via $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane (δ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **3a** (δ = 3.92 ppm, tt, 1H).

**Table S3.** Investigation of halomethylsulfonium reagents

| Entry | Halomethylsulfonium reagent | Yield of the desired product (%) | Conversion (%) |
|---|---|---|---|
| 1 | **1a** (standard conditions) | 95 | 99 |
| 2 | **1b** | Trace | 42 |
| 3 | **1c** | Trace | 7 |
| 4 | **1d** | Trace | 29 |
| 5 | **1e** | 10 | 16 |

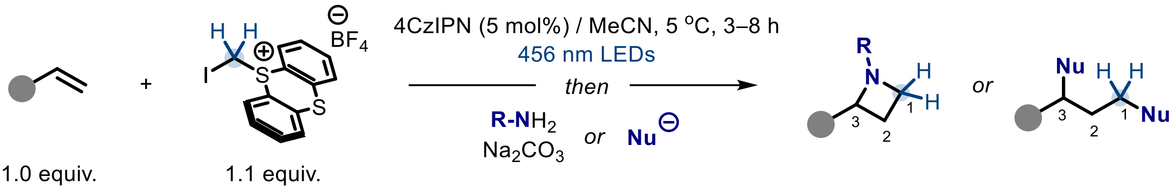
## D. Miscellaneous screening experiments

**Table S4.** Other control experiments

| Entry | Deviation from “standard conditions” | Yield of **3** (%) | Conversion (%) |
|---|---|---|---|
| 1 | **None** | 95 | 99 |
| 2 | 440 nm LEDs | 90 | 92 |
| 3 | 427 nm LEDs | 89 | 99 |
| 4 | w/o 4CzIPN | 21 | 28 |
| 5 | In the dark | < 1 | < 1 |
| 6 | At room temperature | 83 | 99 |

# IV. Synthetic Examples

## A. General procedures



**General Procedure 1 (GP1): Azetidination condition 1**

To a flame-dried 4 mL vial equipped with a magnetic stir bar were added 4CzIPN (7.89 mg, 5 mol%) and **1a** (97.7 mg, 1.1 equiv.). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum. Following evacuation and introduction of argon three times on a Schlenk line, dry MeCN (1.6 mL) was added via syringe. Then, olefin substrate (0.2 mmol, 1.0 equiv.) was added via microliter syringe. (Olefin substrates in solid state were added before capping and MeCN addition) After further sealing with Parafilm, the vial was stirred in an isopropanol bath maintained at 5 (± 2) °C for 3 hours under irradiation by two blue LED Kessil$^{\mathrm{TM}}$ lamps (PR160L-456 nm, 37.5 W). Upon completion of photocatalytic reaction, the vial cap was unscrewed and amine coupling partner (0.8 mmol, 4.0 equiv.) and $Na_2CO_3$ (64.2 mg, 3.0 equiv., 99%) were added. The vial was then capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was vigorously stirred in a pre-heated aluminum block at 80 °C for 13 hours. The crude mixture was purified by flash column chromatography to yield pure azetidine product.

**General Procedure 2 (GP2): Azetidination condition 2**

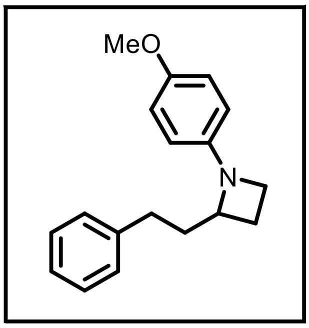
Upon completion of the photocatalytic reaction described in **GP1**, the vial cap was unscrewed and amine coupling partner (3.0 equiv.) and DIPEA (106 μL, 3.0 equiv., 99%) were added. The vial was then capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was vigorously stirred in a pre-heated aluminum block at 60 °C for 13 hours. The crude mixture was purified by flash column chromatography to yield pure azetidine product.

**General Procedure 3 (GP3): 1,3-diazide synthesis.**

Upon completion of the photocatalytic reaction described in **GP1**, the solvent was removed under reduced pressure. DMF (1.6 mL) and sodium azide (39.4 mg, 0.60 mmol, 3.0 equiv., 99%) were added. The vial was then capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was vigorously stirred at room temperature for 24 hours. Upon completion, the crude mixture was diluted with DCM (~10 mL), washed with water (three times) and brine. The combined organic layer was dried with $MgSO_4$, filtered and concentrated with aid of a rotary evaporator. The crude residues were purified by flash column chromatography to yield pure 1,3-diazide product.

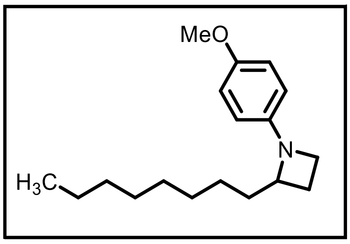
## B. Synthesis and analytical data of homologative azetidination products

### 1-(4-Methoxyphenyl)-2-phenethylazetidine (4):



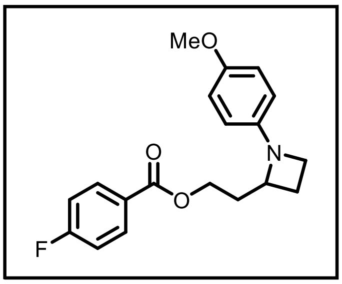
Prepared according to **GP1** using 4-phenyl-1-butene (30 µL, 0.2 mmol, 99%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/acetone 1:0 ~ 10:1 on silica gel (84%, 44.9 mg, off-white solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.32 (t, J = 7.5 Hz, 2H), 7.23 (dd, J = 17.6, 7.7 Hz, 3H), 6.82 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 8.8 Hz, 2H), 3.95 (dddd, J = 15.2, 9.7, 7.4, 3.4 Hz, 2H), 3.77 (s, 3H), 3.52 (q, J = 8.0 Hz, 1H), 2.76 (ddd, J = 15.2, 10.0, 5.5 Hz, 1H), 2.68 (ddd, J = 13.9, 9.9, 6.6 Hz, 1H), 2.30 (qdd, J = 10.0, 6.8, 3.4 Hz, 2H), 2.20 – 2.03 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.44, 147.23, 141.97, 128.51, 128.42, 125.97, 114.78, 113.22, 64.95, 55.89, 50.46, 38.62, 31.31, 23.72. **HRMS** (ESI) calculated for $C_{18}H_{21}NO$ $[M+H]^+$: 268.1696; Found: 268.1694.

### 1-(4-Methoxyphenyl)-2-octylazetidine (6):



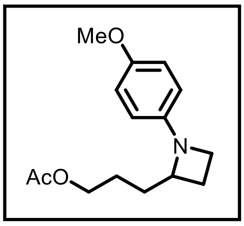
Prepared according to **GP1** using 1-decene (29.5 mg, 0.2 mmol, 95%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (75%, 41.3 mg, orange oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.81 (d, J = 8.3 Hz, 2H), 6.50 (d, J = 8.2 Hz, 2H), 3.89 (q, J = 10.0, 8.9 Hz, 2H), 3.76 (s, 3H), 3.49 (q, J = 8.0 Hz, 1H), 2.28 (td, J = 10.7, 6.2 Hz, 1H), 2.10 (p, J = 8.7 Hz, 1H), 1.95 (dq, J = 14.8, 5.3 Hz, 1H), 1.71 (q, J = 10.7, 10.1 Hz, 1H), 1.40 – 1.25 (m, 12H), 0.91 (t, J = 6.6 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.38, 147.46, 114.76, 113.24, 65.57, 55.90, 50.46, 37.31, 32.01, 29.88, 29.77, 29.39, 24.99, 23.96, 22.79, 14.21. **HRMS** (ESI) calculated for $C_{18}H_{29}NO$ $[M+H]^+$: 276.2322; Found: 276.2324.

### 2-(1-(4-Methoxyphenyl)azetidin-2-yl)ethyl 4-fluorobenzoate (7):



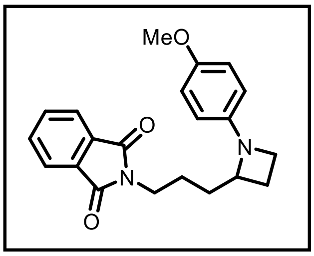
Prepared according to **GP1** using **7-SM** (38.8 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/acetone 1:0 ~ 3:2 on silica gel (74%, 48.7 mg, off-white solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.11 (t, J = 8.5 Hz, 2H), 6.81 (d, J = 8.9 Hz, 2H), 6.51 (d, J = 8.9 Hz, 2H), 4.47 (t, J = 6.4 Hz, 2H), 4.10 (qd, J = 7.8, 3.6 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.75 (s, 3H), 3.54 (q, J = 8.3 Hz, 1H), 2.37 (tdd, J = 10.9, 8.2, 3.4 Hz, 2H), 2.24 (tt, J = 14.5, 8.4 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.85 (d, J = 253.9 Hz), 165.66, 152.62, 146.92, 132.17 (d, J = 9.2 Hz). 126.58 (d, J = 3.0 Hz), 115.62 (d, J = 21.9 Hz), 114.82, 113.20, 62.56, 62.02, 55.86, 50.79, 35.84, 23.83. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -105.63 (tt, J = 8.6, 5.6 Hz). **HRMS** (ESI) calculated for $C_{19}H_{20}FNO_3$ $[M+H]^+$: 330.1500; Found: 330.1500.

**3-(1-(4-Methoxyphenyl)azetidin-2-yl)propyl acetate (8):**



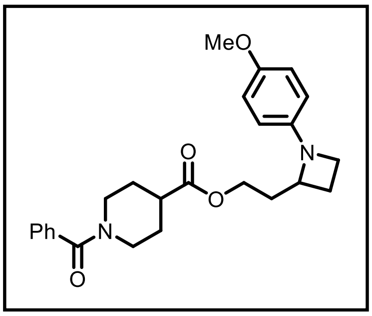
Prepared according to **GP1** using 4-pentenyl acetate (26.2 mg, 0.2 mmol, 98%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (82%, 43.2 mg, yellow oil). **$^1$H NMR** (400 MHz, CDCl$_3$) δ 6.81 (d, 2H), 6.48 (d, 2H), 4.11 (t, J = 6.5 Hz, 2H), 3.95 – 3.85 (m, 2H), 3.75 (s, 3H), 3.50 (q, J = 8.4 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.18 – 2.05 (m, 4H), 2.01 – 1.91 (m, 1H), 1.84 – 1.60 (m, 3H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 171.29, 152.56, 147.18, 114.88, 113.26, 64.79, 64.58, 55.99, 50.45, 33.38, 24.23, 23.57, 21.15. **HRMS** (ESI) calculated for $C_{15}H_{21}NO_3$ [M+H]$^+$: 264.1594; Found: 264.1595.

**2-(3-(1-(4-Methoxyphenyl)azetidin-2-yl)propyl)isoindoline-1,3-dione (9):**



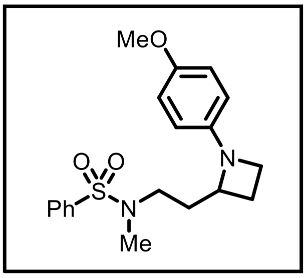
Prepared according to **GP1** using **9-SM** (43.1 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/EA 1:0 ~ 3:1 on silica gel (74%, 52.1 mg, yellow solid). **$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.83 (dd, J = 5.5, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.0 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 8.9 Hz, 2H), 3.96 – 3.82 (m, 2H), 3.74 (d, J = 7.5 Hz, 5H), 3.50 – 3.41 (m, 1H), 2.26 (dtd, J = 11.6, 8.3, 3.3 Hz, 1H), 2.14 – 2.04 (m, 1H), 2.01 – 1.91 (m, 1H), 1.85 – 1.65 (m, 3H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 168.44, 152.36, 147.02, 133.99, 132.17, 123.27, 114.68, 113.16, 64.55, 55.84, 50.36, 38.05, 34.16, 24.03, 23.40. **HRMS** (ESI) calculated for $C_{21}H_{22}N_2O_3$ [M+H]$^+$: 351.1703; Found: 351.1702.

**2-(1-(4-Methoxyphenyl)azetidin-2-yl)ethyl 1-benzoylpiperidine-4-carboxylate (10):**



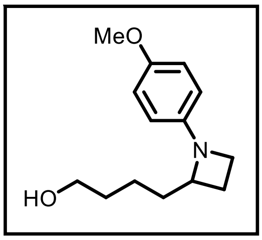
Prepared according to **GP1** using **10-SM** (57.5 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (77 %, 65.1 mg, brown oil). **$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.39 (q, *J* = 5.7, 5.0 Hz, 5H), 6.86 – 6.75 (m, 2H), 6.53 – 6.42 (m, 2H), 4.56 (s, 1H), 4.24 (t, *J* = 6.4 Hz, 2H), 3.99 (qd, *J* = 7.9, 3.6 Hz, 1H), 3.91 (ddd, *J* = 9.6, 6.8, 3.3 Hz, 1H), 3.74 (s, 3H), 3.52 (q, *J* = 8.1 Hz, 1H), 3.02 (s, 2H), 2.56 (tt, *J* = 10.9, 4.1 Hz, 1H), 2.37 – 1.96 (m, 5H), 1.71 (d, *J* = 31.7 Hz, 3H), 1.25 (s, 1H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 174.11, 170.43, 152.50, 146.78, 135.96, 129.67, 128.52, 126.84, 114.67, 113.10, 62.29, 61.50, 55.78, 55.77, 50.68, 46.98 (bs), 41.51 (bs), 41.11, 41.09, 35.61, 29.70, 28.54 (bs), 27.89 (bs), 23.57. **HRMS** (ESI) calculated for $C_{25}H_{30}N_2O_4$ [M+H]$^+$: 423.2279; Found: 423.2279.

**N-(2-(1-(4-Methoxyphenyl)azetidin-2-yl)ethyl)-N-methylbenzenesulfonamide (11):**



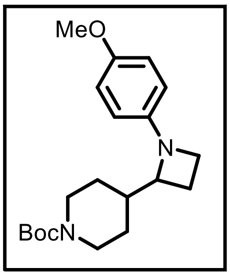
Prepared according to **GP1** using **11-SM** (45.1 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (81%, 58.4 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H), 6.80 (d, J = 8.9 Hz, 2H), 6.44 (d, J = 8.9 Hz, 2H), 4.00 (qd, J = 7.8, 3.4 Hz, 1H), 3.89 (ddd, J = 9.3, 6.9, 3.3 Hz, 1H), 3.75 (s, 3H), 3.51 (q, J = 8.3 Hz, 1H), 3.27 – 3.18 (m, 1H), 3.04 (ddd, J = 13.5, 8.3, 5.4 Hz, 1H), 2.78 (s, 3H), 2.36 (dtd, J = 11.3, 8.2, 3.3 Hz, 1H), 2.20 – 2.09 (m, 2H), 1.93 (tdd, J = 15.0, 10.2, 5.9 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.66, 146.91, 137.69, 132.76, 129.27, 127.52, 114.87, 113.27, 62.82, 55.96, 50.81, 46.62, 35.02, 34.58, 23.62. **HRMS** (ESI) calculated for $C_{19}H_{24}N_2O_3S$ $[M+H]^+$: 361.1580; Found: 361.1579.

**4-(1-(4-Methoxyphenyl)azetidin-2-yl)butan-1-ol (12):**



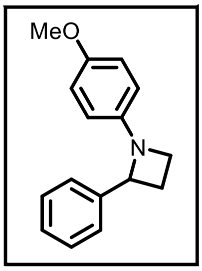
Prepared according to **GP1** using 5-hexen-1-ol (20.5 mg, 0.2 mmol, 98%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 2:3 on silica gel (71%, 33.5 mg, brown solid). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.80 (d, J = 8.9 Hz, 2H), 6.49 (d, J = 8.9 Hz, 2H), 3.94 – 3.84 (m, 2H), 3.75 (s, 3H), 3.67 (t, J = 6.5 Hz, 2H), 3.48 (q, J = 8.4 Hz, 1H), 2.29 (dtd, J = 10.9, 8.1, 3.3 Hz, 1H), 2.10 (dq, J = 10.8, 8.2 Hz, 1H), 1.96 (dddd, J = 13.6, 10.1, 6.2, 3.9 Hz, 1H), 1.73 (dtd, J = 13.8, 9.5, 5.3 Hz, 1H), 1.63 (tt, J = 8.4, 6.6 Hz, 2H), 1.50 – 1.36 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.46, 147.31, 114.79, 113.31, 65.37, 62.87, 55.92, 50.51, 36.89, 32.90, 23.78, 21.19. **HRMS** (ESI) calculated for $C_{14}H_{21}NO_2$ $[M+H]^+$: 236.1645; Found: 236.1642.

***tert*-Butyl 4-(1-(4-methoxyphenyl)azetidin-2-yl)piperidine-1-carboxylate (13):**



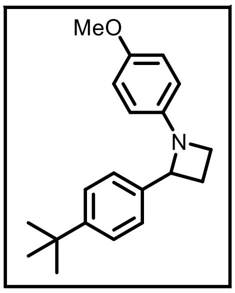
Prepared according to **GP1** using *tert*-butyl 4-vinylpiperidine-1-carboxylate (43.1 mg, 0.2 mmol, 98%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (43%, 29.8mg, yellow oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.80 (d, J = 8.8 Hz, 2H), 6.49 (d, J = 8.8 Hz, 2H), 4.38 – 4.04 (m, 2H), 3.91 (q, J = 7.4 Hz, 1H), 3.84 (q, J = 7.3 Hz, 1H), 3.75 (s, 3H), 3.49 (q, J = 8.0 Hz, 1H), 2.67 (t, J = 12.4 Hz, 2H), 2.24 – 2.11 (m, 2H), 1.94 – 1.81 (m, 1H), 1.76 (d, J = 13.2 Hz, 1H), 1.67 – 1.58 (m, 1H), 1.47 (s, 9H), 1.34 – 1.16 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.04, 152.41, 147.48, 114.75, 113.43, 79.53, 68.31, 55.99, 51.10, 42.35, 28.66, 26.36, 20.18, 20.17. **HRMS** (ESI) calculated for $C_{20}H_{30}N_2O_3$ $[M]^+$: 346.2256; Found: 346.2254.

**1-(4-Methoxyphenyl)-2-phenylazetidine (14):**



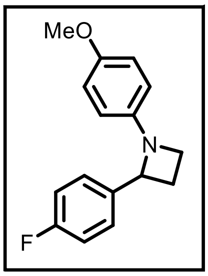
Prepared according to **GP2** using styrene (21.0 mg, 0.2 mmol, 99%) and *p*-anisidine (74.6 mg, 0.6 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 5:1 on silica gel (67%, 32.1 mg, off-white solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.4 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 9.0 Hz, 2H), 4.84 (t, J = 8.0 Hz, 1H), 4.02 (ddd, J = 9.0, 6.5, 2.8 Hz, 1H), 3.74 (s, 3H), 3.73 – 3.64 (m, 1H), 2.61 (dtd, J = 11.0, 8.2, 2.8 Hz, 1H), 2.36 (p, J = 8.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.59, 146.91, 143.94, 128.74, 127.44, 126.06, 114.68, 113.38, 68.01, 55.89, 49.85, 28.01. **HRMS** (ESI) calculated for $C_{16}H_{17}NO$ $[M+H]^+$: 240.1383; Found: 240.1379.

**2-(4-(*tert*-Butyl)phenyl)-1-(4-methoxyphenyl)azetidine (15):**



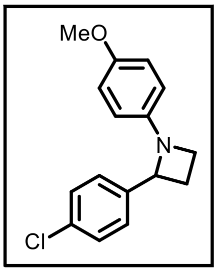
Prepared according to **GP2** using 4-*tert*-butylstyrene (34.5 mg, 0.2 mmol, 93%) and *p*-anisidine (74.6 mg, 0.6 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (61%, 36.0 mg, off-white solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 (s, 4H), 6.78 – 6.71 (m, 2H), 6.47 – 6.38 (m, 2H), 4.79 (t, J = 8.0 Hz, 1H), 3.98 (ddd, J = 9.0, 6.6, 2.9 Hz, 1H), 3.72 (s, 3H), 3.64 (td, J = 8.5, 6.5 Hz, 1H), 2.56 (dtd, J = 10.9, 8.2, 2.9 Hz, 1H), 2.34 (dq, J = 10.7, 8.6 Hz, 1H), 1.33 (s, 9H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.62, 150.39, 147.20, 140.99, 125.84, 125.67, 114.75, 113.49, 67.92, 55.99, 49.96, 34.72, 31.61, 28.07. **HRMS** (ESI) calculated for $C_{20}H_{25}NO$ $[M+H]^+$: 296.2009; Found: 296.2010.

**2-(4-Fluorophenyl)-1-(4-methoxyphenyl)azetidine (16):**



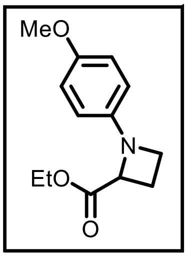
Prepared according to **GP2** using 4-fluorostyrene (24.7 mg, 0.2 mmol, 98%) and *p*-anisidine (74.6 mg, 0.6 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 3:1 on silica gel (79%, 40.4 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.08 (t, J = 8.7 Hz, 2H), 6.82 – 6.74 (m, 2H), 6.44 – 6.37 (m, 2H), 4.80 (t, J = 7.9 Hz, 1H), 4.00 (ddd, J = 9.0, 6.5, 2.8 Hz, 1H), 3.74 (s, 3H), 3.67 (td, J = 8.5, 6.5 Hz, 1H), 2.59 (dtd, J = 10.8, 8.1, 2.8 Hz, 1H), 2.31 (dq, J = 10.6, 8.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.26 (d, J = 245.2 Hz), 152.69, 146.71, 139.70 (d, J = 2.9 Hz), 127.68 (d, J = 8.0 Hz), 115.55 (d, J = 21.3 Hz), 114.71, 113.35, 67.33, 55.87, 49.74, 28.15. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -115.53 (tt, J = 8.7, 5.4 Hz). **HRMS** (ESI) calculated for $C_{16}H_{16}FNO$ $[M+H]^+$: 258.1289; Found: 258.1289.

**2-(4-Chlorophenyl)-1-(4-methoxyphenyl)azetidine (17):**



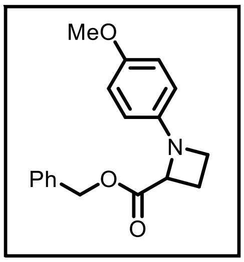
Prepared according to **GP2** using 4-chlorostyrene (28.0 mg, 0.2 mmol, 99%) and *p*-anisidine (74.6 mg, 0.6 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (54%, 29.6 mg, yellow solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, 2H), 7.35 (d, 2H), 6.76 (d, 2H), 6.39 (d, 2H), 4.78 (t, J = 7.9 Hz, 1H), 3.98 (ddd, J = 9.0, 6.5, 2.8 Hz, 1H), 3.73 (s, 3H), 3.66 (td, J = 8.5, 6.5 Hz, 1H), 2.59 (dtd, J = 10.9, 8.1, 2.8 Hz, 1H), 2.29 (dq, J = 10.7, 8.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.80, 146.63, 142.52, 133.14, 128.96, 127.52, 114.79, 113.39, 67.33, 55.95, 49.84, 28.04. **HRMS** (ESI) calculated for $C_{16}H_{16}ClNO$ $[M+H]^+$: 274.0993; Found: 274.0989.

**Ethyl 1-(4-methoxyphenyl)azetidine-2-carboxylate (18):**



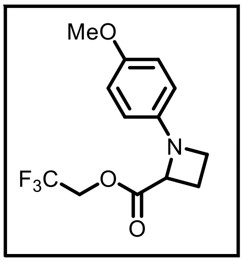
Prepared according to **GP1** using ethyl acrylate (20.2 mg, 0.2 mmol, 99%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner, with modified conditions using **1a** (133 mg, 0.3 mmol, 1.5 equiv.) and 2.0 mL of MeCN at room temperature for 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 3:1 on silica gel (48%, 22.7 mg, light yellow oil). **$^1$H NMR (**500 MHz, $CDCl_3$) δ 6.80 (d, J = 8.4 Hz, 2H), 6.52 (d, J = 8.4 Hz, 2H), 4.38 (t, J = 8.2 Hz, 1H), 4.27 (p, J = 7.3 Hz, 2H), 4.01 – 3.92 (m, 1H), 3.74 (s, 3H), 3.62 (q, J = 7.8 Hz, 1H), 2.61 (p, J = 8.5 Hz, 1H), 2.50 (q, J = 8.1 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 172.78, 153.05, 145.54, 114.63, 113.49, 64.21, 61.26, 55.83, 50.38, 21.67, 14.35. **HRMS** (ESI) calculated for $C_{13}H_{17}NO_3$ $[M+H]^+$: 236.1281; Found: 236.1278.

**Benzyl 1-(4-methoxyphenyl)azetidine-2-carboxylate (19):**



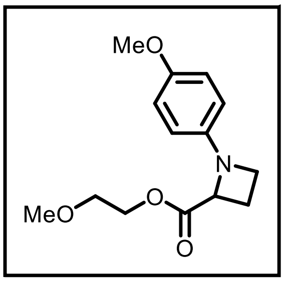
Prepared according to **GP1** using benzyl acrylate (32.8 mg, 0.2 mmol, 98%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner, with modified conditions using **1a** (133 mg, 0.3 mmol, 1.5 equiv.) and 2.0 mL of MeCN at room temperature for 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on silica gel (48%, 28.5 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 6.80 (d, J = 8.9 Hz, 2H), 6.51 (d, J = 8.9 Hz, 2H), 5.32 – 5.18 (m, 2H), 4.49 – 4.41 (m, 1H), 3.97 (ddd, J = 8.6, 6.5, 3.7 Hz, 1H), 3.75 (s, 3H), 3.64 (q, J = 8.0 Hz, 1H), 2.63 (dq, J = 11.0, 8.0 Hz, 1H), 2.52 (dtd, J = 12.4, 8.6, 3.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 172.59, 153.03, 145.35, 135.71, 128.70, 128.47, 128.39, 114.61, 113.46, 66.89, 64.11, 55.81, 50.38, 21.63. **HRMS** (ESI) calculated for $C_{18}H_{19}NO_3$ $[M+H]^+$: 298.1438; Found: 298.1440.

### 2,2,2-Trifluoroethyl 1-(4-methoxyphenyl)azetidine-2-carboxylate (20):



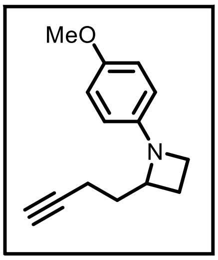
Prepared according to **GP1** using 2,2,2-trifluoroethyl acrylate (31.5 mg, 0.2 mmol, 98%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner, with modified condition using **1a** (133 mg, 0.3 mmol, 1.5 equiv.) and 2.0 mL of MeCN at room temperature for 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on silica gel (43%, 24.9 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.82 (d, J = 8.9 Hz, 2H), 6.49 (d, J = 8.9 Hz, 2H), 4.67 – 4.53 (m, 2H), 4.53 – 4.48 (m, 1H), 3.99 (ddd, J = 8.3, 6.8, 3.8 Hz, 1H), 3.75 (s, 3H), 3.68 (q, J = 8.0 Hz, 1H), 2.68 – 2.54 (m, 2H). **$^{13}$C NMR** (126 MHz, CDCl3) δ 171.29, 153.32, 144.95, 124.08 (q, J = 277.3 Hz), 114.79, 113.40, 63.43, 60.56 (q, J = 36.8 Hz), 55.87, 50.46, 21.66. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -73.71 (t, J = 8.3 Hz). **HRMS** (ESI) calculated for $C_{13}H_{14}F_3NO_3$ $[M+H]^+$: 290.0999; Found: 290.0995.

### 2-Methoxyethyl 1-(4-methoxyphenyl)azetidine-2-carboxylate (21):



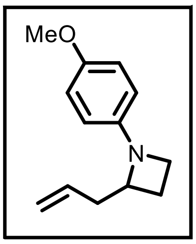
Prepared according to **GP1** using 2-methoxyethyl acrylate (26.6 mg, 0.2 mmol, 98%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner, with modified condition using **1a** (133 mg, 0.3 mmol, 1.5 equiv.) and 2.0 mL of MeCN at room temperature for 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on silica gel (57%, 30.3 mg, brown oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.80 (d, J = 8.9 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 4.48 – 4.30 (m, 3H), 3.96 (ddd, J = 8.7, 6.7, 3.6 Hz, 1H), 3.74 (s, 3H), 3.68 – 3.59 (m, 3H), 3.39 (s, 3H), 2.62 (dq, J = 10.5, 8.0 Hz, 1H), 2.52 (ddt, J = 10.8, 7.8, 4.4 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 172.70, 152.94, 145.33, 114.51, 113.41, 70.35, 63.99, 63.90, 59.03, 55.73, 50.26, 21.63. **HRMS** (ESI) calculated for $C_{14}H_{19}NO_4$ $[M+H]^+$: 266.1387; Found: 266.1387.

### 2-(But-3-yn-1-yl)-1-(4-methoxyphenyl)azetidine (22):



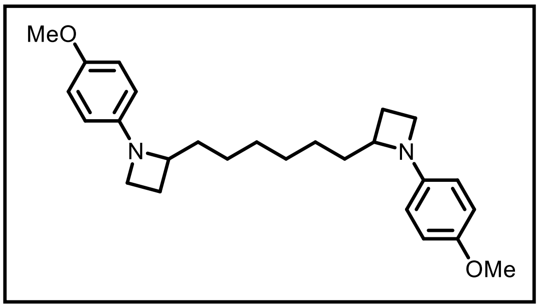
Prepared according to **GP1** using hex-1-en-5-yne (16.5 mg, 0.2 mmol, 97%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on silica gel (52%, 22.6 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.81 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 4.05 (qd, J = 7.9, 3.7 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.75 (s, 3H), 3.51 (q, J = 8.0 Hz, 1H), 2.40 – 2.21 (m, 3H), 2.16 (tdd, J = 14.3, 9.0, 6.0 Hz, 2H), 1.94 (ddt, J = 15.8, 8.6, 4.4 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.53, 147.09, 114.80, 113.25, 84.04, 68.80, 64.08, 55.92, 50.60, 35.55, 23.44, 14.30. **HRMS** (ESI) calculated for $C_{14}H_{17}NO$ $[M+H]^+$: 216.1383; Found: 216.1383.

**2-Allyl-1-(4-methoxyphenyl)azetidine (23):**



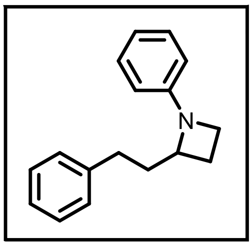
Prepared according to **GP1** using 1,4-pentadiene (13.8 mg, 0.2 mmol, 99%) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) as an amine coupling partner, with modified conditions using **1a** (88.8 mg, 0.2 mmol, 1.0 equiv.) at 5 (± 2) °C for 8 hours for the photocatalytic reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on silica gel (60%, 24.4 mg, light brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.81 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 8.5 Hz, 2H), 5.86 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H), 5.22 – 5.06 (m, 2H), 3.97 (qd, J = 7.8, 4.0 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.76 (s, 3H), 3.51 (q, J = 8.0 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.48 (dt, J = 14.8, 7.7 Hz, 1H), 2.32 – 2.22 (m, 1H), 2.22 – 2.09 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.41, 147.07, 134.04, 117.33, 114.76, 113.25, 64.42, 55.92, 50.43, 41.45, 23.20. **HRMS** (ESI) calculated for $C_{13}H_{17}NO$ $[M+H]^+$: 204.1383; Found: 204.1380.

**1,6-Bis(1-(4-methoxyphenyl)azetidin-2-yl)hexane (24):**



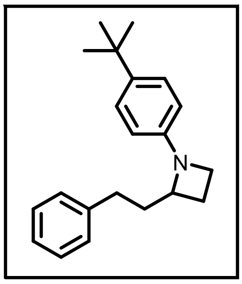
Prepared according to **GP1** using 1,9-decadiene (28.5 mg, 0.2 mmol, 97%) with doubled amount of reagent **1a** (195 mg, 0.44 mmol, 2.2 equiv.) and solvent (3.2 mL). Amine coupling partner *p*-anisidine (199.0 mg, 1.6 mmol, 99%) and $Na_2CO_3$ (129 mg, 1.2 mmol, 99%) were used for the double azetidination reaction. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 5:1 on silica gel (47%, 38.6 mg, off-white solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.82 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.1 Hz, 4H), 3.89 (qd, J = 11.1, 10.2, 5.1 Hz, 4H), 3.76 (s, 6H), 3.49 (q, J = 8.0 Hz, 2H), 2.29 (td, J = 11.2, 5.6 Hz, 2H), 2.11 (p, J = 8.7 Hz, 2H), 1.95 (tq, J = 8.7, 4.2 Hz, 2H), 1.72 (q, J = 10.6, 10.0 Hz, 2H), 1.40 (s, 8H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.38, 147.40, 114.76, 113.23, 65.49, 55.90, 50.45, 37.23, 29.87, 24.90, 23.90. **HRMS** (ESI) calculated for $C_{26}H_{36}N_2O_2$ $[M+H]^+$: 409.2850; Found: 409.2847.

**2-Phenethyl-1-phenylazetidine (25):**



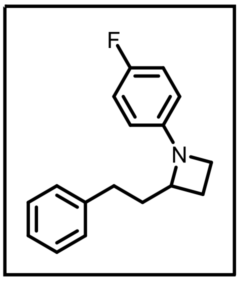
Prepared according to **GP1** using 4-phenyl-1-butene (30 µL, 0.2 mmol, 99%) and aniline (76.0 mg, 0.8 mmol, 98%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 2:3 on silica gel (83%, 39.3 mg, light brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, J = 7.5 Hz, 2H), 7.32 – 7.23 (m, 5H), 6.80 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 4.10 (qd, J = 8.0, 3.4 Hz, 1H), 4.01 (td, J = 8.1, 3.6 Hz, 1H), 3.64 (q, J = 8.0 Hz, 1H), 2.80 (ddd, J = 15.2, 10.0, 5.4 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.45 – 2.30 (m, 2H), 2.24 – 2.16 (m, 1H), 2.13 (dp, J = 14.6, 5.3, 4.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.48, 141.94, 129.02, 128.53, 128.43, 125.99, 117.72, 111.94, 64.56, 49.97, 38.36, 31.24, 23.61. **HRMS** (ESI) calculated for $C_{17}H_{19}N$ $[M+H]^+$: 238.1590; Found: 238.1590.

### 1-(4-(*tert*-Butyl)phenyl)-2-phenethylazetidine (26):



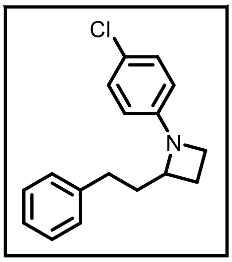
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 4-(*tert*-butyl)aniline (121 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 5:4 on silica gel (86%, 50.3 mg, off-white solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, J = 7.6 Hz, 2H), 7.31 – 7.21 (m, 5H), 6.52 (d, J = 8.6 Hz, 2H), 4.06 (qd, J = 7.7, 3.7 Hz, 1H), 3.98 (ddd, J = 8.6, 6.9, 3.5 Hz, 1H), 3.61 (td, J = 8.6, 7.1 Hz, 1H), 2.79 (ddd, J = 13.7, 10.1, 5.5 Hz, 1H), 2.71 (ddd, J = 13.8, 10.0, 6.6 Hz, 1H), 2.39 – 2.28 (m, 2H), 2.23 – 2.06 (m, 2H), 1.34 (s, 9H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.36, 142.06, 140.46, 128.54, 128.46, 125.98, 125.83, 111.72, 64.65, 50.10, 38.57, 34.02, 31.68, 31.31, 23.66. **HRMS** (ESI) calculated for $C_{21}H_{27}N$ $[M+H]^+$: 294.2216; Found: 294.2216.

### 1-(4-Fluorophenyl)-2-phenethylazetidine (27):



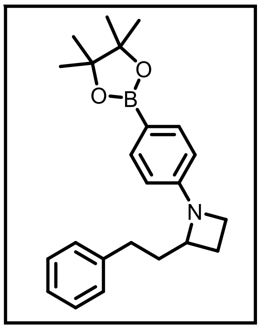
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 4-fluoroaniline (89.8 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (72%, 36.8 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.6 Hz, 2H), 7.25 (q, J = 6.8, 6.0 Hz, 3H), 6.96 – 6.89 (m, 2H), 6.48 – 6.41 (m, 2H), 4.00 (tt, J = 7.6, 3.9 Hz, 1H), 3.97 – 3.92 (m, 1H), 3.59 – 3.51 (m, 1H), 2.81 – 2.72 (m, 1H), 2.68 (ddd, J = 13.9, 9.8, 6.6 Hz, 1H), 2.39 – 2.25 (m, 2H), 2.17 (dq, J = 10.8, 8.1 Hz, 1H), 2.08 (dtd, J = 13.5, 9.5, 5.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 156.23 (d, J = 235.5 Hz), 149.18, 141.89, 128.61, 128.48, 126.10, 115.55 (d, J = 22.5 Hz), 112.91 (d, J = 7.5 Hz), 64.94, 50.45, 38.46, 31.28, 23.67. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -127.66 (tt, J = 8.7, 4.3 Hz). **HRMS** (ESI) calculated for $C_{17}H_{18}FN$ $[M+H]^+$: 256.1496; Found: 256.1497.

### 1-(4-Chlorophenyl)-2-phenethylazetidine (28):



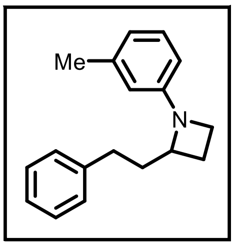
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 4-chloroaniline (104 mg, 0.8 mmol, 98%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (60%, 32.6 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.7 Hz, 3H), 7.13 (d, J = 8.7 Hz, 2H), 6.40 (d, J = 8.3 Hz, 2H), 4.01 (qd, J = 7.7, 3.5 Hz, 1H), 3.93 (td, J = 8.1, 3.7 Hz, 1H), 3.55 (q, J = 8.0 Hz, 1H), 2.73 (ddd, J = 15.3, 10.0, 5.5 Hz, 1H), 2.68 – 2.59 (m, 1H), 2.38 – 2.32 (m, 1H), 2.26 (dddd, J = 13.6, 10.1, 6.5, 3.6 Hz, 1H), 2.14 (dq, J = 10.5, 7.9 Hz, 1H), 2.05 (dtd, J = 14.7, 9.6, 5.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.99, 141.79, 128.92, 128.62, 128.46, 126.13, 122.52, 113.12, 64.69, 50.12, 38.22, 31.20, 23.58. **HRMS** (ESI) calculated for $C_{17}H_{18}ClN$ $[M+H]^+$: 272.1201; Found: 272.1198.

**2-Phenethyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)azetidine (29):**



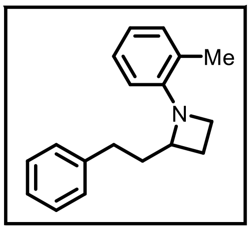
Prepared according to **GP1** using 4-phenyl-1-butene (30 µL, 0.2 mmol, 99%) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (179 mg, 0.8 mmol, 98%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 5:4 on silica gel (44%, 31.7 mg, off-white solid). **$^1$H NMR** (400 MHz, CDCl3) δ 7.64 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 6.6 Hz, 3H), 6.44 (d, J = 8.4 Hz, 2H), 4.11 (d, J = 8.3 Hz, 1H), 3.98 (td, J = 8.0, 3.9 Hz, 1H), 3.64 (q, J = 7.9 Hz, 1H), 2.78 – 2.60 (m, 2H), 2.44 – 2.23 (m, 2H), 2.19 – 1.99 (m, 2H), 1.31 (s, 12H). **$^{13}$C NMR** (126 MHz, CDCl3) δ 154.35, 141.85, 136.08, 128.55, 128.44, 126.04, 110.86, 83.32, 64.23, 49.65, 37.90, 31.12, 24.98, 24.95, 23.45. **HRMS** (ESI) calculated for $C_{23}H_{30}BNO_2$ $[M+H]^+$: 364.2443; Found: 364.2447.

**2-Phenethyl-1-(*m*-tolyl)azetidine (30):**



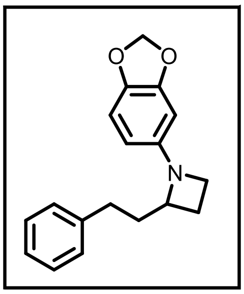
Prepared according to **GP1** using 4-phenyl-1-butene (30 µL, 0.2 mmol, 99%) and *m*-toluidine (86.6 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 5:1 on silica gel (82%, 41.1 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, J = 7.5 Hz, 2H), 7.32 – 7.23 (m, 3H), 7.15 (t, J = 7.7 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 6.38 (d, J = 9.2 Hz, 2H), 4.09 (tt, J = 11.3, 5.6 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.63 (q, J = 8.0 Hz, 1H), 2.84 – 2.69 (m, 2H), 2.41 – 2.35 (m, 2H), 2.35 (s, 3H), 2.23 – 2.08 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.57, 142.00, 138.77, 128.91, 128.52, 128.45, 125.98, 118.71, 112.62, 109.14, 64.48, 50.00, 38.37, 31.23, 23.60, 21.79. **HRMS** (ESI) calculated for $C_{18}H_{21}N$ $[M+H]^+$: 252.1747; Found: 252.1747.

**2-Phenethyl-1-(*o*-tolyl)azetidine (31):**



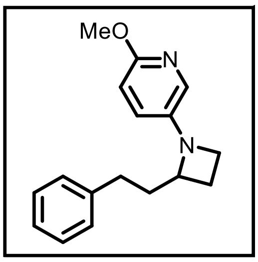
Prepared according to **GP1** using 4-phenyl-1-butene (30 µL, 0.2 mmol, 99%) and the modified amount of *o*-toluidine (86.6 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (72%, 36.2 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.5 Hz, 2H), 7.22 (dd, J = 11.9, 7.1 Hz, 3H), 7.12 – 7.03 (m, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 4.17 (qd, J = 7.9, 3.3 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.50 (q, J = 7.8 Hz, 1H), 2.74 (ddd, J = 15.1, 9.8, 5.7 Hz, 1H), 2.70 – 2.62 (m, 1H), 2.27 (td, J = 11.6, 8.2 Hz, 1H), 2.21 (s, 3H), 2.15 (ddt, J = 10.1, 6.5, 3.6 Hz, 1H), 2.07 (q, J = 8.5 Hz, 1H), 1.97 (dtd, J = 14.7, 9.4, 5.6 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 150.17, 142.07, 131.54, 128.54, 128.51, 126.44, 126.36, 126.01, 119.80, 113.11, 62.86, 52.57, 36.84, 31.41, 23.64, 19.59. **HRMS** (ESI) calculated for $C_{18}H_{21}N$ $[M+H]^+$: 252.1747; Found: 252.1745.

### 1-(Benzo[*d*][1,3]dioxol-5-yl)-2-phenethylazetidine (32):



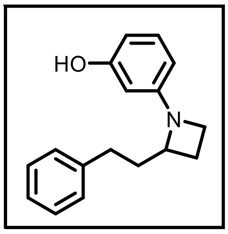
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and benzo[*d*][1,3]dioxol-5-amine (112 mg, 0.8 mmol, 98%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 2:3 on silica gel (73%, 41.1 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.5 Hz, 2H), 7.24 (dd, J = 14.2, 7.3 Hz, 3H), 6.70 (d, J = 8.3 Hz, 1H), 6.16 (d, J = 2.3 Hz, 1H), 5.95 (dd, J = 8.3, 2.3 Hz, 1H), 5.87 (s, 2H), 4.02 – 3.83 (m, 2H), 3.52 (q, J = 8.0 Hz, 1H), 2.80 – 2.62 (m, 2H), 2.30 (ddtd, J = 20.0, 10.1, 7.5, 6.5, 3.5 Hz, 2H), 2.20 – 2.01 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 148.65, 148.23, 141.88, 139.89, 128.54, 128.42, 126.01, 108.55, 103.74, 100.65, 94.94, 64.95, 50.55, 38.37, 31.24, 23.52. **HRMS** (ESI) calculated for $C_{18}H_{19}NO_2$ $[M+H]^+$: 282.1489; Found: 282.1487.

### 2-Methoxy-5-(2-phenethylazetidin-1-yl)pyridine (33):



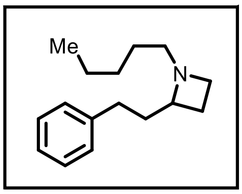
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 6-methoxypyridin-3-amine (101 mg, 0.8 mmol, 98%). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 3:2 on silica gel (57%, 30.6 mg, brown oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 3.0 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.21 (d, J = 7.4 Hz, 3H), 6.85 (dd, J = 8.8, 3.0 Hz, 1H), 6.62 (d, J = 8.8 Hz, 1H), 3.98 – 3.88 (m, 2H), 3.86 (s, 3H), 3.55 – 3.46 (m, 1H), 2.68 (dddd, J = 30.2, 13.8, 9.7, 6.1 Hz, 2H), 2.37 – 2.11 (m, 3H), 2.04 (dtd, J = 13.2, 9.5, 5.5 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 157.68, 143.76, 141.71, 130.06, 128.59, 128.41, 126.08, 124.56, 110.64, 65.26, 53.39, 50.48, 38.50, 31.29, 24.18. **HRMS** (ESI) calculated for $C_{17}H_{20}N_2O$ $[M+H]^+$: 269.1649; Found: 269.1648.

### 3-(2-Phenethylazetidin-1-yl)phenol (34):



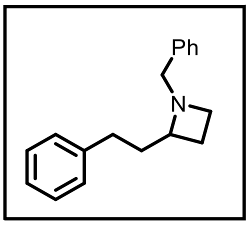
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 3-aminophenol (89.1 mg, 0.8 mmol, 98%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 3:2 on silica gel (78%, 39.6 mg, brown oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.22 (dd, J = 7.8, 2.8 Hz, 3H), 7.04 (t, J = 8.0 Hz, 1H), 6.19 (d, J = 7.3 Hz, 1H), 6.09 (d, J = 8.0 Hz, 1H), 5.96 (s, 1H), 4.90 (s, 1H), 4.03 (qd, J = 7.7, 3.4 Hz, 1H), 3.92 (td, J = 8.0, 3.7 Hz, 1H), 3.57 (q, J = 8.0 Hz, 1H), 2.78 – 2.58 (m, 2H), 2.37 – 2.23 (m, 2H), 2.18 – 2.00 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 156.64, 153.92, 141.84, 130.06, 128.53, 128.46, 126.00, 105.30, 104.92, 99.42, 64.71, 50.06, 38.14, 31.23, 23.54. **HRMS** (ESI) calculated for $C_{17}H_{19}NO$ $[M+H]^+$: 254.1540; Found: 254.1538.

**1-Pentyl-2-phenethylazetidine (35):**



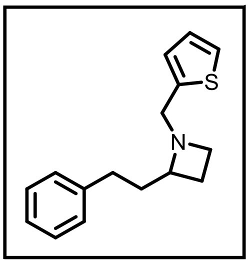
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and amylamine (70.4 mg, 0.8 mmol, 99%) with modified conditions of 60 ºC and 6 hours for the substitution reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on amino-functionalized silica gel (65%, 30.1 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.27 (t, J = 7.4 Hz, 2H), 7.18 (d, J = 7.3 Hz, 3H), 3.39 (t, J = 7.7 Hz, 1H), 2.99 (p, J = 7.6 Hz, 1H), 2.67 (q, J = 8.1 Hz, 1H), 2.57 (q, J = 8.4 Hz, 3H), 2.28 – 2.19 (m, 1H), 2.04 – 1.92 (m, 2H), 1.86 – 1.77 (m, 2H), 1.40 – 1.26 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.33, 128.46, 128.42, 125.81, 66.96, 59.67, 51.82, 38.49, 32.04, 29.89, 27.76, 24.05, 22.73, 14.13. **HRMS** (ESI) calculated for $C_{16}H_{25}N$ $[M+H]^+$: 232.2060; Found: 232.2057.

**1-Benzyl-2-phenethylazetidine (36):**



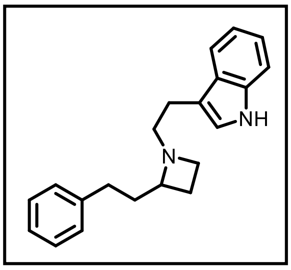
Prepared according to **GP2** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and modified conditions of 5 hours of substitution reaction with benzylamine (43.3 mg, 0.4 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 2:3 on silica gel (55%, 27.7 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.28 (dd, J = 14.6, 5.3 Hz, 7H), 7.19 (d, J = 7.3 Hz, 1H), 7.13 (d, J = 7.4 Hz, 2H), 3.70 (d, J = 12.5 Hz, 1H), 3.49 (d, J = 12.5 Hz, 1H), 3.33 (t, J = 7.7 Hz, 1H), 3.19 (p, J = 7.4 Hz, 1H), 2.82 (q, J = 8.2 Hz, 1H), 2.55 (dhept, J = 14.0, 7.2 Hz, 2H), 2.03 (q, J = 8.6 Hz, 1H), 1.86 (p, J = 9.4 Hz, 1H), 1.76 (dq, J = 14.9, 7.3, 6.6 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.28, 138.55, 129.06, 128.43, 128.40, 128.39, 127.12, 125.80, 66.66, 63.23, 51.75, 37.85, 31.83, 24.09. **HRMS** (ESI) calculated for $C_{18}H_{21}N$ $[M+H]^+$: 252.1747; Found: 252.1745.

**2-Phenethyl-1-(thiophen-2-ylmethyl)azetidine (37):**



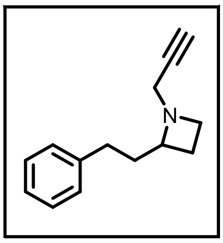
Prepared according to **GP2** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and modified conditions of 5 hours for the substitution reaction with 2-thiophenemethylamine (47.2 mg, 0.4 mmol, 96%). The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 3:1 on silica gel (57%, 29.3 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 2H), 7.21 – 7.09 (m, 4H), 6.91 (t, J = 4.4 Hz, 1H), 6.86 (s, 1H), 3.83 (d, J = 13.5 Hz, 1H), 3.68 (d, J = 13.5 Hz, 1H), 3.36 (t, J = 7.6 Hz, 1H), 3.16 (p, J = 7.5 Hz, 1H), 2.82 (q, J = 8.2 Hz, 1H), 2.59 – 2.46 (m, 2H), 2.00 (q, J = 8.6 Hz, 1H), 1.80 (ddq, J = 36.1, 13.7, 7.6, 6.2 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 142.15, 141.29, 128.42, 128.40, 126.69, 125.83, 125.80, 124.95, 66.43, 56.79, 51.39, 37.78, 31.78, 23.86. **HRMS** (ESI) calculated for $C_{16}H_{19}NS$ $[M+H]^+$: 258.1311; Found: 258.1310.

### 3-(2-(2-Phenethylazetidin-1-yl)ethyl)-1*H*-indole (38):



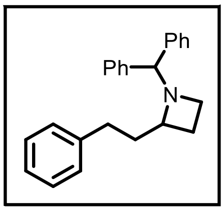
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 2-(indolin-3-yl)ethanamine (128 mg, 0.8 mmol, 96%) with modified conditions of 60 °C and 6 hours for the substitution reaction. The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on amino-functionalized silica gel (42%, 25.6 mg, brown oil). **$^1$H NMR** (500 MHz, CDCl$_3$) δ 8.04 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.29 (d, J = 7.4 Hz, 2H), 7.20 (d, J = 7.7 Hz, 4H), 7.14 (t, J = 7.4 Hz, 1H), 7.03 (s, 1H), 3.52 (t, J = 7.6 Hz, 1H), 3.13 (p, J = 7.7 Hz, 1H), 3.02 – 2.96 (m, 1H), 2.84 (dt, J = 22.5, 8.0 Hz, 3H), 2.65 (dq, J = 23.2, 8.0, 6.9 Hz, 3H), 2.07 (td, J = 14.0, 12.9, 5.6 Hz, 2H), 1.93 – 1.86 (m, 2H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 142.27, 136.41, 128.50, 128.48, 127.65, 125.91, 122.11, 121.57, 119.37, 119.04, 114.61, 111.25, 67.03, 60.00, 51.90, 38.56, 32.10, 24.25, 24.14. **HRMS** (ESI) calculated for $C_{21}H_{24}N_2$ [M+H]$^+$: 305.2012; Found: 305.2013.

### 2-Phenethyl-1-(prop-2-yn-1-yl)azetidine (39):



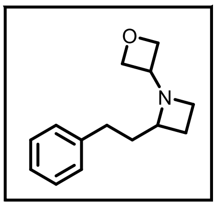
Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and propargylamine (45.0 mg, 0.8 mmol, 98%) with modified conditions of 60 °C and 6 hours for the substitution reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on amino-functionalized silica gel (46%, 18.3 mg, colorless oil). **$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.24 (d, J = 6.8 Hz, 2H), 7.15 (d, J = 6.0 Hz, 3H), 3.40 – 3.20 (m, 4H), 3.06 (q, J = 8.1 Hz, 1H), 2.55 (tp, J = 14.6, 7.0 Hz, 2H), 2.21 (s, 1H), 1.96 (td, J = 16.0, 6.9 Hz, 2H), 1.84 – 1.73 (m, 2H). **$^{13}$C NMR** (126 MHz, CDCl3) δ 142.14, 128.47, 128.43, 125.90, 79.31, 72.94, 64.31, 49.25, 44.50, 38.11, 31.89, 24.19. **HRMS** (ESI) calculated for $C_{14}H_{17}N$ [M+H]$^+$: 200.1434; Found: 200.1433.

### 1-Benzhydryl-2-phenethylazetidine (40):



Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and diphenylmethanamine (151 mg, 0.8 mmol, 97%) with modified conditions of 60 °C and 6 hours for the substitution reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 3:2 on silica gel (69%, 45.2 mg, colorless oil). **$^1$H NMR** (500 MHz, CDCl$_3$) δ 7.52 (d, J = 7.7 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.30 (dddt, J = 28.4, 20.6, 13.4, 7.3 Hz, 9H), 7.02 (d, J = 7.5 Hz, 2H), 4.41 (s, 1H), 3.41 (t, J = 8.1 Hz, 1H), 3.31 (qd, J = 8.7, 3.1 Hz, 1H), 2.77 (q, J = 8.3 Hz, 1H), 2.55 (ddd, J = 14.6, 9.7, 5.2 Hz, 1H), 2.34 (dt, J = 15.8, 8.2 Hz, 1H), 2.09 (q, J = 8.8, 8.3 Hz, 1H), 1.93 (p, J = 9.1 Hz, 1H), 1.54 (dtd, J = 14.4, 9.4, 5.2 Hz, 1H), 1.31 – 1.20 (m, 1H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 143.14, 142.71, 142.29, 128.56, 128.45, 128.36, 128.32, 128.22, 127.61, 127.38, 126.90, 125.60, 78.57, 66.21, 51.48, 37.32, 31.16, 23.14. **HRMS** (ESI) calculated for $C_{24}H_{25}N$ [M+H]$^+$ : 328.2060; Found: 328.2057.

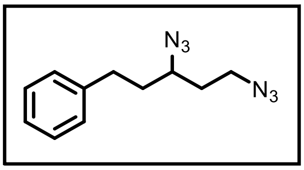
**1-(Oxetan-3-yl)-2-phenethylazetidine (41):**



Prepared according to **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) and 3-aminooxetane (60.3 mg, 0.8 mmol, 97%). The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 4:1 on amino-functionalized silica gel (52%, 22.6 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, J = 7.5 Hz, 2H), 7.17 (dd, J = 18.4, 7.3 Hz, 3H), 4.72 – 4.60 (m, 3H), 4.53 (t, J = 6.1 Hz, 1H), 3.82 (p, J = 6.4 Hz, 1H), 3.35 (ddd, J = 8.9, 6.9, 2.4 Hz, 1H), 3.18 (qd, J = 8.1, 5.1 Hz, 1H), 3.04 (q, J = 8.3 Hz, 1H), 2.54 (qdd, J = 13.9, 9.6, 6.4 Hz, 2H), 2.05 (dtd, J = 10.3, 7.8, 2.4 Hz, 1H), 1.95 – 1.79 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.92, 128.58, 128.42, 126.05, 76.31, 74.72, 64.35, 58.53, 46.74, 38.41, 31.88, 23.96. **HRMS** (ESI) calculated for $C_{14}H_{19}NO$ $[M+H]^+$: 218.1539; Found: 218.1539.

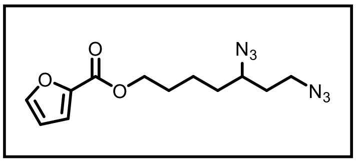
## C. Synthesis and analytical data of homologative diazidation products

**(3,5-Diazidopentyl)benzene (42):**



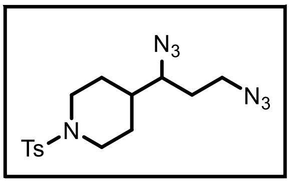
Prepared according to **GP3** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%) with modified conditions using 5.0 equivalents of $NaN_3$ (65.7 mg, 1.0 mmol, 99%) and MeCN (1.6 mL) for 48 hours for diazidation reaction. The product was purified by flash column chromatography with *n*-hexane 100% on silica gel (95%, 43.8 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 (t, J = 7.5 Hz, 2H), 7.21 (dd, J = 12.7, 7.2 Hz, 3H), 3.44 (tq, J = 10.4, 5.2, 4.4 Hz, 3H), 2.81 (ddd, J = 14.8, 9.1, 6.0 Hz, 1H), 2.71 (dt, J = 13.9, 7.9 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.78 (dddd, J = 23.3, 20.0, 11.0, 6.2 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 140.95, 128.80, 128.56, 126.44, 59.56, 48.45, 36.43, 33.88, 32.44. **HRMS** (ESI) calculated for $C_{11}H_{14}N_6$ $[M+H]^+$: 231.1353; Found: 231.1359.

**5,7-Diazidoheptyl furan-2-carboxylate (43):**



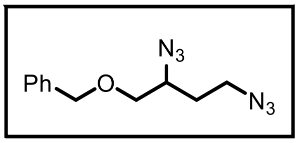
Prepared according to **GP3** using **43-SM** (38.8 mg, 0.2 mmol). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (78%, 45.6 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 1.6, 0.9 Hz, 1H), 7.18 (dd, J = 3.5, 0.9 Hz, 1H), 6.51 (dd, J = 3.5, 1.7 Hz, 1H), 4.33 (t, J = 6.5 Hz, 2H), 3.44 (h, J = 6.7 Hz, 3H), 1.83 – 1.74 (m, 3H), 1.73 – 1.67 (m, 1H), 1.66 – 1.59 (m, 3H), 1.56 – 1.48 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 158.92, 146.48, 144.92, 118.07, 112.01, 64.66, 60.04, 48.46, 34.30, 33.79, 28.64, 22.71. **HRMS** (ESI) calculated for $C_{12}H_{16}N_6O_3$ $[M+Na]^+$: 315.1176; Found: 315.1177.

**4-(1,3-Diazidopropyl)-1-tosylpiperidine (44):**



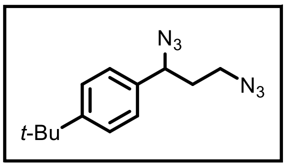
Prepared according to **GP3** using **44-SM** (53.1 mg, 0.2 mmol). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 6:1 on silica gel (79%, 57.4 mg, white solid). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 3.87 (d, J = 11.6 Hz, 2H), 3.49 (ddd, J = 11.7, 6.6, 4.7 Hz, 1H), 3.40 (ddd, J = 12.2, 8.9, 5.9 Hz, 1H), 3.28 (ddd, J = 9.8, 5.5, 3.3 Hz, 1H), 2.44 (s, 3H), 2.21 (t, J = 11.8 Hz, 2H), 1.83 – 1.67 (m, 3H), 1.61 (dt, J = 9.6, 5.1 Hz, 1H), 1.54 – 1.35 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 143.80, 133.15, 129.83, 127.88, 64.24, 48.44, 46.28, 46.23, 40.24, 30.77, 28.10, 27.55, 21.70. **HRMS** (ESI) calculated for $C_{15}H_{21}N_7O_2S$ $[M+Na]^+$: 386.1369; Found: 386.1367.

### ((2,4-Diazidobutoxy)methyl)benzene (45):



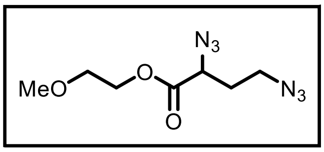
Prepared according to **GP3** using allyl benzyl ether (28.2 mg, 0.2 mmol, 95%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (70%, 34.5 mg, colorless oil). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 4.58 (d, J = 2.1 Hz, 2H), 3.69 (ddq, J = 10.3, 6.8, 3.3 Hz, 1H), 3.61 (dt, J = 10.2, 3.0 Hz, 1H), 3.54 (dd, J = 9.3, 6.6 Hz, 1H), 3.43 (q, J = 7.2, 5.8 Hz, 2H), 1.80 – 1.72 (m, 1H), 1.68 (dq, J = 13.6, 6.8 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.78, 128.68, 128.05, 127.80, 73.60, 72.74, 58.97, 48.27, 30.44. **HRMS** (ESI) calculated for $C_{11}H_{14}N_6O$ $[M+Na]^+$: 269.1121; Found: 269.1118.

### 1-(*tert*-Butyl)-4-(1,3-diazidopropyl)benzene (46):



Prepared according to **GP3** using 4-*tert*-butylstyrene (34.5 mg, 0.2 mmol, 93%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (72%, 37.2 mg, white solid). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 4.58 (dd, J = 8.6, 6.0 Hz, 1H), 3.43 (dt, J = 13.4, 7.0 Hz, 1H), 3.33 (dt, J = 12.4, 6.2 Hz, 1H), 2.10 – 1.99 (m, 1H), 1.99 – 1.88 (m, 1H), 1.33 (s, 9H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 151.80, 135.73, 126.72, 126.07, 63.12, 48.39, 35.55, 34.79, 31.44. **HRMS** (ESI) calculated for $C_{13}H_{18}N_6$ $[M-CH_3]^+$: 243.1353; Found: 243.1360.

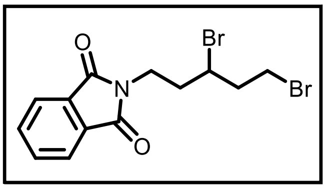
### 2-Methoxyethyl 2,4-diazidobutanoate (47):



Prepared according to **GP3** using 2-methoxyethyl acrylate (26.6 mg, 0.2 mmol, 98%) with modified conditions using **1a** (18.3 mg, 0.3 mmol, 1.5 equiv.) and 2.0 mL of MeCN at room temperature for 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with n-hexane/DCM = 1:0 ~ 1:1 on silica gel (52%, 23.7 mg, pale yellow oil). **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 4.37 (q, J = 4.7 Hz, 2H), 4.12 (dd, J = 8.9, 4.9 Hz, 1H), 3.64 (t, J = 4.6 Hz, 2H), 3.50 – 3.45 (m, 2H), 3.39 (s, 3H), 2.13 – 2.05 (m, 1H), 1.95 (ddt, J = 14.5, 8.8, 5.8 Hz, 1H).**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 170.06, 70.19, 65.00, 59.27, 59.13, 47.63, 30.82. HRMS (ESI) calculated for $C_7H_{12}N_6O_3$ $[M+H]^+$: 229.1044; Found: 229.1045.

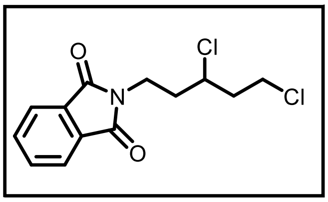
## D. Synthesis and analytical data of homologative dihalogenation products

### 2-(3,5-Dibromopentyl)isoindoline-1,3-dione (48):



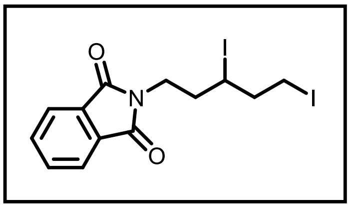
Upon completion of the photocatalytic reaction described in **GP1** using *N*-(3-buten-1-yl)phthalimide (41.1 mg, 0.2 mmol, 98%), the vial cap was unscrewed and magnesium bromide (113 mg, 0.6 mmol, 98%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at 60 °C for 16 hours, and the product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (64%, 48.0 mg, brown solid). **$^{1}$H NMR** (500 MHz, CDCl$_3$) δ 7.86 (dd, J = 5.5, 3.0 Hz, 2H), 7.73 (dd, J = 5.5, 3.0 Hz, 2H), 4.20 (tt, J = 8.9, 4.5 Hz, 1H), 3.96 (ddd, J = 14.0, 8.1, 6.0 Hz, 1H), 3.86 (ddd, J = 14.0, 8.2, 6.4 Hz, 1H), 3.62 – 3.56 (m, 2H), 2.39 – 2.30 (m, 2H), 2.28 – 2.20 (m, 2H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 168.30, 134.22, 132.14, 123.49, 51.05, 41.34, 37.37, 36.41, 30.79. **HRMS** (ESI) calculated for $C_{13}H_{13}Br_2NO_2$ [M+Na]$^+$: 395.9205; Found: 395.9205.

### 2-(3,5-Dichloropentyl)isoindoline-1,3-dione (49):



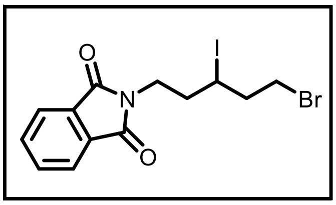
Upon completion of the photocatalytic reaction described in **GP1** using *N*-(3-buten-1-yl)phthalimide (41.1 mg, 0.2 mmol, 98%), the vial cap was unscrewed and tetrabutylammonium chloride (344 mg, 1.2 mmol, 97%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at 40 °C for 16 hours, and the product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (68%, 38.9 mg, yellow solid). **$^{1}$H NMR** (500 MHz, CDCl$_3$) δ 7.86 (dd, J = 5.4, 3.1 Hz, 2H), 7.73 (dd, J = 5.5, 3.0 Hz, 2H), 4.17 (tt, J = 9.0, 3.9 Hz, 1H), 3.95 (ddd, J = 14.1, 8.4, 5.9 Hz, 1H), 3.87 (ddd, J = 14.1, 8.3, 6.4 Hz, 1H), 3.78 – 3.68 (m, 2H), 2.24 – 2.15 (m, 3H), 2.11 (dtd, J = 14.5, 8.7, 5.7 Hz, 1H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 168.40, 134.27, 132.21, 123.55, 57.23, 41.56, 40.92, 36.96, 35.57. **HRMS** (ESI) calculated for $C_{13}H_{13}Cl_2NO_2$ [M+Na]$^+$: 308.0215; Found: 308.2013.

### 2-(3,5-Diiodopentyl)isoindoline-1,3-dione (50):



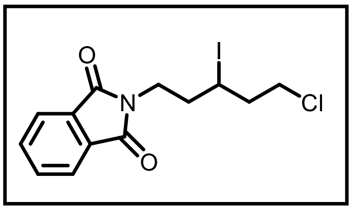
Upon completion of the photocatalytic reaction described in **GP1** using *N*-(3-buten-1-yl)phthalimide (41.1 mg, 0.2 mmol, 98%), the vial cap was unscrewed and potassium iodide (100 mg, 0.6 mmol, 99.5%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at room temperature for 13 hours, and the product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (86%, 80.7 mg, pale yellow solid). **$^{1}$H NMR** (500 MHz, CDCl$_3$) δ 7.86 (dd, J = 0.0 Hz, 2H), 7.73 (dd, 2H), 4.13 (tt, J = 9.0, 4.4 Hz, 1H), 3.92 (ddd, 1H), 3.82 (ddd, 1H), 3.39 (ddd, J = 10.0, 7.2, 4.8 Hz, 1H), 3.26 (ddd, J = 10.0, 8.3, 7.0 Hz, 1H), 2.38 – 2.24 (m, 2H), 2.25 – 2.15 (m, 2H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) δ 168.32, 134.24, 132.15, 123.52, 43.15, 38.62, 38.02, 32.62, 5.37. **HRMS** (ESI) calculated for $C_{13}H_{13}I_2NO_2$ [M+Na]$^+$: 491.8928; Found: 491.8924.

### 2-(5-Bromo-3-iodopentyl)isoindoline-1,3-dione (51):



Upon completion of the photocatalytic reaction described in **GP1** using *N*-(3-buten-1-yl)phthalimide (41.1 mg, 0.2 mmol, 98%), the vial cap was unscrewed and magnesium bromide (41.3 mg, 0.22 mmol, 98%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at room temperature for 16 hours, and the product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (68%, 57.4 mg, pale yellow solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 5.4, 3.0 Hz, 2H), 7.73 (dd, J = 5.5, 3.0 Hz, 2H), 4.22 (tt, J = 9.0, 4.2 Hz, 1H), 3.99 – 3.89 (m, 1H), 3.89 – 3.79 (m, 1H), 3.60 (ddd, J = 10.8, 6.7, 4.6 Hz, 1H), 3.51 (td, J = 9.8, 9.3, 6.0 Hz, 1H), 2.44 – 2.33 (m, 1H), 2.33 – 2.18 (m, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 168.37, 134.29, 132.17, 123.57, 42.52, 38.86, 38.08, 32.95, 29.97. **HRMS** (ESI) calculated for $C_{13}H_{13}BrINO_2$ $[M+Na]^+$: 443.9066; Found: 443.9066.

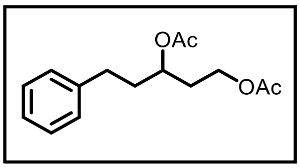
### 2-(5-Chloro-3-iodopentyl)isoindoline-1,3-dione (52):



Upon completion of the photocatalytic reaction described in **GP1** using *N*-(3-buten-1-yl)phthalimide (41.1 mg, 0.2 mmol, 98%), the vial cap was unscrewed and tetrabutylammonium chloride (85.6 mg, 0.3 mmol, 97%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at room temperature for 16 hours, and the product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (63%, 47.6 mg, pale yellow solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 5.6, 3.1 Hz, 2H), 7.73 (dd, J = 5.8, 3.1 Hz, 2H), 4.24 (tt, J = 9.1, 4.2 Hz, 1H), 3.94 (ddd, J = 14.0, 8.3, 5.7 Hz, 1H), 3.82 (ddd, J = 14.1, 8.5, 6.3 Hz, 1H), 3.74 (dt, J = 11.0, 5.6 Hz, 1H), 3.67 (td, J = 10.8, 9.8, 5.5 Hz, 1H), 2.30 (ddt, J = 15.6, 9.4, 4.1 Hz, 2H), 2.26 – 2.18 (m, 1H), 2.18 – 2.09 (m, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 168.33, 134.24, 132.15, 123.52, 44.53, 42.51, 38.94, 38.08, 28.58. **HRMS** (ESI) calculated for $C_{13}H_{13}ClINO_2$ $[M+Na]^+$: 399.9571; Found: 399.9568.

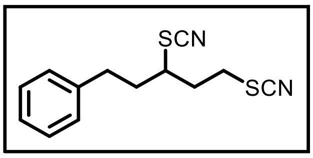
## E. Synthesis and analytical data of other homologative difunctionalization products

### 5-Phenylpentane-1,3-diyl diacetate (53):



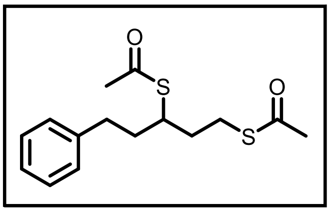
Upon completion of the photocatalytic reaction described in **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%), the vial cap was unscrewed and cesium acetate (115 mg, 0.6 mmol, 99.9%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at 60 °C for 13 hours, and the product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 3:2 on silica gel (48%, 25.4 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.6 Hz, 2H), 7.18 (dd, J = 14.1, 7.3 Hz, 3H), 5.04 (td, J = 7.4, 3.7 Hz, 1H), 4.10 (t, J = 6.7 Hz, 2H), 2.64 (tt, J = 13.3, 6.7 Hz, 2H), 2.04 (s, 6H), 1.92 (dq, J = 13.0, 6.1 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 171.10, 170.77, 141.38, 128.57, 128.40, 126.13, 70.90, 60.87, 36.00, 33.17, 31.74, 21.20, 21.02. **HRMS** (ESI) calculated for $C_{15}H_{20}O_4$ $[M+Na]^+$: 287.1254; Found: 287.1252.

**(3,5-Dithiocyanatopentyl)benzene (54):**



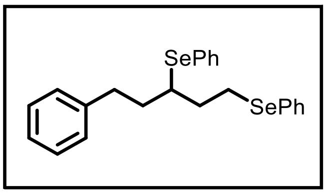
Upon completion of the photocatalytic reaction described in **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%), the vial cap was unscrewed and potassium thiocyanate (41.2 mg, 0.42 mmol, 99%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at 60 ºC for 13 hours, and the product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 5:1 on silica gel (76%, 39.9 mg, light yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.5 Hz, 2H), 7.23 (dd, J = 18.5, 7.5 Hz, 3H), 3.20 (dt, J = 13.1, 6.5 Hz, 1H), 3.11 (dq, J = 12.7, 6.9 Hz, 1H), 3.03 (dt, J = 14.4, 7.8 Hz, 1H), 2.95 (dt, J = 14.1, 7.1 Hz, 1H), 2.80 (dt, J = 14.8, 8.0 Hz, 1H), 2.31 (qd, J = 15.9, 15.1, 6.8 Hz, 2H), 2.15 (q, J = 7.3 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.48, 128.85, 128.45, 126.68, 111.24, 109.48, 47.81, 36.84, 35.27, 32.83, 30.92. **HRMS** (ESI) calculated for $C_{13}H_{14}N_2S_2$ $[M+Na]^+$: 285.0490; Found: 285.0487.

***S,S′*-(5-Phenylpentane-1,3-diyl) diethanethioate (55):**



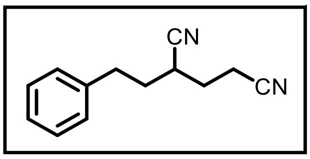
Upon completion of the photocatalytic reaction described in **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%), the vial cap was unscrewed and potassium thioacetate (117 mg, 1.0 mmol, 98%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at 60 ºC for 13 hours, and the product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 10:1 on silica gel (64%, 37.9 mg, brown oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 2H), 7.13 (d, J = 7.4 Hz, 3H), 3.58 (tt, J = 8.5, 5.2 Hz, 1H), 2.95 (ddd, J = 14.1, 9.1, 5.5 Hz, 1H), 2.82 (ddd, J = 13.6, 9.0, 6.7 Hz, 1H), 2.65 (dddd, J = 38.7, 13.4, 10.2, 5.7 Hz, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 1.97 – 1.75 (m, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 195.74, 195.49, 141.45, 128.54, 128.49, 126.11, 43.60, 36.75, 34.93, 33.19, 30.95, 30.72, 26.57. **HRMS** (ESI) calculated for $C_{15}H_{20}O_2S_2$ $[M+Na]^+$: 319.0797; Found: 319.0794.

**(5-Phenylpentane-1,3-diyl)bis(phenylselane) (56):**



To a flame-dried 4 mL vial with a magnetic stir bar was added diphenyl diselenide (126 mg, 0.4 mmol, 99%), EtOH (2.0 mL) and $NaBH_4$ (40.0 mg, 1.0 mmol, 95%), sequentially. The mixture was stirred at room temperature for 1 hour, followed by transfer to the completed photocatalytic reaction mixture described in **GP1** using 4-phenyl-1-butene (30 μL, 0.2 mmol, 99%). The combined reaction mixture was stirred at 80 ºC for 13 hours. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 10:1 on silica gel (90%, 82.5 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 4H), 7.34 – 7.21 (m, 9H), 7.18 – 7.13 (m, 2H), 3.26 (p, J = 6.7 Hz, 1H), 3.16 (dt, J = 12.2, 7.6 Hz, 1H), 3.08 (dt, J = 12.2, 7.6 Hz, 1H), 2.86 (ddd, J = 14.8, 8.7, 6.8 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.08 – 2.02 (m, 2H), 1.95 (dtd, J = 8.6, 6.7, 1.9 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.58, 135.34, 132.92, 130.03, 129.17, 129.11, 128.55, 128.50, 128.45, 127.74, 127.02, 126.02, 45.75, 37.16, 35.95, 33.92, 26.04. **HRMS** (ESI) calculated for $C_{23}H_{24}Se_2$ $[M+Na]^+$: 483.0100; Found: 483.0098.

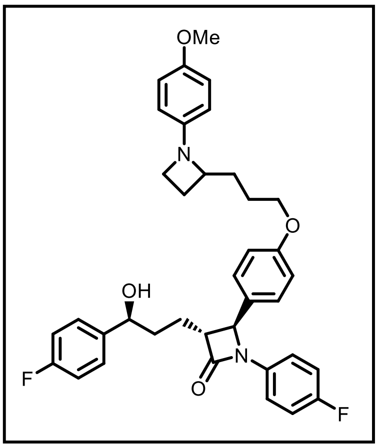
**2-Phenethylpentanedinitrile (57):**



Upon completion of the photocatalytic reaction described in **GP1** using 4-phenyl-1-butene (30 µL, 0.2 mmol, 99%), the solvent was removed under reduced pressure. The vial cap was unscrewed and sodium cyanide (30.3 mg, 0.6 mmol, 97%) was added. Then the vial was capped, followed by five cycles of evacuation and argon back-filling. Dry DMF (1.6 mL) was added, and the reaction mixture was stirred at 60 °C for 13 hours. After completion of reaction, the crude mixture was diluted with EA and washed with water and brine. Combined organic layers were evaporated under reduced pressure, and the product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 3:1 on silica gel (63%, 25.0 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 (t, J = 7.5 Hz, 2H), 7.26 (dd, J = 24.9, 7.5 Hz, 3H), 2.95 (ddd, J = 14.2, 8.9, 5.2 Hz, 1H), 2.80 (dt, J = 14.8, 8.2 Hz, 1H), 2.72 (tt, J = 9.6, 5.6 Hz, 1H), 2.63 (dt, J = 16.8, 6.7 Hz, 1H), 2.55 (dt, J = 16.8, 7.9 Hz, 1H), 2.00 (tq, J = 22.9, 7.9, 6.5 Hz, 4H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.48, 128.92, 128.46, 126.82, 120.17, 118.03, 33.68, 33.19, 30.38, 28.29, 15.43. **HRMS** (ESI) calculated for $C_{13}H_{14}N_2$ $[M+Na]^+$: 221.1049; Found: 221.1046.

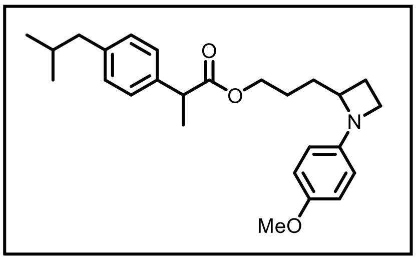
## F. Synthesis and analytical data of synthetic applications

### (3*R*,4*S*)-1-(4-Fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)-4-(4-(3-(1-(4-methoxyphenyl)azetidin-2-yl)propoxy)phenyl)azetidin-2-one (58):



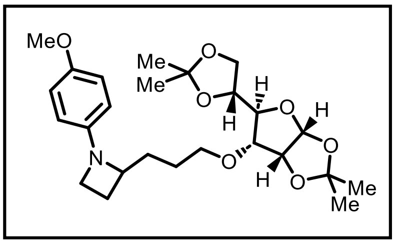
Prepared according to **GP1** using **58-SM** (95.4 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (78%, 95.6 mg, brown solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.6, 5.4 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.13 – 7.06 (m, 2H), 7.03 (t, J = 8.7 Hz, 2H), 6.91 (td, J = 8.5, 3.5 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.81 – 6.76 (m, 2H), 6.52 – 6.42 (m, 3H), 4.71 (d, J = 8.7 Hz, 1H), 4.64 (d, J = 11.3 Hz, 1H), 4.03 – 3.92 (m, 3H), 3.91 – 3.85 (m, 1H), 3.74 (s, 3H), 3.49 (q, J = 8.0 Hz, 1H), 2.45 – 2.33 (m, 2H), 2.33 – 2.25 (m, 1H), 2.24 – 2.18 (m, 1H), 2.15 – 2.02 (m, 3H), 1.91 – 1.78 (m, 3H), 1.71 (q, J = 13.2, 12.3 Hz, 1H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) 171.25, 162.17 (d, J = 245.2 Hz), 159.51 (d, J = 243.6 Hz), 158.85 & 158.82, 152.33, 147.14 & 147.12, 138.40 (d, J = 3.1 Hz), 133.27 (d J = 2.9 Hz), 133.05, 127.87, 127.48 (d, J = 8.0 Hz) & 122.44 (d, J = 7.7 Hz), 122.41 (d, J = 7.8 Hz), 115.47 (d, J = 22.4 Hz), 115.15 (d, J = 21.5 Hz), 114.73, 114.60, 113.19, 81.57, 79.21, 67.84, 64.81, 55.84, 52.84, 50.35, 33.30, 32.73, 27.80, 24.65, 23.52. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -115.01 – -115.51 (m), -117.46 – -117.77 (m). **HRMS** (ESI) calculated for $C_{37}H_{38}F_2N_2O_4$ $[M+H]^+$: 613.2873; Found: 613.2873.

### 3-(1-(4-methoxyphenyl)azetidin-2-yl)propyl 2-(4-isobutylphenyl)propanoate (59):



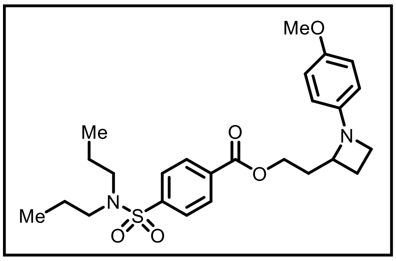
Prepared according to **GP1** using **73** (54.9 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (80%, 65.5 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, J = 7.9 Hz, 2H), 7.09 (dd, J = 8.1, 2.6 Hz, 2H), 6.82 – 6.76 (m, 2H), 6.46 – 6.40 (m, 2H), 4.11 (td, J = 6.5, 1.3 Hz, 2H), 3.85 (ddt, J = 8.7, 6.9, 3.4 Hz, 2H), 3.75 (s, 3H), 3.70 (q, J = 7.1 Hz, 1H), 3.46 (tdd, J = 8.7, 6.8, 3.1 Hz, 1H), 2.43 (dd, J = 7.2, 4.4 Hz, 2H), 2.26 – 2.17 (m, 1H), 2.07 – 1.96 (m, 1H), 1.91 – 1.78 (m, 2H), 1.73 – 1.60 (m, 3H), 1.50 (d, J = 7.2 Hz, 3H), 0.89 (s, 3H), 0.88 (s, 3H).**$^{13}$C NMR** (126 MHz, $CDCl_3$, *one carbon merged with others*) δ 174.95, 152.51, 147.20, 140.71, 137.98, 129.50, 127.34, 114.85, 113.23, 64.76, 56.01, 50.41, 45.40, 45.23, 33.30 & 33.24, 30.35, 24.21 & 24.16, 23.57 & 23.50, 22.57, 18.66. **HRMS** (ESI) calculated for $C_{26}H_{35}NO_3$ $[M+H]^+$: 410.2690; Found: 410.2691.

### 2-(3-(((3a*R*,5*R*,6*R*,6a*R*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)propyl)-1-(4-methoxyphenyl)azetidine (60):



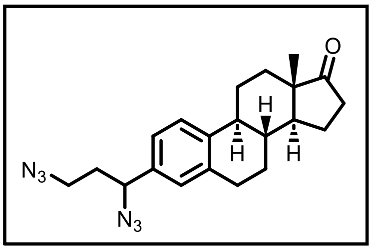
Prepared according to **GP1** using **60-SM** (65.7 mg, 0.2 mmol) and p-anisidine (99.5 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (61%, 56.6 mg, brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.80 (d, J = 8.8 Hz, 2H), 6.47 (d, J = 8.9 Hz, 2H), 5.87 (dd, J = 9.9, 3.7 Hz, 1H), 4.53 (dd, J = 10.5, 3.7 Hz, 1H), 4.32 (dt, J = 7.9, 6.0 Hz, 1H), 4.14 – 4.07 (m, 2H), 4.00 (dd, J = 8.6, 5.7 Hz, 1H), 3.93 – 3.86 (m, 3H), 3.75 (s, 3H), 3.66 (dtd, J = 9.3, 6.3, 2.7 Hz, 1H), 3.58 (tt, J = 9.5, 6.3 Hz, 1H), 3.49 (q, J = 8.1 Hz, 1H), 2.28 (dtd, J = 11.3, 8.3, 3.3 Hz, 1H), 2.11 (dtd, J = 11.1, 8.1, 3.5 Hz, 1H), 1.97 (tdd, J = 13.8, 5.8, 3.9 Hz, 1H), 1.77 (dtd, J = 13.7, 9.6, 5.1 Hz, 1H), 1.72 – 1.57 (m, 2H), 1.50 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.31 (d, J = 4.9 Hz, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.52, 147.30, 114.87, 113.25, 111.94, 109.14, 105.47, 82.75 & 82.69, 82.40 & 82.36, 81.39 & 81.37, 72.73 & 72.69, 70.80 & 70.59, 67.47 & 67.45, 65.07 & 65.04, 56.00, 50.48 & 50.46, 33.57 & 33.54, 27.04, 27.01, 26.44 & 26.43, 25.63 & 25.61, 25.30, 23.68 & 23.58. **HRMS** (ESI) calculated for $C_{25}H_{37}NO_7$ $[M+H]^+$ : 464.2643; Found: 464.2641.

### 2-(1-(4-Methoxyphenyl)azetidin-2-yl)ethyl 4-(*N,N*-dipropylsulfamoyl)benzoate (61):



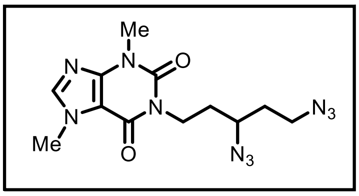
Prepared according to **GP1** using **61-SM** (67.9 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (67%, 63.6 mg, yellow solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 6.49 (d, J = 8.9 Hz, 2H), 4.50 (t, J = 6.4 Hz, 2H), 4.10 (qd, J = 7.8, 3.6 Hz, 1H), 3.93 (ddd, J = 8.6, 6.8, 3.3 Hz, 1H), 3.74 (s, 3H), 3.53 (q, 1H), 3.16 – 3.03 (m, 4H), 2.37 (ttd, J = 11.0, 7.8, 7.3, 3.5 Hz, 2H), 2.30 – 2.18 (m, 2H), 1.54 (h, J = 7.4 Hz, 4H), 0.86 (t, J = 7.4 Hz, 6H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.34, 152.64, 146.86, 144.37, 133.58, 130.28, 127.13, 114.81, 113.22, 62.55, 62.46, 55.88, 50.82, 50.05, 35.68, 23.75, 22.06, 11.27.**HRMS** (ESI) calculated for $C_{25}H_{34}N_2O_5S$ $[M+H]^+$ : 475.2261; Found: 475.2261.

### (8*R*,9*S*,13*S*,14*S*)-3-(1,3-Diazidopropyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (62):



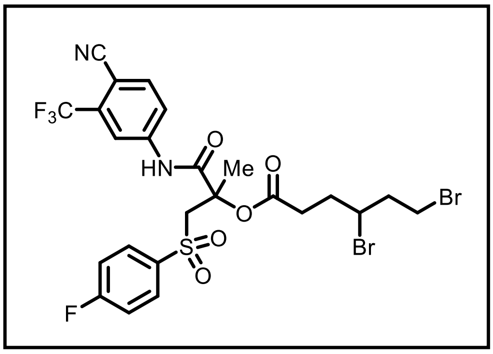
Prepared according to **GP3** using **62-SM** (56.1 mg, 0.2 mmol). The product was purified by flash column chromatography eluted with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (45%, 34.1 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 7.03 (s, 1H), 4.54 (t, J = 7.3 Hz, 1H), 3.42 (dt, J = 13.3, 6.9 Hz, 1H), 3.33 (dt, J = 12.4, 6.2 Hz, 1H), 2.93 (dd, J = 9.3, 4.3 Hz, 2H), 2.51 (dd, J = 19.0, 8.7 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.35 – 2.27 (m, 1H), 2.16 (q, J = 9.3 Hz, 1H), 2.10 – 2.00 (m, 3H), 2.00 – 1.87 (m, 2H), 1.63 (q, J = 11.5, 10.5 Hz, 2H), 1.50 (tq, J = 21.3, 11.4, 9.6 Hz, 4H), 0.92 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 220.83, 140.38, 137.36, 136.12, 127.58 & 127.53, 126.11, 124.32 & 124.25, 63.11 & 63.05, 50.59, 48.32, 48.05, 44.47, 38.09, 35.94, 35.50 & 35.45, 31.67, 29.54 & 29.52, 26.50, 25.75, 21.69, 13.94. **HRMS** (ESI) calculated for $C_{21}H_{26}N_6O$ $[M+Na]^+$: 401.2060; Found: 401.2061.

**1-(3,5-Diazidopentyl)-3,7-dimethyl-3,4,5,7-tetrahydro-1*H*-purine-2,6-dione (63):**



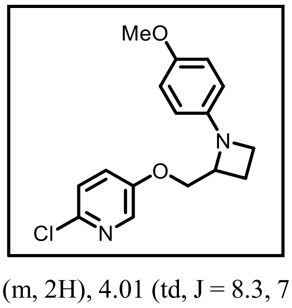
Prepared according to **GP3** using **63-SM** (47.2 mg, 0.2 mmol). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (90%, 60.2 mg, yellow oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 4.14 (hept, J = 7.1, 6.7 Hz, 2H), 3.98 (s, 3H), 3.57 (s, 3H), 3.45 (qd, J = 12.3, 6.6 Hz, 2H), 1.89 (dq, J = 14.4, 7.2, 6.7 Hz, 3H), 1.82 – 1.64 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 155.28, 151.57, 149.07, 141.77, 107.76, 58.23, 48.27, 38.43, 33.84, 33.79, 32.83, 29.90. **HRMS** (ESI) calculated for $C_{12}H_{16}N_{10}O_2$ $[M-H_2]^+$: 332.1469; Found: 332.1458.

**1-((4-Cyano-3-(trifluoromethyl)phenyl)amino)-3-((4-fluorophenyl)sulfonyl)-2-methyl-1-oxopropan-2-yl 4,6-dibromohexanoate (64):**



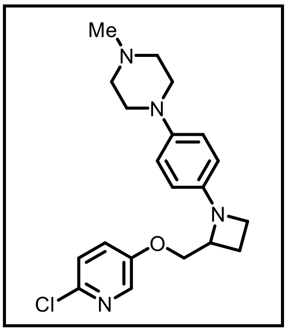
Upon completion of the photocatalytic reaction described in **GP1** using **64-SM** (103 mg, 0.2 mmol), the vial cap was unscrewed and magnesium bromide (113 mg, 0.6 mmol, 98%) was added. The vial was capped, followed by five quick cycles of evacuation and argon back-filling. The reaction mixture was stirred at 60 °C for 16 hours, and the product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (80%, 109.8 mg, yellow solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, J = 12.3 Hz, 1H), 8.11 (dd, J = 8.5, 2.2 Hz, 1H), 7.96 (ddd, J = 8.5, 6.0, 2.2 Hz, 1H), 7.90 (dd, J = 8.8, 4.9 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 7.22 (t, J = 8.4 Hz, 2H), 4.38 (qd, J = 9.1, 4.5 Hz, 1H), 4.28 (dd, 1H), 4.00 (dd, J = 14.1, 2.6 Hz, 1H), 3.68 – 3.54 (m, 2H), 2.94 – 2.79 (m, 2H), 2.47 – 2.28 (m, 3H), 2.27 – 2.15 (m, 1H), 1.89 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 170.98, 169.55 & 169.49, 166.34 (d, J = 258.2 Hz), 141.18, 136.04, 135.96 (d, J = 4.1 Hz), 134.77 – 133.94 (m), 131.09 (d, J = 9.6 Hz) & 131.07 (d, J = 9.7 Hz), 123.06, 122.28 (q, J = 274.0 Hz), 118.46 (q, J = 4.1 Hz), 117.04 (d, J = 22.5 Hz), 115.51, 105.74, 80.72 & 80.67, 58.39, 54.49 & 54.11, 41.86 & 41.56, 33.66, 33.63 & 33.31, 31.06 & 30.75, 24.72 & 24.69. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -62.13 (d, J = 5.0 Hz), -102.02 (tt, J = 8.6, 5.0 Hz). **HRMS** (ESI) calculated for $C_{24}H_{22}Br_2F_4N_2O_5S$ $[M+Na]^+$: 706.9444; Found: 706.9450.

**2-Chloro-5-((1-(4-methoxyphenyl)azetidin-2-yl)methoxy)pyridine (66):**



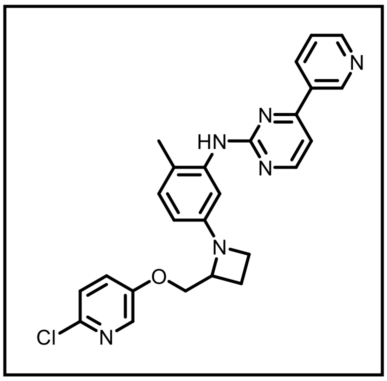
Prepared according to **GP1** using **65** (33.9 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%) with modified conditions using 0.3 mmol of **1a** (133 mg) and 2.0 mL of MeCN at room temperature and 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 4:1 on silica gel (53%, 32.3 mg, off-white solid). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 1H), 7.27 (d, J = 10.2 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 8.9 Hz, 2H), 4.34 (p, J = 7.5, 6.7 Hz, 1H), 4.30 – 4.19 (m, 2H), 4.01 (td, J = 8.3, 7.7, 3.9 Hz, 1H), 3.77 (s, 3H), 3.65 (q, J = 8.2 Hz, 1H), 2.39 (dtd, J = 19.3, 11.0, 9.7, 6.0 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 154.35, 152.79, 146.22, 142.91, 136.88, 125.22, 124.51, 114.70, 113.40, 72.87, 63.18, 55.84, 50.78, 20.37. **HRMS** (ESI) calculated for $C_{16}H_{17}ClN_2O_2$ $[M+H]^+$: 305.1052; Found: 305.1050

**1-(4-(2-(((6-Chloropyridin-3-yl)oxy)methyl)azetidin-1-yl)phenyl)-4-methylpiperazine (67):**



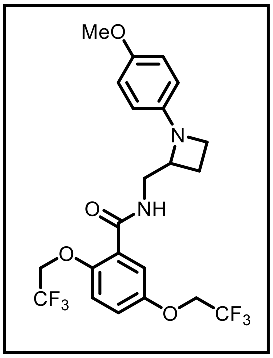
Prepared according to **GP1** using **65** (33.9 mg, 0.2 mmol) and 4-(4-methylpiperazin-1-yl)aniline (156 mg, 0.8 mmol, 98%), with modified conditions using 0.3 mmol of **1a** (133 mg) and 2.0 mL of MeCN at room temperature and 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with DCM/MeOH = 1:0 ~ 9:1 on silica gel (46%, 34.3 mg, brown solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.23 (s, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 8.3 Hz, 2H), 4.33 (p, J = 6.6 Hz, 1H), 4.28 – 4.15 (m, 2H), 3.99 (td, J = 7.9, 3.8 Hz, 1H), 3.64 (q, J = 8.1 Hz, 1H), 3.12 (d, J = 5.3 Hz, 4H), 2.65 (t, J = 4.9 Hz, 4H), 2.39 (s, 5H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 154.36, 146.35, 144.13, 142.91, 136.87, 125.24, 124.54, 118.54, 113.20, 72.84, 63.07, 55.25, 50.67, 50.61, 45.97, 20.42. **HRMS** (ESI) calculated for $C_{20}H_{25}ClN_4O$ $[M+H]^+$: 373.1790; Found: 373.1787

***N*-(5-(2-(((6-Chloropyridin-3-yl)oxy)methyl)azetidin-1-yl)-2-methylphenyl)-4-(pyridin-3-yl)pyrimidin-2-amine (68):**



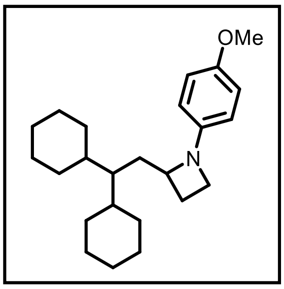
Prepared according to **GP1** using **65** (33.9 mg, 0.2 mmol) and 6-methyl-*N*-(4-(pyridin-3-yl)pyrimidin-2-yl)benzene-1,3-diamine (238 mg, 0.8 mmol, 98%), with modified conditions using 0.3 mmol of **1a** (133 mg) and 2.0 mL of MeCN at room temperature and 5 hours for the photocatalytic reaction. The product was purified by flash column chromatography with DCM/EA = 1:0 ~ 4:5 on silica gel (36%, 33.0 mg, brown solid). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.28 (d, J = 1.8 Hz, 1H), 8.70 – 8.65 (m, 1H), 8.46 (s, 1H), 8.30 (dt, J = 8.0, 1.8 Hz, 1H), 7.99 (d, J = 2.5 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.37 (dd, J = 7.9, 4.8 Hz, 1H), 7.13 (p, J = 6.0, 5.4 Hz, 3H), 7.07 (d, J = 8.2 Hz, 1H), 7.02 (s, 1H), 6.36 (dd, J = 8.1, 2.4 Hz, 1H), 4.49 – 4.41 (m, 1H), 4.28 – 4.17 (m, 2H), 4.05 (ddd, J = 8.6, 7.1, 3.9 Hz, 1H), 3.75 (q, J = 7.7 Hz, 1H), 2.46 (dtd, J = 12.4, 8.8, 8.1, 4.4 Hz, 1H), 2.39 (q, J = 7.8 Hz, 1H), 2.28 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 162.53, 160.68, 159.13, 154.22, 151.45, 150.67, 148.63, 142.70, 137.85, 136.83, 134.38, 132.76, 130.79, 124.90, 124.30, 123.47, 117.57, 108.19, 107.42, 105.30, 72.36, 62.97, 50.48, 20.42, 17.22. **HRMS** (ESI) calculated for $C_{25}H_{23}ClN_6O$ $[M+H]^+$: 459.1695; Found: 459.1695

***N*-((1-(4-Methoxyphenyl)azetidin-2-yl)methyl)-2,5-bis(2,2,2-trifluoroethoxy)benzamide (70):**



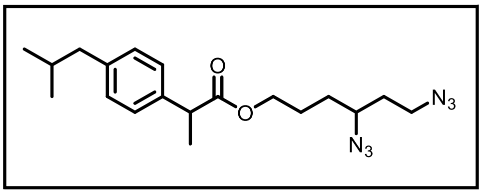
Prepared according to **GP1** using **69** (71.5 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/EA = 1:0 ~ 1:1 on silica gel (62%, 60.9 mg, yellow-brown oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.9 Hz, 1H), 7.07 – 6.99 (m, 2H), 6.81 – 6.75 (m, 2H), 6.62 – 6.56 (m, 2H), 4.84 (qd, *J* = 8.3, 4.1 Hz, 1H), 4.43 – 4.29 (m, 5H), 4.16 (ddd, *J* = 14.7, 9.6, 1.3 Hz, 1H), 3.79 – 3.68 (m, 4H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.07 – 1.91 (m, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 161.70, 153.01, 152.31, 151.98, 142.34, 123.48 (q, J = 278.8 Hz), 123.27 (q, J = 278.1 Hz), 120.84, 119.65, 119.30, 117.01, 115.04, 114.21, 78.51, 69.07 (q, J = 35.1 Hz), 66.52 (q, J = 35.7 Hz), 60.36, 55.85, 41.46, 35.42. **$^{19}$F NMR** (471 MHz, $CDCl_3$) δ -73.84 (t, *J* = 8.3 Hz), -73.98 (t, *J* = 7.8 Hz). **HRMS** (ESI) calculated for $C_{22}H_{22}F_6N_2$ $[M+H]^+$: 493.1557; Found: 493.1561.

### 2-(2,2-Dicyclohexylethyl)-1-(4-methoxyphenyl)azetidine (72):



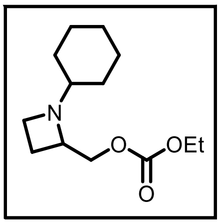
Prepared according to **GP1** using **71** (44.1 mg, 0.2 mmol) and *p*-anisidine (99.5 mg, 0.8 mmol, 99%). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 3:2 on silica gel (48%, 34.1 mg, brown solid). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.82 (d, *J* = 8.6 Hz, 2H), 6.50 (d, *J* = 8.5 Hz, 2H), 3.90 (dddd, *J* = 25.1, 9.3, 7.2, 3.3 Hz, 2H), 3.76 (s, 3H), 3.44 (q, *J* = 8.0 Hz, 1H), 2.23 (ddt, *J* = 11.0, 8.0, 3.9 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.94 (ddd, *J* = 13.0, 8.6, 3.7 Hz, 1H), 1.71 (tdd, *J* = 17.2, 9.7, 3.8 Hz, 10H), 1.52 (d, *J* = 9.9 Hz, 1H), 1.48 – 1.33 (m, 2H), 1.33 – 0.89 (m, 11H). **$^{13}$C NMR** (101 MHz, $CDCl_3$, *one carbon merged with others*) δ 152.40, 147.49, 114.77, 113.48, 65.76, 55.91, 50.11, 45.74, 40.37, 39.85, 36.03, 32.35, 32.29, 31.39, 29.46, 27.35, 27.27, 27.14, 27.02, 26.89, 24.25. **HRMS** (ESI) calculated for $C_{24}H_{37}NO$ $[M+H]^+$: 356.2948; Found: 356.2949.

### 4,6-Diazidohexyl 2-(4-isobutylphenyl)propanoate (75):



Prepared according to **GP3** using **73** (54.9 mg, 0.2 mmol). The product was purified by flash column chromatography with *n*-hexane/DCM = 1:0 ~ 1:1 on silica gel (81%, 60.3 mg, colorless oil). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 4.09 (qd, J = 11.9, 6.1 Hz, 2H), 3.69 (q, J = 7.2 Hz, 1H), 3.43 – 3.32 (m, 3H), 2.45 (d, J = 7.1 Hz, 2H), 1.84 (dt, J = 13.6, 6.6 Hz, 1H), 1.69 (ddt, J = 36.0, 14.4, 7.3 Hz, 4H), 1.48 (t, J = 7.3 Hz, 5H), 0.90 (s, 3H), 0.89 (s, 3H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 174.86, 140.79, 137.92, 129.53, 127.32, 64.06 & 63.99, 59.67 & 59.65, 48.35, 45.34 & 45.32, 45.19, 33.71, 31.02 & 30.97, 30.36, 25.33 & 25.29, 22.55, 18.54 & 18.50. **HRMS** (ESI) calculated for $C_{19}H_{28}N_6O$ $[M+Na]^+$: 395.2166; Found: 395.2168.

### (1-Cyclohexylazetidin-2-yl)methyl ethyl carbonate (79):



Prepared according to **GP1** using allyl ethyl carbonate (**76**, 26.8 mg, 0.2 mmol, 97%) and cyclohexylamine (**77**, 80.1 mg, 0.8 mmol, 99%), with modified conditions of 60 ºC and 6 hours for the substitution reaction. The product was purified by flash column chromatography with *n*-hexane/acetone = 1:0 ~ 5:1 on amino-functionalized silica gel (48%, 23.2 mg, colorless oil). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.23 (dd, J = 11.1, 4.4 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 4.06 (dd, J = 11.0, 6.9 Hz, 1H), 3.37 (tq, J = 7.5, 4.6 Hz, 2H), 2.83 (q, J = 8.4 Hz, 1H), 2.11 – 2.02 (m, 2H), 1.96 (p, J = 8.9 Hz, 1H), 1.78 (d, J = 12.9 Hz, 1H), 1.74 – 1.66 (m, 3H), 1.58 (d, J = 11.3 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.15 (td, J = 23.5, 22.4, 12.2 Hz, 3H), 0.96 (dq, J = 20.8, 11.0, 10.4 Hz, 2H). **$^{13}$C NMR** (126 MHz, $CDCl_3$, *one carbon merged with others*) δ 155.30, 71.85, 66.44, 64.11, 62.30, 49.84, 31.12, 29.94, 26.00, 24.64, 20.99, 14.39. **HRMS** (ESI) calculated for $C_{13}H_{23}NO_3$ $[M+H]^+$: 242.1751; Found: 242.1748.

## G. Low-yielding or unsuccessful substrates

Attempts to synthesize azetidine products using tertiary alkylamines (e.g., *tert*-butylamine and 1-adamantylamine) were unsuccessful, resulting in side reactions such as monosubstitution and elimination.

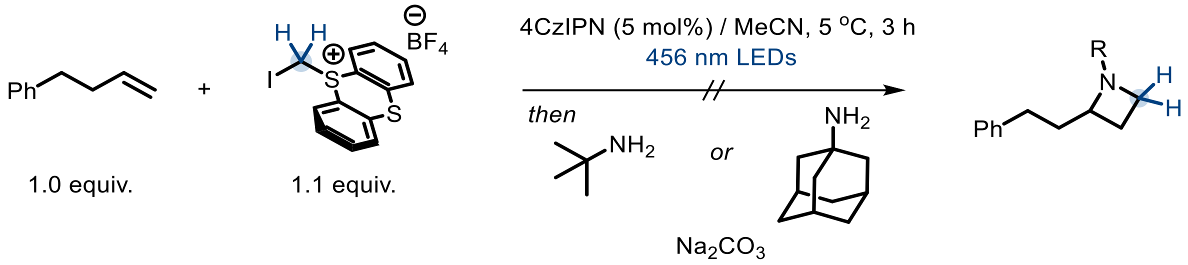
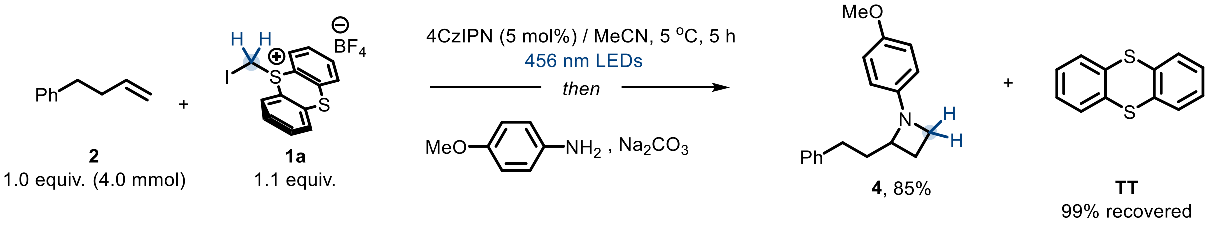


**Fig. S4.** Attempted azetidination reactions with tertiary alkylamines

## H. Scale-up reaction



To an oven-dried two-neck round bottom flask equipped with a magnetic stir bar were added 4CzIPN (158 mg, 5.0 mol%) and **1a** (1.95 g, 1.1 equiv.). The flask was capped with rubber septa and purged with argon via Schlenk technique. Dry MeCN (32.0 mL) and 4-phenyl-1-butene (613 μL, 1.0 equiv, 98%) were added sequentially under an argon atmosphere. The reaction mixture was stirred in an isopropanol bath maintained at 5 (± 2) °C for 5 hours under irradiation by two blue LED Kessil$^{\text{TM}}$ lamps (PR160L-456 nm, 37.5 W), which were positioned ~5.0 cm away from the flask. Upon completion, an oven-dried reflux condenser was connected, followed by addition of *p*-anisidine (1.99 g, 4.0 equiv., 99%) and $Na_2CO_3$ (1.28 g, 3.0 equiv., 99%). The flask was evacuated and backfilled with argon five times and the reaction mixture was allowed to stir at 80 °C for 13 hours. Upon completion, the crude mixture was purified via flash column chromatography with *n*-hexane/acetone 1:0 ~ 3:1 on silica gel. The desired azetidine product **4** was obtained in 85% yield (909 mg), and thianthrene was recovered in 99% yield (white powder, 942 mg).

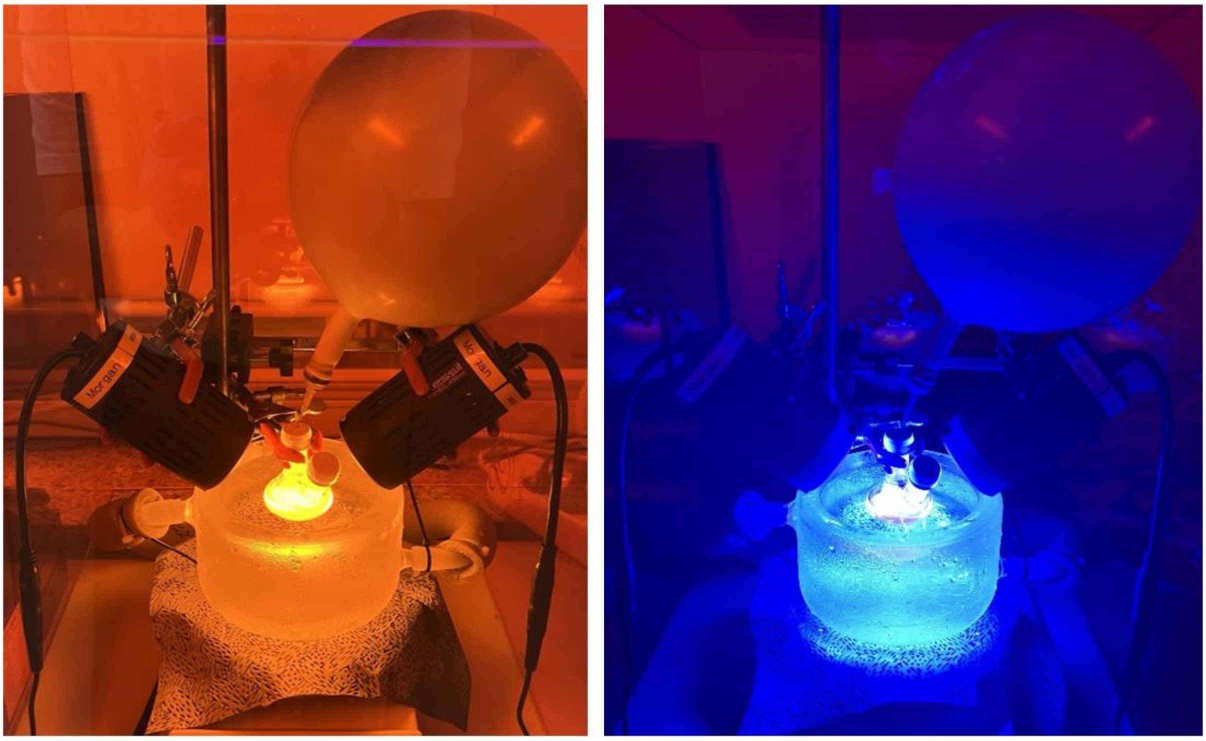
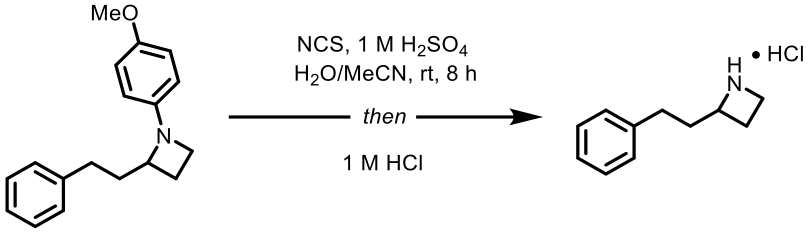


**Fig. S5.** Photographic demonstration of the reaction setup for 4.0 mmol scale reaction.

## I. PMP deprotection of azetidine 4



4 5

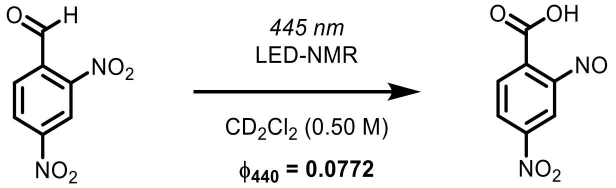
To a flame-dried 4 mL vial with a magnetic stir bar was added 1-(4-methoxyphenyl)-2-phenethylazetidine (**4**, 26.7 mg, 0.1 mmol). The vial was capped, evacuated and filled with argon by Schlenk technique three times. A mixture of degassed water and MeCN (1:1 v/v, 0.055 M) was added via syringe, followed by portionwise addition of *N*-chlorosuccinimide (53.4 mg, 0.4 mmol, 4.0 equiv.) and 1 M aqueous sulfuric acid solution (0.1 mL, 1.0 equiv.). Following five quick cycles of evacuation and argon back-filling, the mixture was stirred at room temperature for 8 hours. Upon completion, the mixture was basified with saturated $NaHCO_3$ solution at 0 ºC and extracted with $Et_2O$ three times. The combined organic layers were washed with water and brine three times, respectively, and dried over anhydrous $MgSO_4$. After filtration, the crude mixture was concentrated carefully under ~670 hPa of pressure using a rotary evaporator. The crude residue was passed through a basic aluminum oxide with $Et_2O$ and concentrated under ~670 hPa of pressure. 1 M HCl solution in $Et_2O$ (1.0 mL) was added to the mixture, and the mixture was concentrated under reduced pressure to afford the desired NH-azetidine **5** (89%, 17.6 mg, white solid). **$^1$H NMR** (400 MHz, $D_2O$) δ 7.45 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 4.50 (p, *J* = 8.0 Hz, 1H), 4.06 (q, *J* = 9.6 Hz, 1H), 3.89 (td, *J* = 10.3, 5.3 Hz, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.53 (dtd, *J* = 12.2, 8.9, 5.3 Hz, 1H), 2.43 – 2.13 (m, 3H). **$^{13}$C NMR** (126 MHz, $D_2O$) δ 140.40, 128.86, 128.49, 126.54, 61.06, 43.07, 34.69, 30.28, 24.54. **HRMS** (ESI) calculated for $C_{11}H_{15}N$ $[M+H]^+$: 162.1277; Found: 162.1275.

## V. Mechanistic Investigations

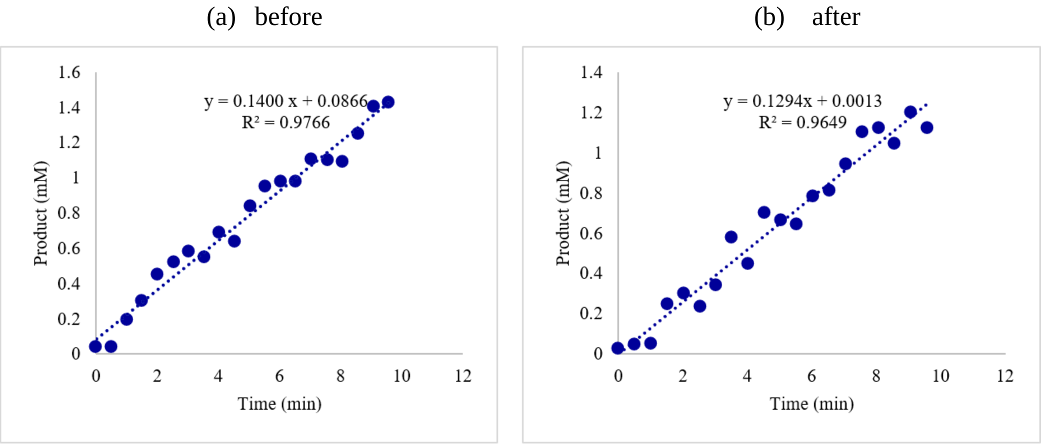
### A. Quantum yield measurement for the photocatalytic 1,3-dielectrophile formation

The 445 nm Prizmatix© Collimated Modular Mic-LED, coupled with a BLCC-04 LED current controller, was employed as the light source for the LED-NMR kinetic monitoring. To determine the photon flux, the LED source was calibrated using the photoreaction of 2,4-dinitrobenzaldehyde to give 4-nitro-2-nitrosobenzoic acid as the product. The formation of 4-nitro-2-nitrosobenzoic acid was monitored by a time-course $^1$H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard.

**Determination of the photon flux**



In an argon-filled glovebox, 2,4-dinitrobenzaldehyde (100 mg, 0.5 mmol, 98%) and 1,1,2,2-tetrachloroethane (53 µL, 0.5 mmol, 99%) were added to a 1 mL volumetric flask. $CD_2Cl_2$ was then added to reach 1.0 mL of total solution. After sufficient dissolution, 400 µL of the solution was transferred to the PhotoNMR sampling device (NE-379-5-Br, New Era) consisting of a coaxial inner cell and a 5 mm NMR sample tube. The NMR tube was further sealed with Parafilm and wrapped in aluminum foil to prevent background reactions caused by ambient light sources. The NMR tubes were removed from the glovebox, and the optical fiber connected to Mic-LED was placed into the coaxial inner cell. After taking off the aluminum foil, the tube was inserted into the NMR machine. Upon turning on the light source, the formation of 4-nitro-2-nitrosobenzoic acid was monitored by $^1$H NMR spectroscopy recorded every 30 seconds for a total duration of 600 seconds. The photon flux of the light source in the current setup was measured as the average of two separate experiments conducted before and after the photocatalytic 1,3-dielectrophile formation monitoring described below.


(a) before

(b) after

**Fig. S6.** Initial rates of photochemical (445 nm) transformation of 2,4-dinitrobenzaldehyde conducted before and after the photocatalytic 1,3-dielectrophile formation.

The resulting initial rate $k_0$ in average was determined as

$$k_0 = 0.135\ \text{mM/min} = 2.25 \times 10^{-6}\ \text{M/s}$$

$$k_0 = \phi \times (1 - 10^{-\varepsilon bC}) \times I_0$$

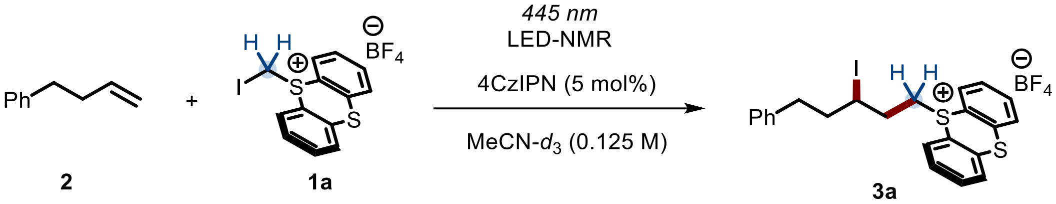
The following parameters were obtained from the report by Reibarkh and coworkers[16],

$$\varepsilon = 23.4\ \text{M}^{-1}\text{cm}^{-1},\ b = 0.11\ \text{cm},\ \phi = 0.0772$$

$$k_0 = 2.25 \times 10^{-6}\ \text{M/s} = 0.0772 \times 0.948 \times I_0$$

$$\therefore\ I_0 = 3.07 \times 10^{-5}\ \text{M/s}$$

**Quantum yield measurement**



In an argon-filled glovebox, **1a** (61.3 mg, 0.137 mmol), 4-phenyl-1-butene (**2**, 19 µL, 0.125 mmol, 99%), and 1,1,2,2-tetrachloroethane (11.6 µL, 0.11 mmol, 99%) were added to a 1 mL volumetric flask. MeCN-$d_3$ was then added to reach 1.0 mL of total solution. After sufficient dissolution, 400 µL of the solution was transferred to the PhotoNMR sampling device (NE-379-5-Br, New Era) consisting of a coaxial inner cell and a 5 mm NMR sample tube. The NMR tube was further sealed with Parafilm, and wrapped in aluminum foil to prevent background reactions caused by ambient light sources. The NMR tube was removed from the glovebox, and the optical fiber connected to Mic-LED was placed into the coaxial inner cell. After taking off the aluminum foil, the NMR tube was inserted into the NMR machine. Upon turning on the light source, the formation of **3a** was monitored by $^1$H NMR spectroscopy recorded every 3 minutes for a total duration of 27 minutes.

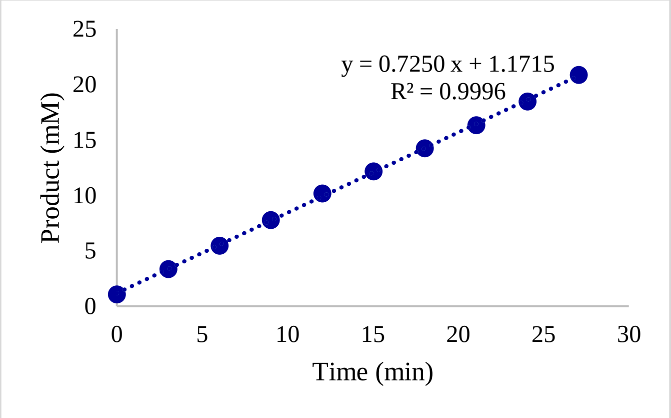


**Fig. S7.** Initial rate of photocatalysed 1,3-dielectrophile formation reaction under 445 nm irradiation

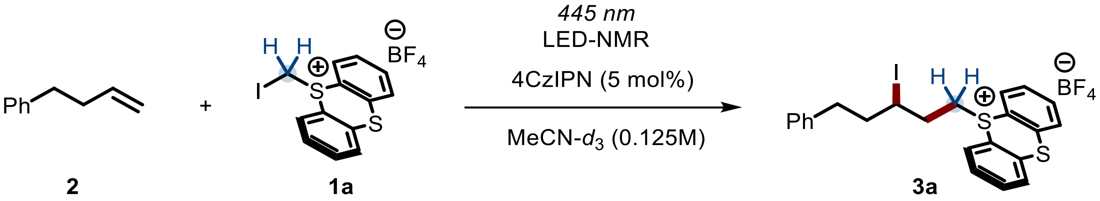
The resulting initial rate $k_0$ and quantum yield $\phi$ was determined as

$$k_0 = 0.725\ \text{mM/min} = 1.21 \times 10^{-5}\ \text{M/s}$$

$$k_0 = 1.21 \times 10^{-5}\ \text{M/s} = \phi \times I_0 = \phi \times 3.07 \times 10^{-5}\ \text{M/s}$$

$$\therefore\ \phi = 0.39$$

### B. Light on-off experiment



In an argon-filled glovebox, **1a** (61.3 mg, 0.137 mmol), 4-phenyl-1-butene (**2**, 19 μL, 0.125 mmol, 99%), and 1,1,2,2-tetrachloroethane (11.6 μL, 0.11 mmol, 99%) were added to a 1 mL volumetric flask. MeCN-$d_3$ was then added to reach 1.0 mL of total solution. After sufficient dissolution, 400 μL of the solution was transferred to a 5 mm thin wall NMR tube. The coaxial inserts were placed, followed by further sealing with Parafilm and aluminum foil wrapping. The NMR tube was removed from the glovebox, and the optical fiber connected to Mic-LED was placed into the coaxial inner cell. After taking off the aluminum foil, the NMR tube was inserted into the NMR machine. Upon turning on the light source, the formation of **3a** was monitored by $^1$H NMR spectroscopy recorded every 3 minutes for a total duration of 177 minutes with alternating sequence of light irradiation and darkness (30 minutes interval).

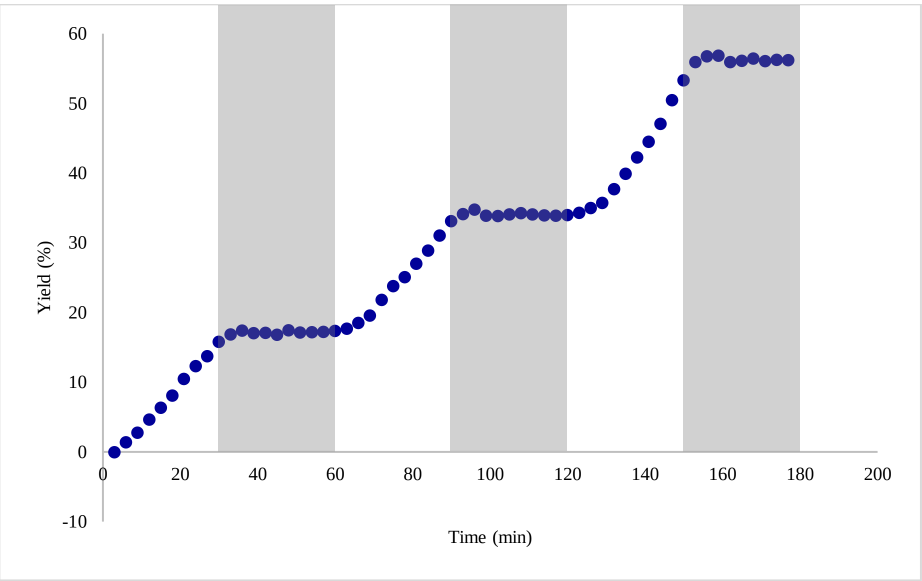


**Fig. S8**. Light on-off experiment (white area indicates irradiation and grey area indicates darkness)

## C. Electrochemical measurements

Cyclic voltammetry (CV) experiments were conducted using a three-electrode cell setup comprising an Ag/AgCl (3 M NaCl) reference electrode, a 3 mm glassy carbon disk working electrode, and a Pt wire counter electrode. Samples were prepared at a substrate concentration of 5.0 mM in MeCN with 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. Before measurements, the sample solution was bubbled with argon for 5 minutes. All experiments were performed at a scan rate of 100 mV/s within the selected potential window. The working electrode was polished, and all electrodes were rinsed thoroughly between each measurement. Reduction potential values were referenced to Saturated Calomel Electrode (SCE) by converting the Ag/AgCl (3 M NaCl) reference values, subtracting 0.035 V to all potentials. The reduction potential was estimated as the half-peak potential ($E_{p/2}$) where the current is half of the value of the peak current[17].

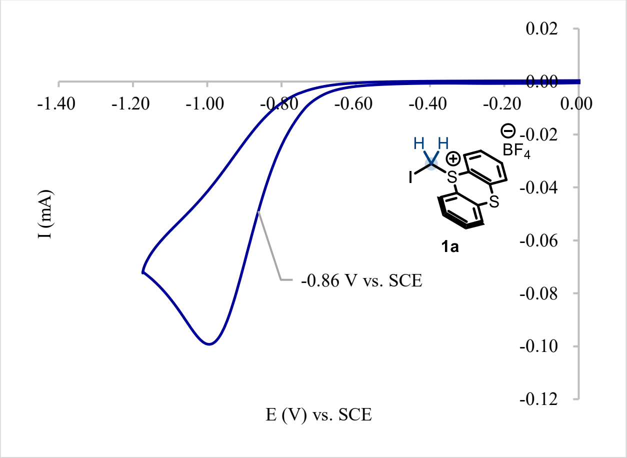


**Fig. S9**. Cyclic voltammogram of **1a**

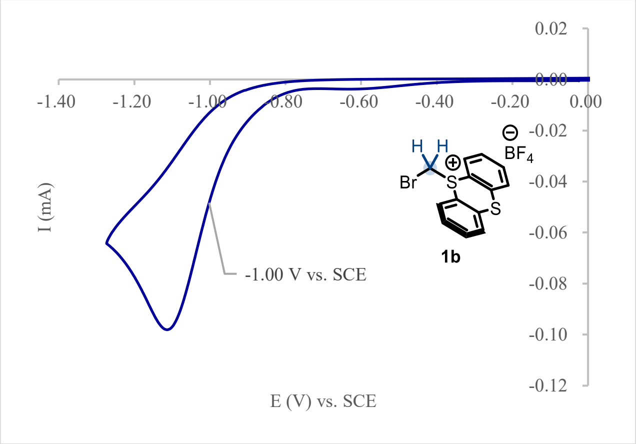


**Fig. S10**. Cyclic voltammogram of **1b**

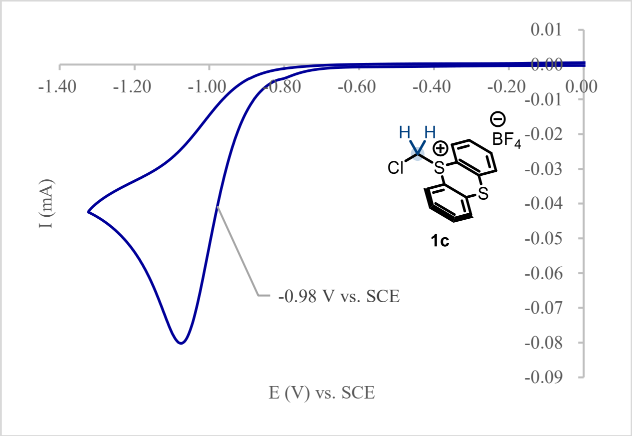


**Fig. S11**. Cyclic voltammogram of **1c**

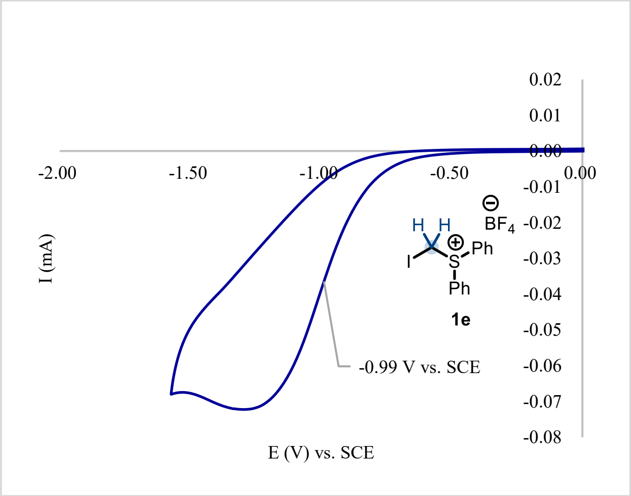


**Fig. S12**. Cyclic voltammogram of **1e**

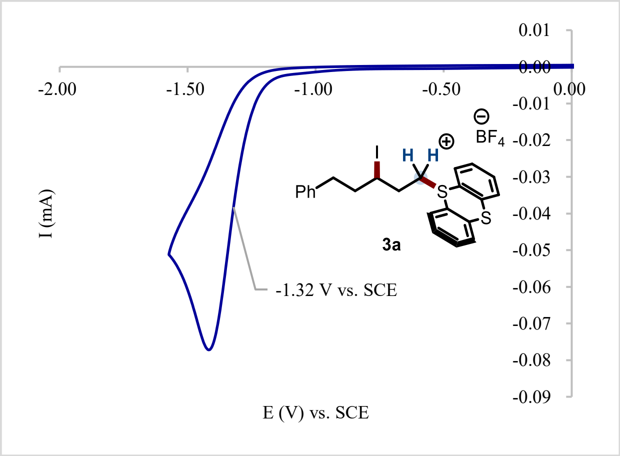


**Fig. S13.** Cyclic voltammogram of **3**

※ Note: cyclic voltammogram of **1d** could not be obtained due to its low stability in MeCN.

## D. UV-vis spectroscopy

UV-vis absorption spectra were collected using Agilent 8453 UV-visible Spectrophotometer. Samples were prepared in a 3 mL, 1 cm cuvette right before the measurements. UV-vis absorption spectra of **1a**, **2**, and 4CzIPN were measured.

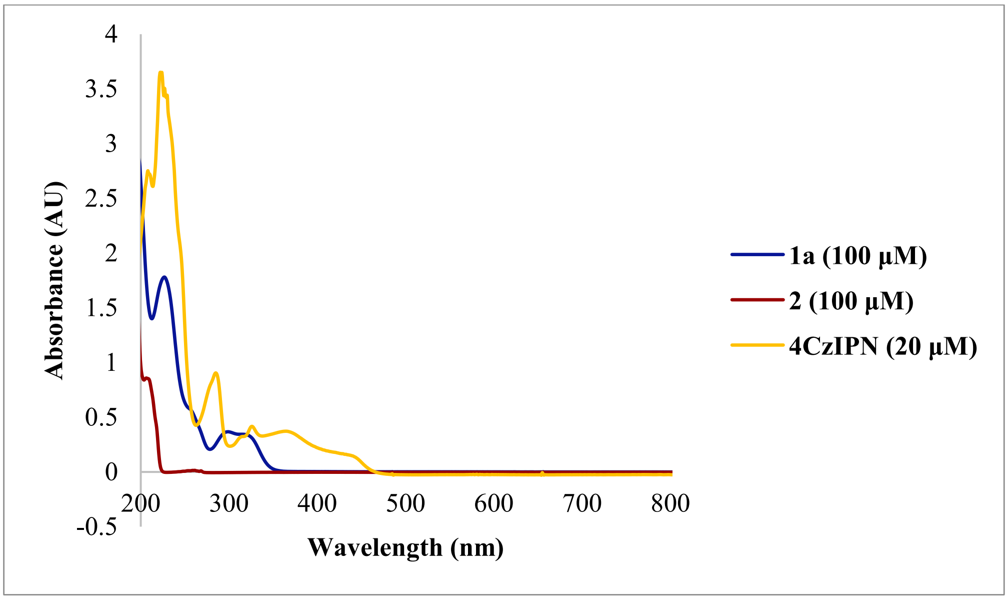


**Fig. S14.** UV-vis absorption spectra of **1a** (100 µM, blue), **2** (100 µM, red) and 4CzIPN (20 µM, yellow) in MeCN.

## E. Time-resolved photoluminescence quenching study

Emission lifetime of 4CzIPN in the presence of varying concentrations of **1a** and **2** were measured using the time-correlated single photon counting (TCSPC) technique. Stock solutions of 4CzIPN (0.15 mM, 2.13 mg dissolved in 18 mL of MeCN), **1a** (37.5 mM, 389 mg dissolved in 18 mL of MeCN), and **2** (37.5 mM, 100 μL in 18.0 mL of MeCN) were prepared in an argon-filled glovebox. Using these stock solutions, 3.0 mL of samples containing 1.0 μM of 4CzIPN were prepared with varying concentrations of the indicated quencher (0.0 mM, 5.0 mM, 10.0 mM, 15.0 mM, 20.0 mM, 25.0 mM) in a 3.0 mL, 1.0 cm air-tight quartz cuvette with a screw-cap. All samples were prepared in an argon-filled glovebox and further sealed with Parafilm. TCSPC traces of the freshly prepared samples were recorded upon 450 nm excitation with measurement time range of 200 ns. The lifetime of 4CzIPN was measured to 19.7 ns, which was comparable to the previous report[18]. The Stern-Volmer plots were constructed using the $\tau_0/\tau$ ratio and the concentrations of quencher, where $\tau_0$ represents fluorescence lifetime at 0.0 mM quencher. The slope of the plot provided a Stern-Volmer constant ($K_{sv}$) value of 1.7 $M^{-1}$ when **1a** was employed as a quencher. However, no significant decay was observed with the alkene substrate **2** as a quencher.

Using the Stern-Volmer relationship[19],

$$\tau_0/\tau = 1 + K_{SV}[Q] = 1 + \tau_0 k_q [Q]$$

$$K_{SV} = \tau_0 k_q$$

$$k_q = K_{SV} / \tau_0 = (1.7\ M^{-1}) / (19.7\ ns) = 8.6 \times 10^{-7}\ M^{-1}\ s^{-1}$$

where $\tau_0$ = fluorescence lifetime of 4CzIPN in the absence of quencher, $\tau$ = fluorescence lifetime of 4CzIPN in the presence of quencher, $K_{SV}$ = Stern-Volmer constant, $[Q]$ = quencher concentration, and $k_q$ = bimolecular quenching constant

**Table S5**. Stern-Volmer quenching study of 4CzIPN with varying concentrations of **1a**

| Entry | **[1a]** (mM) | $\tau$ (ns) | $\tau_0/\tau$ |
|---|---|---|---|
| 1 | 0.0 | 19.72 | 1.0000 |
| 2 | 5.0 | 19.69 | 1.0019 |
| 3 | 10.0 | 19.44 | 1.0146 |
| 4 | 15.0 | 19.30 | 1.0218 |
| 5 | 20.0 | 19.20 | 1.0272 |
| 6 | 25.0 | 18.93 | 1.0421 |

**Table S6**. Stern-Volmer quenching study of 4CzIPN with varying concentrations of **2**

| Entry | **[2]** (mM) | $\tau$ (ns) | $\tau_0/\tau$ |
|---|---|---|---|
| 1 | 0.0 | 19.45 | 1.0000 |
| 2 | 5.0 | 19.37 | 1.0043 |
| 3 | 10.0 | 19.46 | 0.9995 |
| 4 | 15.0 | 19.50 | 0.9975 |
| 5 | 20.0 | 19.48 | 0.9988 |
| 6 | 25.0 | 19.44 | 1.0007 |

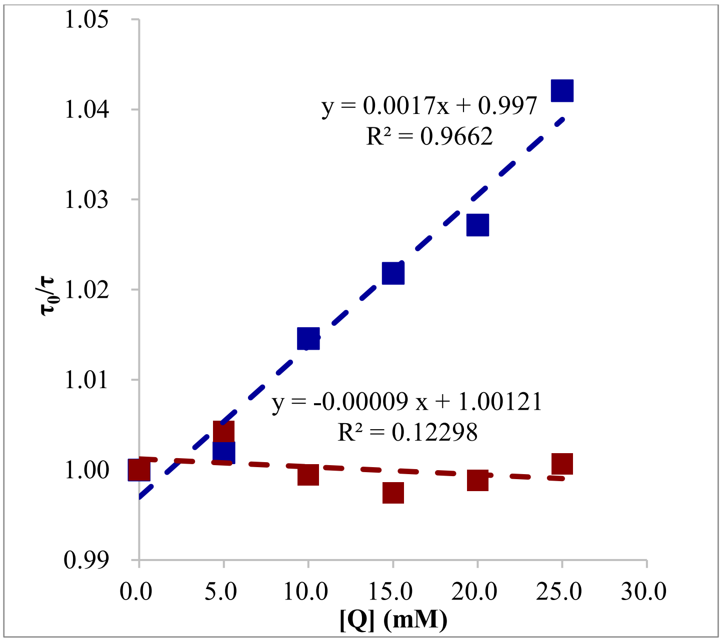
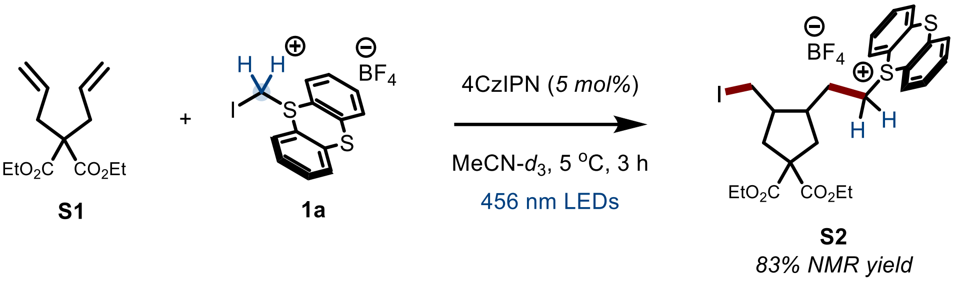


**Fig. S15.** Stern-Volmer plot of 4CzIPN quenched by **1a** or **2** in MeCN. (Blue: **1a** as quencher, red: **2** as quencher)

## F. Radical clock experiments

### Experiment 1



To a flame-dried 4 mL vial with a magnetic stir bar were added 4CzIPN (5 mol%) and **1a** (12.2 mg, 0.0275 mol, 1.1 equiv.). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon via Schlenk line. Dry MeCN-$d_3$ (0.2 mL) and **S1** (6.1 µL, 0.025 mmol, 1.0 equiv.) were added sequentially, using syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred in an isopropanol bath maintained at 5 (± 2) °C for 3 hours under irradiation by two blue LED Kessil$^{TM}$ lamps (PR160L-456 nm, 37.5 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. The reaction mixture was diluted with MeCN-$d_3$ (~0.2 mL) to a total volume ~0.4 mL, transferred to an NMR tube, and analyzed by $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane ($\delta$ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **S2** ($\delta$ = 3.84 ppm, ddd, 1H).

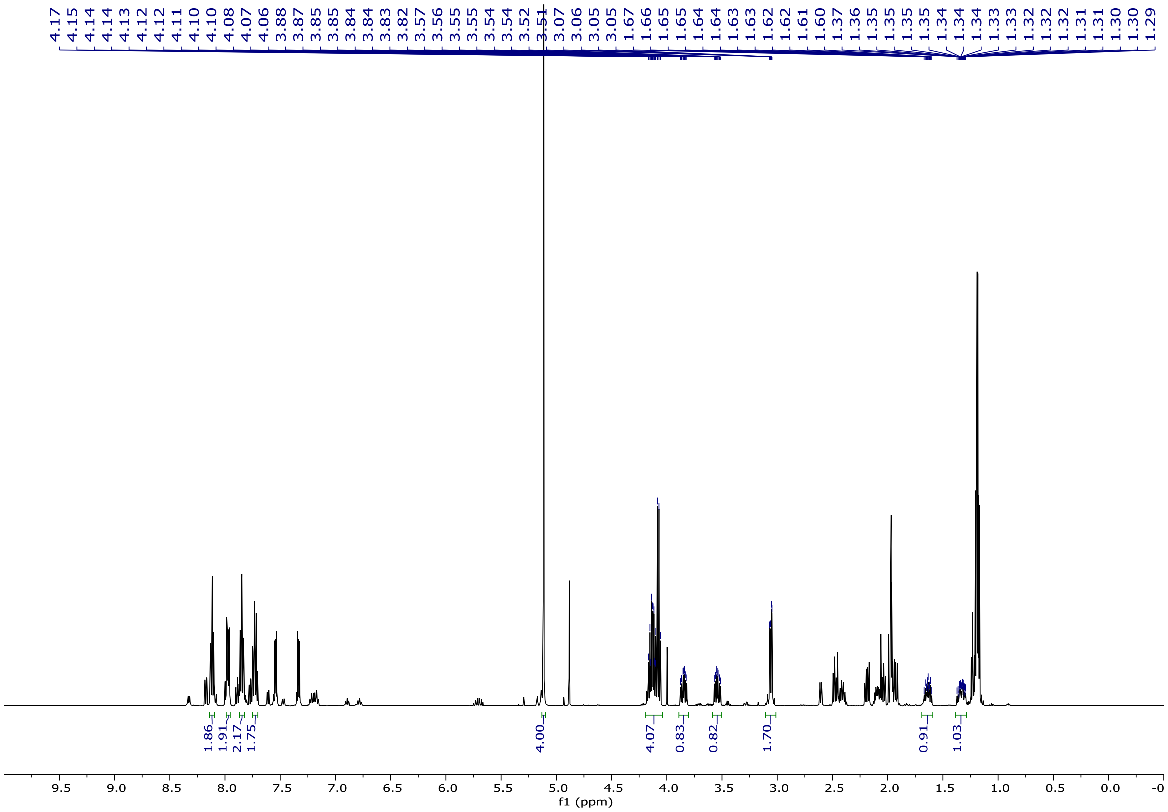
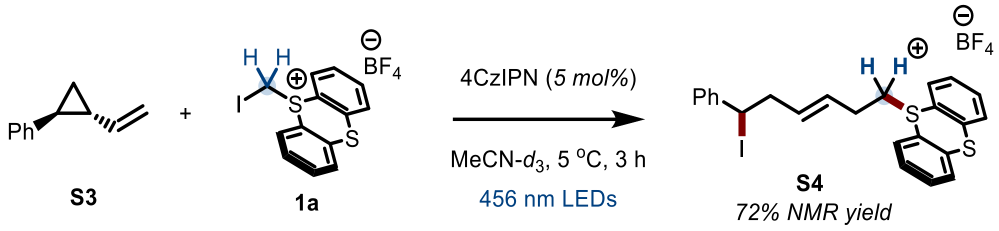


**Fig. S16.** $^1$H NMR spectrum for radical clock experiment using **S1** (83%, **S2**)

## Experiment 2



To a flame-dried 4 mL vial with a magnetic stir bar were added 4CzIPN (5 mol%) and **1a** (12.2 mg, 0.0275 mol, 1.1 equiv.). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon via Schlenk line. Dry MeCN-$d_3$ (0.2 mL) and **S3** (3.61 mg, 0.025 mmol, 1.0 equiv.) were added sequentially, using syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred in an isopropanol bath maintained at 5 (± 2) °C for 3 hours under irradiation by two blue LED Kessil$^{TM}$ lamps (PR160L-456 nm, 37.5 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. The reaction mixture was diluted with MeCN-$d_3$ (~0.2 mL) to a total volume ~0.4 mL, transferred to an NMR tube, and analyzed by $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane (δ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **S4** (δ = 5.33 ppm, t, 1H).

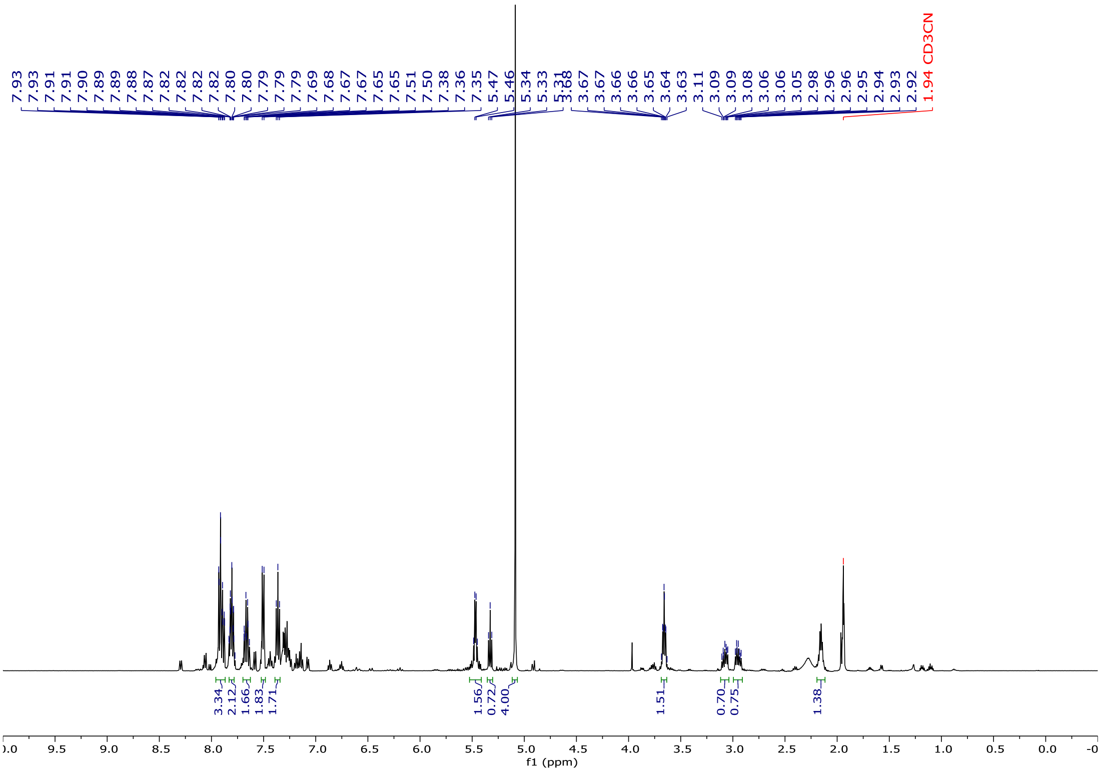
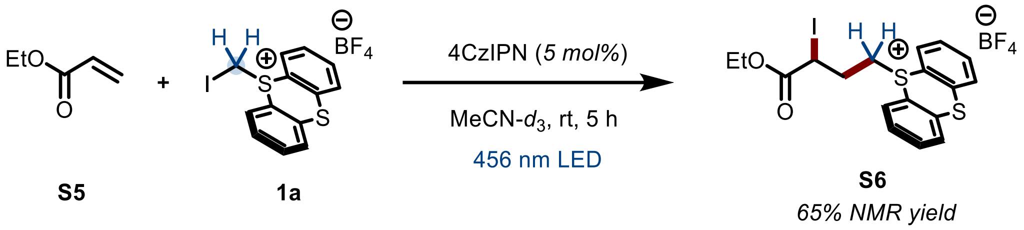


**Fig. S17.** $^1$H NMR spectrum for radical clock experiment using **S3** (72%, **S4**)

## G. Polarity-mismatched radical addition



To a flame-dried 4 mL vial with a magnetic stir bar were added 4CzIPN (5 mol%) and **1a** (16.7 mg, 0.0275 mol, 1.5 equiv.). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon via Schlenk line. Dry MeCN-$d_3$ (0.25 mL) and **S5** (2.7 µL, 0.025 mmol, 99%) were added sequentially, using syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred at room temperature (maintained by a household cooling fan) for 5 hours under irradiation by a blue LED Kessil™ lamp (PR160L-456 nm, 37.5 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. The reaction mixture was diluted with MeCN-$d_3$ (~0.15 mL) to a total volume ~0.4 mL, transferred to an NMR tube, and analyzed by $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane (δ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **S6** (δ = 3.76 ppm, ddd, 1H).

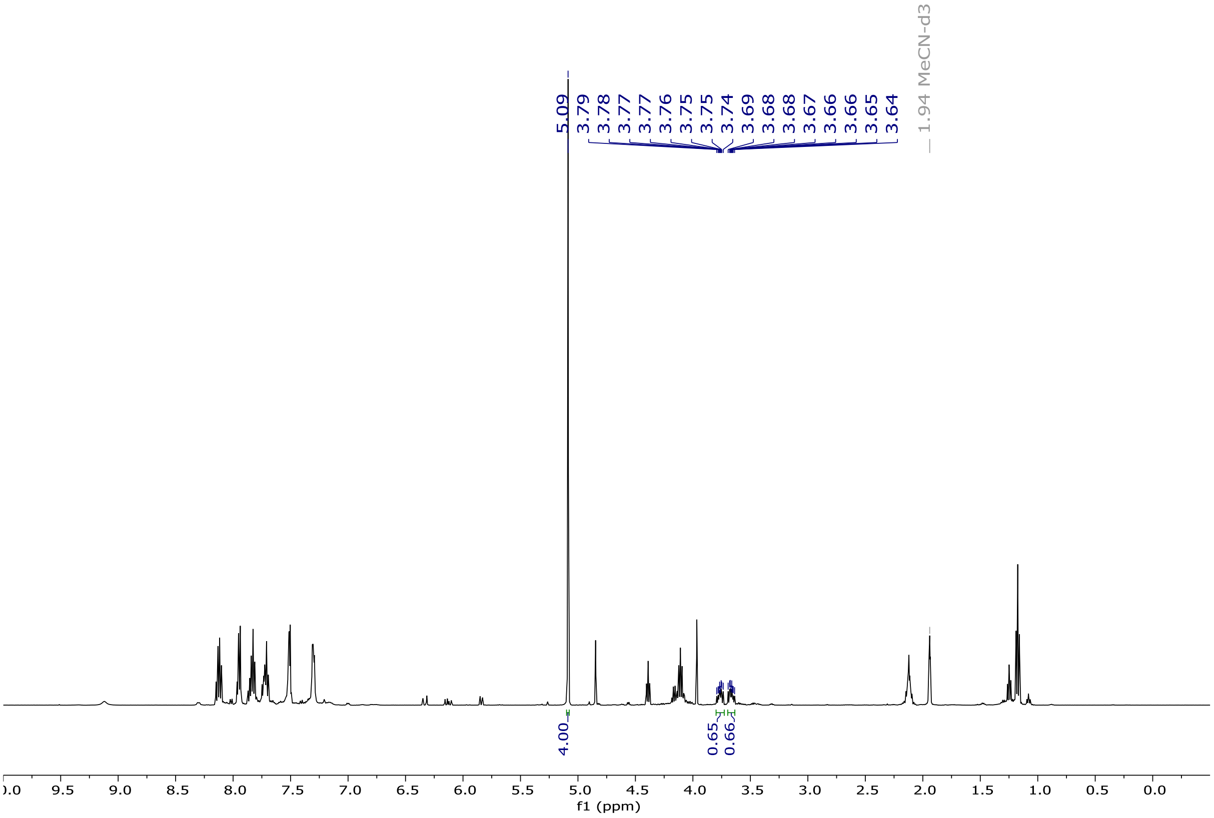
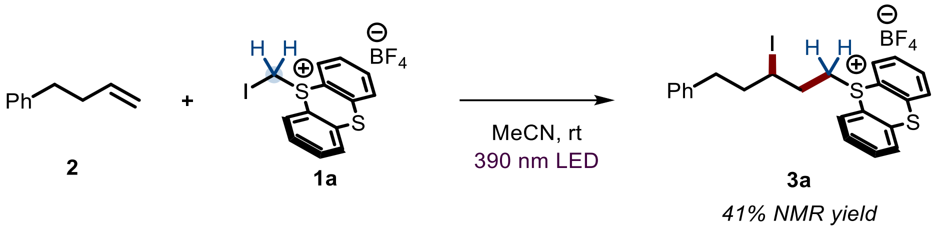


**Fig. S18.** $^1$H NMR spectrum for polarity-mismatched radical addition experiment using **S5** (65%, **S6**)

## H. Direct Photolysis of 1a in the presence of alkene substrate



To a flame-dried 4 mL vial with a magnetic stir bar was added **1a** (12.2 mg, 0.0275 mol, 1.1 equiv.). The vial was capped with a screw-thread open-top cap fitted with a PTFE-lined silicone septum, followed by evacuation and introduction of argon via Schlenk line. Dry MeCN-*d*3 (0.2 mL) and **2** (3.8 µL, 0.025 mmol, 98%) were added sequentially, using syringe and microliter syringe, respectively. After further sealing with Parafilm, the vial was stirred at room temperature (maintained by a household cooling fan) for 3 hours under irradiation by two blue LED Kessil™ lamps (PR160L-390 nm, 39 W). After completion, dibromomethane (3.5 µL, 0.05 mmol, 99%) – an internal standard for $^1$H NMR analysis – was added. The reaction mixture was diluted with MeCN-*d*3 (~0.2 mL) to a total volume ~0.4 mL, transferred to an NMR tube, and analyzed by $^1$H NMR spectroscopy. The yields were determined by relative integration between dibromomethane (δ = 5.09 ppm, s, 2H, integrated to 4.0) and the product **3a** (δ = 3.92 ppm, tt, 1H).

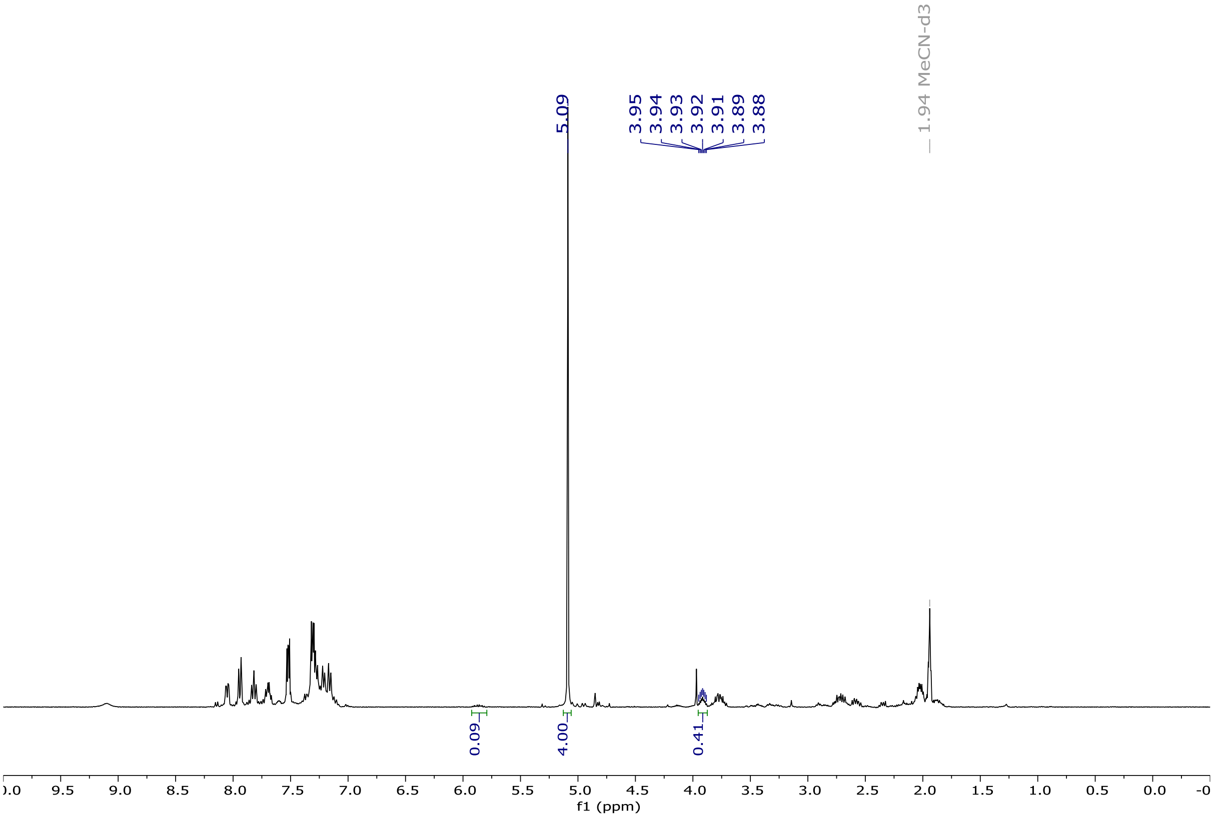


**Fig. S19.** $^1$H NMR spectrum for direct photolysis experiment using **1a** and **2** (41%, **3a**)

# VI. Crystallographic Data

## Crystallographic data of 1a (CCDC 2416218)

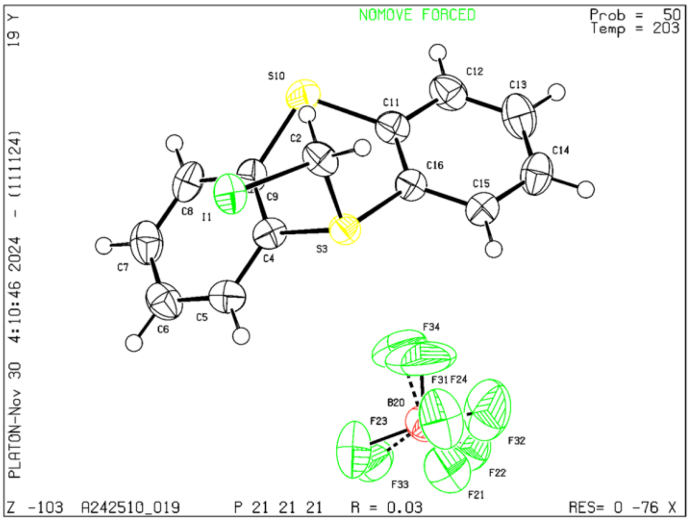


**Fig. S20.** Crystallographic data of **1a**

**Table S7**. Crystal data and structure refinement for **1a**

| | | |
|---|---|---|
| Empirical formula | $C_{13}$ $H_{10}$ B $F_4$ I $S_2$ | |
| Formula weight | 444.04 | |
| Temperature | 203(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | $P2_12_12_1$ | |
| Unit cell dimensions | a = 9.2891(4) Å | α = 90° |
| | b = 10.3259(4) Å | β = 90° |
| | c = 15.9566(6) Å | γ = 90° |
| Volume | 1530.53(11) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.927 Mg/m$^3$ | |
| Absorption coefficient | 2.395 mm$^{-1}$ | |
| F(000) | 856 | |
| Crystal size | 0.085 x 0.067 x 0.053 mm$^3$ | |
| Theta range for data collection | 2.537 to 27.993°. | |
| Index ranges | –12<=h<=12, –13<=k<=13, –21<=l<=21 | |
| Reflections collected | 36690 | |
| Independent reflections | 3689 [R(int) = 0.0794] | |
| Completeness to theta = 25.242° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7456 and 0.5988 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3689 / 150 / 228 | |
| Goodness-of-fit on F$^2$ | 1.254 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0336, wR2 = 0.0781 | |
| R indices (all data) | R1 = 0.0597, wR2 = 0.0997 | |
| Absolute structure parameter | 0.006(12) | |
| Extinction coefficient | 0.0114(10) | |
| Largest diff. peak and hole | 1.318 and –0.720 e·Å$^{-3}$ | |

## Crystallographic data of 9 (CCDC 2416216)

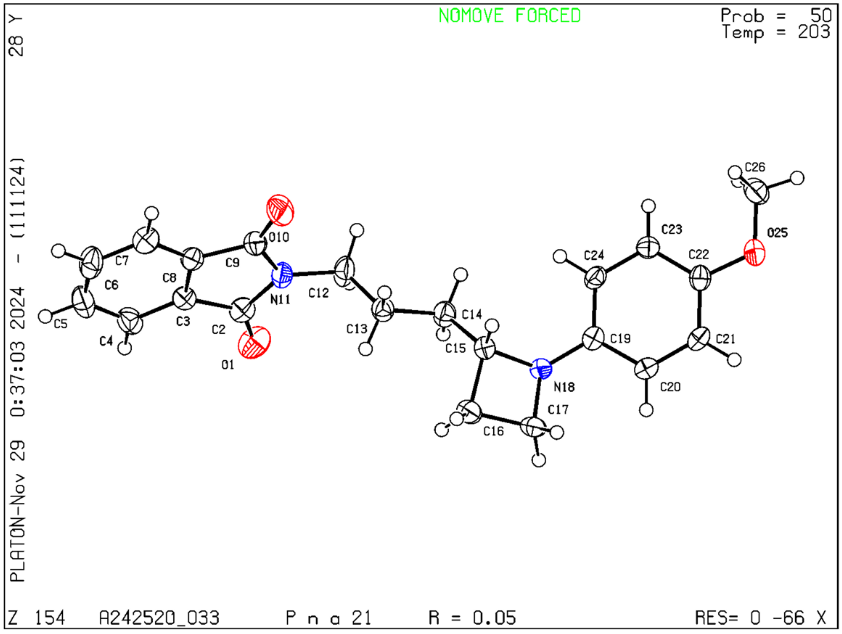


**Fig. S21.** Crystallographic data of **9**

**Table S8.** Crystal data and structure refinement for **9**

| | | |
|---|---|---|
| Empirical formula | $C_{21} H_{22} N_2 O_3$ | |
| Formula weight | 350.40 | |
| Temperature | 203(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | *Pna*$2_1$ | |
| Unit cell dimensions | a = 27.8530(14) Å | α = 90° |
| | b = 10.8984(6) Å | β = 90° |
| | c = 5.9988(3) Å | γ = 90° |
| Volume | 1820.95(16) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.278 Mg/m$^3$ | |
| Absorption coefficient | 0.086 mm$^{-1}$ | |
| F(000) | 744 | |
| Crystal size | 0.177 x 0.031 x 0.028 mm$^3$ | |
| Theta range for data collection | 2.882 to 27.103°. | |
| Index ranges | –35<=h<=35, –13<=k<=13, –6<=l<=7 | |
| Reflections collected | 13100 | |
| Independent reflections | 3841 [R(int) = 0.0882] | |
| Completeness to theta = 25.242° | 99.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7455 and 0.6677 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3841 / 1 / 236 | |
| Goodness-of-fit on F$^2$ | 1.087 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0458, wR2 = 0.0815 | |
| R indices (all data) | R1 = 0.0640, wR2 = 0.0879 | |
| Absolute structure parameter | 0.1(10) | |
| Largest diff. peak and hole | 0.148 and –0.181 e·Å$^{-3}$ | |

**Crystallographic data of 24 (CCDC 2416215)**

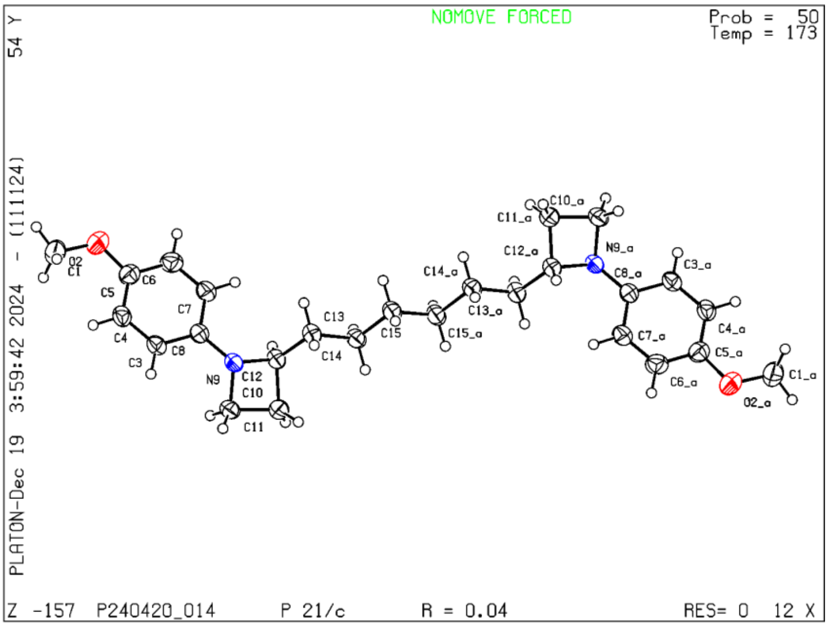


**Fig. S22.** Crystallographic data of **24**

**Table S9.** Crystal data and structure refinement for **24**

| | | |
|---|---|---|
| Empirical formula | $C_{26} H_{36} N_2 O_2$ | |
| Formula weight | 408.57 | |
| Temperature | 173(2) K | |
| Wavelength | 0.700 Å | |
| Crystal system | Monoclinic | |
| Space group | *P*2$_1$/*c* | |
| Unit cell dimensions | a = 5.2650(11) Å | α = 90° |
| | b = 9.1090(18) Å | β = 95.74(3)° |
| | c = 24.390(5) Å | γ = 90° |
| Volume | 1163.9(4) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.166 Mg/m$^3$ | |
| Absorption coefficient | 0.070 mm$^{-1}$ | |
| F(000) | 444 | |
| Crystal size | 0.092 x 0.019 x 0.017 mm$^3$ | |
| Theta range for data collection | 1.653 to 27.036°. | |
| Index ranges | –6<=h<=6, –11<=k<=11, –31<=l<=31 | |
| Reflections collected | 9673 | |
| Independent reflections | 2608 [R(int) = 0.0721] | |
| Completeness to theta = 24.835° | 98.2 % | |
| Absorption correction | Empirical | |
| Max. and min. transmission | 1.000 and 0.943 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2608 / 0 / 141 | |
| Goodness-of-fit on F$^2$ | 1.025 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0448, wR2 = 0.1010 | |
| R indices (all data) | R1 = 0.0758, wR2 = 0.1126 | |
| Extinction coefficient | 0.076(5) | |
| Largest diff. peak and hole | 0.157 and –0.126 e·Å$^{-3}$ | |

## Crystallographic data of 61 (CCDC 2416217)

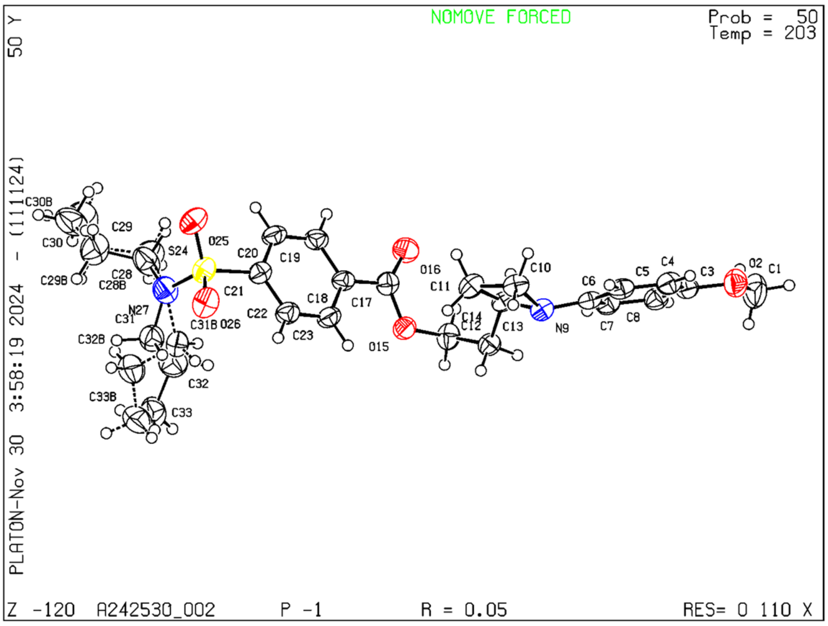


**Fig. S23.** Crystallographic data of **61**

**Table S10.** Crystal data and structure refinement for **61**

| | | |
|---|---|---|
| Empirical formula | $C_{25} H_{34} N_2 O_5 S$ | |
| Formula weight | 474.60 | |
| Temperature | 203(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | *P*-1 | |
| Unit cell dimensions | a = 6.3005(3) Å | α = 78.8922(17)° |
| | b = 9.6133(5) Å | β = 86.2453(16)° |
| | c = 21.9526(12) Å | γ = 72.9680(14)° |
| Volume | 1247.45(11) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.264 Mg/m$^3$ | |
| Absorption coefficient | 0.167 mm$^{-1}$ | |
| F(000) | 508 | |
| Crystal size | 0.097 x 0.072 x 0.022 mm$^3$ | |
| Theta range for data collection | 2.598 to 25.500°. | |
| Index ranges | –7<=h<=7, –11<=k<=11, –26<=l<=26 | |
| Reflections collected | 32789 | |
| Independent reflections | 4637 [R(int) = 0.0848] | |
| Completeness to theta = 25.242° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7452 and 0.7043 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4637 / 174 / 359 | |
| Goodness-of-fit on F$^2$ | 1.133 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0517, wR2 = 0.0887 | |
| R indices (all data) | R1 = 0.0823, wR2 = 0.0997 | |
| Largest diff. peak and hole | 0.171 and –0.295 e·Å$^{-3}$ | |

# VII. Computational Studies

## A. General Computational Information

All calculations were performed using density functional theory (DFT)[20] implemented in Gaussian 16 suite of programs[21], using High-Performance Computing Resources in the Institute for Basic Science (IBS) Research Solution Center. Geometry optimizations were performed using (U)B3LYP[22,23] functional with Grimme's D3[24] dispersion and a mixed basis set of LANL2DZ (iodine, I) and 6-311+G** for all other atoms. Frequency calculations were performed at the same level as that used for geometry optimizations, wherein thermochemistry correction energy (G – E) was acquired. All stationary points were characterized by frequency calculations to confirm their identity as either local minima (zero imaginary frequencies) or first-order saddle points (one imaginary frequency). For transition structures, an intrinsic reaction coordinate calculation (IRC) was conducted to ensure transit between desired reactant and product minima[25,26]. With the optimized geometries of intermediates and transition structures, single-point energy calculations were re-evaluated at (U)B3LYP functional with Grimme's D3 dispersion and a different basis set combination of SDD (I)[27] and 6-311++G**[28-32] for others. The solvent effect was reflected by using the SMD[33] solvation model and carried out at the same level as single-point calculations (solvent = acetonitrile). Finally, to increase the accuracy of the integration grid, we used the *int* = *ultrafine* option for all types of calculations. Three-dimensional molecular structures were visualized using CYLview[34]. Visualizations of molecular orbitals were prepared using ChemCraft version 1.0 program (hydrogen atoms are omitted for clarity). The final solution phase Gibbs free energies were calculated as follows:

$$G_{sol} = E_{sol} + (G - E) \quad - \quad (\text{eq } 1)$$

$$\Delta G_{sol} = \Sigma G_{sol} \text{ for products} - \Sigma G_{sol} \text{ for reactants} \quad - \quad (\text{eq } 2)$$

## B. Computational details for iodide ion

The entropy of single atom species (e.g. $I^-$) was computed separately based on the Sackur-Tetrode equation as shown below[35]. The computed entropy of $I^-$ was 40.428 cal $mol^{-1}$ $K^{-1}$, that was used for the computational studies.

$$S_t = \frac{3}{2} RlnM + \frac{5}{2} RlnT - RlnP + Rln\left[\frac{(2\pi k)(2\pi k)^{\frac{3}{2}} R e^{\frac{5}{2}}}{h^3 N_o^{\frac{5}{2}}}\right] \quad - (\text{eq } 3)$$

$$S_t = \frac{3}{2} RlnM + \frac{5}{2} RlnT - 9.686 J K^{-1} mol^{-1} \text{ at } P = 1\, atm \quad - (\text{eq } 4)$$

## C. DFT Energy Landscape

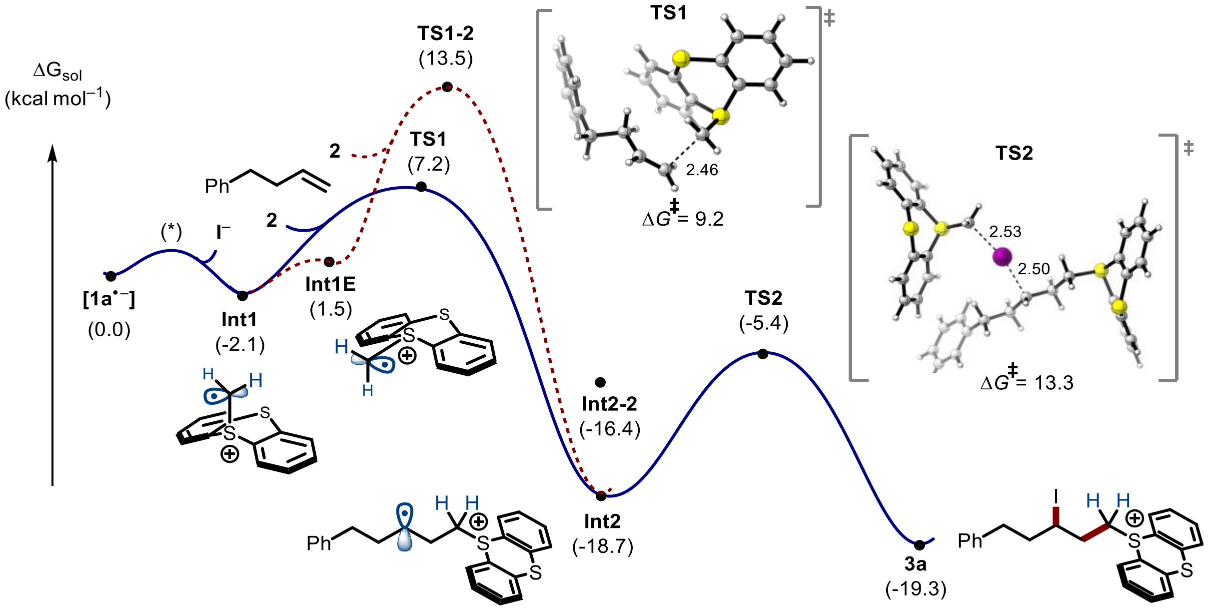


**Fig. S24**. Computed reaction profiles at SMD(MeCN)-(U)B3LYP-D3/SDD(I)+6-311++g**//(U)B3LYP-D3/LANL2DZ(I)+6-311+g** level of theory. ΔG in kcal mol$^{-1}$. Bond distances in Å

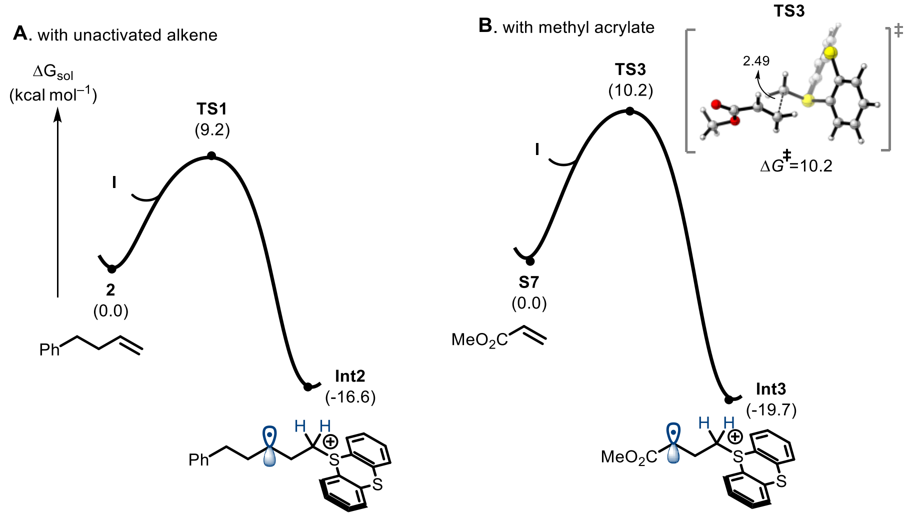


**Fig. S25**. Scrutiny of electron demand in radical addition step. (A) with unactivated alkene (**2**) and (B) with methyl acrylate (**S7**).

## D. Frontier molecular orbitals (FMO) of reagents 1a, 1b, and 1c

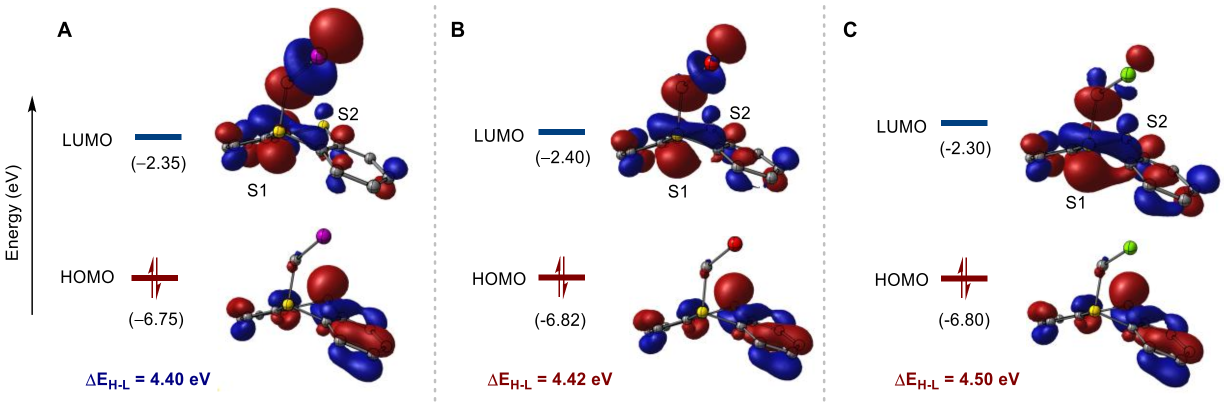


**Fig. S26.** Computed FMOs of each reagent: (A) reagent **1a**, (B) reagent **1b**, and (C) reagent **1c**. ΔE$_{H-L}$ = the energy gap between HOMO and LUMO (E in eV, isovalue = 0.04)

## E. Frontier molecular orbitals of α-thianthrenium methyl radical

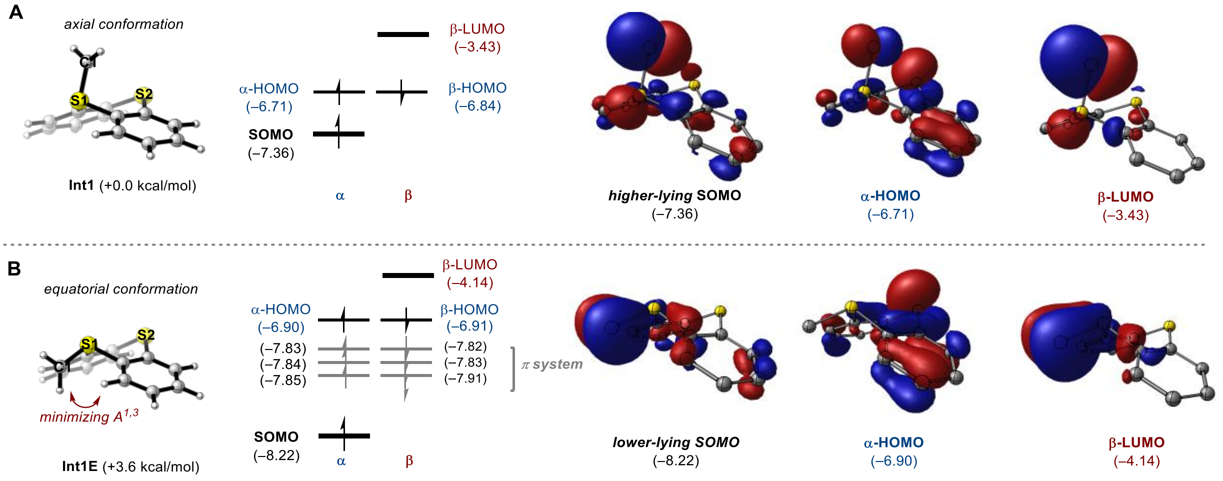


**Fig. S27.** Computed structures, electronic structures and molecular orbitals of (A) axial conformer **Int1** and (B) equatorial conformer **Int1E** (isovalue: 0.04).

## F. Energy components from DFT calculations

**Table S11**. Computed energies of the optimized geometries

| | **$E_{sol}$(SCF) (hartree)** | **G-E (hartree)** | **$G_{sol}$ (kcal/mol)** |
|---|---|---|---|
| **1a** | -1309.21698 | 0.147385 | -821452.952 |
| **1b** | -3871.947451 | 0.148625 | -2429588.61 |
| **1c** | -1758.025457 | 0.150337 | -1103082.459 |
| **[$1a^{\bullet-}$]** | -1309.34998467 | 0.142531 | -821539.460 |
| **2** | -388.40302114 | 0.153363 | -243630.155 |
| **Int1** | -1297.73282089 | 0.146208 | -814247.278 |
| **Int1E** | -1297.72631927 | 0.145439 | -814243.681 |
| **TS1** | -1686.145756 | 0.324273 | -1057868.153 |
| **TS1-2** | -1686.136225 | 0.324869 | -1057861.798 |
| **Int2** | -1686.18623 | 0.323409 | -1057894.093 |
| **Int2-2** | -1686.186268 | 0.327245 | -1065100.357 |
| **TS2** | -2995.405713 | 0.494557 | -1879333.705 |
| **3a** | -1697.672597 | 0.325855 | -1065100.357 |
| $I^-$ (iodide ion) | -11.60733162 | -0.016848 | -7294.277 |
| **S7** | -306.5769817 | 0.064453 | -192339.370 |
| **TS3** | -1604.312657 | 0.229744 | -1006576.465 |
| **Int3** | -1604.367045 | 0.236511 | -1006606.347 |

## G. Global electrophilicity index and radical stability score

### Global electrophilicity index

To gain deeper insight into the electrophilic nature of α-thianthrenium methyl radical (**I**), the global electrophilicity index ($\omega$), originally introduced by Parr et al.[36] was evaluated through DFT calculations using the following formalism.

$$\omega = \frac{\mu^2}{2\eta} - \text{ (eq 5)}$$

where μ is the electronic chemical potential[37] and $\eta$ is the chemical hardness[38]. These two quantities were defined as $\mu = -(I + A)/2$ and $\eta = (I - A)$, and are calculated using the vertical ionization energy I and electron affinity A.

To contextualize the use of global electrophilicity in understanding radical polarity, we looked to the literatures. In 2007, De Proft and coworkers demonstrated that electrophilicity scales correlate well with experimental and theoretical reaction data through principal component analysis (PCA)[38]. They compiled a database of 35 radicals, including carbon- and heteroatom-centered radicals (heteroatoms = nitrogen, oxygen, sulfur, and halogens). More recently, Nagib and colleagues introduced a radical polarity database by evaluating the global electrophilicity of over 500 radicals, calculated at the B3LYP-D3/6-311+G** level[39]. We benchmarked these elegant studies to quantitatively determine the electrophilicity of radicals **Int1** and **Int1E**. For consistency, the electrophilicity indices were calculated using the B3LYP-D3/6-311+G* level of theory for all atoms except iodine, for which the SDD basis set was employed. To calculate the global electrophilicity index of **Int1** and **Int1E**, the $BF_4^-$ anion was included to avoid theoretical errors arising from truncation. Indeed, the positively charged and neutral radicals fall far apart on the scale of the global electrophilic index, precluding a direct head-to-head comparison. To provide both quantitative and qualitative context for the electrophilic nature of the α-thianthrenium methyl radical, the radical polarities of 354 carbon-centered radicals frequently encountered in organic synthesis were retrieved from the report by Nagib[39] and are presented in **Table S12** alongside the newly calculated electrophilicity indices.

### Radical stability score

Traditionally, the stability of organic radicals has been assessed based on the radical stabilization energy (RSE) scale, where the RSE for a carbon-centered radical (R•) is defined by the difference between the C–H bond dissociation energies (BDEs) of methane and R–H[40]. However, the RSE scale only reflects thermodynamic stabilization and does not effectively consider the kinetic aspects. Consequently, the value is not sufficient to describe the kinetic accessibility of organic radicals involved in chemical reactions. Recent computational studies by John and Paton[41] disclosed an alternative method to quantitatively understand radical stability based on two molecular descriptors: maximum spin density (max. spin) and percent buried volume ($\%V_{\text{bur}}$). Combining these two key computational descriptors, a new quantitative metric that captures both thermodynamic and kinetic considerations – Radical Stability Score (RSS) – was defined as follows:

$$\text{RSS} = \%V_{\text{bur}} + 50 \times (1 - \text{max. spin}) \; - \text{(eq 6)}$$

The factor of 50 in the equation 6 ensures approximately equal weight is given to the spin and buried volume terms. This metric preserves the thermodynamic information contained in traditional metrics derived from BDE values while also allowing for differentiation between sterically distinct radical centers, providing a more comprehensive understanding of radical stability. In this study, we therefore quantified radical stability based on RSS scale in lieu of the traditional thermodynamic RSE scale.

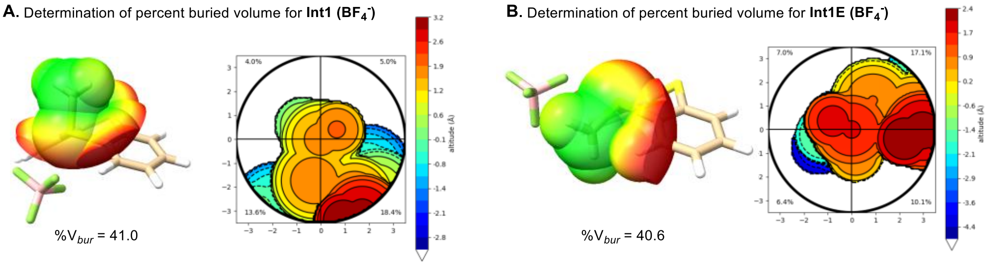
## Maximum spin density

The maximum spin densities in this study were computed according to the procedure reported in the previous study[41]. Mulliken spin densities for all atoms in each molecule were calculated using the B3LYP-D3/SDD(I)+6-311+G** level of theory, based on geometries from the database constructed by Nagib[39]. The computed spin density values for each atom were then normalized. The absolute magnitudes of heavy atom spin densities were summed, neglecting the small spin values on hydrogen atoms, and then converted to fractional spins that sum to one. The atom with the highest fractional spin density was identified as the radical center and its fractional spin density was considered to be the maximum spin density. The computed maximum spin densities of all radicals were enumerated in **Table S12**.

## Buried volume

The percent buried volumes (%$V_{\mathrm{bur}}$) in this study were computed according to the procedure reported in the previous study[41]. The percent buried volumes were evaluated from the optimized molecular geometry using SEQCROW, bundled with UCSF ChimeraX[42]. The atom with the highest fractional spin density was selected as the center for the buried volume calculation, using numerical integration on a Cartesian grid with a spacing of 0.05 Å. Voxel occupancies were determined based on the unscaled atomic Bond radii for all atoms, in conjunction with a sphere radius of R = 3.5 Å. Hydrogen atoms were not included in the calculation of %$V_{\mathrm{Bur}}$ values to consider only heavy atoms. For accuracy, the percent buried volume was measured both in the presence and absence of $BF_4^-$, and no significant differences were observed. The computed buried volumes were enumerated in **Table S12**.

**A.** Determination of percent buried volume for **Int1 ($BF_4^-$)** **B.** Determination of percent buried volume for **Int1E ($BF_4^-$)**



**C.** Determination of percent buried volume for **Int1** **D.** Determination of percent buried volume for **Int1E**

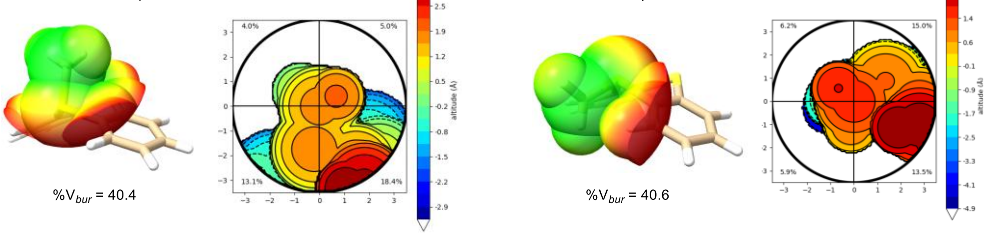


**Fig. S28.** Percent buried volume and steric map. (**A**) **Int1 ($BF_4^-$)**, (B) **Int1E ($BF_4^-$)**, (**C**) **Int1** and (**D**) **Int1E**.

**Table S12.** Computed global electrophilicity index and radical stability score

| **IUPAC Name** | max. spin. | $\%V_{\mathrm{bur}}$ | **RSS** | $\omega$ |
|---|---|---|---|---|
| 3,5-Bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl | 0.42 | 52 | 81.2 | 0.73 |
| *tert*-butyl | 0.94 | 42.3 | 45.1 | 0.66 |
| Cyclopentyl | 0.93 | 40.4 | 43.8 | 0.68 |
| 2-Methylbutan-2-yl | 0.94 | 47.8 | 51 | 0.70 |
| Propan-2-yl | 0.99 | 32.9 | 33.7 | 0.72 |
| Adamantan-1-yl | 0.76 | 57.8 | 69.7 | 0.74 |
| Butan-2-yl | 0.96 | 38.9 | 40.7 | 0.74 |
| Cyclobutyl | 0.97 | 36.1 | 37.5 | 0.75 |
| 1-(1*H*-Pyrrol-2-yl)ethyl | 0.41 | 39.9 | 69.2 | 0.79 |
| Cyclohepta-2,4,6-trien-1-yl | 0.29 | 39.5 | 74.8 | 0.80 |
| 3-Ethylbicyclo[1.1.1]pentan-1-yl | 0.73 | 43.7 | 57.1 | 0.88 |
| Ethyl | 1 | 23.6 | 23.8 | 0.89 |
| Butyl | 0.96 | 30.2 | 32.1 | 0.91 |
| (4-Aminophenyl)methyl | 0.38 | 32.5 | 63.8 | 0.91 |
| Propyl | 0.97 | 29.8 | 31.3 | 0.92 |
| 2-Methylbut-3-en-2-yl | 0.41 | 45.4 | 74.9 | 0.95 |
| Cyclohexa-2,5-dien-1-yl | 0.3 | 38.3 | 73.2 | 0.95 |
| Cyclohexa-2,4-dien-1-yl | 0.3 | 38.2 | 73.1 | 0.95 |
| Hex-5-en-1-yl | 0.92 | 33.2 | 37.2 | 0.96 |
| 2,2-Dimethylpropyl | 0.89 | 41.7 | 47.2 | 0.96 |
| 1-(Furan-2-yl)ethyl | 0.38 | 38.9 | 69.9 | 0.97 |
| But-3-en-2-yl | 0.42 | 27.6 | 56.9 | 0.98 |
| (4-Methoxyphenyl)methyl | 0.38 | 32.6 | 63.8 | 1.03 |
| Cyclopropyl | 0.94 | 29.1 | 32 | 1.04 |
| 2-Phenylpropan-2-yl | 0.41 | 50.3 | 79.9 | 1.04 |
| 1-(Thiophen-2-yl)ethyl | 0.36 | 40.9 | 72.9 | 1.06 |
| (4-Hydroxyphenyl)methyl | 0.38 | 32.5 | 63.8 | 1.06 |
| Prop-1-en-2-yl | 0.93 | 29.8 | 33.5 | 1.08 |
| 1-Phenylethyl | 0.39 | 41.6 | 72.2 | 1.12 |
| But-3-yn-2-yl | 0.48 | 33.3 | 59.2 | 1.15 |
| Prop-2-en-1-yl | 0.41 | 27.3 | 56.7 | 1.16 |
| Methyl | 1 | 14 | 14 | 1.21 |
| Benzyl | 0.37 | 32.6 | 64 | 1.24 |
| Prop-1-en-1-yl | 0.9 | 26.9 | 31.8 | 1.25 |
| Ethenyl | 0.97 | 20.3 | 21.7 | 1.25 |
| 2-Phenylbut-3-en-2-yl | 0.28 | 52.9 | 88.8 | 1.31 |
| [4-(Trimethylsilyl)phenyl]methyl | 0.36 | 32.6 | 64.8 | 1.32 |
| 9,10-Dihydroanthracen-9-yl | 0.25 | 48.6 | 86.3 | 1.33 |
| 1-Phenylprop-2-en-1-yl | 0.26 | 44.5 | 81.4 | 1.34 |
| (4-Bromophenyl)methyl | 0.36 | 32.6 | 64.5 | 1.42 |
| Diphenylmethyl | 0.25 | 49.4 | 87.2 | 1.43 |
| Triphenylmethyl | 0.25 | 66 | 103.6 | 1.44 |
| (4-Iodophenyl)methyl | 0.36 | 32.6 | 64.8 | 1.46 |
| [4-(Trifluoromethyl)phenyl]methyl | 0.37 | 32.6 | 64.2 | 1.67 |

| | | | | |
|---|---|---|---|---|
| (4-Carboxyphenyl)methyl | 0.35 | 32.6 | 65 | 1.75 |
| 9*H*-Fluoren-9-yl | 0.29 | 44.6 | 80.3 | 1.77 |
| Cyclopenta-2,4-dien-1-yl | 0.4 | 35.5 | 65.7 | 1.88 |
| Ethynyl | 0.94 | 18.7 | 21.6 | 3.37 |
| 2-Methyloxolan-2-yl | 0.73 | 45.8 | 59.5 | 0.52 |
| Oxolan-2-yl | 0.85 | 36.9 | 44.4 | 0.52 |
| 2-Hydroxypropan-2-yl | 0.85 | 37.7 | 45.3 | 0.58 |
| 1-Ethoxyethyl | 0.89 | 36.1 | 41.7 | 0.59 |
| 1,3-Dioxolan-2-yl | 0.82 | 33.1 | 41.9 | 0.59 |
| 1-Hydroxyethyl | 0.88 | 28.3 | 34.4 | 0.60 |
| 2-Methyl-2,3-dihydrofuran-2-yl | 0.8 | 43.8 | 54.1 | 0.61 |
| 2,3-Dihydrofuran-2-yl | 0.82 | 34.9 | 44 | 0.64 |
| Hydroxymethyl | 0.9 | 20.2 | 25.2 | 0.71 |
| Methoxymethyl | 0.89 | 26.5 | 31.9 | 0.72 |
| 1-(Acetyloxy)ethyl | 0.91 | 36.6 | 41.2 | 0.88 |
| 1-[(2,2-Dimethylpropanoyl)oxy]ethyl | 0.89 | 38.7 | 44.4 | 0.88 |
| Oxan-4-yl | 0.9 | 42.9 | 47.9 | 0.88 |
| Oxan-3-yl | 0.96 | 42.3 | 44.2 | 0.92 |
| 3-Hydroxypropyl | 0.95 | 30.2 | 32.9 | 0.97 |
| 2-Hydroxyethyl | 0.99 | 27.3 | 27.7 | 0.99 |
| 3-Oxocyclohexyl | 0.92 | 43.2 | 47.3 | 1.00 |
| 3-Methoxypropyl | 0.87 | 30.4 | 36.7 | 1.01 |
| Benzoyl | 0.61 | 34 | 53.4 | 1.04 |
| (Acetyloxy)methyl | 0.92 | 27.6 | 31.4 | 1.05 |
| 4-Oxocyclohexyl | 0.92 | 43.3 | 47.5 | 1.05 |
| *N*,*N*-Dimethylcarbamoyl | 0.61 | 35.1 | 54.7 | 1.06 |
| 2-Methoxyethyl | 0.97 | 31.6 | 33 | 1.08 |
| Acetyl | 0.68 | 25.2 | 41.4 | 1.08 |
| 1-(Benzoyloxy)ethyl | 0.83 | 37.6 | 45.9 | 1.10 |
| Formyl | 0.75 | 16.9 | 29.5 | 1.17 |
| 2,2,2-Trifluoro-1-hydroxyethyl | 0.81 | 35.3 | 44.9 | 1.21 |
| 2,2-Dimethoxypropyl | 0.91 | 45.4 | 49.7 | 1.23 |
| 1-[(2,2,2-Trifluoroacetyl)oxy]ethyl | 0.85 | 37.1 | 44.5 | 1.31 |
| 1-Ethoxy-2-methyl-1-oxopropan-2-yl | 0.73 | 46.7 | 60.4 | 1.38 |
| Methoxycarbonyl | 0.73 | 27.9 | 41.6 | 1.42 |
| 1-Ethoxy-1-oxopropan-2-yl | 0.75 | 37.6 | 50 | 1.55 |
| 3-Oxobutan-2-yl | 0.65 | 39.6 | 57.2 | 1.63 |
| (Dimethylcarbamoyl)methyl | 0.74 | 33.9 | 47 | 1.66 |
| 2-Oxocyclohexyl | 0.63 | 44.6 | 63.2 | 1.68 |
| 1,1,1,3,3,3-Hexafluoro-2-hydroxypropan-2-yl | 0.76 | 51 | 62.9 | 1.70 |
| 2-Oxocyclopentyl | 0.66 | 41.1 | 58.3 | 1.74 |
| 1,4-Dimethoxy-1,4-dioxobutan-2-yl | 0.73 | 42.3 | 55.6 | 1.76 |
| 2-(*tert*-Butoxy)-2-oxoethyl | 0.74 | 29.5 | 42.3 | 1.80 |
| 2-Ethoxy-2-oxoethyl | 0.75 | 28.5 | 40.8 | 1.84 |
| 4-(Acetyloxy)-1-methoxy-1-oxopentan-2-yl | 0.73 | 47.4 | 61 | 1.88 |
| 2-Oxo-2-phenylethyl | 0.65 | 33.4 | 50.9 | 2.06 |
| 2,3-Dioxobutyl | 0.58 | 34 | 54.9 | 2.39 |

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|---|---|---|---|---|
| 1,3-Diethoxy-1,3-dioxopropan-2-yl | 0.62 | 41.8 | 60.9 | 2.40 |
| 1,3-Dimethoxy-1,3-dioxopropan-2-yl | 0.62 | 41.9 | 61.1 | 2.45 |
| 1-Methoxy-1,3-dioxo-3-phenylpropan-2-yl | 0.55 | 46.4 | 68.7 | 2.50 |
| 1-Methoxy-1,3-dioxobutan-2-yl | 0.55 | 43.8 | 66.4 | 2.60 |
| 2,4-Dioxopentan-3-yl | 0.51 | 46 | 70.5 | 2.66 |
| 1,3-Dioxo-1-phenylbutan-2-yl | 0.5 | 48.6 | 73.5 | 2.75 |
| 2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-yl | 0.57 | 45.6 | 67.1 | 3.01 |
| Pyrrolidin-2-yl | 0.82 | 38.2 | 47.1 | 0.34 |
| 1-[Bis(propan-2-yl)amino]ethyl | 0.7 | 53.2 | 68 | 0.37 |
| Imidazolidin-2-yl | 0.81 | 36 | 45.5 | 0.39 |
| 1-(Diethylamino)ethyl | 0.82 | 46.6 | 55.8 | 0.42 |
| 1-Methylpyrrolidin-2-yl | 0.82 | 44.2 | 53.2 | 0.42 |
| 1-Methylpiperidin-2-yl | 0.8 | 47.6 | 57.8 | 0.44 |
| 1-Aminoethyl | 0.86 | 30 | 37.1 | 0.44 |
| 1-(Methylamino)ethyl | 0.66 | 45.6 | 62.7 | 0.45 |
| Aminomethyl | 0.85 | 20.3 | 27.9 | 0.50 |
| Piperidin-2-yl | 0.78 | 41.5 | 52.4 | 0.51 |
| 1-[Methyl(phenyl)amino]ethyl | 0.86 | 36.8 | 44 | 0.59 |
| Morpholin-3-yl | 0.84 | 40 | 48 | 0.59 |
| 4-Methylmorpholin-3-yl | 0.77 | 46.4 | 57.9 | 0.59 |
| 1-[(*tert*-Butoxy)carbonyl]pyrrolidin-2-yl | 0.83 | 44.8 | 53.4 | 0.61 |
| 1-Phenylpyrrolidin-2-yl | 0.59 | 46.7 | 67 | 0.61 |
| 1-(Phenylamino)ethyl | 0.64 | 39.1 | 57.2 | 0.63 |
| 1-(*N*-Methylacetamido)ethyl | 0.81 | 43.8 | 53.3 | 0.67 |
| 1-Acetylpyrrolidin-2-yl | 0.8 | 45.1 | 55.2 | 0.68 |
| 1-Methylpiperidin-4-yl | 0.94 | 42.8 | 45.7 | 0.69 |
| 1-(Diphenylamino)ethyl | 0.65 | 49 | 66.6 | 0.71 |
| Piperidin-3-yl | 0.94 | 42.9 | 45.7 | 0.72 |
| 1-(*N*-Phenylacetamido)ethyl | 0.76 | 46.7 | 58.7 | 0.75 |
| Pyrrolidin-3-yl | 0.96 | 39.8 | 41.7 | 0.76 |
| 4-[(*tert*-Butoxy)carbonyl]morpholin-3-yl | 0.82 | 46.9 | 55.8 | 0.78 |
| Piperidin-4-yl | 0.9 | 43 | 48 | 0.80 |
| [(Methoxycarbonyl)amino]methyl | 0.86 | 28.6 | 35.5 | 0.81 |
| 1-Methylpiperidin-3-yl | 0.94 | 43 | 45.8 | 0.81 |
| (*N*-Methylacetamido)methyl | 0.82 | 34.8 | 43.7 | 0.83 |
| 4-Acetylmorpholin-3-yl | 0.83 | 47.2 | 55.8 | 0.86 |
| 1-[(*tert*-Butoxy)carbonyl]piperidin-4-yl | 0.93 | 43.6 | 47.1 | 0.89 |
| 1-[(*tert*-Butoxy)carbonyl]pyrrolidin-3-yl | 0.95 | 39.5 | 42.1 | 0.90 |
| (2-Oxopyrrolidin-1-yl)methyl | 0.79 | 34.1 | 44.4 | 0.90 |
| Acetamidomethyl | 0.82 | 30.8 | 39.6 | 0.93 |
| 2-Aminoethyl | 0.99 | 28.4 | 29 | 0.98 |
| 1-Trifluoromethanesulfonylpyrrolidin-2-yl | 0.83 | 50.7 | 59.2 | 1.00 |
| 3-(Dimethylamino)bicyclo[1.1.1]pentan-1-yl | 0.75 | 44.5 | 56.8 | 1.00 |
| 1-(4-Methylbenzenesulfonyl)pyrrolidin-2-yl | 0.73 | 52 | 65.4 | 1.01 |
| 3-Aminopropyl | 0.94 | 32.6 | 35.7 | 1.01 |
| 1-(4-Methylbenzenesulfonamido)pentyl | 0.7 | 51.4 | 66.5 | 1.01 |
| 1-[(*tert*-Butoxy)carbonyl]azetidin-3-yl | 0.94 | 35.7 | 38.6 | 1.02 |

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|---|---|---|---|---|
| 1-(4-Methylbenzenesulfonyl)piperidin-2-yl | 0.75 | 54.5 | 67 | 1.03 |
| (4-Methylbenzenesulfonamido)methyl | 0.78 | 33.9 | 44.9 | 1.09 |
| 1-(4-Methylbenzenesulfonamido)pentan-3-yl | 0.91 | 48 | 52.3 | 1.10 |
| 5-(4-Methylbenzenesulfonamido)pentan-2-yl | 0.85 | 47.1 | 54.5 | 1.10 |
| 1-(4-Methylbenzenesulfonamido)pentan-2-yl | 0.85 | 46.9 | 54.6 | 1.18 |
| (Trifluoromethanesulfonamido)methyl | 0.86 | 33.8 | 40.6 | 1.19 |
| (2,5-Dioxopyrrolidin-1-yl)methyl | 0.77 | 34.5 | 45.9 | 1.30 |
| (2,2,2-Trifluoroacetamido)methyl | 0.73 | 28.7 | 42.1 | 1.33 |
| (1,3-Dioxo-2,3-dihydro-1*H*-isoindol-2-yl)methyl | 0.72 | 34.3 | 48.2 | 1.38 |
| 1-Cyano-1-methylethyl | 0.56 | 41.4 | 63.6 | 1.49 |
| 1-Cyanoethyl | 0.56 | 32.2 | 54.1 | 1.68 |
| Cyanomethyl | 0.55 | 23.2 | 45.5 | 2.00 |
| Dicyano(phenyl)methyl | 0.29 | 48.3 | 83.9 | 2.92 |
| Dicyanomethyl | 0.4 | 31.2 | 61.3 | 3.00 |
| Tricyanomethyl | 0.32 | 39.2 | 73.1 | 4.08 |
| 3-Aminophenyl | 0.8 | 38.1 | 48.1 | 1.30 |
| 4-Aminophenyl | 0.8 | 37.6 | 47.6 | 1.33 |
| 3-*tert*-Butylphenyl | 0.73 | 38.7 | 52.3 | 1.34 |
| 2-*tert*-Butylphenyl | 0.73 | 50.6 | 64.1 | 1.34 |
| 2-(Acetyloxy)phenyl | 0.76 | 46.7 | 58.8 | 1.36 |
| 3-Methylphenyl | 0.76 | 38.1 | 50.3 | 1.36 |
| 4-*tert*-Butylphenyl | 0.77 | 37.6 | 49.2 | 1.38 |
| 2-Methylphenyl | 0.74 | 43.2 | 56.4 | 1.38 |
| 4-Methylphenyl | 0.78 | 37.6 | 48.6 | 1.39 |
| 3-Methoxyphenyl | 0.71 | 38.6 | 52.9 | 1.39 |
| 3-Acetamidophenyl | 0.72 | 38.5 | 52.7 | 1.39 |
| 4-Methoxyphenyl | 0.79 | 37.6 | 48.2 | 1.40 |
| Phenyl | 0.79 | 37.7 | 48 | 1.41 |
| 3-Hydroxyphenyl | 0.81 | 37.9 | 47.2 | 1.43 |
| 1,1'-Biphenyl-3-yl | 0.71 | 38.5 | 52.9 | 1.44 |
| 3-(Methylsulfanyl)phenyl | 0.73 | 38.5 | 52.2 | 1.45 |
| 4-Hydroxyphenyl | 0.79 | 37.6 | 48.1 | 1.45 |
| 4-Acetamidophenyl | 0.79 | 37.5 | 48 | 1.46 |
| 2-Aminophenyl | 0.79 | 41.8 | 52.1 | 1.47 |
| 1,1'-Biphenyl-4-yl | 0.77 | 37.6 | 49 | 1.48 |
| 1,1'-Biphenyl-2-yl | 0.65 | 46.1 | 63.6 | 1.48 |
| 3-(Acetyloxy)phenyl | 0.74 | 38.7 | 51.6 | 1.52 |
| 4-(Acetyloxy)phenyl | 0.77 | 37.6 | 48.9 | 1.52 |
| 3-Acetylphenyl | 0.76 | 38.2 | 50.4 | 1.52 |
| 4-(Methylsulfanyl)phenyl | 0.78 | 37.7 | 48.6 | 1.53 |
| 4-Sulfanylphenyl | 0.77 | 37.6 | 49.1 | 1.54 |
| 3-Sulfanylphenyl | 0.76 | 38.1 | 50.2 | 1.55 |
| 4-Fluorophenyl | 0.79 | 37.7 | 48.3 | 1.58 |
| 2-(Methylsulfanyl)phenyl | 0.76 | 38.2 | 50 | 1.59 |
| 3-Carboxyphenyl | 0.8 | 47.9 | 58.1 | 1.60 |
| 3-fFuorophenyl | 0.81 | 37.9 | 47.5 | 1.60 |
| 2-Methoxyphenyl | 0.8 | 46.3 | 56.3 | 1.61 |

| | | | | |
|---|---|---|---|---|
| 2-Sulfanylphenyl | 0.75 | 42.6 | 55.3 | 1.61 |
| 2-Carboxyphenyl | 0.77 | 44.3 | 55.6 | 1.61 |
| 4-Chlorophenyl | 0.79 | 37.7 | 48.3 | 1.62 |
| 4-Bromophenyl | 0.77 | 37.5 | 49 | 1.64 |
| 4-Acetylphenyl | 0.78 | 37.7 | 48.5 | 1.64 |
| 4-Iodophenyl | 0.77 | 37.7 | 49.2 | 1.64 |
| 2-Acetylphenyl | 0.76 | 47 | 59.2 | 1.65 |
| 4-Carboxyphenyl | 0.79 | 37.8 | 48.1 | 1.65 |
| 3-Chlorophenyl | 0.79 | 38.1 | 48.5 | 1.66 |
| 3-Bromophenyl | 0.8 | 38.1 | 48.3 | 1.71 |
| 3-(Trifluoromethyl)phenyl | 0.75 | 38.3 | 51 | 1.72 |
| 4-(Trifluoromethyl)phenyl | 0.8 | 37.7 | 47.9 | 1.73 |
| 2-Acetamidophenyl | 0.68 | 42.2 | 58.4 | 1.75 |
| 3-Iodophenyl | 0.79 | 38.1 | 48.7 | 1.76 |
| 2-Hydroxyphenyl | 0.79 | 41.4 | 52.1 | 1.78 |
| 2-(Trifluoromethyl)phenyl | 0.73 | 45.4 | 58.9 | 1.80 |
| 2-Chlorophenyl | 0.7 | 42 | 56.8 | 1.81 |
| 2-Iodophenyl | 0.74 | 43.3 | 56.2 | 1.82 |
| 2-Bromophenyl | 0.76 | 42.6 | 54.8 | 1.83 |
| 3-Cyanophenyl | 0.75 | 38.1 | 50.6 | 1.85 |
| 2-Fluorophenyl | 0.79 | 39.7 | 50.4 | 1.85 |
| 4-Cyanophenyl | 0.78 | 37.8 | 48.8 | 1.86 |
| 3-Nitrophenyl | 0.79 | 38.2 | 48.8 | 1.89 |
| 4-Nitrophenyl | 0.81 | 37.7 | 47.2 | 1.93 |
| 2-Cyanophenyl | 0.72 | 41.8 | 55.9 | 1.93 |
| 2-Nitrophenyl | 0.61 | 43.7 | 63 | 2.04 |
| Pyridin-2-yl | 0.79 | 35.6 | 46.3 | 1.17 |
| Pyrimidin-2-yl | 0.84 | 33.7 | 41.8 | 1.24 |
| 2,4,6-Trimethylphenyl | 0.75 | 55.3 | 67.7 | 1.34 |
| Pyrazin-2-yl | 0.76 | 34.7 | 46.6 | 1.38 |
| Pyrimidin-4-yl | 0.79 | 34.9 | 45.3 | 1.39 |
| 1*H*-Pyrrol-3-yl | 0.87 | 34.2 | 40.8 | 1.57 |
| Pyridin-3-yl | 0.79 | 36.9 | 47.3 | 1.59 |
| Pyridin-4-yl | 0.8 | 37.1 | 46.9 | 1.60 |
| 2,4-Dimethoxyphenyl | 0.79 | 46.3 | 56.7 | 1.60 |
| 1*H*-Pyrazol-3-yl | 0.86 | 32 | 38.8 | 1.65 |
| Thiophen-3-yl | 0.86 | 36.2 | 43.4 | 1.77 |
| 2,4,6-Trimethoxyphenyl | 0.5 | 48.5 | 73.4 | 1.78 |
| 3,5-Difluorophenyl | 0.81 | 38 | 47.6 | 1.82 |
| 1*H*-pyrrol-2-yl | 0.88 | 33.9 | 39.9 | 1.84 |
| Furan-3-yl | 0.86 | 33.9 | 41 | 1.89 |
| 1*H*-indol-2-yl | 0.72 | 34.5 | 48.6 | 1.92 |
| 5-Methyl-2-(methylsulfamoyl)phenyl | 0.73 | 48.9 | 62.3 | 1.93 |
| Furan-2-yl | 0.89 | 32.5 | 37.9 | 2.01 |
| 1-Benzofuran-3-yl | 0.84 | 37.9 | 46.1 | 2.02 |
| Thiophen-2-yl | 0.9 | 36.4 | 41.7 | 2.05 |
| 3,5-Bis(trifluoromethyl)phenyl | 0.69 | 39 | 54.7 | 2.05 |

| | | | | |
|---|---|---|---|---|
| 1-Benzofuran-2-yl | 0.84 | 33.2 | 41.1 | 2.09 |
| *1H*-Indol-3-yl | 0.78 | 38 | 48.9 | 2.22 |
| 1,3-Oxazol-2-yl | 0.86 | 30.3 | 37.3 | 2.22 |
| 1,3-Benzoxazol-2-yl | 0.81 | 31.1 | 40.7 | 2.31 |
| Pentafluorophenyl | 0.6 | 42.3 | 62.1 | 3.09 |
| 1-(Methylsulfanyl)ethyl | 0.79 | 38.4 | 48.8 | 0.75 |
| (Methylsulfanyl)methyl | 0.8 | 29.7 | 39.6 | 0.79 |
| Thian-2-yl | 0.73 | 43.2 | 56.8 | 0.80 |
| Sulfanylmethyl | 0.84 | 25 | 33.2 | 0.83 |
| 1-(Phenylsulfanyl)ethyl | 0.63 | 41.2 | 59.5 | 0.87 |
| 1,3-Dithian-2-yl | 0.59 | 43 | 63.3 | 0.95 |
| 1-(Trimethylsilyl)ethyl | 0.92 | 47.3 | 51.1 | 1.02 |
| 1-[Dimethyl(methylamino)silyl]ethyl | 0.96 | 46.7 | 48.6 | 1.07 |
| Fluoromethyl | 0.96 | 16.6 | 18.6 | 1.08 |
| 3-Fluoropropyl | 0.94 | 30 | 32.8 | 1.12 |
| 3-Sulfanylpropyl | 0.95 | 33.6 | 36.2 | 1.12 |
| Chloromethyl | 0.92 | 22.5 | 26.7 | 1.14 |
| Bromomethyl | 0.92 | 24.8 | 29 | 1.20 |
| Difluoromethyl | 0.9 | 19.3 | 24.1 | 1.20 |
| 2-Sulfanylethyl | 0.82 | 30.1 | 38.9 | 1.23 |
| Iodomethyl | 0.92 | 26.9 | 31.1 | 1.24 |
| Dichloromethyl | 0.84 | 30.2 | 38.4 | 1.26 |
| (Trimethylsilyl)methyl | 0.94 | 38.1 | 40.9 | 1.27 |
| 1-(Ethanesulfinyl)ethyl | 0.89 | 42.1 | 47.4 | 1.28 |
| 3-Chloropropyl | 0.88 | 30.2 | 36.1 | 1.29 |
| 3,3,3-Trifluoropropyl | 0.91 | 32.5 | 36.8 | 1.33 |
| [Dimethyl(phenyl)silyl]methyl | 0.91 | 40.5 | 44.9 | 1.35 |
| 1,2-Difluoroethyl | 0.91 | 29.2 | 33.7 | 1.38 |
| (Methoxydimethylsilyl)methyl | 0.97 | 39.4 | 40.8 | 1.39 |
| 1-(Benzenesulfinyl)ethyl | 0.86 | 44.4 | 51.4 | 1.45 |
| Trichloromethyl | 0.77 | 38 | 49.6 | 1.48 |
| 1-(Aminosulfinyl)ethyl | 0.92 | 41.1 | 45.4 | 1.48 |
| 2-Fluoroethyl | 0.96 | 26.7 | 28.9 | 1.51 |
| Methanesulfinylmethyl | 0.87 | 32.9 | 39.6 | 1.57 |
| 2-Chloroethyl | 0.84 | 28.9 | 36.9 | 1.58 |
| 1,2-Dichloroethyl | 0.78 | 36.3 | 47.3 | 1.63 |
| Trifluoromethyl | 0.88 | 21.9 | 28.1 | 1.67 |
| 1-(Ethanesulfonyl)ethyl | 0.85 | 44.4 | 52.1 | 1.68 |
| 1-(Methylsulfamoyl)ethyl | 0.87 | 45.9 | 52.6 | 1.71 |
| 1-(Phenylsulfamoyl)ethyl | 0.7 | 47.4 | 62.3 | 1.82 |
| 2,2,2-Trifluoroethyl | 0.86 | 38.3 | 45.4 | 1.84 |
| 1-(Benzenesulfonyl)ethyl | 0.74 | 46 | 59.1 | 1.86 |
| Nonafluorobutyl | 0.8 | 45.3 | 55.3 | 1.87 |
| 1-(Methoxysulfonyl)ethyl | 0.88 | 45.3 | 51.3 | 1.88 |
| 2,2,2-Trichloroethyl | 0.94 | 31.2 | 34 | 1.91 |
| (Benzenesulfonyl)methyl | 0.79 | 37.2 | 47.8 | 2.14 |
| Difluoro(phenyl)methyl | 0.35 | 37.8 | 70.2 | 1.20 |

| | | | | |
|---|---|---|---|---|
| (4-Chlorophenyl)methyl | 0.36 | 32.6 | 64.6 | 1.39 |
| (4-Fluorophenyl)methyl | 0.37 | 32.6 | 64.1 | 1.26 |
| (4-Cyanophenyl)methyl | 0.32 | 32.6 | 66.8 | 1.88 |
| (4-Methylphenyl)methyl | 0.36 | 32.5 | 64.3 | 1.16 |
| Cyclohexyl | 0.94 | 43.7 | 46.8 | 0.81 |
| 1,3-Oxazolidin-2-yl | 0.83 | 34.6 | 43.1 | 0.47 |
| 4-Phenylmorpholin-3-yl | 0.64 | 49 | 66.9 | 0.75 |
| 2-Ethoxy-1,1-difluoro-2-oxoethyl | 0.69 | 33.6 | 49.1 | 1.57 |
| 2-Ethoxy-1-fluoro-2-oxoethyl | 0.71 | 31.2 | 45.8 | 1.65 |
| 1,1-Dichloro-2-oxobutyl | 0.57 | 46.1 | 67.5 | 2.01 |
| 1,1,3,3,3-Pentachloro-2-oxopropyl | 0.53 | 50.9 | 74.5 | 2.58 |
| (tert-Butoxy)methyl | 0.88 | 35 | 40.8 | 0.62 |
| Trimethoxymethyl | 0.85 | 48.9 | 56.4 | 0.70 |
| 1,4-Dioxan-2-yl | 0.86 | 38.8 | 45.9 | 0.77 |
| 2-Oxopropyl | 0.66 | 30.8 | 47.8 | 1.94 |
| Cyanodifluoromethyl | 0.53 | 28.2 | 51.8 | 1.84 |
| Dichloro(cyano)methyl | 0.49 | 38.3 | 63.9 | 2.14 |
| (3-Cyanophenyl)methyl | 0.36 | 32.5 | 64.7 | 1.68 |
| (3-Nitrophenyl)methyl | 0.36 | 32.5 | 64.7 | 1.73 |
| (4-Nitrophenyl)methyl | 0.35 | 32.6 | 64.9 | 2.16 |
| 1-(Dimethylamino)-2-phenylpropan-2-yl | 0.41 | 58.8 | 88.4 | 1.15 |
| 1-(Dimethylamino)-2-(4-fluorophenyl)propan-2-yl | 0.4 | 58.9 | 89 | 1.18 |
| 1-(Dimethylamino)-2-(4-chlorophenyl)propan-2-yl | 0.39 | 58.7 | 89.4 | 1.28 |
| 2-(4-Cyanophenyl)-1-(dimethylamino)propan-2-yl | 0.34 | 58.8 | 92 | 1.69 |
| 1-(Dimethylamino)-2-(4-methylphenyl)propan-2-yl | 0.39 | 59 | 89.6 | 1.08 |
| 1-(Dimethylamino)-2-(4-methoxyphenyl)propan-2-yl | 0.4 | 58.9 | 89 | 0.99 |
| (3,4-Dichlorophenyl)methyl | 0.36 | 32.6 | 64.6 | 1.57 |
| (3,5-Dichlorophenyl)methyl | 0.36 | 32.7 | 64.5 | 1.68 |
| (3-Chlorophenyl)methyl | 0.37 | 32.6 | 64.2 | 1.46 |
| (3-Fluorophenyl)methyl | 0.38 | 32.5 | 63.7 | 1.42 |
| [3-(Trifluoromethyl)phenyl]methyl | 0.37 | 32.5 | 64 | 1.56 |
| [3,5-Bis(trifluoromethyl)phenyl]methyl | 0.36 | 32.7 | 64.6 | 1.90 |
| (3-Methoxyphenyl)methyl | 0.37 | 32.6 | 63.9 | 1.24 |
| (4-*tert*-butylphenyl)methyl | 0.36 | 32.5 | 64.7 | 1.18 |
| (3-Methylphenyl)methyl | 0.37 | 32.6 | 64.3 | 1.21 |
| 1-Ethenyl-5-oxopyrrolidin-2-yl | 0.77 | 45.1 | 56.7 | 0.90 |
| 1-Ethenyl-5-oxopyrrolidin-3-yl | 0.95 | 38.8 | 41.4 | 1.06 |
| 1-(Ethylamino)ethyl | 0.86 | 37.4 | 44.5 | 0.46 |
| (Dimethoxymethoxy)methyl | 0.9 | 29.9 | 34.7 | 0.80 |
| 2-(*tert*-Butoxy)-1-phenylethyl | 0.37 | 52.7 | 84.2 | 1.24 |
| 2-(*tert*-Butoxy)-1-(4-methylphenyl)ethyl | 0.36 | 52.6 | 84.5 | 1.18 |
| 2-(*tert*-Butoxy)-1-(4-methoxyphenyl)ethyl | 0.37 | 52.3 | 84 | 1.06 |
| 2-(*tert*-Butoxy)-1-(4-chlorophenyl)ethyl | 0.37 | 46 | 77.6 | 1.30 |
| 2-(*tert*-Butoxy)-1-[4-(methoxycarbonyl)phenyl]ethyl | 0.35 | 53.1 | 85.4 | 1.64 |
| 2-(*tert*-Butoxy)-1-(4-nitrophenyl)ethyl | 0.35 | 52.4 | 84.8 | 2.09 |
| 1-[1,1'-Biphenyl]-4-yl-2-(tert-butoxy)ethyl | 0.32 | 52.8 | 86.8 | 1.40 |
| 2-(*tert*-Butoxy)-1-(4-fluorophenyl)ethyl | 0.37 | 46.1 | 77.4 | 1.18 |

| | | | | |
|---|---|---|---|---|
| 1-Hydroxypentyl | 0.84 | 34.9 | 43.1 | 0.61 |
| Hexan-2-yl | 0.96 | 39.3 | 41.5 | 0.74 |
| 1-(Acetoxy)pentyl | 0.93 | 41.9 | 45.2 | 0.88 |
| Pentyl | 0.96 | 30.2 | 32.2 | 0.91 |
| Nonyl | 0.96 | 30.2 | 32.1 | 0.91 |
| Undecyl | 0.96 | 30.3 | 32.5 | 0.92 |
| [(2,2-Dimethylpropanoyl)oxy]methyl | 0.91 | 29.7 | 34.2 | 1.04 |
| 1-(Acetyloxy)pentyl | 0.93 | 45.4 | 48.7 | 1.05 |
| (5*R*)-3,4,5-Tris(acetyloxy)-6-[(acetyloxy)methyl]oxan-2-yl | 0.62 | 48.5 | 67.4 | 1.07 |
| 1-(Acetyloxy)-2-methylpropyl | 0.88 | 50.5 | 56.7 | 1.10 |
| 1-(Acetyloxy)-2-(4-methoxyphenyl)ethyl | 0.74 | 47 | 60.1 | 1.12 |
| 1-(Acetyloxy)-2-phenylethyl | 0.9 | 48 | 53 | 1.12 |
| 1-(Acetyloxy)-2-(4-fluorophenyl)ethyl | 0.81 | 47.8 | 57.6 | 1.18 |
| 2-(Trimethoxysilyl)phenyl | 0.74 | 51.2 | 64.2 | 1.39 |
| 2-(Dimethylcarbamoyl)phenyl | 0.77 | 49.6 | 61.2 | 1.54 |
| 4-(Ethoxycarbonyl)phenyl | 0.79 | 37.7 | 48.2 | 1.58 |
| [4-(Methoxycarbonyl)phenyl]methyl | 0.35 | 32.5 | 65.1 | 1.67 |
| Octadecafluorooctyl | 0.78 | 46.9 | 57.9 | 1.89 |
| 4-Chloropentan-2-yl | 0.95 | 42 | 44.4 | 0.85 |
| 4-Chlorobutan-2-yl | 0.97 | 41.4 | 42.9 | 0.87 |
| 3-Chloropropan-1-yl | 0.97 | 32.4 | 34 | 1.06 |
| 2,6-Dichloroheptan-4-yl | 0.86 | 50.5 | 57.7 | 0.99 |
| 2-Methoxy-2-oxoethyl | 0.75 | 28.6 | 41 | 1.87 |
| 1,1-Difluoropropan-1-yl | 0.83 | 35 | 43.6 | 1.05 |
| 2,2-Difluoropropan-1-yl | 0.92 | 34.5 | 38.4 | 1.48 |
| 1,1,2,2-Tetrafluoropropan-1-yl | 0.85 | 39.6 | 47.1 | 1.50 |
| 2,2-Dichloropropan-1-yl | 0.86 | 39.4 | 46.4 | 1.65 |
| 2-Chloro-2-methylpropan-1-yl | 0.84 | 40.6 | 48.8 | 1.47 |
| **Int1 ($BF_4^-$)** | 0.64 | 41 | 58.9 | 2.31 |
| **Int1E ($BF_4^-$)** | 0.73 | 40.6 | 54.2 | 2.67 |

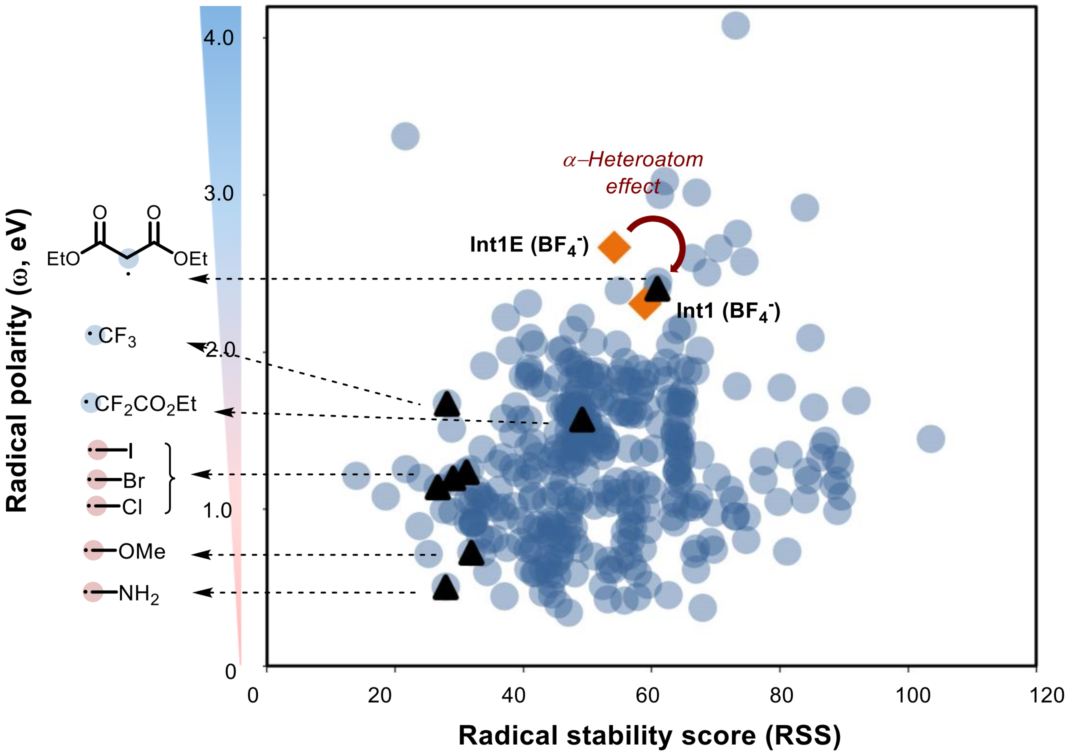

**Fig. S29.** Radical polarity and radical stability score plots

## H. Cartesian Coordinates, Structures and Computed Gibbs Free Energies for the Optimized Structures and Transition States

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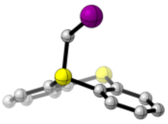
### 1a



Charge 1, multiplicity 1

| | | | |
|---|---|---|---|
| C | -2.344815000000 | -1.598209000000 | 0.296206000000 |
| C | -1.178654000000 | -1.367430000000 | -0.428033000000 |
| C | -0.598245000000 | -0.095337000000 | -0.444394000000 |
| C | -1.227853000000 | 0.924875000000 | 0.284167000000 |
| C | -2.381244000000 | 0.692345000000 | 1.038809000000 |
| C | -2.942943000000 | -0.578398000000 | 1.037739000000 |
| C | 1.166393000000 | 2.385091000000 | 0.256329000000 |
| C | 1.773596000000 | 1.357026000000 | -0.477771000000 |
| C | 3.169911000000 | 1.295964000000 | -0.491860000000 |
| H | 3.665873000000 | 0.502750000000 | -1.038577000000 |
| C | 3.920126000000 | 2.234563000000 | 0.211308000000 |
| C | 3.298806000000 | 3.232846000000 | 0.961813000000 |
| C | 1.911827000000 | 3.309365000000 | 0.991888000000 |
| H | -2.777740000000 | -2.591311000000 | 0.297510000000 |
| H | -0.705030000000 | -2.178585000000 | -0.968251000000 |
| H | -2.832367000000 | 1.494416000000 | 1.611478000000 |
| H | -3.839221000000 | -0.771478000000 | 1.613395000000 |
| H | 5.001351000000 | 2.170406000000 | 0.188369000000 |
| H | 3.889440000000 | 3.948488000000 | 1.519349000000 |
| H | 1.413703000000 | 4.083826000000 | 1.562496000000 |
| S | 0.877237000000 | 0.135594000000 | -1.415284000000 |
| S | -0.602756000000 | 2.597021000000 | 0.259595000000 |
| C | -0.994927000000 | 3.125689000000 | -1.473218000000 |
| H | -0.647195000000 | 2.364539000000 | -2.165504000000 |
| H | -2.077145000000 | 3.233066000000 | -1.498441000000 |
| I | -0.081692000000 | 5.012177000000 | -1.961309000000 |

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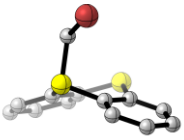
### 1b



Charge 1, multiplicity 1

| | | | |
|---|---|---|---|
| C | -2.349328000000 | -1.589154000000 | 0.288099000000 |
| C | -1.180849000000 | -1.360595000000 | -0.433095000000 |
| C | -0.597322000000 | -0.089844000000 | -0.447174000000 |
| C | -1.226833000000 | 0.931261000000 | 0.280399000000 |
| C | -2.381458000000 | 0.700288000000 | 1.034107000000 |
| C | -2.946706000000 | -0.568850000000 | 1.029566000000 |
| C | 1.172570000000 | 2.392112000000 | 0.252419000000 |
| C | 1.778374000000 | 1.358156000000 | -0.474940000000 |
| C | 3.174441000000 | 1.293297000000 | -0.485894000000 |
| H | 3.669415000000 | 0.495378000000 | -1.026618000000 |
| C | 3.925741000000 | 2.235655000000 | 0.211288000000 |
| C | 3.305836000000 | 3.241670000000 | 0.952553000000 |
| C | 1.918938000000 | 3.321049000000 | 0.981256000000 |
| H | -2.784643000000 | -2.581224000000 | 0.287327000000 |
| H | -0.707886000000 | -2.172456000000 | -0.972812000000 |
| H | -2.831286000000 | 1.502380000000 | 1.607790000000 |
| H | -3.844531000000 | -0.760503000000 | 1.603272000000 |
| H | 5.006846000000 | 2.168731000000 | 0.190514000000 |
| H | 3.897400000000 | 3.960864000000 | 1.504522000000 |
| H | 1.421840000000 | 4.100115000000 | 1.546545000000 |
| S | 0.881225000000 | 0.138148000000 | -1.413989000000 |
| S | -0.596492000000 | 2.600610000000 | 0.263392000000 |
| C | -0.989124000000 | 3.137881000000 | -1.478201000000 |
| H | -0.621982000000 | 2.386306000000 | -2.171532000000 |
| H | -2.072740000000 | 3.232569000000 | -1.509151000000 |
| Br | -0.165010000000 | 4.845453000000 | -1.851836000000 |

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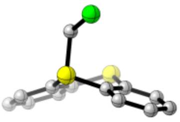
### 1c



Charge 1, multiplicity 1

| | | | |
|---|---|---|---|
| C | -2.352753000000 | -1.582639000000 | 0.279712000000 |
| C | -1.181837000000 | -1.354298000000 | -0.437457000000 |
| C | -0.596381000000 | -0.084326000000 | -0.447648000000 |
| C | -1.226691000000 | 0.936185000000 | 0.280385000000 |
| C | -2.383811000000 | 0.705169000000 | 1.030479000000 |
| C | -2.951065000000 | -0.56297300000 | 1.021289000000 |
| C | 1.176736000000 | 2.396272000000 | 0.255271000000 |
| C | 1.781788000000 | 1.362012000000 | -0.472687000000 |
| C | 3.177793000000 | 1.297802000000 | -0.485708000000 |
| H | 3.672310000000 | 0.499695000000 | -1.026537000000 |
| C | 3.929897000000 | 2.241631000000 | 0.208722000000 |
| C | 3.310945000000 | 3.248839000000 | 0.949114000000 |
| C | 1.924048000000 | 3.327219000000 | 0.980838000000 |
| H | -2.789273000000 | -2.574151000000 | 0.275799000000 |
| H | -0.708393000000 | -2.165782000000 | -0.977280000000 |
| H | -2.833624000000 | 1.506448000000 | 1.605273000000 |
| H | -3.850922000000 | -0.754436000000 | 1.591813000000 |
| H | 5.010971000000 | 2.175283000000 | 0.185925000000 |
| H | 3.903146000000 | 3.969637000000 | 1.498247000000 |
| H | 1.427699000000 | 4.106472000000 | 1.546629000000 |
| S | 0.884080000000 | 0.142531000000 | -1.411604000000 |
| S | -0.591707000000 | 2.602497000000 | 0.272741000000 |
| C | -0.982587000000 | 3.148291000000 | -1.478303000000 |
| H | -0.628970000000 | 2.383191000000 | -2.164510000000 |
| H | -2.066017000000 | 3.252512000000 | -1.501889000000 |
| Cl | -0.198945000000 | 4.696220000000 | -1.810806000000 |

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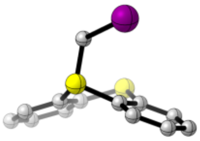
### [1a$^{\bullet-}$]



Charge 0, multiplicity 2

| | | | |
|---|---|---|---|
| C | -2.311770000000 | -1.715914000000 | 0.392763000000 |
| C | -1.164623000000 | -1.483195000000 | -0.360173000000 |
| C | -0.608425000000 | -0.201172000000 | -0.416827000000 |
| C | -1.225694000000 | 0.836831000000 | 0.290586000000 |
| C | -2.360690000000 | 0.596769000000 | 1.066840000000 |
| C | -2.905521000000 | -0.681797000000 | 1.118020000000 |
| C | 1.080732000000 | 2.350624000000 | 0.187149000000 |
| C | 1.718867000000 | 1.303536000000 | -0.486486000000 |
| C | 3.116197000000 | 1.247701000000 | -0.471036000000 |
| H | 3.624078000000 | 0.435261000000 | -0.977265000000 |
| C | 3.847584000000 | 2.220399000000 | 0.203046000000 |
| C | 3.200159000000 | 3.247682000000 | 0.886524000000 |
| C | 1.811627000000 | 3.313459000000 | 0.880417000000 |
| H | -2.732080000000 | -2.714145000000 | 0.427261000000 |
| H | -0.686228000000 | -2.298159000000 | -0.891300000000 |
| H | -2.819816000000 | 1.413068000000 | 1.613684000000 |
| H | -3.787793000000 | -0.869849000000 | 1.717844000000 |
| H | 4.929978000000 | 2.167041000000 | 0.201282000000 |
| H | 3.771087000000 | 4.007523000000 | 1.405190000000 |
| H | 1.296788000000 | 4.129854000000 | 1.369937000000 |
| S | 0.850615000000 | 0.045843000000 | -1.407300000000 |
| S | -0.702814000000 | 2.574423000000 | 0.110929000000 |
| C | -0.981457000000 | 3.183538000000 | -1.482251000000 |
| H | -0.597199000000 | 2.592364000000 | -2.302882000000 |
| H | -1.970838000000 | 3.613113000000 | -1.567960000000 |
| I | 0.463673000000 | 5.604502000000 | -1.740184000000 |

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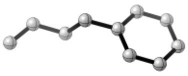
## 2



Charge 0, multiplicity 1

| | | | |
|---|---|---|---|
| C | -0.941771000000 | 1.077651000000 | -0.114772000000 |
| H | -0.490226000000 | 0.166334000000 | -0.496501000000 |
| H | -2.018547000000 | 1.073354000000 | 0.013309000000 |
| C | -0.205879000000 | 2.148368000000 | 0.175751000000 |
| H | -0.699933000000 | 3.040758000000 | 0.559295000000 |
| C | 1.286610000000 | 2.236978000000 | 0.039810000000 |
| H | 1.682755000000 | 1.317348000000 | -0.402695000000 |
| H | 1.547230000000 | 3.053845000000 | -0.644768000000 |
| C | 1.988318000000 | 2.497628000000 | 1.394310000000 |
| H | 1.578420000000 | 3.410810000000 | 1.839318000000 |
| H | 1.747746000000 | 1.678706000000 | 2.079052000000 |
| C | 3.485921000000 | 2.627231000000 | 1.245927000000 |
| C | 4.071850000000 | 3.861651000000 | 0.944235000000 |
| C | 4.316746000000 | 1.507171000000 | 1.357092000000 |
| C | 5.448366000000 | 3.975635000000 | 0.758655000000 |
| H | 3.443050000000 | 4.742734000000 | 0.858489000000 |
| C | 5.694212000000 | 1.615230000000 | 1.172485000000 |
| H | 3.879876000000 | 0.542058000000 | 1.594714000000 |
| C | 6.264996000000 | 2.851035000000 | 0.871569000000 |
| H | 5.883719000000 | 4.942279000000 | 0.530035000000 |
| H | 6.321655000000 | 0.735716000000 | 1.267158000000 |
| H | 7.336407000000 | 2.937909000000 | 0.730470000000 |

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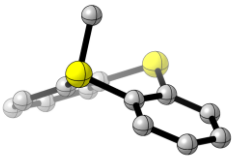
## Int1



Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -2.089048000000 | -2.035744000000 | -0.131543000000 |
| C | -1.212377000000 | -1.457347000000 | -1.047685000000 |
| C | -0.631612000000 | -0.216973000000 | -0.773764000000 |
| C | -0.962805000000 | 0.409835000000 | 0.435569000000 |
| C | -1.808104000000 | -0.175806000000 | 1.376607000000 |
| C | -2.380634000000 | -1.408844000000 | 1.079831000000 |
| C | 1.428878000000 | 1.872880000000 | 0.281784000000 |
| C | 1.723100000000 | 1.223320000000 | -0.925141000000 |
| C | 3.060484000000 | 1.156222000000 | -1.322328000000 |
| H | 3.322333000000 | 0.646366000000 | -2.241595000000 |
| C | 4.054729000000 | 1.722308000000 | -0.526448000000 |
| C | 3.742767000000 | 2.336902000000 | 0.686159000000 |
| C | 2.417749000000 | 2.409292000000 | 1.104869000000 |
| H | -2.531218000000 | -2.998044000000 | -0.359812000000 |
| H | -0.963697000000 | -1.975214000000 | -1.966130000000 |
| H | -2.025324000000 | 0.325332000000 | 2.312486000000 |
| H | -3.049891000000 | -1.875491000000 | 1.791399000000 |
| H | 5.087041000000 | 1.661869000000 | -0.849437000000 |
| H | 4.525205000000 | 2.758321000000 | 1.304375000000 |
| H | 2.158209000000 | 2.884668000000 | 2.043405000000 |
| S | 0.468954000000 | 0.510348000000 | -1.975535000000 |
| S | -0.282768000000 | 2.030237000000 | 0.792719000000 |
| C | -0.977440000000 | 3.032980000000 | -0.472985000000 |
| H | -0.401353000000 | 3.890976000000 | -0.791227000000 |
| H | -2.029316000000 | 2.897919000000 | -0.684282000000 |

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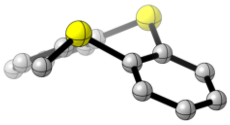
## Int1E



Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -3.076361000000 | 0.729198000000 | 2.009602000000 |
| C | -2.996242000000 | -0.656967000000 | 1.884116000000 |
| C | -1.795742000000 | -1.257946000000 | 1.512370000000 |
| C | -0.695339000000 | -0.440174000000 | 1.279008000000 |
| C | -0.752356000000 | 0.951282000000 | 1.387557000000 |
| C | -1.968108000000 | 1.533273000000 | 1.753734000000 |
| S | 0.949730000000 | -1.126670000000 | 0.902644000000 |
| C | 1.407906000000 | -0.138973000000 | -0.558144000000 |
| C | 1.297813000000 | 1.244877000000 | -0.403066000000 |
| S | 0.689062000000 | 1.975266000000 | 1.112791000000 |
| C | 1.901386000000 | -0.728501000000 | -1.717035000000 |
| C | 2.314922000000 | 0.103602000000 | -2.754905000000 |
| C | 2.225144000000 | 1.488360000000 | -2.620736000000 |
| C | 1.710800000000 | 2.060084000000 | -1.459348000000 |
| C | 0.588036000000 | -2.710022000000 | 0.229121000000 |
| H | -4.012418000000 | 1.191476000000 | 2.298257000000 |
| H | -3.863123000000 | -1.275579000000 | 2.079650000000 |
| H | -1.726408000000 | -2.335790000000 | 1.431462000000 |
| H | -2.041887000000 | 2.611294000000 | 1.829260000000 |
| H | 1.986645000000 | -1.804048000000 | -1.812064000000 |
| H | 2.711009000000 | -0.334142000000 | -3.662591000000 |
| H | 2.547424000000 | 2.130828000000 | -3.431043000000 |
| H | 1.620740000000 | 3.135763000000 | -1.369475000000 |
| H | 1.093799000000 | -3.558576000000 | 0.667797000000 |
| H | -0.116431000000 | -2.787917000000 | -0.588966000000 |

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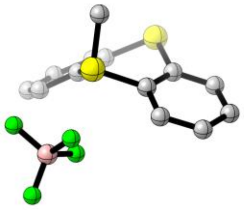
## Int1 (BF$_4^-$)



Charge 0, multiplicity 2

| | | | |
|---|---|---|---|
| C | -2.072509000000 | -2.026694000000 | -0.135983000000 |
| C | -1.211355000000 | -1.445880000000 | -1.065355000000 |
| C | -0.647866000000 | -0.195347000000 | -0.803852000000 |
| C | -0.976402000000 | 0.438851000000 | 0.400620000000 |
| C | -1.791597000000 | -0.152016000000 | 1.361313000000 |
| C | -2.353039000000 | -1.393613000000 | 1.073917000000 |
| C | 1.406367000000 | 1.895970000000 | 0.247528000000 |
| C | 1.708774000000 | 1.245817000000 | -0.955295000000 |
| C | 3.048562000000 | 1.159317000000 | -1.338983000000 |
| H | 3.313245000000 | 0.642938000000 | -2.253839000000 |
| C | 4.039192000000 | 1.711089000000 | -0.528493000000 |
| C | 3.716608000000 | 2.318504000000 | 0.684073000000 |
| C | 2.388090000000 | 2.404216000000 | 1.092786000000 |
| H | -2.503137000000 | -2.997832000000 | -0.350729000000 |
| H | -0.957651000000 | -1.968998000000 | -1.979494000000 |
| H | -1.961042000000 | 0.351722000000 | 2.305836000000 |
| H | -2.997906000000 | -1.867536000000 | 1.803397000000 |
| H | 5.075416000000 | 1.637076000000 | -0.837407000000 |
| H | 4.496148000000 | 2.715821000000 | 1.322083000000 |
| H | 2.105241000000 | 2.838762000000 | 2.044484000000 |
| S | 0.456130000000 | 0.528160000000 | -2.008293000000 |
| S | -0.310791000000 | 2.071856000000 | 0.749657000000 |
| C | -0.96661600000E0 | 3.003961000000 | -0.585021000000 |
| H | -0.400620000000 | 3.868150000000 | -0.903044000000 |
| H | -2.018483000000 | 2.878067000000 | -0.799589000000 |
| F | 0.328380000000 | 1.500377000000 | 5.225412000000 |
| F | 0.602625000000 | 3.094901000000 | 3.564412000000 |
| F | -1.366797000000 | 1.891458000000 | 3.692464000000 |
| F | 0.574055000000 | 0.862483000000 | 3.008750000000 |

| | | | |
|---|---|---|---|
| B | 0.034971000000 | 1.841930000000 | 3.923521000000 |

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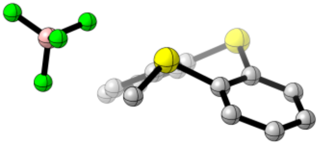
## Int1E (BF$_4^-$)



Charge 0, multiplicity 2

| | | | |
|---|---|---|---|
| C | -3.295618000000 | 1.326666000000 | 1.563148000000 |
| C | -2.573543000000 | 0.431411000000 | 2.349183000000 |
| C | -1.190165000000 | 0.328803000000 | 2.216808000000 |
| C | -0.560350000000 | 1.141756000000 | 1.282688000000 |
| C | -1.261607000000 | 2.046340000000 | 0.482318000000 |
| C | -2.647977000000 | 2.128022000000 | 0.626117000000 |
| S | 1.256032000000 | 1.142740000000 | 1.116064000000 |
| C | 1.389558000000 | 1.024978000000 | -0.699326000000 |
| C | 0.666677000000 | 1.953381000000 | -1.453959000000 |
| S | -0.432412000000 | 3.127993000000 | -0.677668000000 |
| C | 2.259479000000 | 0.119770000000 | -1.301327000000 |
| C | 2.421198000000 | 0.152259000000 | -2.684145000000 |
| C | 1.713698000000 | 1.078320000000 | -3.448590000000 |
| C | 0.831481000000 | 1.967414000000 | -2.841342000000 |
| C | 1.756356000000 | -0.464698000000 | 1.611665000000 |
| H | -4.370720000000 | 1.403068000000 | 1.675132000000 |
| H | -3.076634000000 | -0.181170000000 | 3.087058000000 |
| H | -0.618916000000 | -0.321153000000 | 2.868069000000 |
| H | -3.209662000000 | 2.812826000000 | 0.002482000000 |
| H | 2.819110000000 | -0.588126000000 | -0.702294000000 |
| H | 3.102439000000 | -0.543537000000 | -3.158238000000 |
| H | 1.838290000000 | 1.101690000000 | -4.524619000000 |
| H | 0.260847000000 | 2.669083000000 | -3.437698000000 |
| H | 2.478898000000 | -0.512051000000 | 2.416515000000 |
| H | 1.208192000000 | -1.310804000000 | 1.220813000000 |
| B | 1.535439000000 | 0.192230000000 | 4.661992000000 |
| F | 2.892240000000 | -0.079652000000 | 4.368618000000 |
| F | 1.331844000000 | 0.518511000000 | 5.980948000000 |
| F | 0.761637000000 | -0.946565000000 | 4.274318000000 |
| F | 1.119950000000 | 1.275340000000 | 3.798689000000 |

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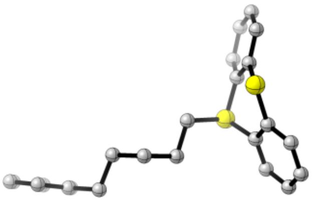
## Int2



Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -4.185956000000 | 3.704993000000 | -0.245219000000 |
| C | -4.239068000000 | 2.519863000000 | -0.973305000000 |
| C | -3.450141000000 | 1.426936000000 | -0.601059000000 |
| C | -2.616900000000 | 1.563269000000 | 0.518146000000 |
| C | -2.587734000000 | 2.737291000000 | 1.274787000000 |
| C | -3.371757000000 | 3.815806000000 | 0.882106000000 |
| C | -2.484685000000 | -1.230011000000 | 0.726344000000 |
| C | -3.315433000000 | -1.343192000000 | -0.396606000000 |
| C | -3.991860000000 | -2.550571000000 | -0.598658000000 |
| H | -4.654085000000 | -2.656589000000 | -1.449750000000 |
| C | -3.833652000000 | -3.602833000000 | 0.298492000000 |
| C | -3.025859000000 | -3.464611000000 | 1.427503000000 |
| C | -2.352305000000 | -2.269287000000 | 1.650226000000 |
| H | -4.803665000000 | 4.541118000000 | -0.550021000000 |
| H | -4.904839000000 | 2.433796000000 | -1.823849000000 |
| H | -1.954847000000 | 2.806892000000 | 2.151836000000 |
| H | -3.350215000000 | 4.733859000000 | 1.455484000000 |
| H | -4.365339000000 | -4.530595000000 | 0.124675000000 |
| H | -2.923394000000 | -4.279933000000 | 2.132342000000 |
| H | -1.722854000000 | -2.146186000000 | 2.523720000000 |
| S | -3.545609000000 | -0.047458000000 | -1.598117000000 |
| S | -1.521537000000 | 0.245142000000 | 1.020132000000 |
| C | -0.228352000000 | 0.208003000000 | -0.344630000000 |
| H | -0.764776000000 | 0.236744000000 | -1.291287000000 |
| H | 0.311542000000 | 1.144082000000 | -0.191875000000 |
| C | 0.681745000000 | -1.022698000000 | -0.214061000000 |
| H | 0.083888000000 | -1.929924000000 | -0.337431000000 |
| H | 1.127223000000 | -1.044802000000 | 0.788452000000 |
| C | 1.747081000000 | -0.925256000000 | -1.258408000000 |
| H | 1.588758000000 | -1.428080000000 | -2.206039000000 |
| C | 3.033055000000 | -0.228401000000 | -0.989835000000 |
| H | 3.419702000000 | 0.236818000000 | -1.901605000000 |
| H | 2.894117000000 | 0.575938000000 | -0.256456000000 |
| C | 4.133000000000 | -1.190442000000 | -0.434827000000 |
| H | 4.314104000000 | -1.977166000000 | -1.172492000000 |
| H | 3.754993000000 | -1.680600000000 | 0.467901000000 |
| C | 5.412925000000 | -0.451041000000 | -0.127044000000 |
| C | 5.645731000000 | 0.074342000000 | 1.148007000000 |
| C | 6.368209000000 | -0.234818000000 | -1.125776000000 |
| C | 6.805501000000 | 0.797599000000 | 1.421337000000 |
| H | 4.919929000000 | -0.094561000000 | 1.938253000000 |
| C | 7.528761000000 | 0.488057000000 | -0.857140000000 |
| H | 6.207582000000 | -0.643502000000 | -2.118774000000 |
| C | 7.749788000000 | 1.007778000000 | 0.417706000000 |
| H | 6.975639000000 | 1.189696000000 | 2.417698000000 |
| H | 8.263005000000 | 0.639791000000 | -1.640098000000 |
| H | 8.654542000000 | 1.565685000000 | 0.629091000000 |

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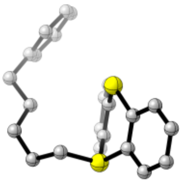
## Int2-2



Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -1.573307000000 | -0.400076000000 | 2.393232000000 |
| C | -0.954769000000 | -1.104397000000 | 1.365299000000 |
| C | 0.220612000000 | -0.617165000000 | 0.788062000000 |
| C | 0.743128000000 | 0.593242000000 | 1.263847000000 |
| C | 0.150931000000 | 1.279833000000 | 2.327190000000 |
| C | -1.017363000000 | 0.779211000000 | 2.889397000000 |
| C | 3.208414000000 | -0.017543000000 | 0.074295000000 |
| C | 2.668160000000 | -1.225364000000 | -0.389365000000 |
| C | 3.553297000000 | -2.243910000000 | -0.757478000000 |
| H | 3.161424000000 | -3.193400000000 | -1.102511000000 |
| C | 4.928123000000 | -2.050015000000 | -0.661302000000 |
| C | 5.448942000000 | -0.852800000000 | -0.169833000000 |
| C | 4.586286000000 | 0.168804000000 | 0.209689000000 |
| H | -2.493486000000 | -0.787269000000 | 2.811420000000 |
| H | -1.395548000000 | -2.023876000000 | 1.000958000000 |
| H | 0.591386000000 | 2.198165000000 | 2.697272000000 |
| H | -1.492211000000 | 1.310131000000 | 3.704710000000 |
| H | 5.596868000000 | -2.851212000000 | -0.951942000000 |
| H | 6.518931000000 | -0.716128000000 | -0.077931000000 |
| H | 4.975951000000 | 1.102493000000 | 0.598397000000 |
| S | 0.922847000000 | -1.539453000000 | -0.563554000000 |
| S | 2.158080000000 | 1.363948000000 | 0.498292000000 |
| C | 1.540864000000 | 1.955129000000 | -1.163576000000 |
| H | 2.459866000000 | 2.294016000000 | -1.644557000000 |
| H | 1.168916000000 | 1.076698000000 | -1.686943000000 |
| C | 0.481206000000 | 3.086383000000 | -1.024085000000 |
| H | 0.879160000000 | 3.982164000000 | -1.503226000000 |
| H | 0.360793000000 | 3.344093000000 | 0.040205000000 |
| C | -0.847525000000 | 2.715829000000 | -1.602156000000 |
| H | -1.231882000000 | 3.269902000000 | -2.449881000000 |
| C | -1.602557000000 | 1.573334000000 | -1.024284000000 |
| H | -1.023883000000 | 0.647447000000 | -1.156291000000 |
| H | -1.674067000000 | 1.691930000000 | 0.067480000000 |
| C | -3.009804000000 | 1.314181000000 | -1.588101000000 |
| H | -2.951209000000 | 1.190602000000 | -2.673993000000 |
| H | -3.651978000000 | 2.178227000000 | -1.396585000000 |
| C | -3.586178000000 | 0.070531000000 | -0.948798000000 |
| C | -4.387299000000 | 0.152982000000 | 0.193634000000 |
| C | -3.243564000000 | -1.197076000000 | -1.433873000000 |
| C | -4.831241000000 | -1.000312000000 | 0.840664000000 |
| H | -4.671925000000 | 1.127624000000 | 0.577539000000 |
| C | -3.683284000000 | -2.353008000000 | -0.790853000000 |

| | | | |
|---|---|---|---|
| H | -2.634790000000 | -1.279516000000 | -2.329469000000 |
| C | -4.475398000000 | -2.257732000000 | 0.354106000000 |
| H | -5.465602000000 | -0.917078000000 | 1.716288000000 |
| H | -3.421676000000 | -3.326641000000 | -1.190377000000 |
| H | -4.829383000000 | -3.154842000000 | 0.848826000000 |

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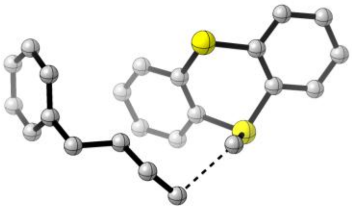
**TS1**



(*i* = –157.5655)

Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -1.469444000000 | -0.715541000000 | 1.873023000000 |
| C | -0.713822000000 | -1.319237000000 | 0.873211000000 |
| C | 0.469476000000 | -0.723907000000 | 0.427079000000 |
| C | 0.861196000000 | 0.490581000000 | 1.004338000000 |
| C | 0.136626000000 | 1.073862000000 | 2.045563000000 |
| C | -1.038497000000 | 0.466620000000 | 2.475336000000 |
| C | 3.476334000000 | 0.028777000000 | 0.161838000000 |
| C | 3.066708000000 | -1.175813000000 | -0.425920000000 |
| C | 4.037018000000 | -2.148495000000 | -0.682782000000 |
| H | 3.743070000000 | -3.096050000000 | -1.118514000000 |
| C | 5.370424000000 | -1.911390000000 | -0.358967000000 |
| C | 5.757426000000 | -0.717346000000 | 0.249909000000 |
| C | 4.806331000000 | 0.261157000000 | 0.516599000000 |
| H | -2.398501000000 | -1.177846000000 | 2.181320000000 |
| H | -1.045282000000 | -2.253157000000 | 0.436679000000 |
| H | 0.477991000000 | 1.997165000000 | 2.499032000000 |
| H | -1.618831000000 | 0.919571000000 | 3.269178000000 |
| H | 6.109022000000 | -2.676482000000 | -0.565623000000 |
| H | 6.793036000000 | -0.548268000000 | 0.516629000000 |
| H | 5.092542000000 | 1.195402000000 | 0.985524000000 |
| S | 1.377561000000 | -1.531058000000 | -0.876341000000 |
| S | 2.307358000000 | 1.372539000000 | 0.420789000000 |
| C | 1.888327000000 | 1.943633000000 | -1.199243000000 |
| H | 2.539956000000 | 2.745727000000 | -1.521854000000 |
| H | 1.584400000000 | 1.187062000000 | -1.908569000000 |
| C | -0.141126000000 | 3.331026000000 | -1.147902000000 |
| H | 0.353011000000 | 4.162581000000 | -1.635315000000 |
| H | -0.120601000000 | 3.320092000000 | -0.063398000000 |
| C | -0.978708000000 | 2.510569000000 | -1.827653000000 |
| H | -1.073412000000 | 2.629862000000 | -2.905393000000 |
| C | -1.720170000000 | 1.380665000000 | -1.199604000000 |
| H | -1.274960000000 | 0.440007000000 | -1.551028000000 |
| H | -1.584140000000 | 1.403636000000 | -0.117155000000 |
| C | -3.233201000000 | 1.327185000000 | -1.515047000000 |
| H | -3.381298000000 | 1.205482000000 | -2.592696000000 |
| H | -3.698848000000 | 2.274691000000 | -1.231785000000 |
| C | -3.870715000000 | 0.184359000000 | -0.756919000000 |
| C | -4.557117000000 | 0.411803000000 | 0.439190000000 |
| C | -3.713039000000 | -1.134787000000 | -1.197089000000 |
| C | -5.072466000000 | -0.651309000000 | 1.181264000000 |
| H | -4.698000000000 | 1.429231000000 | 0.790059000000 |
| C | -4.220825000000 | -2.200779000000 | -0.457287000000 |
| H | -3.197061000000 | -1.328807000000 | -2.132864000000 |
| C | -4.900022000000 | -1.961914000000 | 0.738547000000 |
| H | -5.616019000000 | -0.455137000000 | 2.098731000000 |
| H | -4.102523000000 | -3.215691000000 | -0.820348000000 |
| H | -5.307530000000 | -2.788822000000 | 1.308562000000 |

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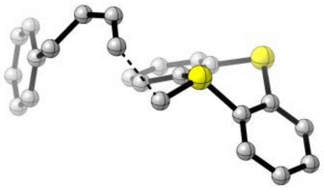
**TS1-2**



(*i* = –250.7857)

Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -0.728891000000 | -2.827171000000 | -0.319441000000 |
| C | -1.309677000000 | -1.690847000000 | 0.240589000000 |
| C | -0.609356000000 | -0.486102000000 | 0.258930000000 |
| C | 0.658753000000 | -0.441854000000 | -0.307837000000 |
| C | 1.272445000000 | -1.581763000000 | -0.841663000000 |
| C | 0.562153000000 | -2.783141000000 | -0.841698000000 |
| S | 1.646532000000 | 1.064871000000 | -0.454523000000 |
| C | 3.166018000000 | 0.514126000000 | 0.384411000000 |
| C | 3.742985000000 | -0.634618000000 | -0.163202000000 |
| S | 2.937610000000 | -1.514381000000 | -1.501377000000 |
| C | 3.741497000000 | 1.205915000000 | 1.442452000000 |
| C | 4.959635000000 | 0.750937000000 | 1.944052000000 |
| C | 5.566742000000 | -0.378235000000 | 1.395417000000 |
| C | 4.958634000000 | -1.081456000000 | 0.357544000000 |
| H | -1.276217000000 | -3.761915000000 | -0.331512000000 |
| H | -2.307791000000 | -1.726644000000 | 0.658446000000 |
| H | -1.069609000000 | 0.392867000000 | 0.684385000000 |
| H | 1.027160000000 | -3.678044000000 | -1.236875000000 |
| H | 3.265141000000 | 2.081377000000 | 1.865267000000 |
| H | 5.430727000000 | 1.280383000000 | 2.762857000000 |
| H | 6.512914000000 | -0.727474000000 | 1.790577000000 |
| H | 5.415434000000 | -1.979055000000 | -0.041225000000 |
| C | 0.858455000000 | 2.276463000000 | 0.542317000000 |
| H | 0.351038000000 | 1.925307000000 | 1.432450000000 |
| H | 1.462469000000 | 3.170895000000 | 0.624252000000 |
| C | -0.679962000000 | 3.402164000000 | -0.822962000000 |
| H | -1.193074000000 | 3.716828000000 | 0.077203000000 |
| H | 0.118189000000 | 4.048340000000 | -1.166873000000 |
| C | -1.260468000000 | 2.538660000000 | -1.708547000000 |
| H | -0.769836000000 | 2.398389000000 | -2.669761000000 |
| C | -2.477849000000 | 1.700175000000 | -1.494730000000 |
| H | -2.173726000000 | 0.650860000000 | -1.610927000000 |
| H | -3.152707000000 | 1.872230000000 | -2.342721000000 |
| C | -3.230263000000 | 1.883502000000 | -0.163884000000 |
| H | -3.921613000000 | 2.728559000000 | -0.252394000000 |
| H | -2.531554000000 | 2.161946000000 | 0.630128000000 |
| C | -3.976274000000 | 0.645323000000 | 0.293967000000 |
| C | -3.968482000000 | 0.287529000000 | 1.646553000000 |
| C | -4.668179000000 | -0.173227000000 | -0.605948000000 |
| C | -4.621931000000 | -0.861397000000 | 2.090829000000 |
| H | -3.445934000000 | 0.913657000000 | 2.363751000000 |
| C | -5.321481000000 | -1.323834000000 | -0.167069000000 |
| H | -4.702027000000 | 0.081889000000 | -1.659306000000 |
| C | -5.296854000000 | -1.675223000000 | 1.182186000000 |
| H | -4.603347000000 | -1.119487000000 | 3.143495000000 |
| H | -5.853602000000 | -1.943838000000 | -0.879430000000 |
| H | -5.806068000000 | -2.568931000000 | 1.523109000000 |

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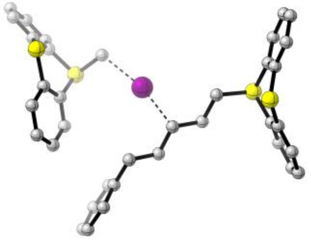
**TS2**



(*i* = –191.7008)

Charge 2, multiplicity 2

| | | | |
|---|---|---|---|
| C | -6.579657000000 | -4.209804000000 | 1.214102000000 |
| C | -6.557496000000 | -2.938157000000 | 1.781022000000 |
| C | -5.995969000000 | -1.864968000000 | 1.082792000000 |
| C | -5.459580000000 | -2.114328000000 | -0.188803000000 |

| | | | |
|---|---|---|---|
| C | -5.512864000000 | -3.379074000000 | -0.779801000000 |
| C | -6.070179000000 | -4.433316000000 | -0.065346000000 |
| C | -5.694688000000 | 0.617950000000 | -0.785676000000 |
| C | -6.223872000000 | 0.840570000000 | 0.493747000000 |
| C | -6.971047000000 | 2.003784000000 | 0.703752000000 |
| H | -7.408861000000 | 2.190569000000 | 1.677227000000 |
| C | -7.178846000000 | 2.902648000000 | -0.339240000000 |
| C | -6.673042000000 | 2.649865000000 | -1.614994000000 |
| C | -5.931972000000 | 1.496717000000 | -1.846323000000 |
| H | -7.023517000000 | -5.027673000000 | 1.768831000000 |
| H | -6.996484000000 | -2.771027000000 | 2.757484000000 |
| H | -5.121870000000 | -3.535656000000 | -1.778410000000 |
| H | -6.113885000000 | -5.420169000000 | -0.508347000000 |
| H | -7.765505000000 | 3.795312000000 | -0.158380000000 |
| H | -6.861811000000 | 3.340829000000 | -2.426797000000 |
| H | -5.540610000000 | 1.282335000000 | -2.834020000000 |
| S | -5.989124000000 | -0.265555000000 | 1.871833000000 |
| S | -4.678031000000 | -0.810008000000 | -1.125668000000 |
| C | -3.115973000000 | -0.492051000000 | -0.166504000000 |
| H | -3.392691000000 | -0.413596000000 | 0.884155000000 |
| H | -2.533832000000 | -1.400395000000 | -0.327767000000 |
| C | -2.412772000000 | 0.760718000000 | -0.681755000000 |
| H | -3.097583000000 | 1.617095000000 | -0.595149000000 |
| H | -2.164745000000 | 0.666378000000 | -1.743512000000 |
| C | -1.177641000000 | 1.127091000000 | 0.112032000000 |
| H | -1.267907000000 | 0.964861000000 | 1.185440000000 |
| C | -0.504888000000 | 2.416657000000 | -0.274211000000 |
| H | -1.270968000000 | 3.206026000000 | -0.210047000000 |
| H | -0.214022000000 | 2.378130000000 | -1.327922000000 |
| I | 0.507097000000 | -0.675237000000 | -0.311644000000 |
| C | 2.591074000000 | -2.117221000000 | -0.411656000000 |
| H | 2.709644000000 | -2.454342000000 | 0.611637000000 |
| H | 2.311627000000 | -2.868381000000 | -1.144574000000 |
| C | 5.354494000000 | -2.317627000000 | -0.871723000000 |
| C | 4.329025000000 | 0.037178000000 | 0.241991000000 |
| C | 5.894602000000 | -2.834739000000 | -2.051959000000 |
| C | 5.830009000000 | -2.694649000000 | 0.392846000000 |
| C | 4.828287000000 | -0.356321000000 | 1.491437000000 |
| C | 4.105665000000 | 1.378370000000 | -0.074258000000 |
| C | 6.911500000000 | -3.778714000000 | -1.969099000000 |
| H | 5.522982000000 | -2.507274000000 | -3.015944000000 |
| C | 6.856186000000 | -3.641326000000 | 0.452561000000 |
| C | 5.053246000000 | 0.635212000000 | 2.451109000000 |
| H | 3.743865000000 | 1.661242000000 | -1.054954000000 |
| C | 4.338803000000 | 2.350174000000 | 0.891931000000 |
| C | 7.378685000000 | -4.185135000000 | -0.718608000000 |
| H | 7.338692000000 | -4.190751000000 | -2.874540000000 |
| H | 7.257708000000 | -3.936139000000 | 1.414814000000 |
| C | 4.798381000000 | 1.971621000000 | 2.153116000000 |
| H | 5.454805000000 | 0.360260000000 | 3.419226000000 |
| H | 4.156204000000 | 3.390707000000 | 0.657124000000 |
| H | 8.174802000000 | -4.916832000000 | -0.651866000000 |
| H | 4.988799000000 | 2.726483000000 | 2.906629000000 |
| S | 3.987798000000 | -1.167535000000 | -1.033655000000 |
| S | 5.189508000000 | -2.047507000000 | 1.926524000000 |
| C | 0.681113000000 | 2.815871000000 | 0.616354000000 |
| H | 1.373251000000 | 1.971234000000 | 0.687633000000 |
| H | 0.319963000000 | 3.001133000000 | 1.632164000000 |
| C | 1.448949000000 | 4.021270000000 | 0.120016000000 |
| C | 2.006795000000 | 4.035030000000 | -1.165116000000 |
| C | 1.680792000000 | 5.115181000000 | 0.957845000000 |
| C | 2.782215000000 | 5.108420000000 | -1.597442000000 |
| H | 1.841105000000 | 3.198503000000 | -1.837611000000 |
| C | 2.457973000000 | 6.192421000000 | 0.529995000000 |
| H | 1.257113000000 | 5.125144000000 | 1.956890000000 |
| C | 3.014053000000 | 6.190599000000 | -0.747382000000 |
| H | 3.205043000000 | 5.103270000000 | -2.595640000000 |
| H | 2.625892000000 | 7.032376000000 | 1.194012000000 |
| H | 3.616710000000 | 7.026618000000 | -1.081621000000 |

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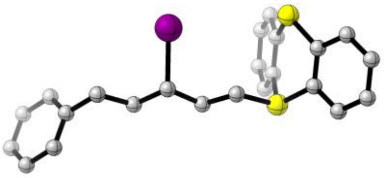
## **3a**



Charge 1, multiplicity 1

| | | | |
|---|---|---|---|
| C | -2.042443000000 | 3.407542000000 | 1.868345000000 |
| C | -2.582957000000 | 2.908864000000 | 0.687347000000 |
| C | -2.716334000000 | 1.529538000000 | 0.498541000000 |
| C | -2.286293000000 | 0.679343000000 | 1.526123000000 |
| C | -1.778852000000 | 1.174877000000 | 2.729847000000 |
| C | -1.651891000000 | 2.548598000000 | 2.896273000000 |
| C | -3.822059000000 | -1.397281000000 | 0.431301000000 |
| C | -4.256931000000 | -0.522203000000 | -0.574262000000 |
| C | -5.424249000000 | -0.852121000000 | -1.271293000000 |
| H | -5.791957000000 | -0.186054000000 | -2.042827000000 |
| C | -6.122677000000 | -2.015505000000 | -0.962922000000 |
| C | -5.692538000000 | -2.859062000000 | 0.061936000000 |
| C | -4.539469000000 | -2.546589000000 | 0.771900000000 |
| H | -1.946347000000 | 4.479206000000 | 1.994347000000 |
| H | -2.918443000000 | 3.589096000000 | -0.086418000000 |
| H | -1.477344000000 | 0.494037000000 | 3.517279000000 |
| H | -1.251909000000 | 2.944717000000 | 3.820956000000 |
| H | -7.024363000000 | -2.252499000000 | -1.514670000000 |
| H | -6.252435000000 | -3.751840000000 | 0.309753000000 |
| H | -4.194454000000 | -3.189475000000 | 1.573350000000 |
| S | -3.402876000000 | 0.967872000000 | -1.044344000000 |
| S | -2.303485000000 | -1.094425000000 | 1.321523000000 |
| C | -0.998617000000 | -1.366701000000 | 0.025275000000 |
| H | -1.084525000000 | -2.428268000000 | -0.213705000000 |
| H | -1.289701000000 | -0.769214000000 | -0.837087000000 |
| C | 0.378670000000 | -0.988892000000 | 0.562975000000 |
| H | 0.700311000000 | -1.734902000000 | 1.298950000000 |
| H | 0.345473000000 | -0.022399000000 | 1.072492000000 |
| C | 1.443948000000 | -0.922840000000 | -0.536311000000 |
| H | 1.379765000000 | -1.784305000000 | -1.202428000000 |
| C | 2.849400000000 | -0.782563000000 | 0.036257000000 |
| H | 2.974411000000 | -1.593743000000 | 0.766655000000 |
| H | 2.931751000000 | 0.153458000000 | 0.597597000000 |
| I | 0.966444000000 | 0.783223000000 | -1.901340000000 |
| C | 3.993385000000 | -0.883093000000 | -0.986342000000 |
| H | 3.896159000000 | -1.821044000000 | -1.543470000000 |
| H | 3.909583000000 | -0.072165000000 | -1.713745000000 |
| C | 5.342239000000 | -0.822936000000 | -0.305517000000 |
| C | 5.980473000000 | -1.989925000000 | 0.125773000000 |
| C | 5.955142000000 | 0.409033000000 | -0.054709000000 |
| C | 7.202362000000 | -1.929272000000 | 0.793894000000 |
| H | 5.524759000000 | -2.955469000000 | -0.072784000000 |
| C | 7.176306000000 | 0.474277000000 | 0.613624000000 |
| H | 5.478131000000 | 1.323381000000 | -0.394465000000 |
| C | 7.802634000000 | -0.695698000000 | 1.041181000000 |
| H | 7.688681000000 | -2.843842000000 | 1.113800000000 |
| H | 7.642534000000 | 1.436441000000 | 0.792980000000 |
| H | 8.755330000000 | -0.646896000000 | 1.555544000000 |

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## $I^-$ (iodide ion)

Charge –1, multiplicity 1

| | | | |
|---|---|---|---|
| I | -0.088375000000 | 4.994383000000 | -1.966830000000 |

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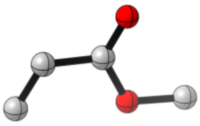
## **S7**



Charge 0, multiplicity 1

| | | | |
|---|---|---|---|
| C | -0.853652000000 | 1.061298000000 | -0.150842000000 |
| H | -0.357642000000 | 0.203133000000 | -0.588108000000 |
| H | -1.927096000000 | 1.005049000000 | -0.010334000000 |
| C | -0.171070000000 | 2.149559000000 | 0.203038000000 |
| H | -0.656317000000 | 3.014114000000 | 0.641339000000 |
| C | 1.294539000000 | 2.315057000000 | 0.048559000000 |
| O | 1.891323000000 | 3.315401000000 | 0.378546000000 |
| O | 1.898630000000 | 1.237162000000 | -0.497728000000 |
| C | 3.323622000000 | 1.340920000000 | -0.672109000000 |

| | | | |
|---|---|---|---|
| H | 3.815902000000 | 1.490846000000 | 0.290366000000 |
| H | 3.631198000000 | 0.397562000000 | -1.118273000000 |
| H | 3.567738000000 | 2.176554000000 | -1.330335000000 |

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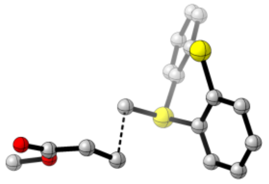
## TS3



(*i* = –197.546)

Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -2.041972000000 | -2.163122000000 | 0.092018000000 |
| C | -1.001112000000 | -1.644323000000 | -0.673956000000 |
| C | -0.679568000000 | -0.286255000000 | -0.596862000000 |
| C | -1.430196000000 | 0.521147000000 | 0.268711000000 |
| C | -2.455425000000 | 0.002827000000 | 1.062359000000 |
| C | -2.762407000000 | -1.349650000000 | 0.967142000000 |
| C | 0.645659000000 | 2.392172000000 | 0.284858000000 |
| C | 1.379467000000 | 1.573028000000 | -0.582749000000 |
| C | 2.764522000000 | 1.757471000000 | -0.648566000000 |
| H | 3.357706000000 | 1.126986000000 | -1.300270000000 |
| C | 3.381533000000 | 2.726602000000 | 0.137333000000 |
| C | 2.639581000000 | 3.508811000000 | 1.023342000000 |
| C | 1.262161000000 | 3.338884000000 | 1.104940000000 |
| H | -2.277437000000 | -3.217964000000 | 0.018138000000 |
| H | -0.424549000000 | -2.295332000000 | -1.320359000000 |
| H | -3.007454000000 | 0.648139000000 | 1.735681000000 |
| H | -3.557608000000 | -1.765007000000 | 1.573151000000 |
| H | 4.455520000000 | 2.853796000000 | 0.073858000000 |
| H | 3.129563000000 | 4.244440000000 | 1.648558000000 |
| H | 0.671950000000 | 3.941147000000 | 1.785702000000 |
| S | 0.647739000000 | 0.322368000000 | -1.620438000000 |
| S | -1.141444000000 | 2.293014000000 | 0.356331000000 |
| C | -1.666306000000 | 2.924995000000 | -1.207109000000 |
| H | -1.250494000000 | 2.467529000000 | -2.093320000000 |
| H | -2.668041000000 | 3.333317000000 | -1.196034000000 |
| C | -0.661837000000 | 5.190168000000 | -1.401569000000 |
| H | 0.371844000000 | 4.882067000000 | -1.301512000000 |
| H | -1.211790000000 | 5.411810000000 | -0.495058000000 |
| C | -1.173311000000 | 5.514697000000 | -2.608567000000 |
| H | -0.589722000000 | 5.428440000000 | -3.517799000000 |
| C | -2.556274000000 | 6.006180000000 | -2.819344000000 |
| O | -2.934152000000 | 6.496777000000 | -3.854377000000 |
| O | -3.341044000000 | 5.826593000000 | -1.731961000000 |
| C | -4.689736000000 | 6.345340000000 | -1.844463000000 |
| H | -5.214941000000 | 5.853906000000 | -2.664080000000 |
| H | -5.164601000000 | 6.127674000000 | -0.890942000000 |
| H | -4.662909000000 | 7.419903000000 | -2.026672000000 |

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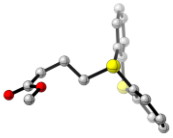
## Int3



Charge 1, multiplicity 2

| | | | |
|---|---|---|---|
| C | -2.276180000000 | -1.791699000000 | -0.093870000000 |
| C | -1.158599000000 | -1.356475000000 | -0.800313000000 |
| C | -0.698972000000 | -0.043788000000 | -0.654681000000 |
| C | -1.394500000000 | 0.806185000000 | 0.216769000000 |
| C | -2.493778000000 | 0.364493000000 | 0.956939000000 |
| C | -2.939673000000 | -0.941488000000 | 0.791108000000 |
| C | 0.862492000000 | 2.467729000000 | 0.350081000000 |
| C | 1.536293000000 | 1.606690000000 | -0.526969000000 |
| C | 2.932922000000 | 1.668483000000 | -0.568132000000 |
| H | 3.478795000000 | 1.001428000000 | -1.224802000000 |
| C | 3.620532000000 | 2.564488000000 | 0.245431000000 |
| C | 2.936744000000 | 3.393570000000 | 1.135124000000 |
| C | 1.549023000000 | 3.342050000000 | 1.196227000000 |
| H | -2.617055000000 | -2.812165000000 | -0.220518000000 |
| H | -0.629309000000 | -2.039174000000 | -1.454408000000 |
| H | -2.996053000000 | 1.035304000000 | 1.644188000000 |
| H | -3.796069000000 | -1.293241000000 | 1.352216000000 |
| H | 4.702391000000 | 2.597425000000 | 0.199150000000 |
| H | 3.479380000000 | 4.073158000000 | 1.779877000000 |
| H | 1.003769000000 | 3.978437000000 | 1.883386000000 |
| S | 0.720883000000 | 0.451672000000 | -1.611196000000 |
| S | -0.921679000000 | 2.517725000000 | 0.408220000000 |
| C | -1.401578000000 | 3.270368000000 | -1.227160000000 |
| H | -1.027468000000 | 2.613437000000 | -2.010448000000 |
| H | -2.491634000000 | 3.255426000000 | -1.200718000000 |
| C | -0.862196000000 | 4.705048000000 | -1.340404000000 |
| H | 0.229447000000 | 4.694616000000 | -1.328365000000 |
| H | -1.216007000000 | 5.290174000000 | -0.484106000000 |
| C | -1.357138000000 | 5.324931000000 | -2.606970000000 |
| H | -0.694381000000 | 5.478461000000 | -3.448520000000 |
| C | -2.732876000000 | 5.753366000000 | -2.798806000000 |
| O | -3.141765000000 | 6.291167000000 | -3.805993000000 |
| O | -3.513575000000 | 5.482146000000 | -1.716131000000 |
| C | -4.888033000000 | 5.924468000000 | -1.815060000000 |
| H | -5.382795000000 | 5.435269000000 | -2.655041000000 |
| H | -5.353115000000 | 5.643850000000 | -0.873028000000 |
| H | -4.925322000000 | 7.005038000000 | -1.956961000000 |

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## Additional Discussion

We designed a series of experiments to gain insight into the reaction mechanism (Fig. S30). Photoluminescence decay study using time-correlated single photon counting (TCSPC) revealed concentration-dependent quenching of 4CzIPN* by **1a**, with a quenching rate constant ($k_q$) of 8.6 x $10^7$ $M^{-1}$ $s^{-1}$, and no quenching by substrate **2** (Fig. S30A). Cyclic voltammetry measurements provide a diagnostic for the nature of excited-state decay to imply electron transfer between 4CzIPN* [$E(PC^{\bullet+}/PC^{*}) = -1.04$ V versus SCE][43] and **1a** [$E_{p/2} = -0.86$ V versus SCE]. In contrast, the pre-isolated 1,3-dielectrophile **3a** exhibited a more negative potential [$E_{p/2} = -1.31$ V versus SCE], accounting for its stability against potential reagents (**1b** and **1c**) also fell within the potential range for direct reduction by photocatalyst. To reconcile these opposite reaction outcomes provoked by halogen substituents, the frontier molecular orbitals (FMO) of **1a** were examined in comparison with those of **1c** as a control (Fig. S30B). While both possess apparently identical HOMOs localized on the sulfur atom (S2), a striking difference in the LUMO compositions was observed. As shown in Fig. S30B, **1a** has a lowest-lying LUMO with prominent antibonding character between p(C1) and p(I) orbitals, rendering the C–I bond reactive preferentially over the C–S bond. Conversely, the LUMO of **1c** is dominated by σ* orbital of C1–S1 group. These theoretical analyses underscore the centrality of reagent's LUMO in achieving chemoselectivity, distinct from the canonical reactivity in sulfonium chemistry.

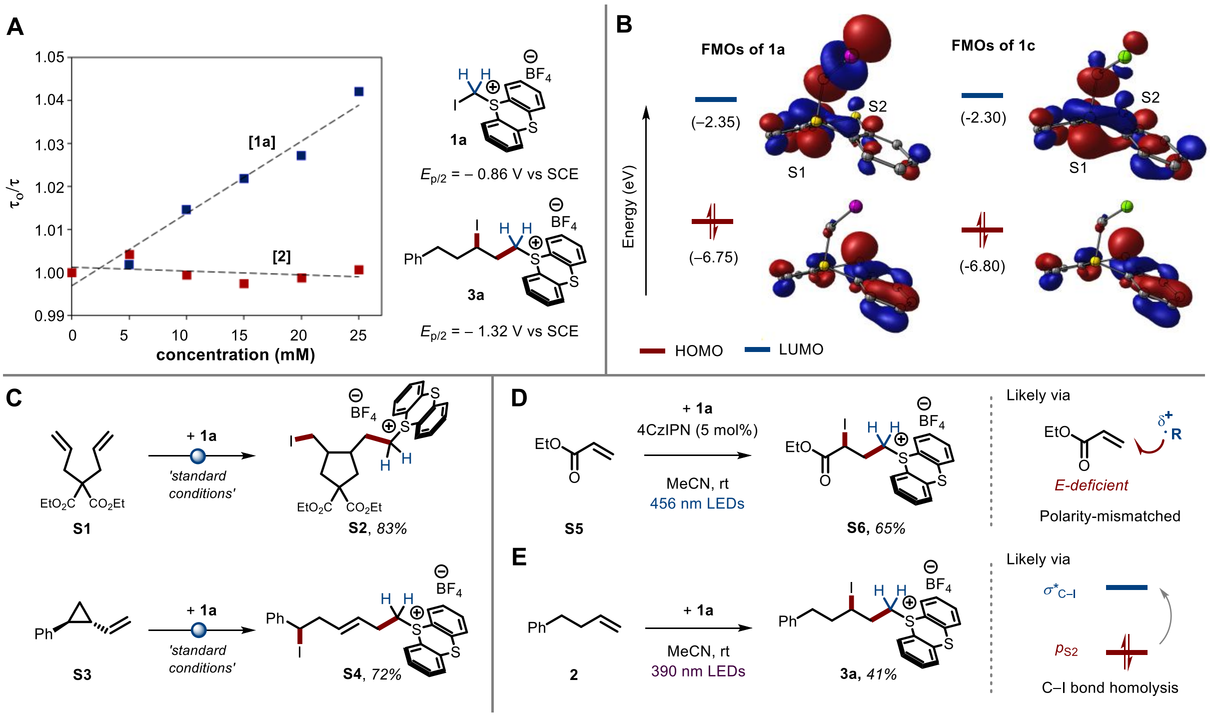

**Fig. S30. Mechanistic Studies.** (**A**) Photoluminescence decay study and electrochemical experiment. $E_{p/2}$ = half-peak potential. SCE = Saturated calomel electrode. (**B**) Frontier molecular orbital (FMO) analysis. (**C**) Radical clock experiments. (**D**) Polarity-mismatched radical addition. (**E**) Direct photolysis.

We next designed a series of experiments to gather mechanistic insight into the post-initiation step. Radical clock substrate **S1** underwent difunctionalization accompanied by cyclization to form cyclopentane **S2** (Fig.

S30C). The reaction of cyclopropyl-substituted alkene **S3** with **1a** resulted in ring-opening product **S4**, supporting the radical intermediacy. Surprisingly, scrutiny of electronic demand revealed that the present system is amenable to functionalization of electron-deficient alkene **S5**, affording **S6** in good yield (Fig. S30D). This observation runs counter to the general paradigm dictated by radical polarity effects and underpins the unprecedented ambiphilic behavior of α-thianthrenium methyl radical **I**. This case study further corroborates that radical-polar crossover mechanism, among commonly proposed pathways[44], might not be implicated in the C–I bond-forming event, as accessing a carbocation adjacent to an electron-withdrawing substituent is prohibitively unfavorable. By inference, the reaction likely proceeds through radical propagation by the action of reagent **1a**. To lend support to this mechanistic feasibility, we considered a non-redox-assisted activation where the common intermediate **Int1** could be generated through a homolysis induced by an $n_{S2} \rightarrow \sigma^*_{C\text{–}I}$ transition. Evidently, exposure of **1a** to 390 nm irradiation in the presence of alkene **2** without the photocatalyst produced the identical product **3a**, albeit with a diminution in yield and mass balance (Fig. S30E).

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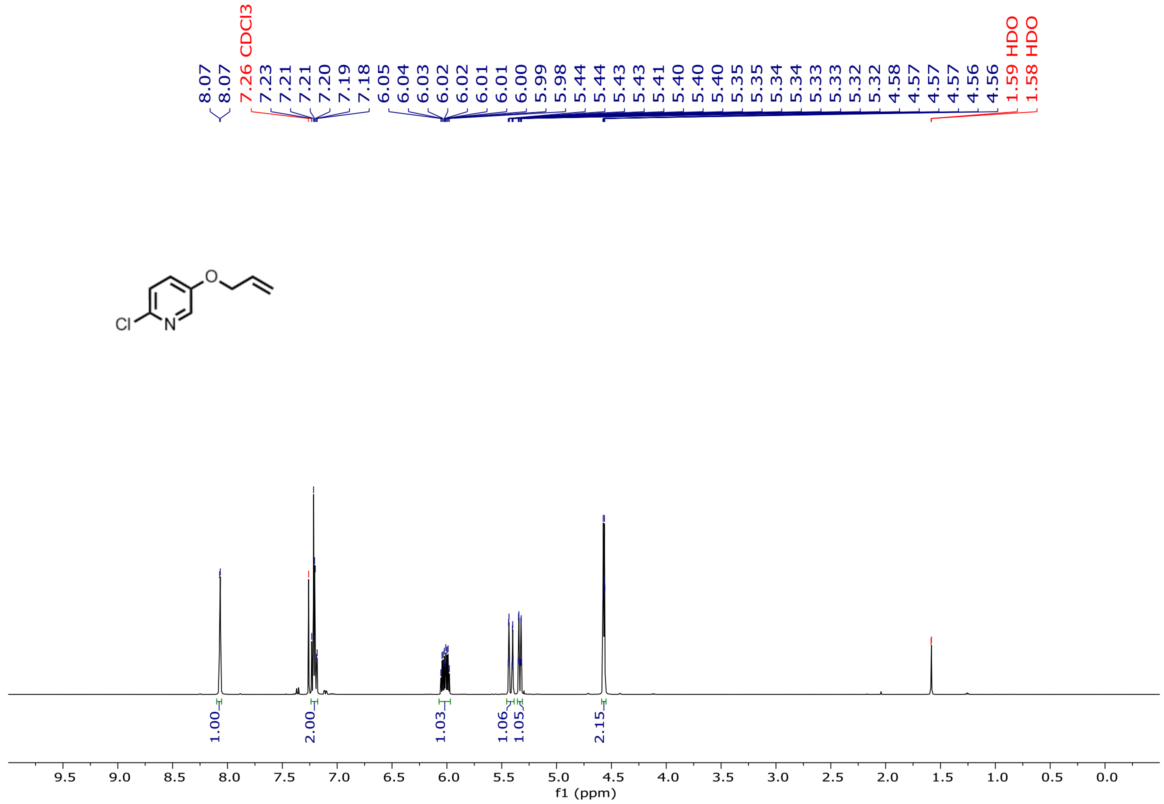
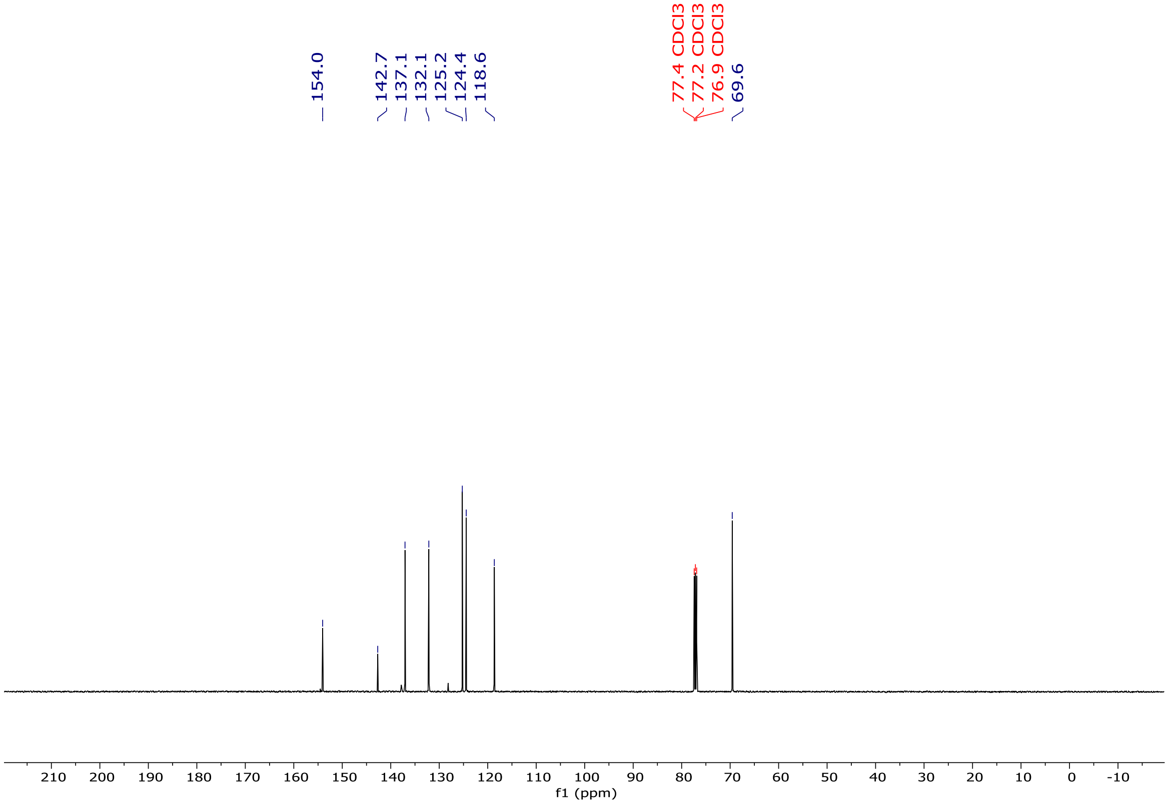
# IX. NMR Spectral Copies

## $^{1}$H NMR spectrum of 65 in $CDCl_3$. (500 MHz)



## $^{13}$C NMR spectrum of 65 in $CDCl_3$. (126 MHz)



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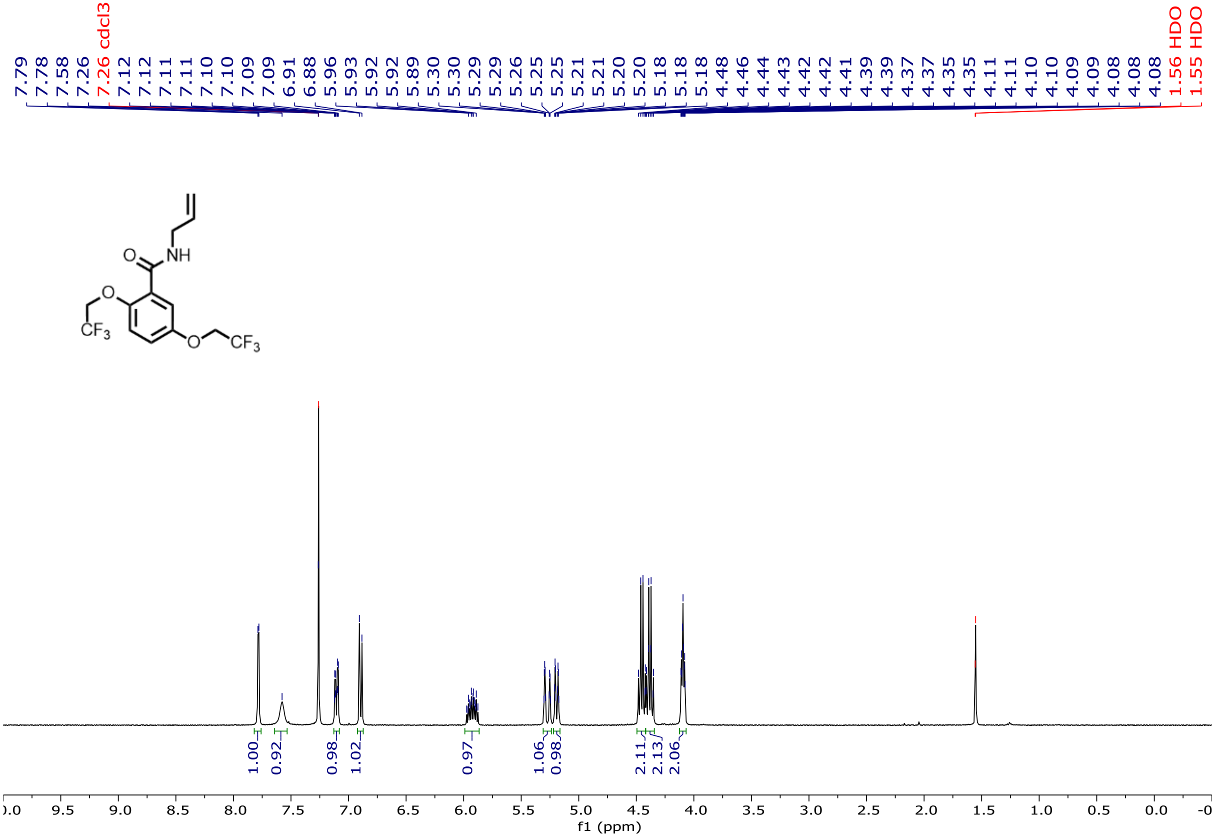

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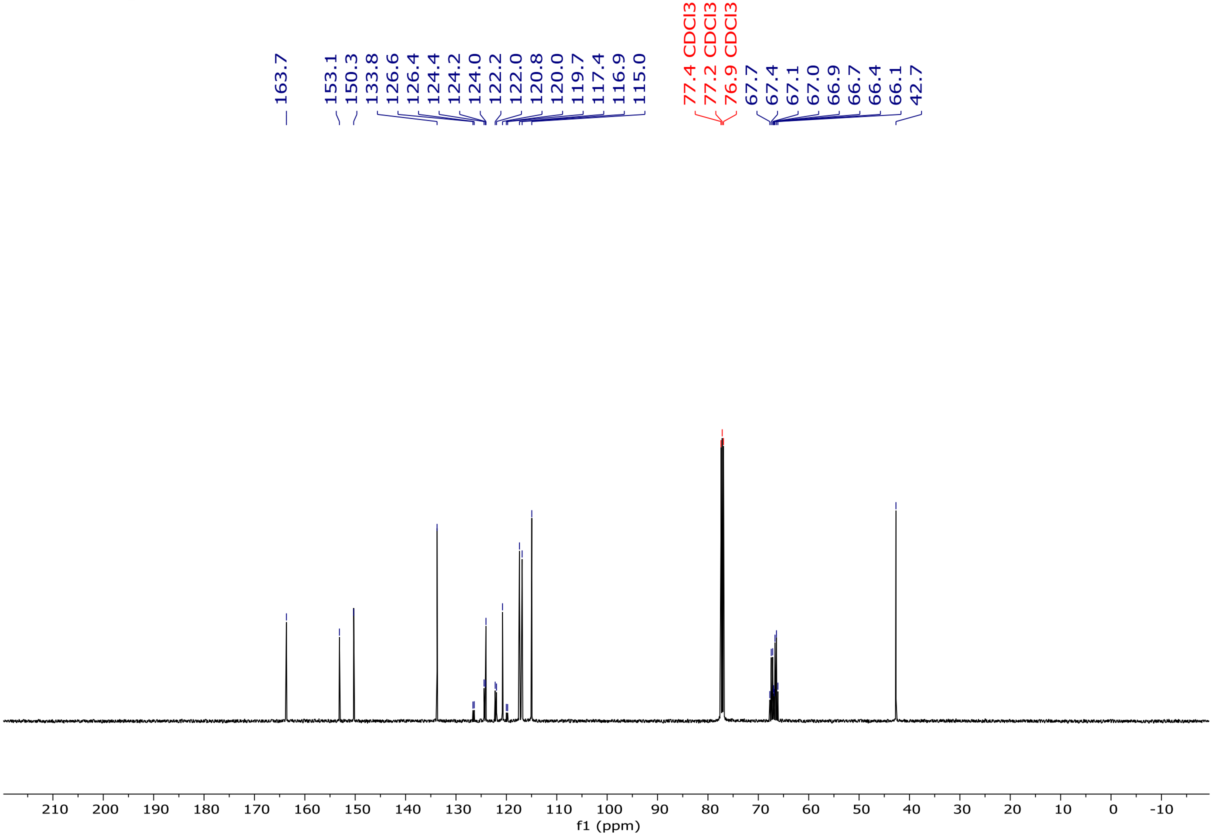
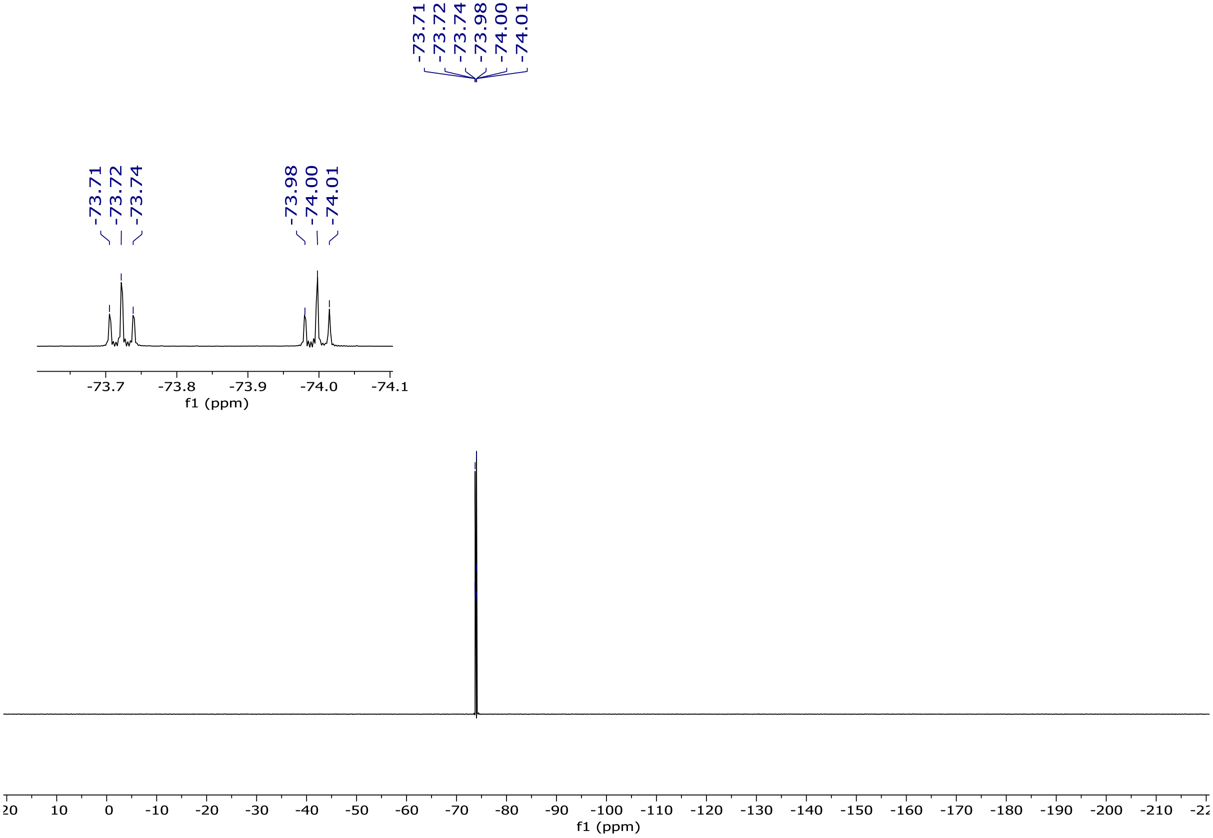


$^{19}$**F NMR spectrum of 69 in CDCl$_3$. (471 MHz)**



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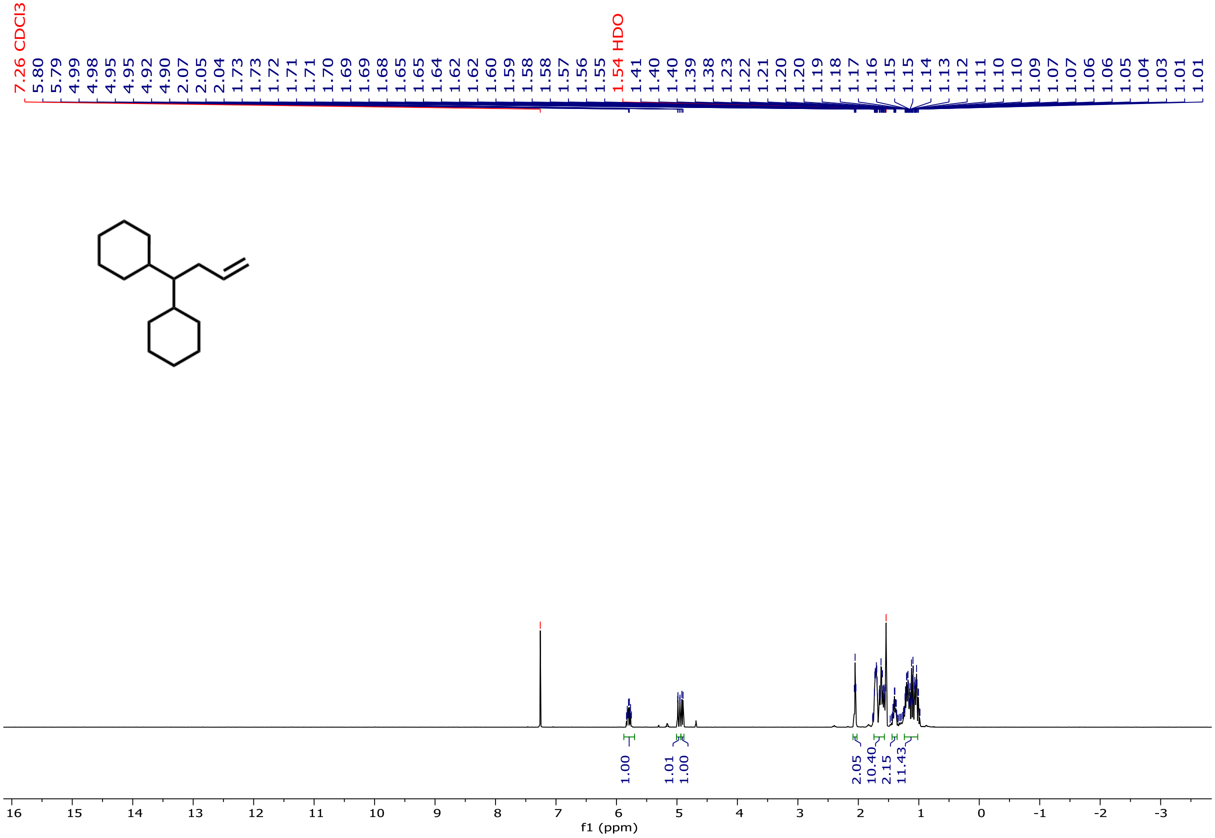

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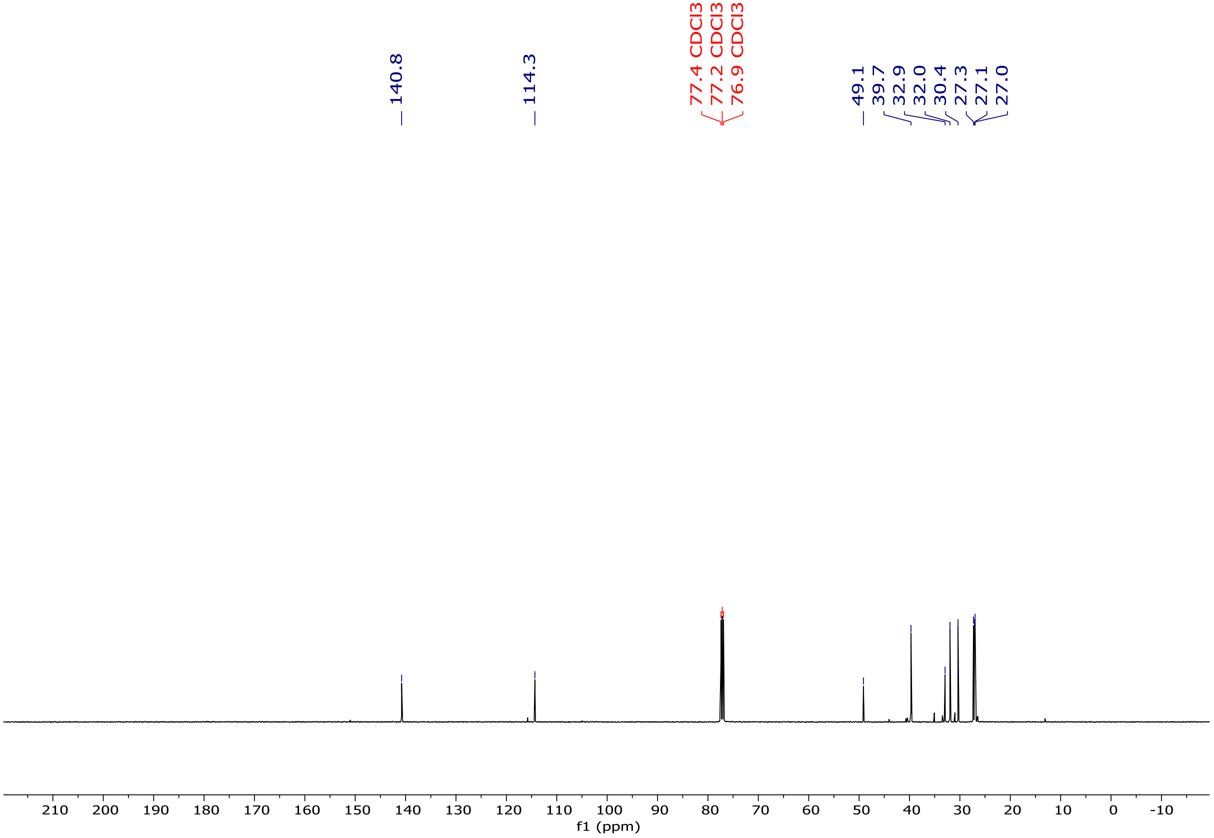

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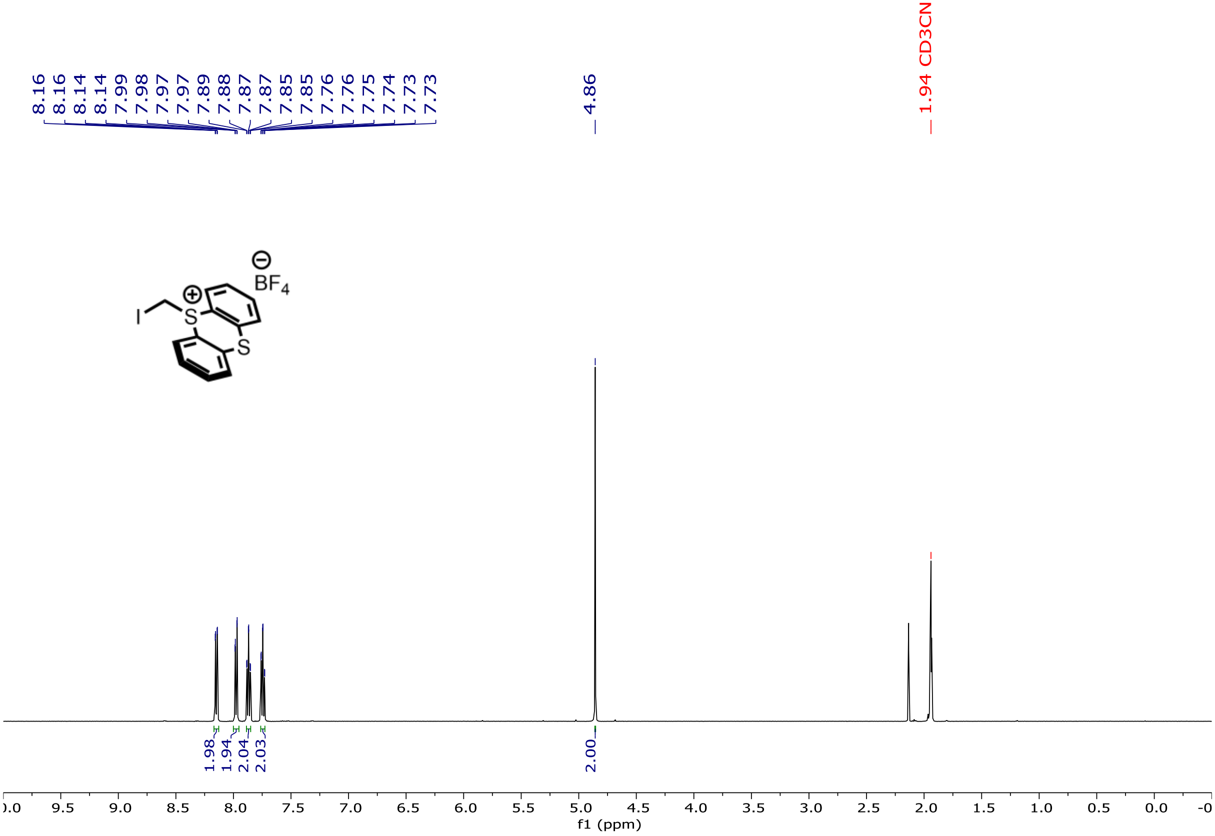

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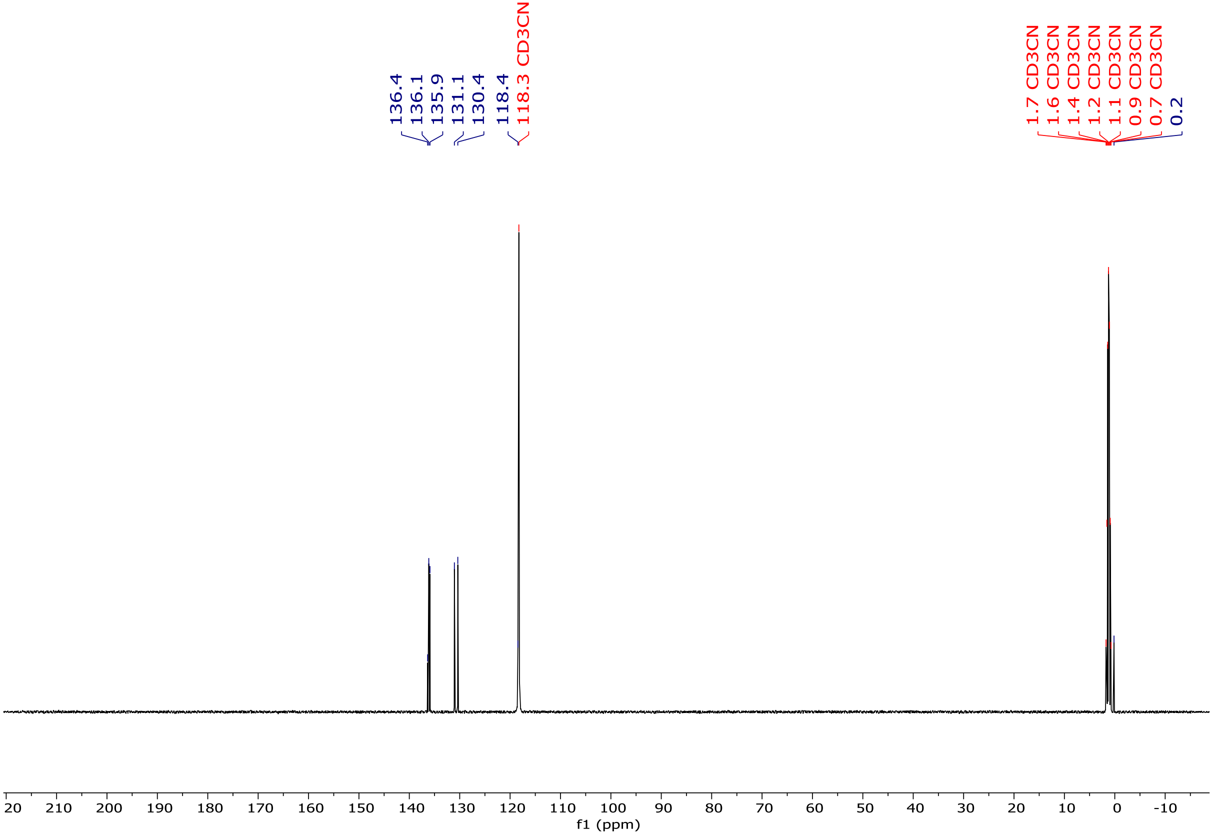

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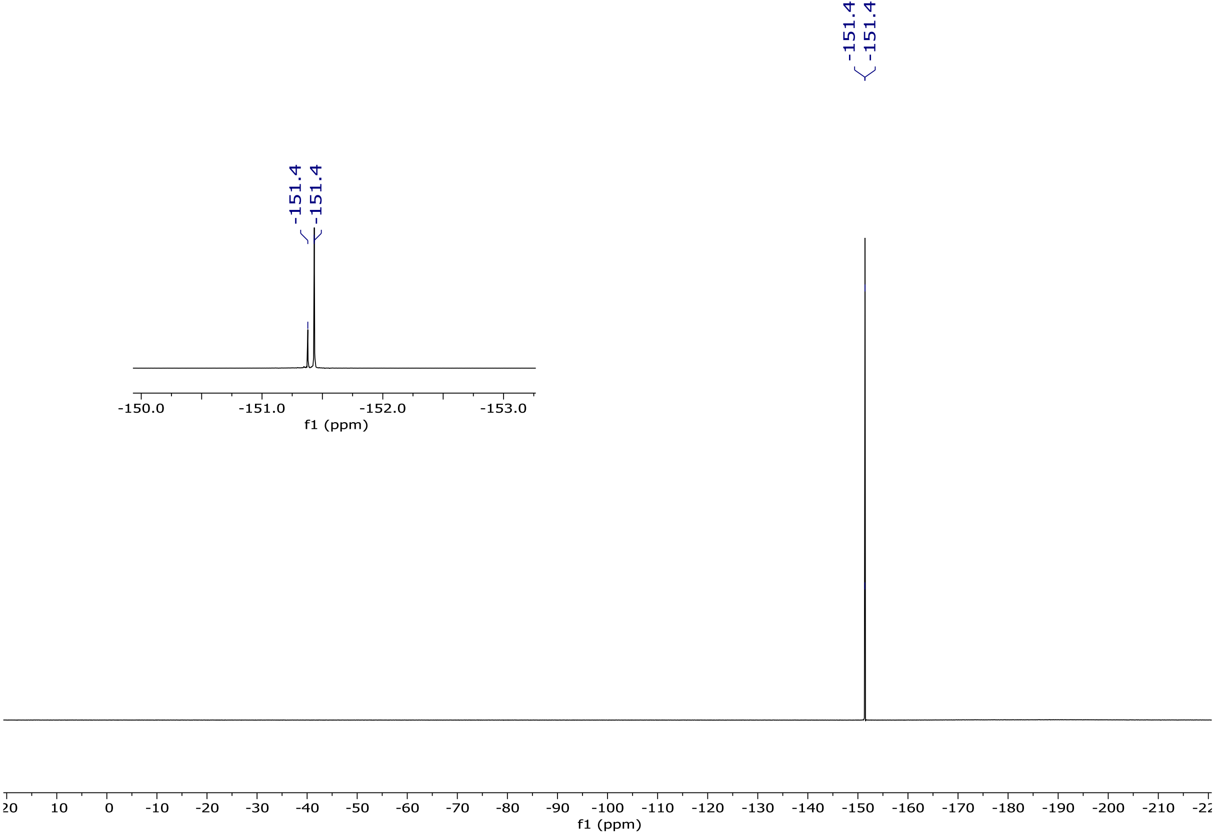

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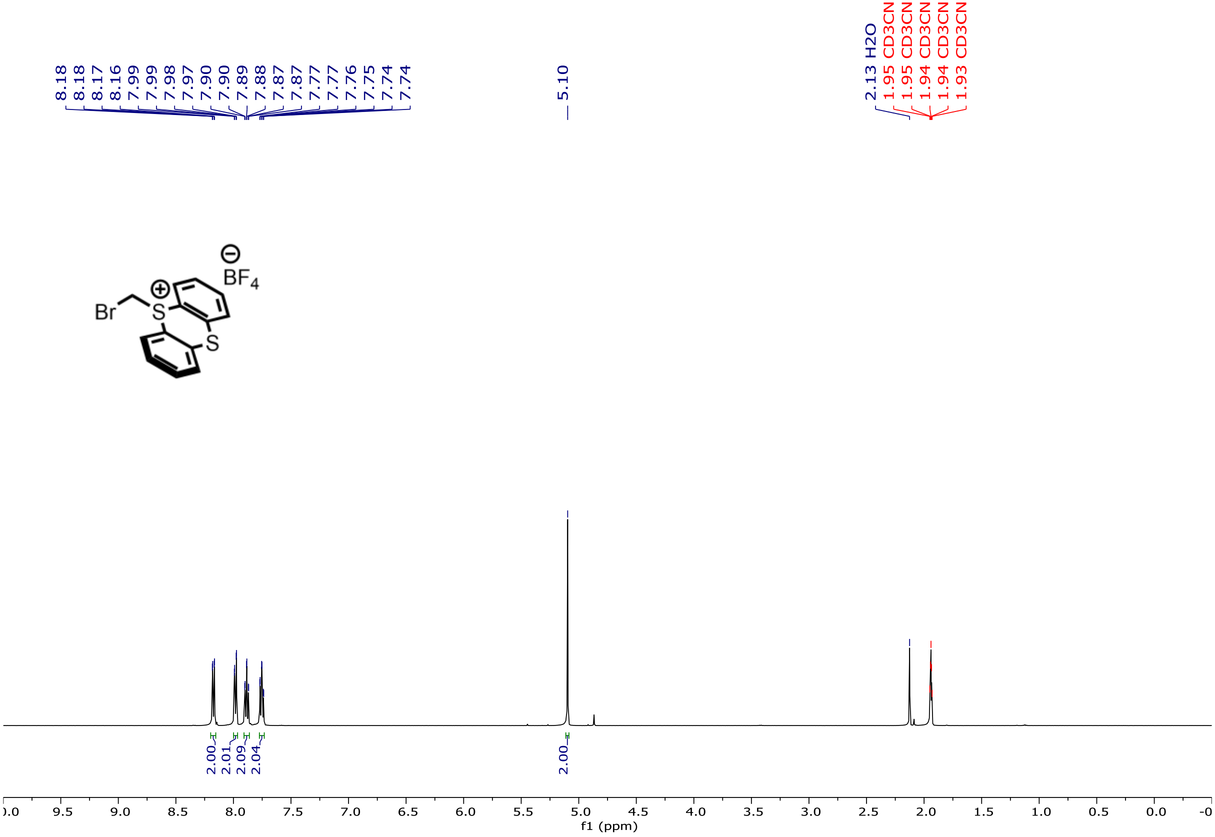

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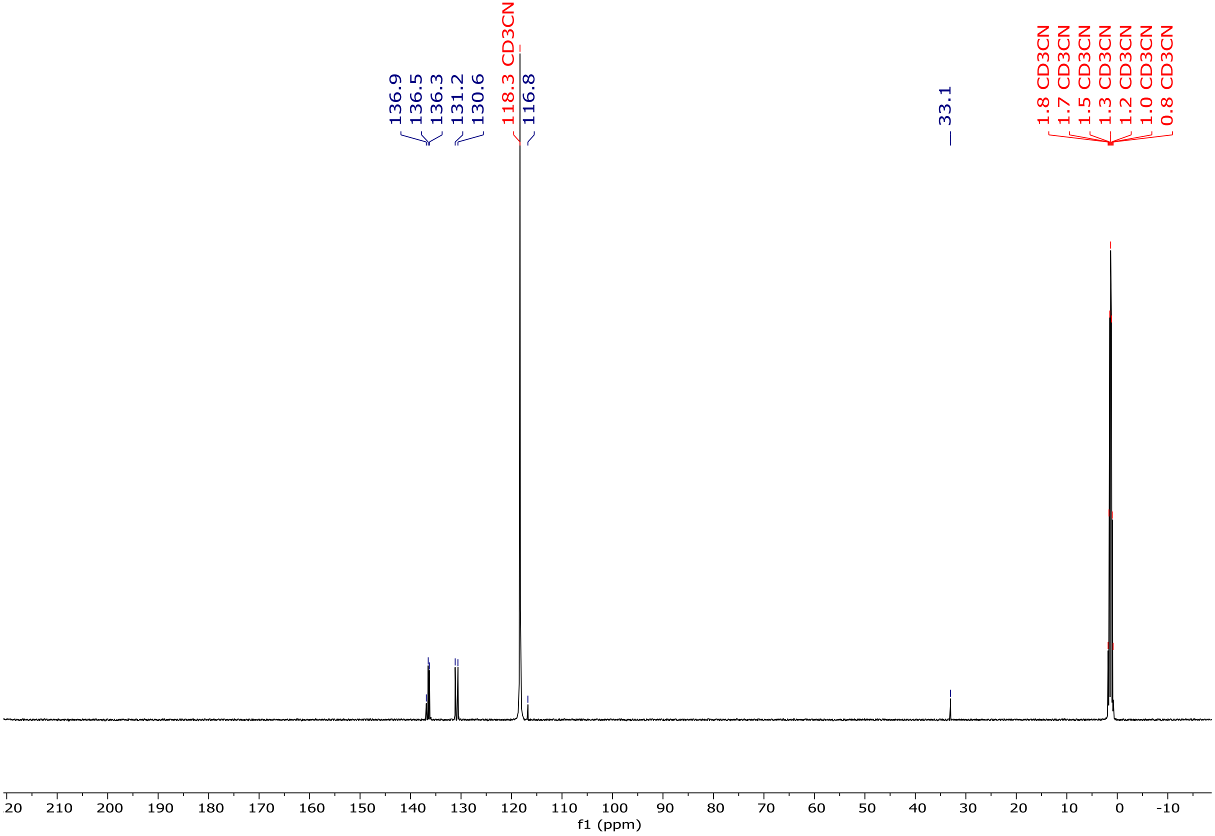

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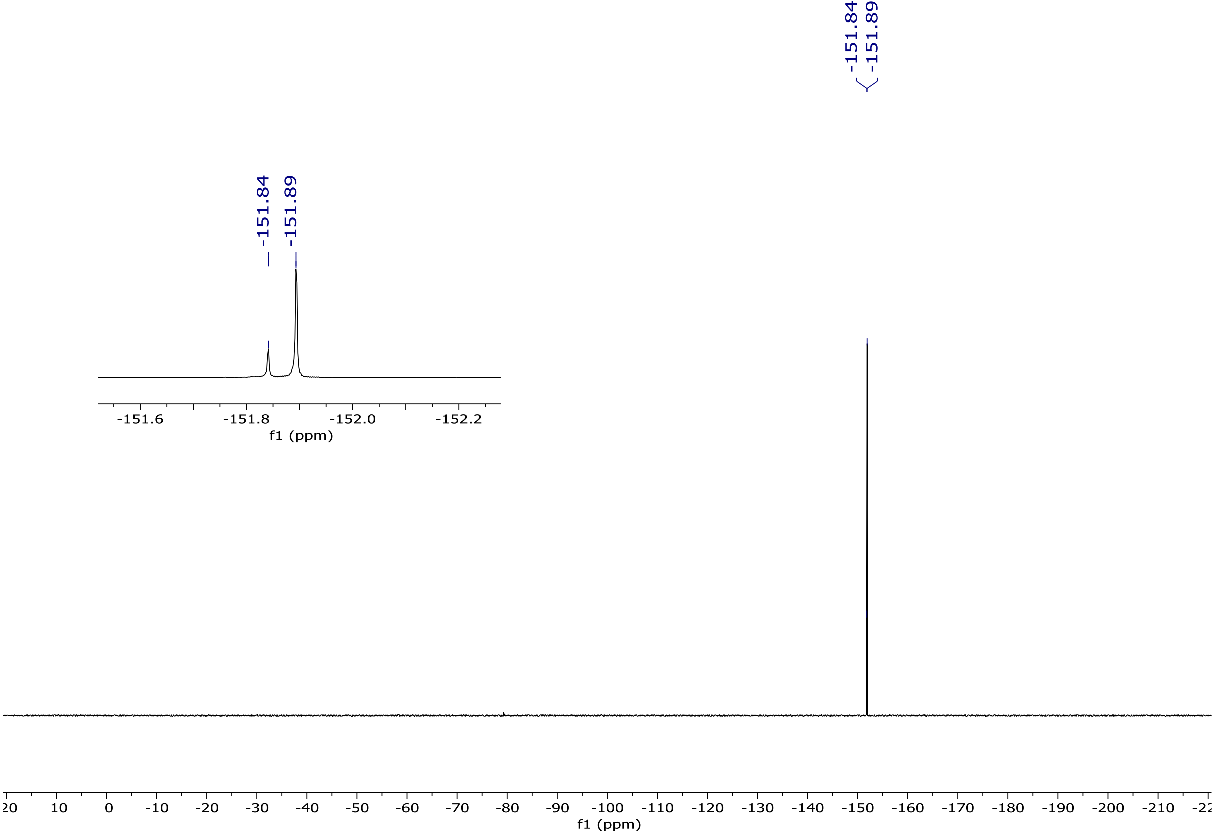

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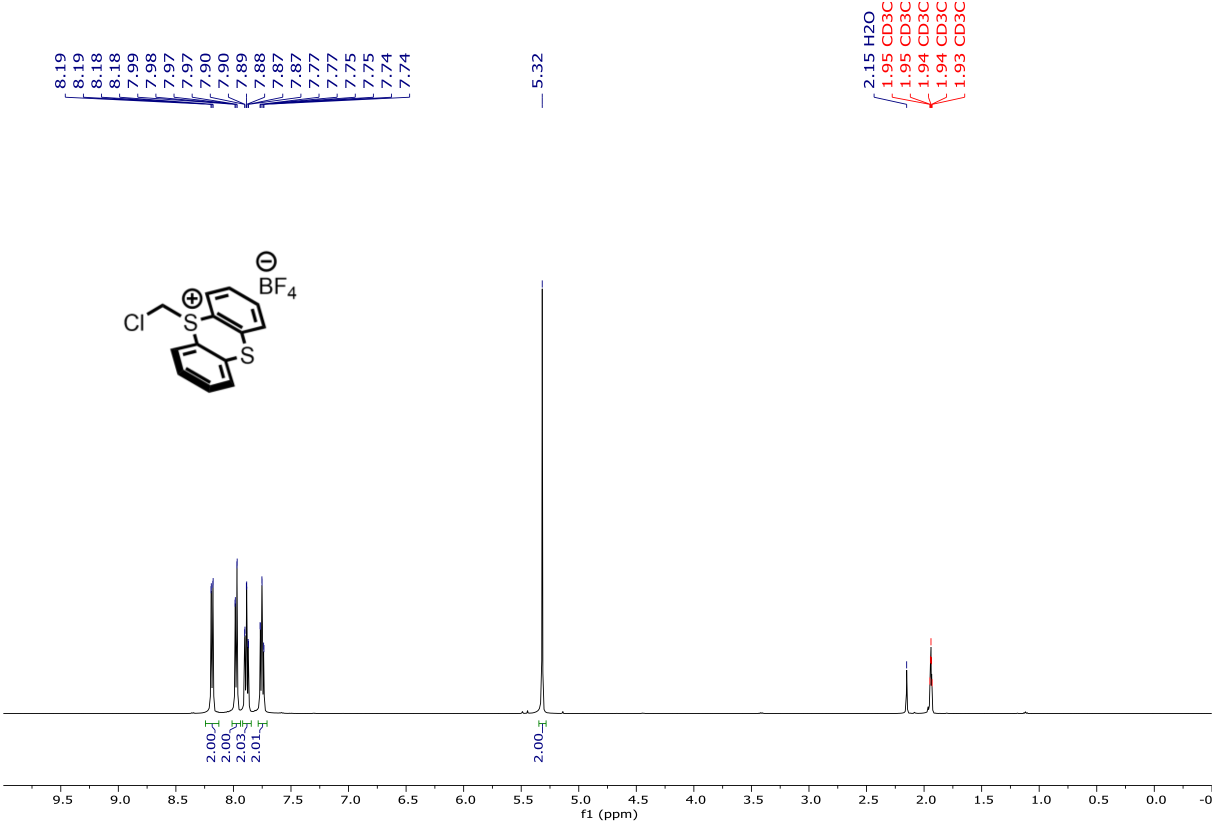

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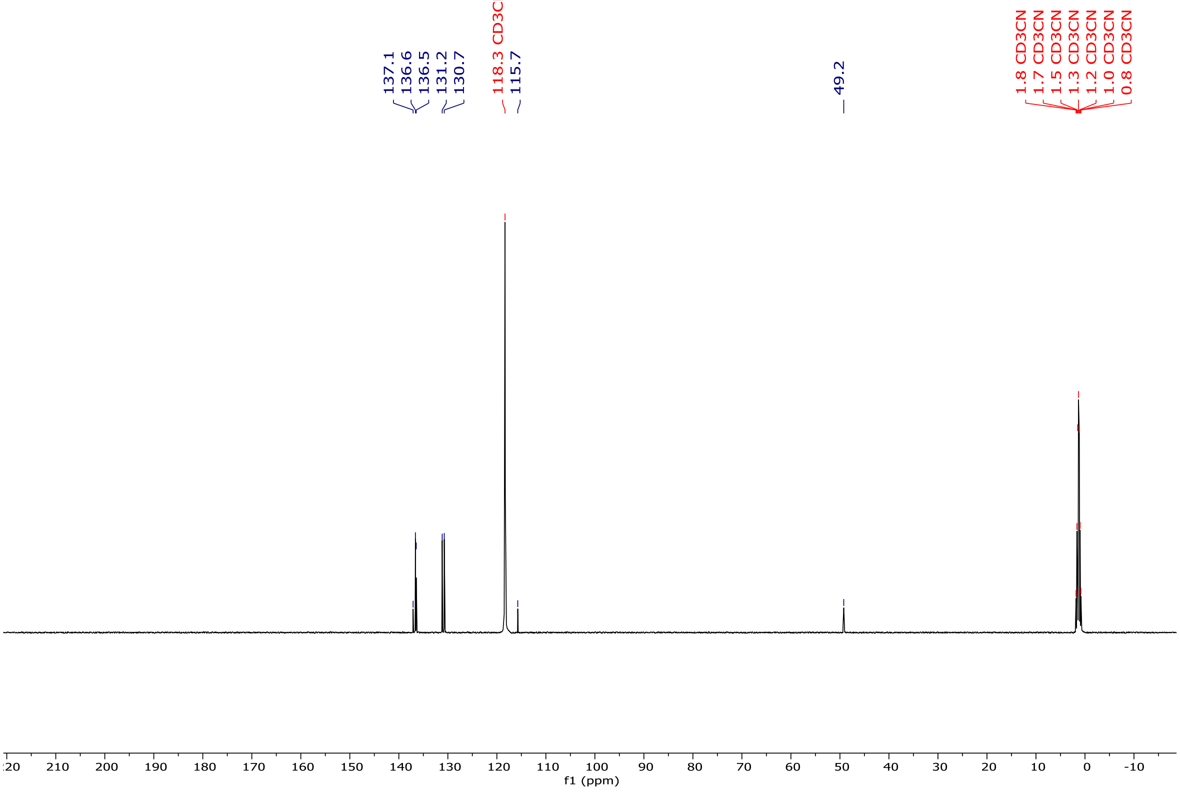

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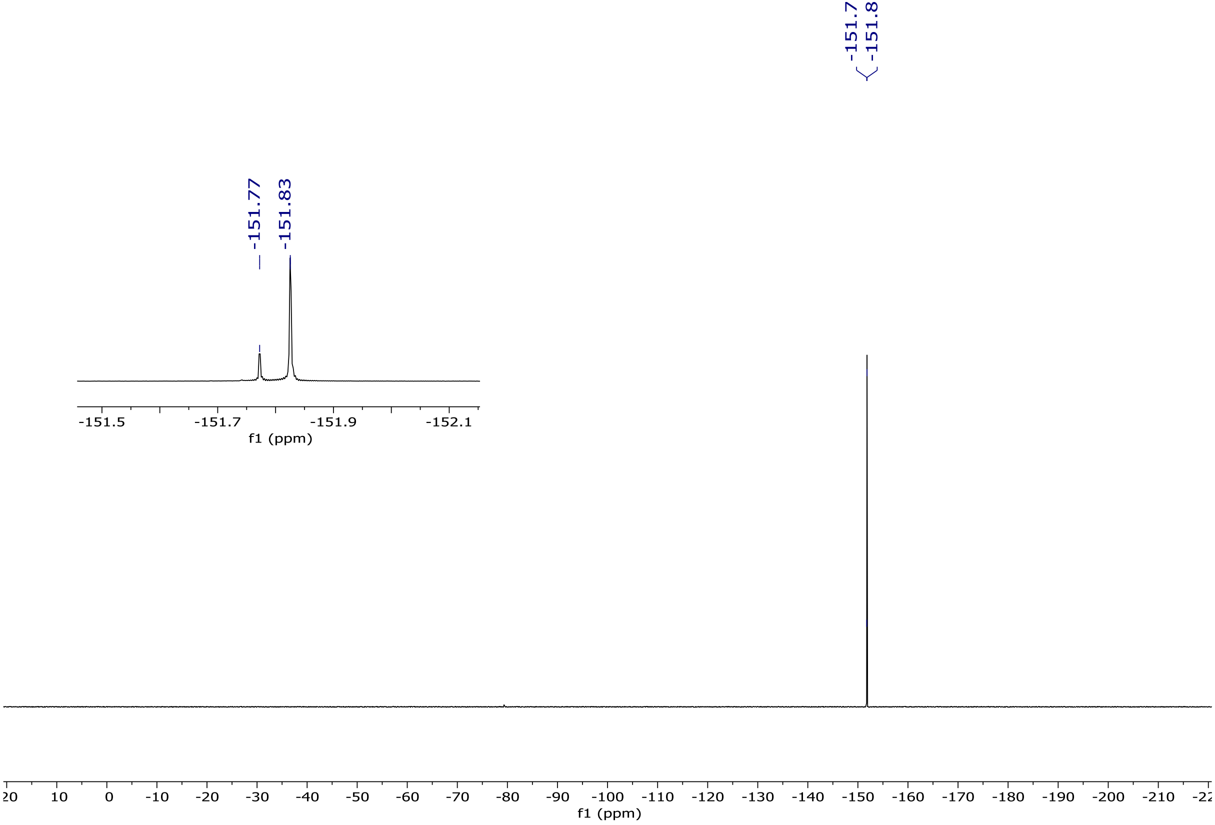

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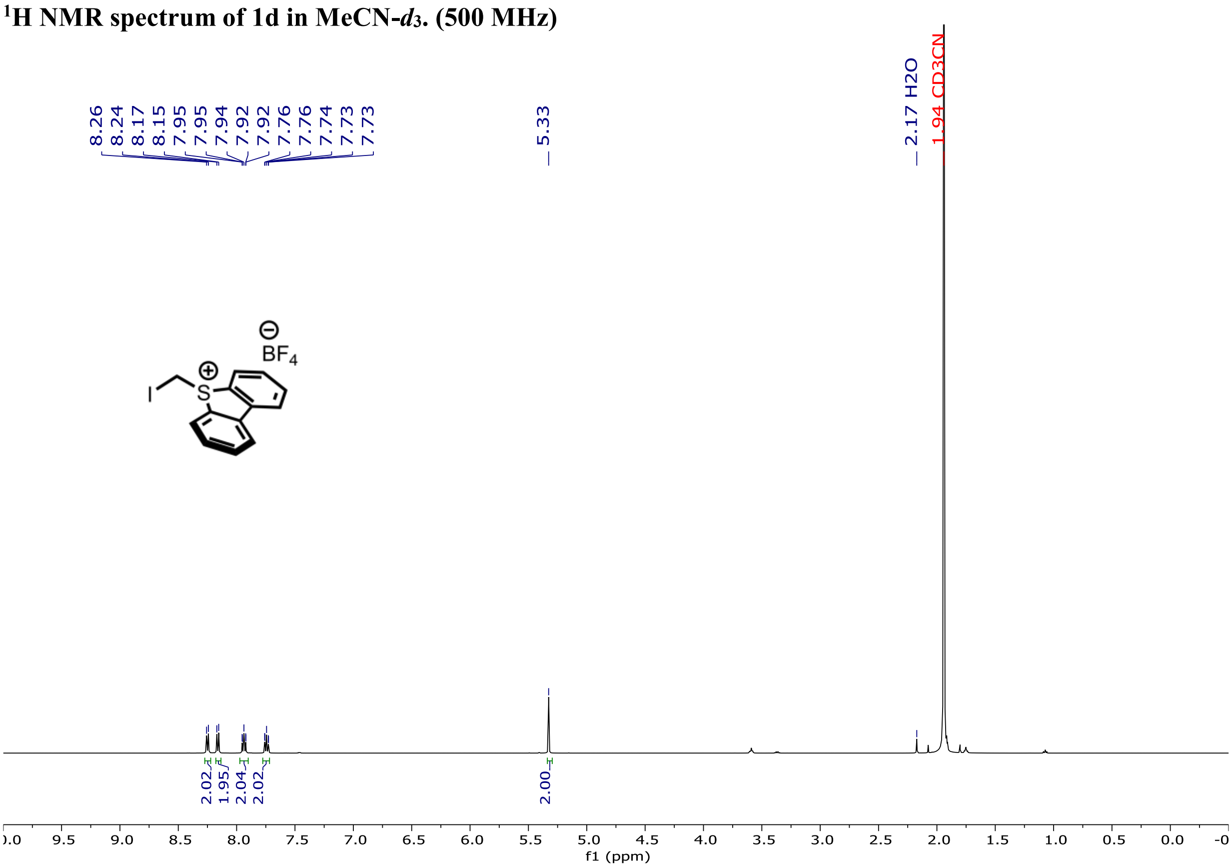

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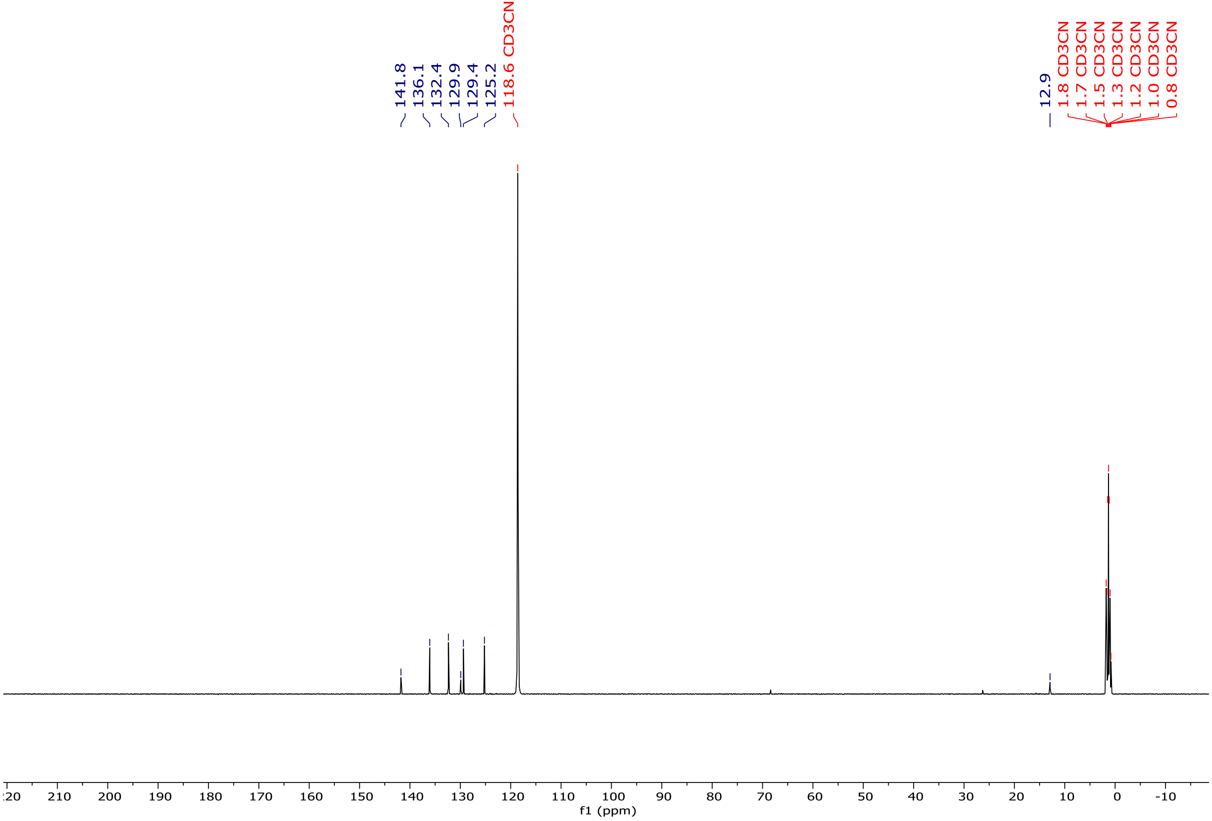

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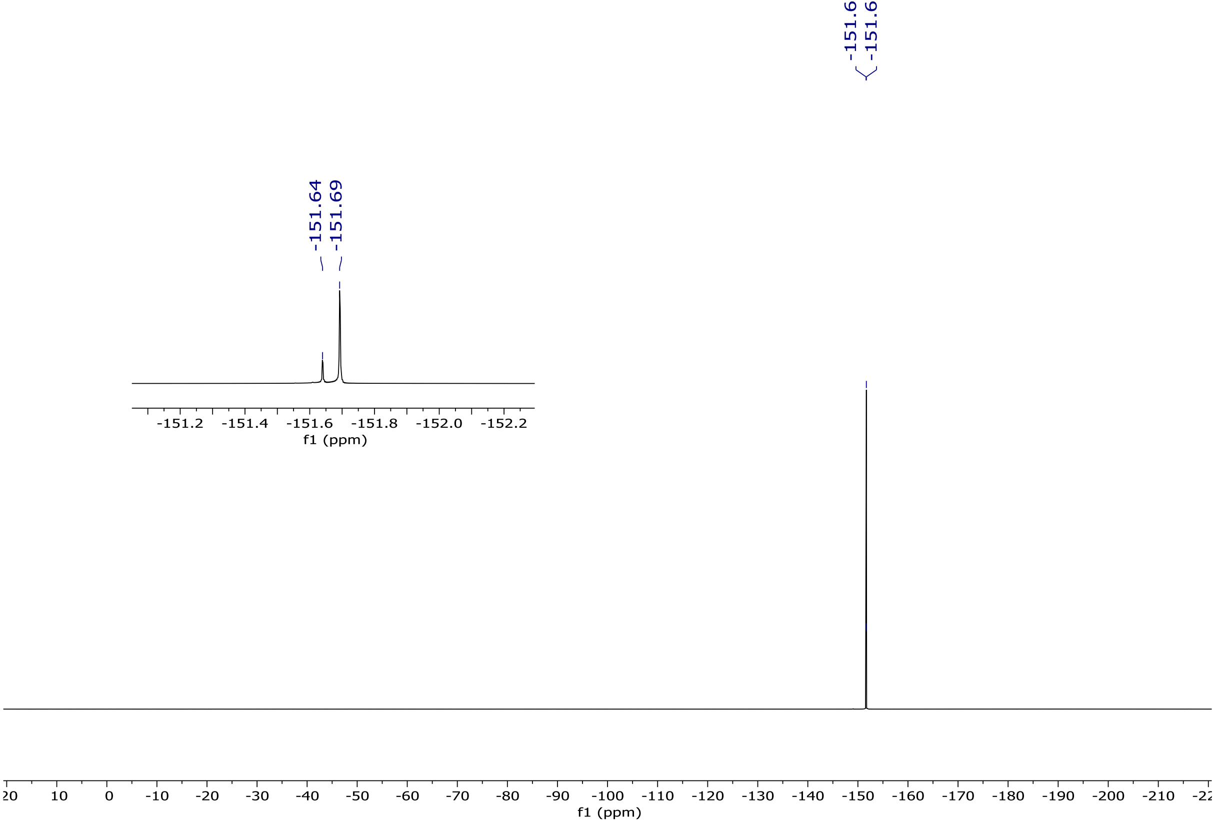

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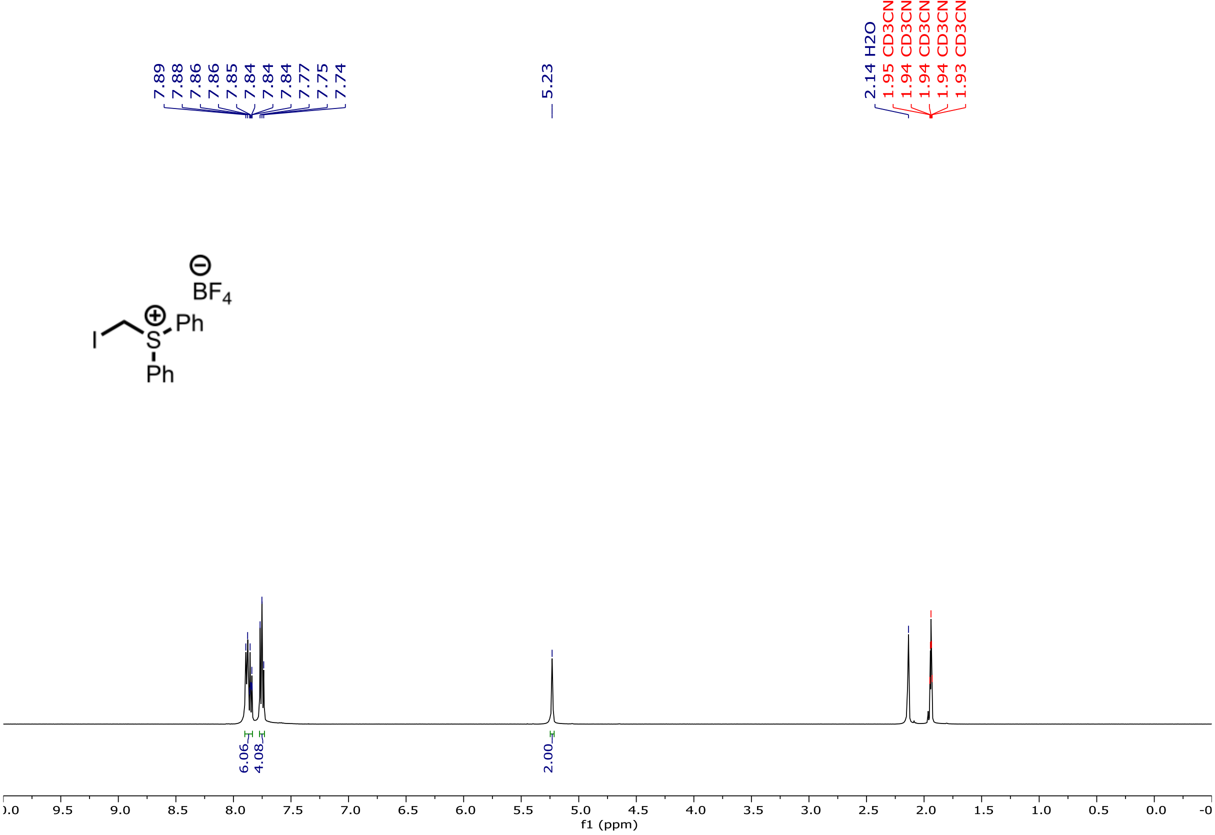

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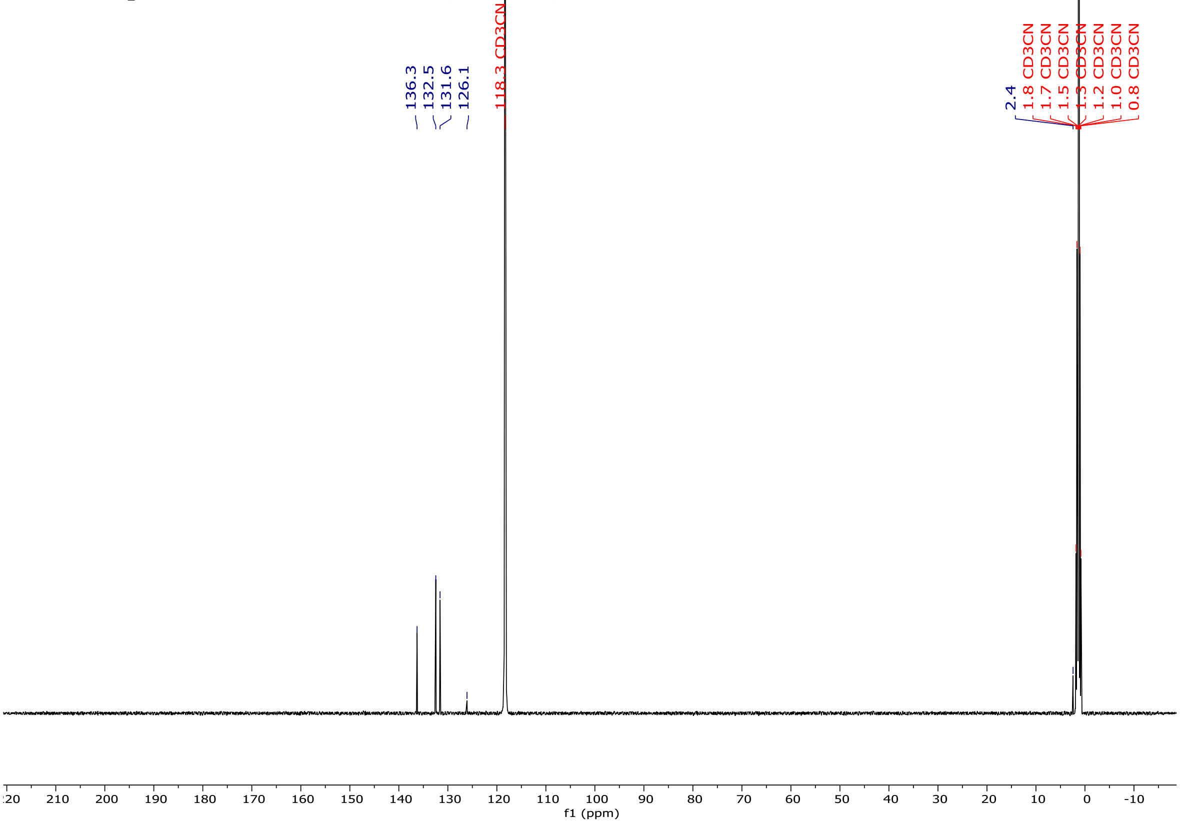

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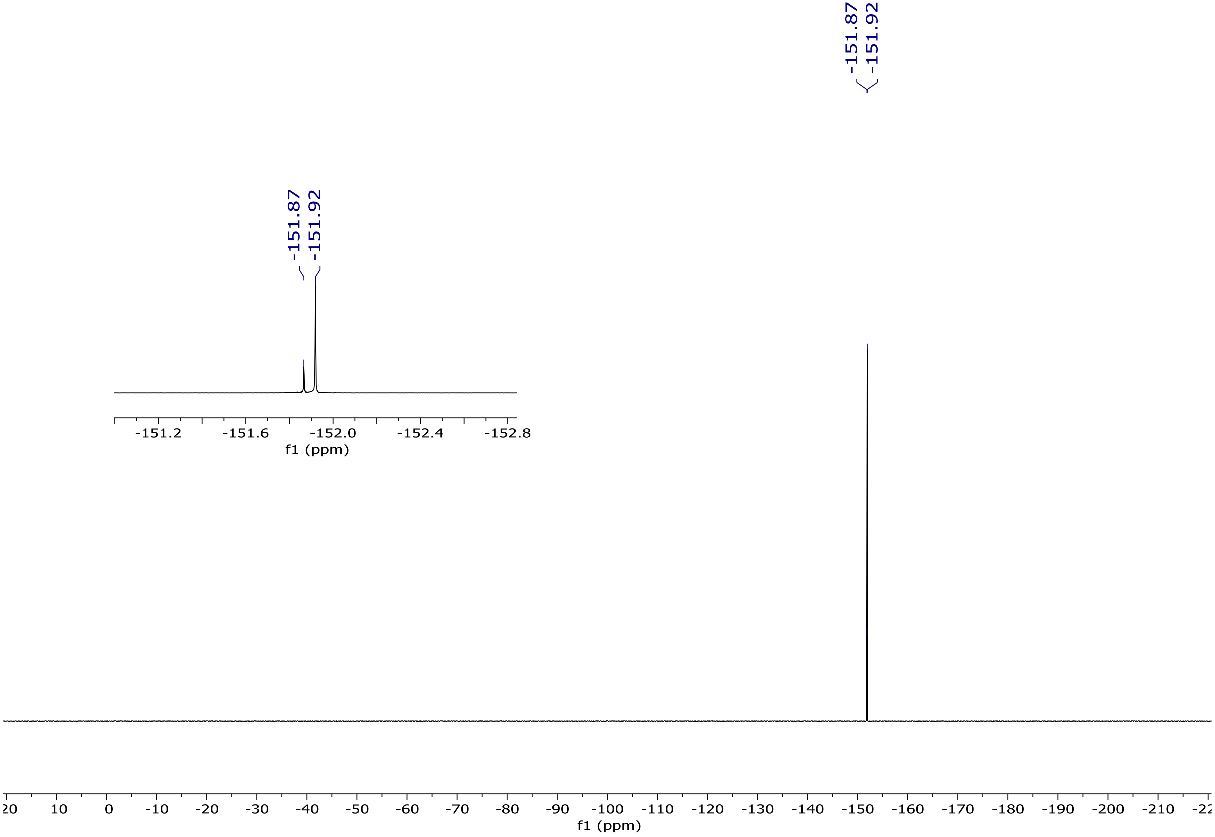

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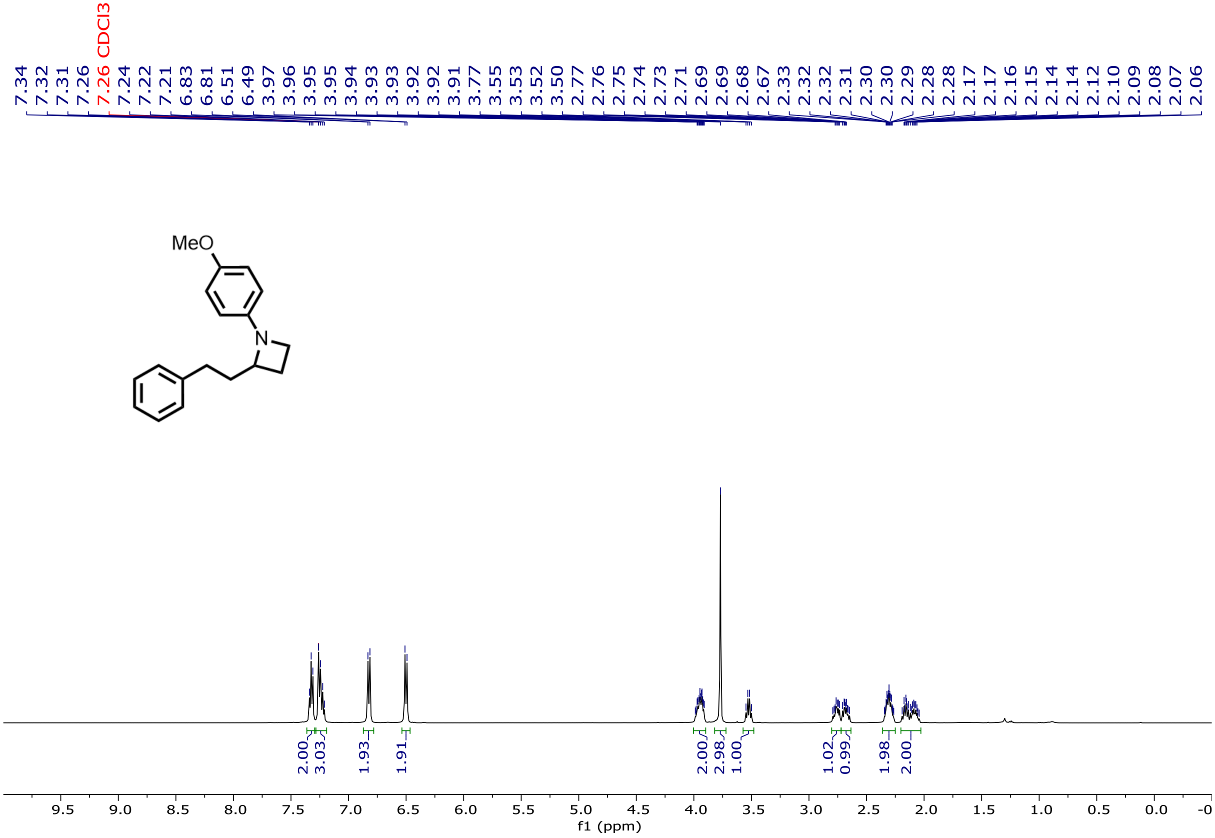

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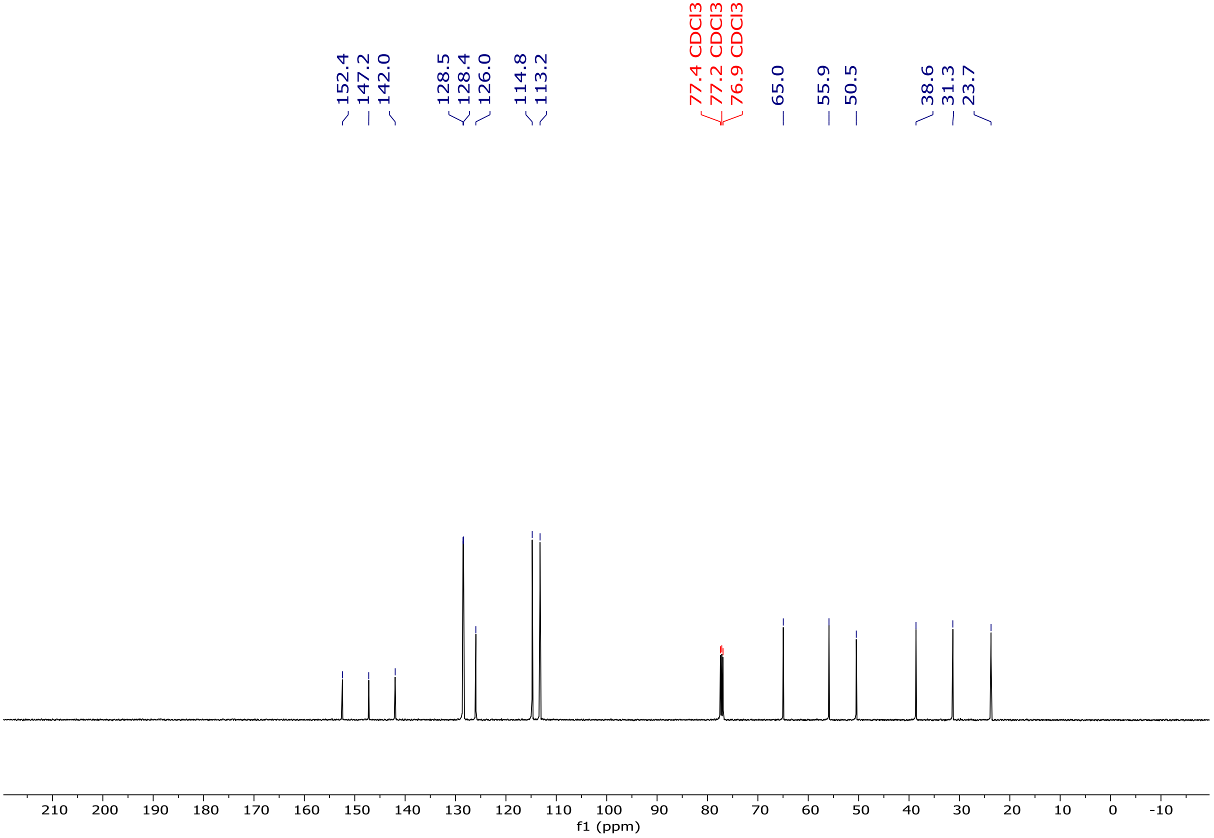

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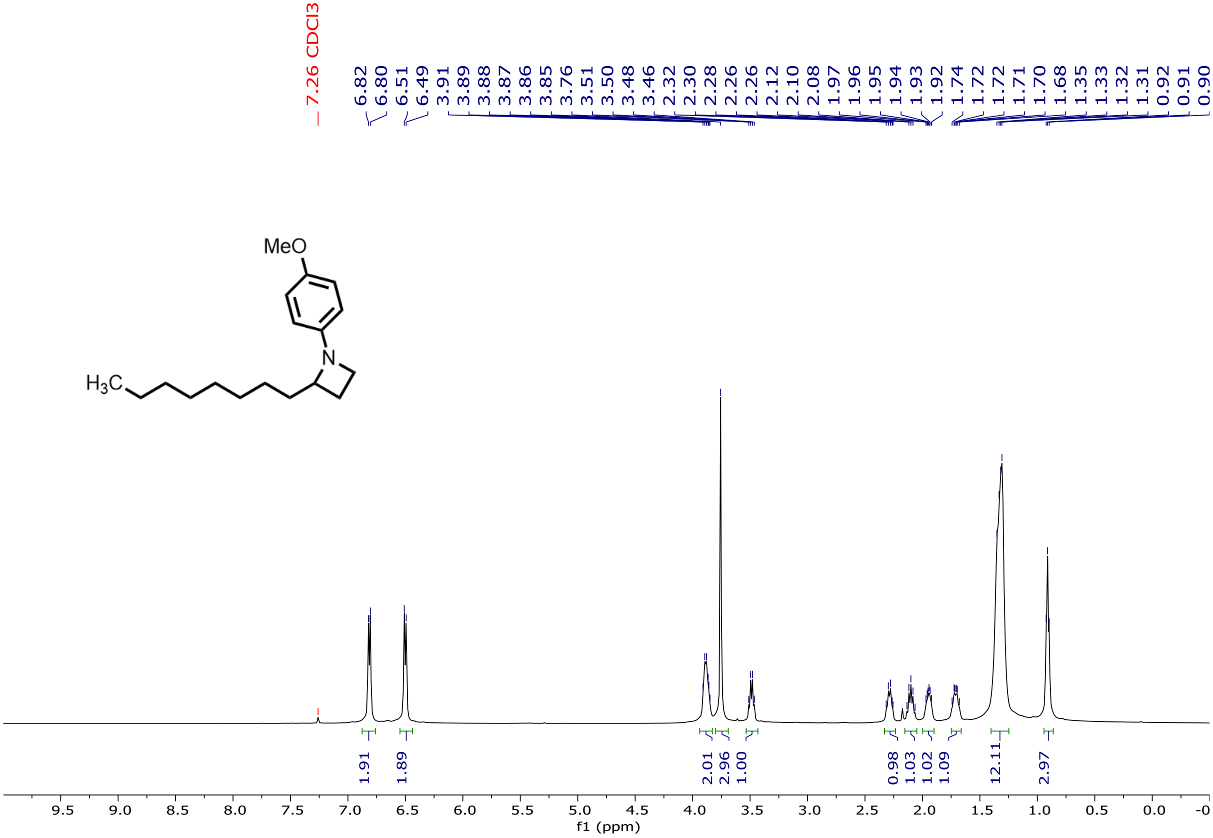

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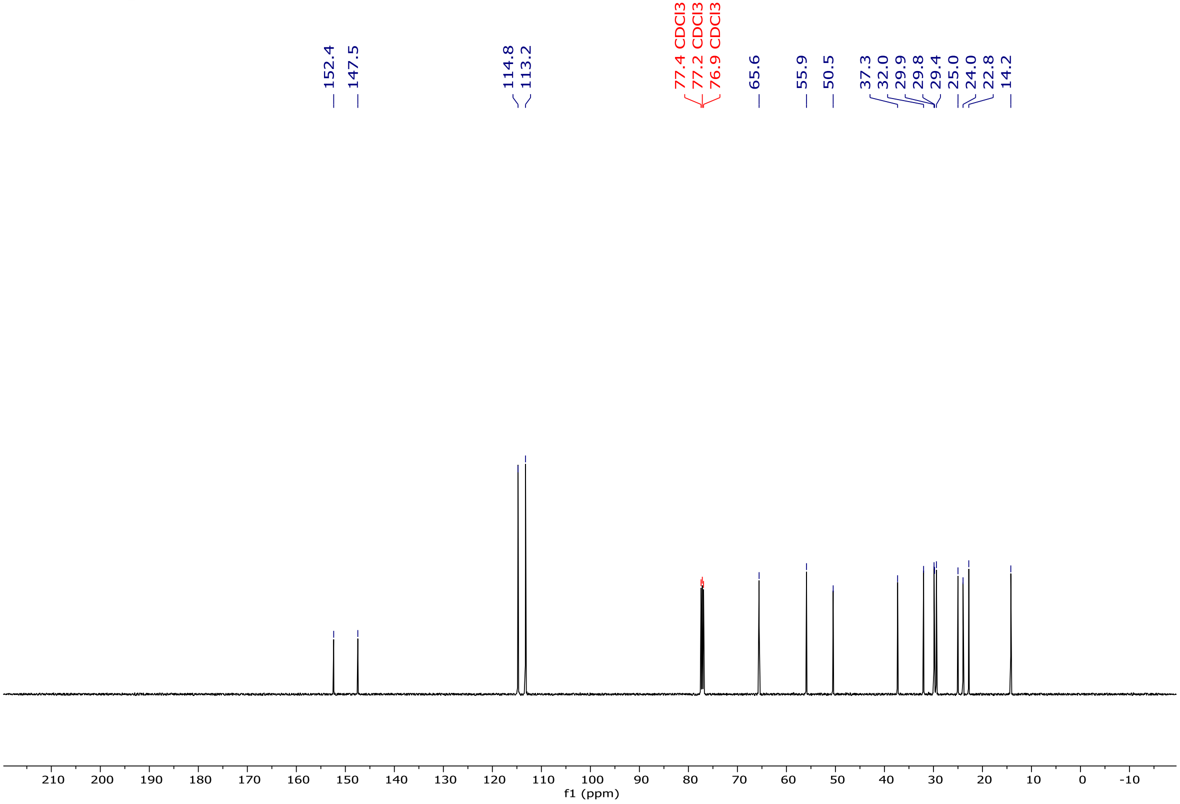

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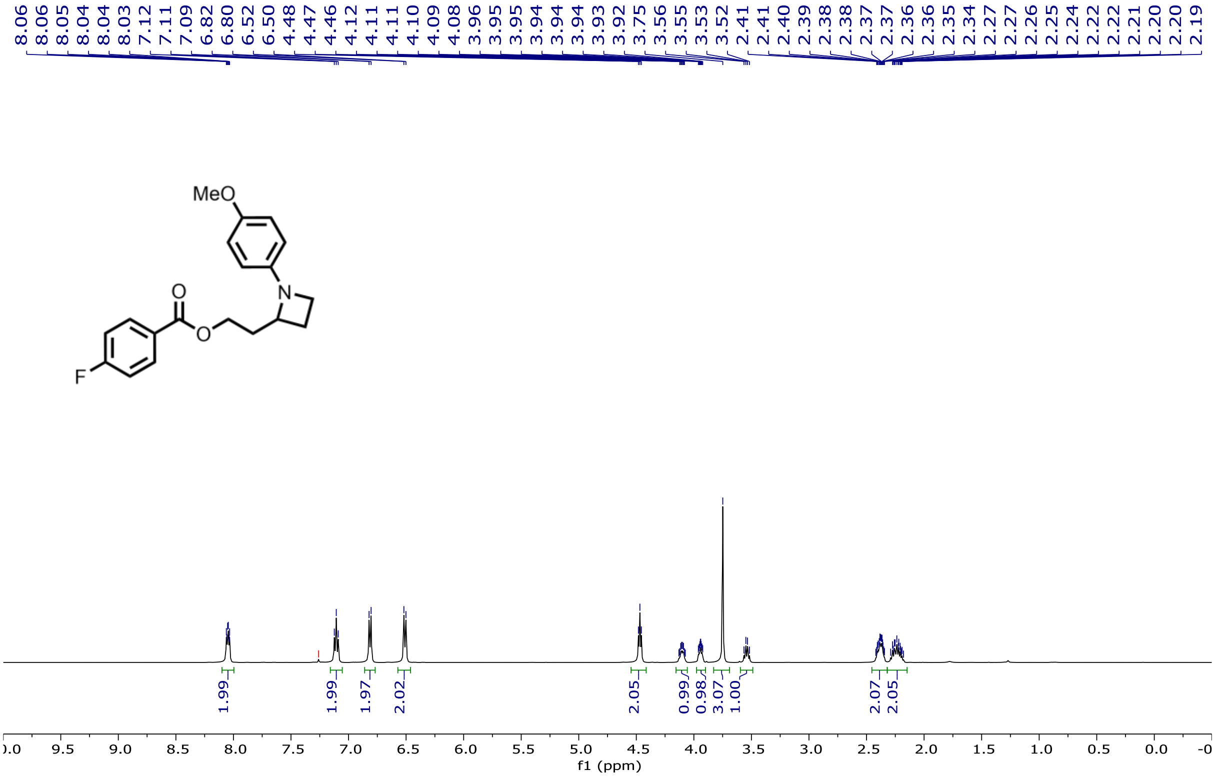

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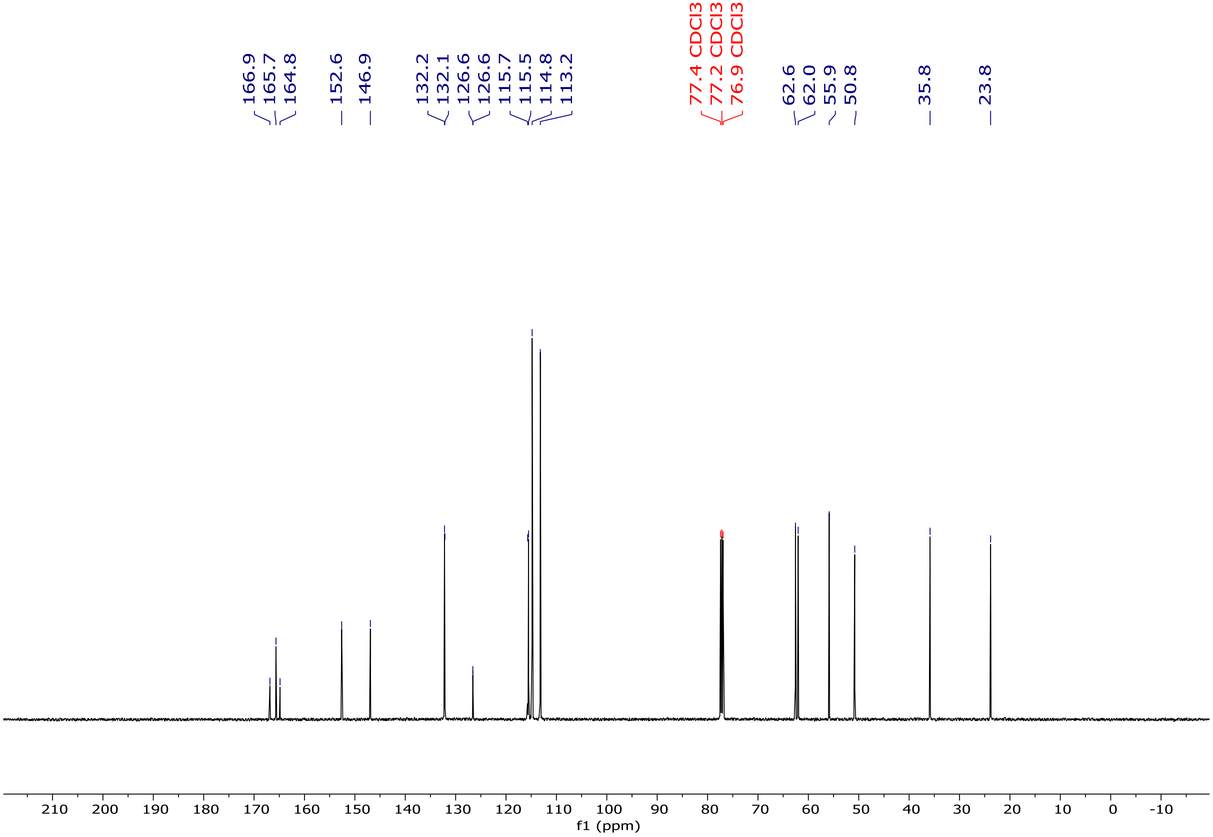

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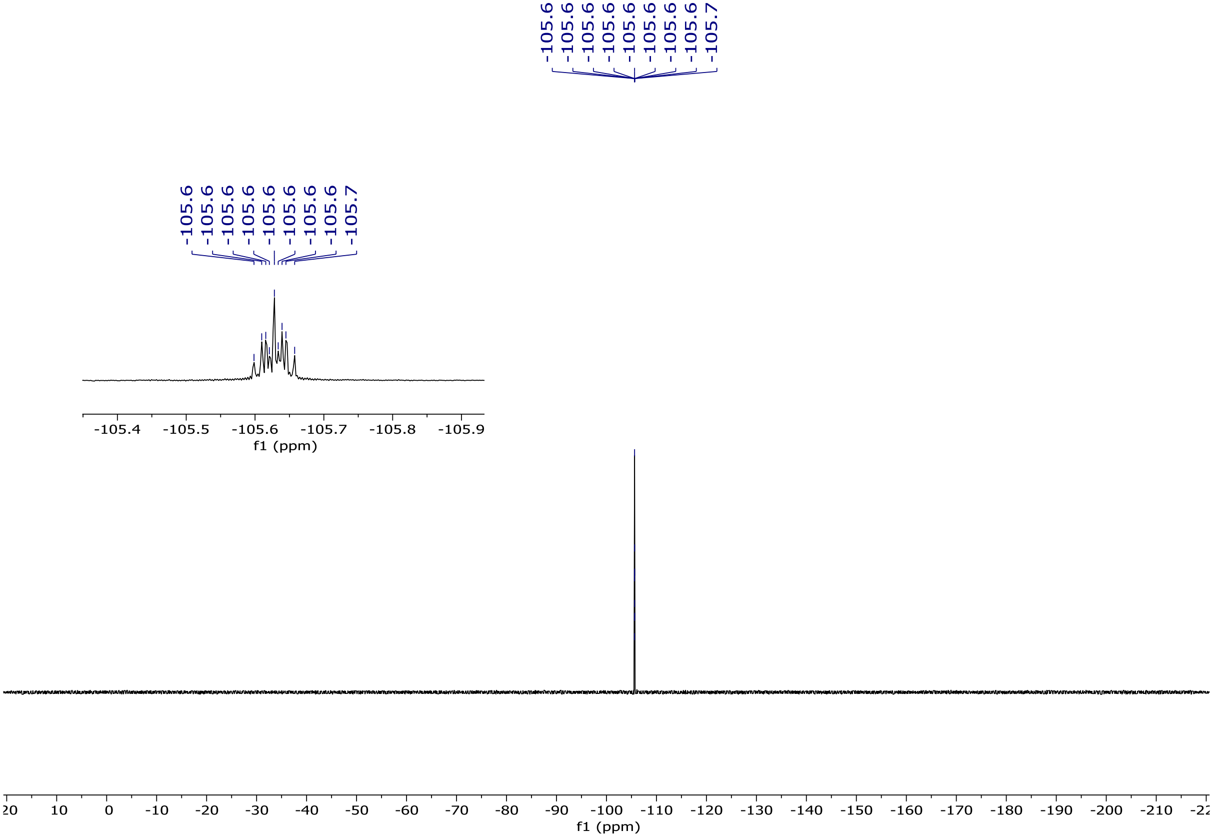

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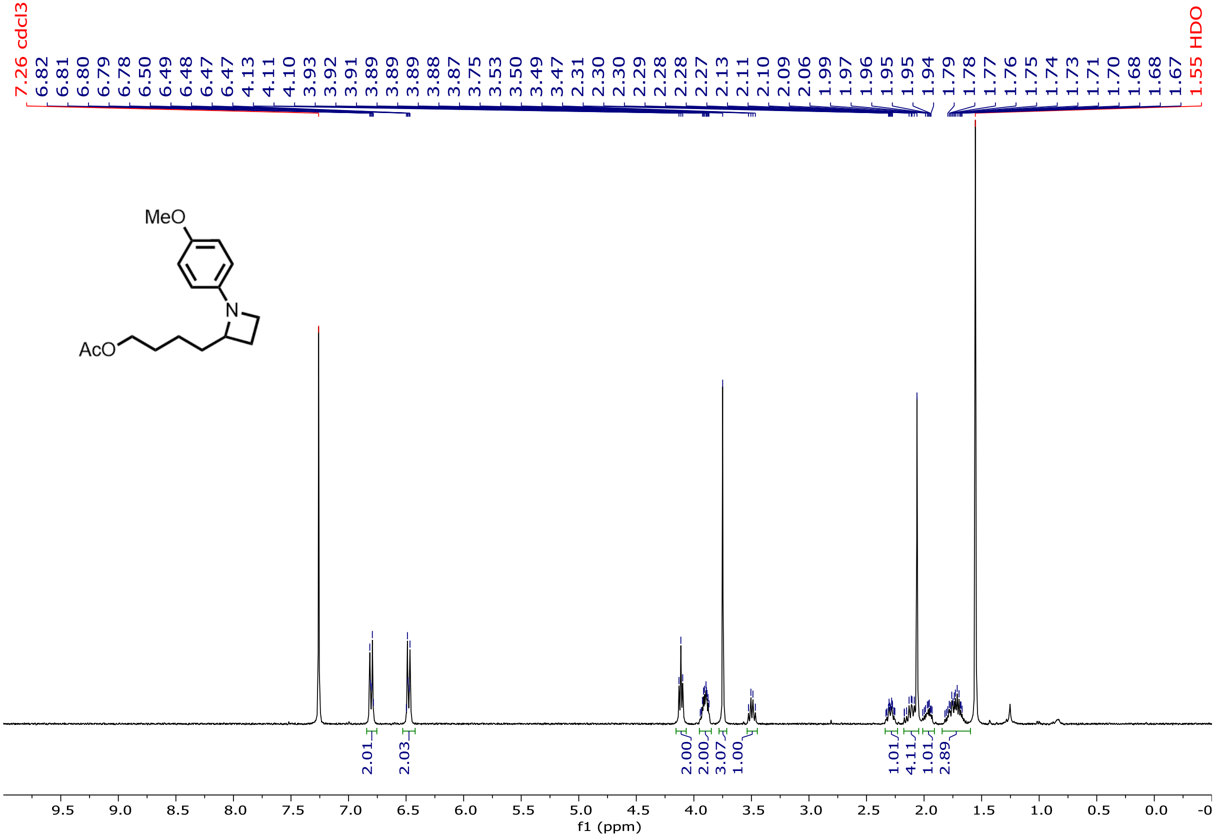

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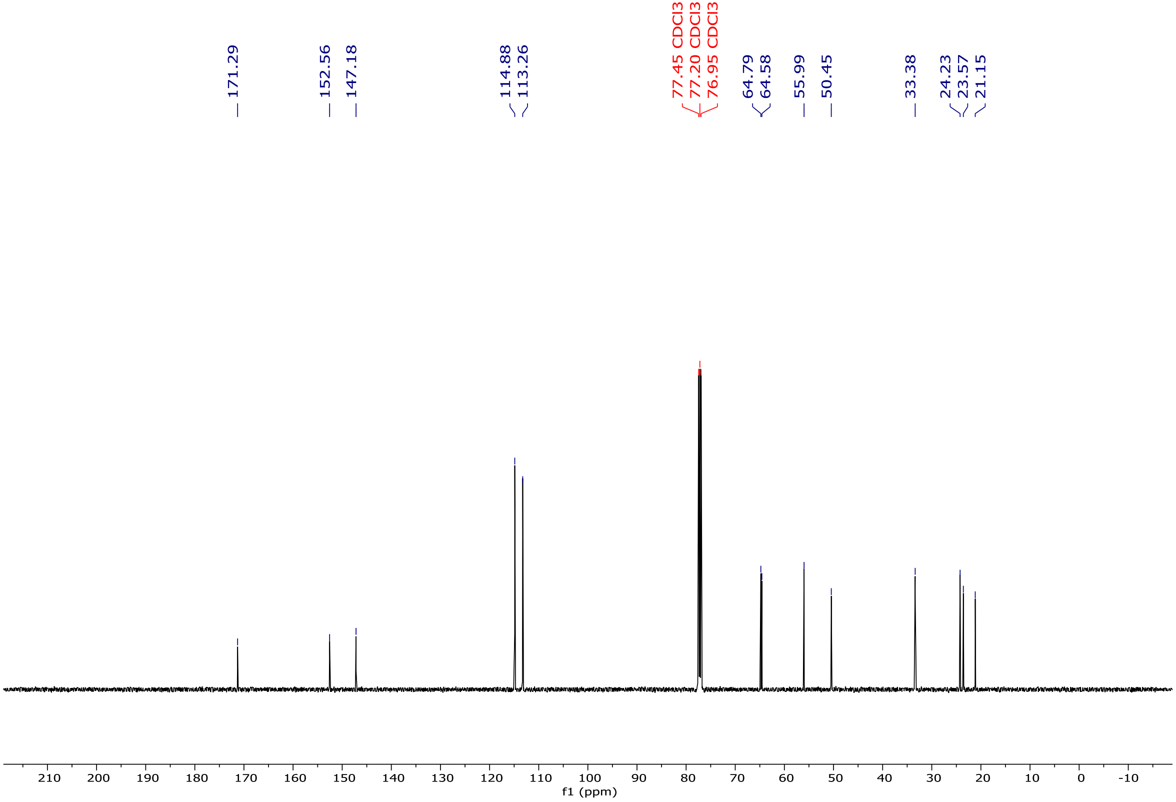

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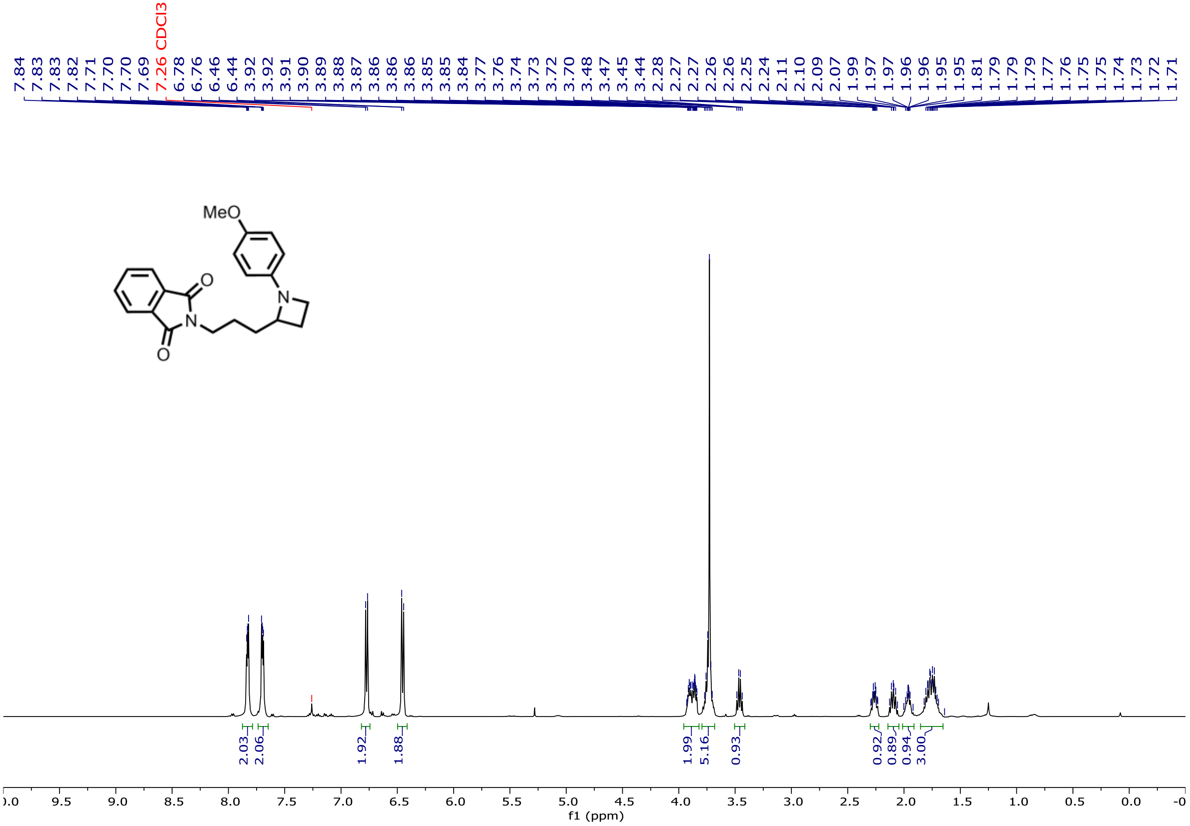

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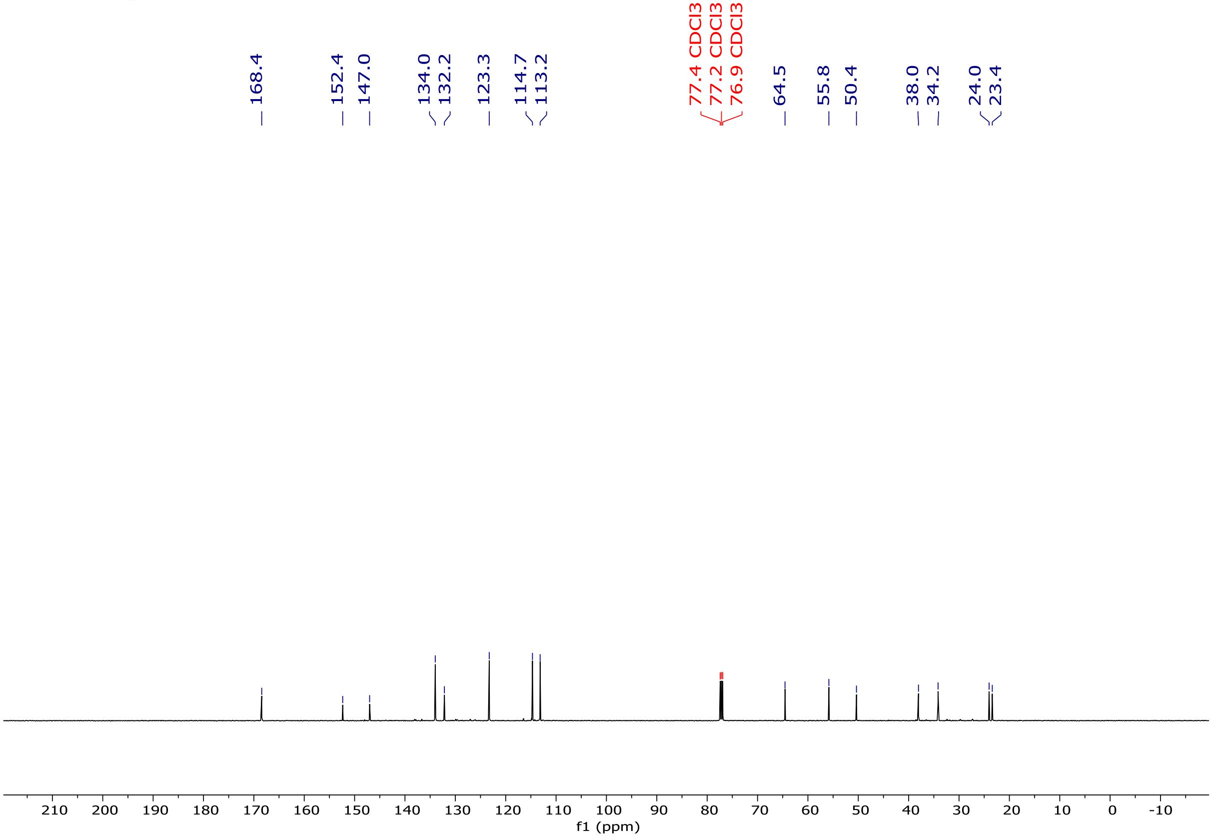

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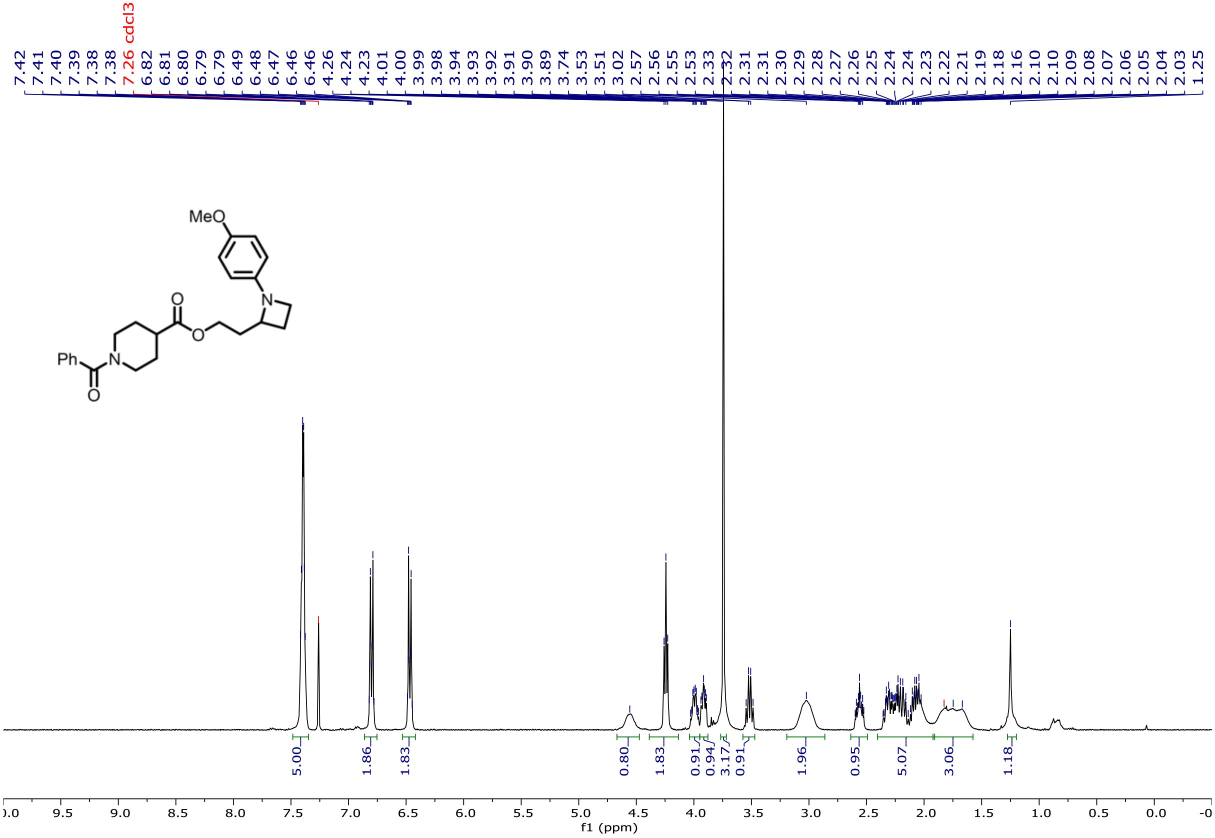

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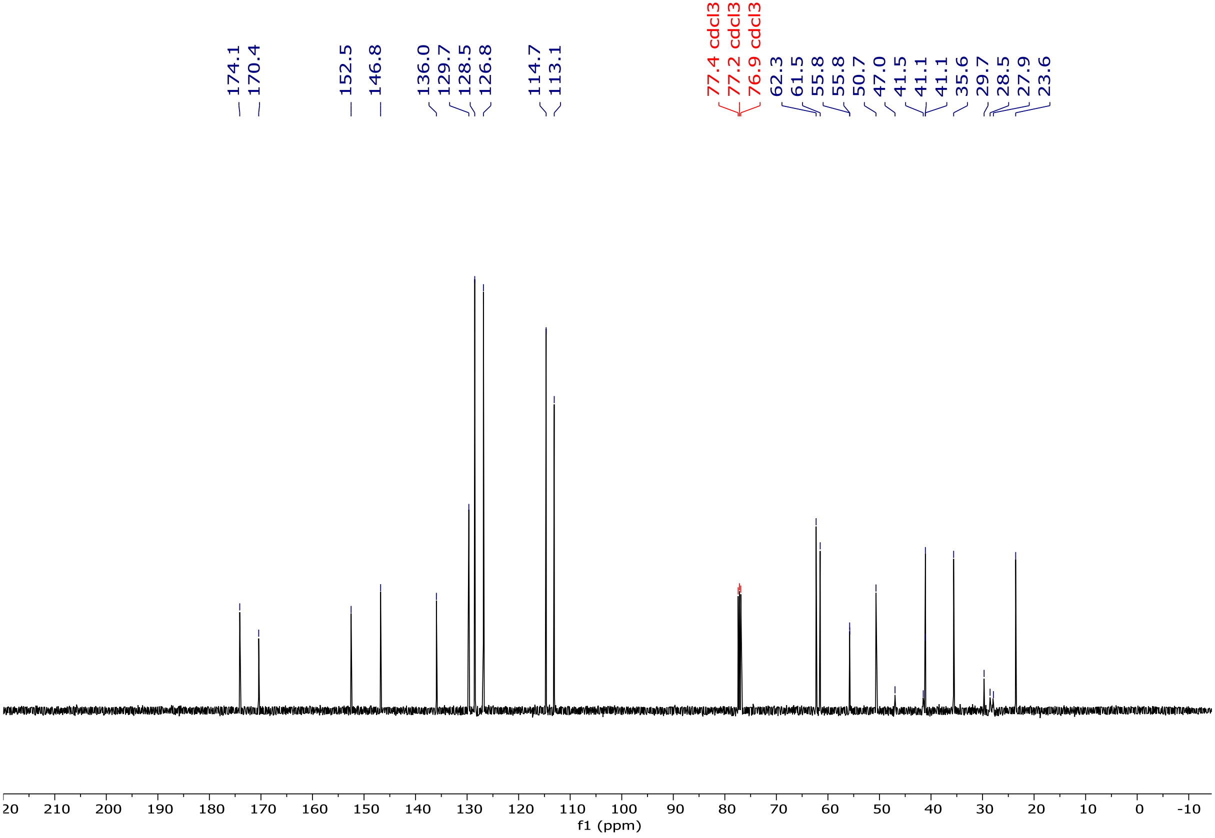

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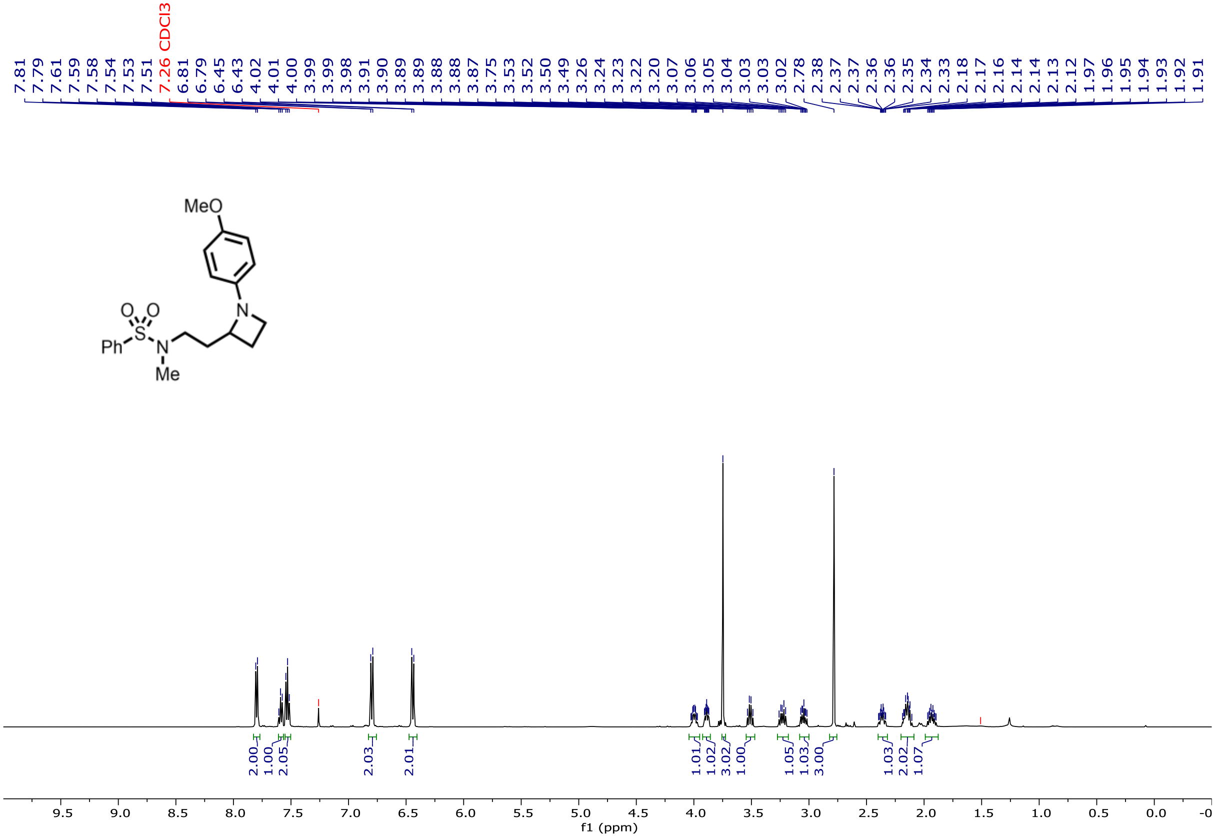

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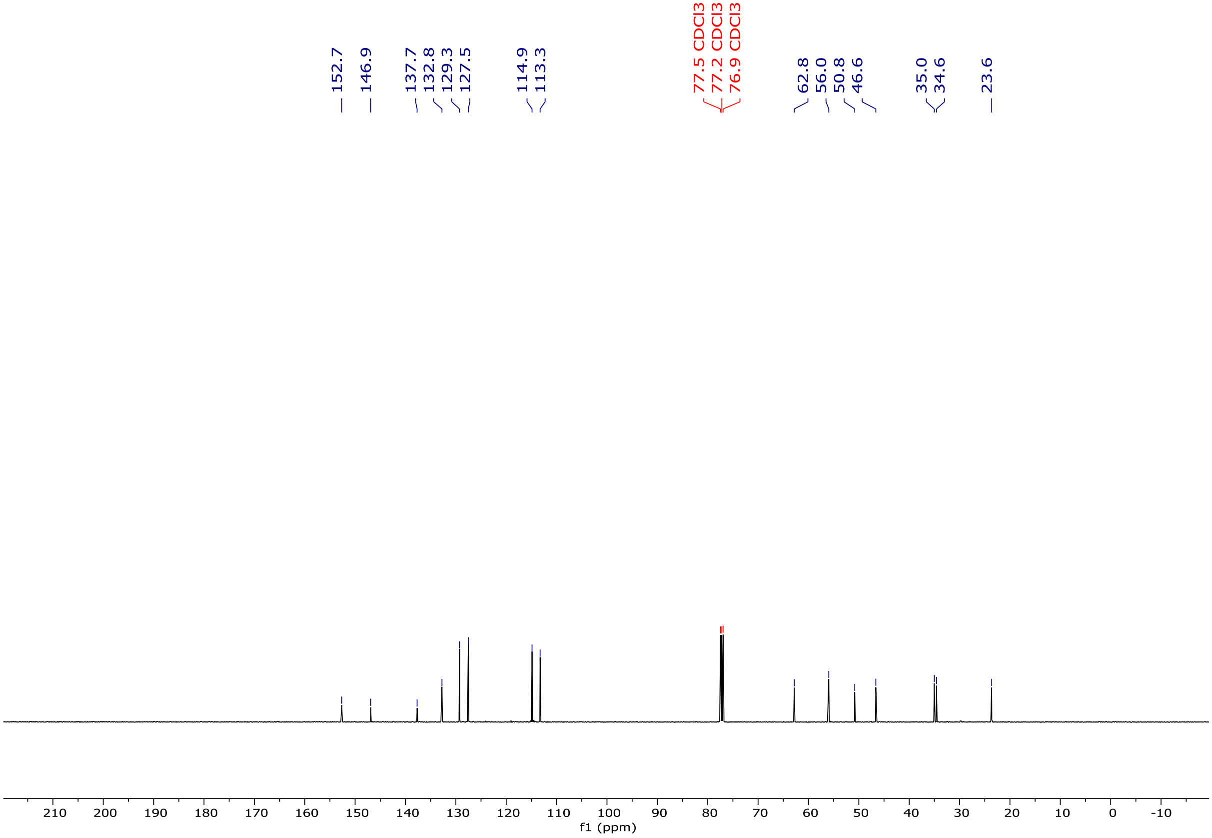

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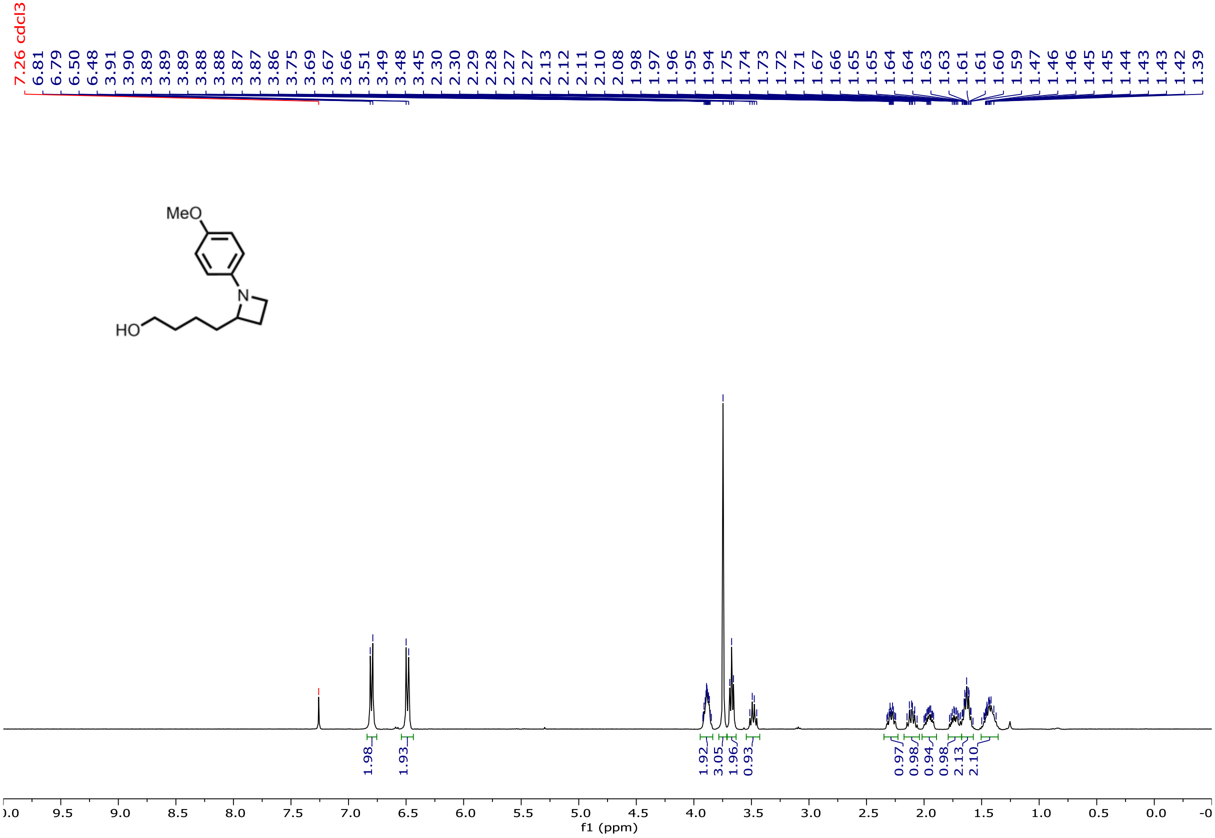

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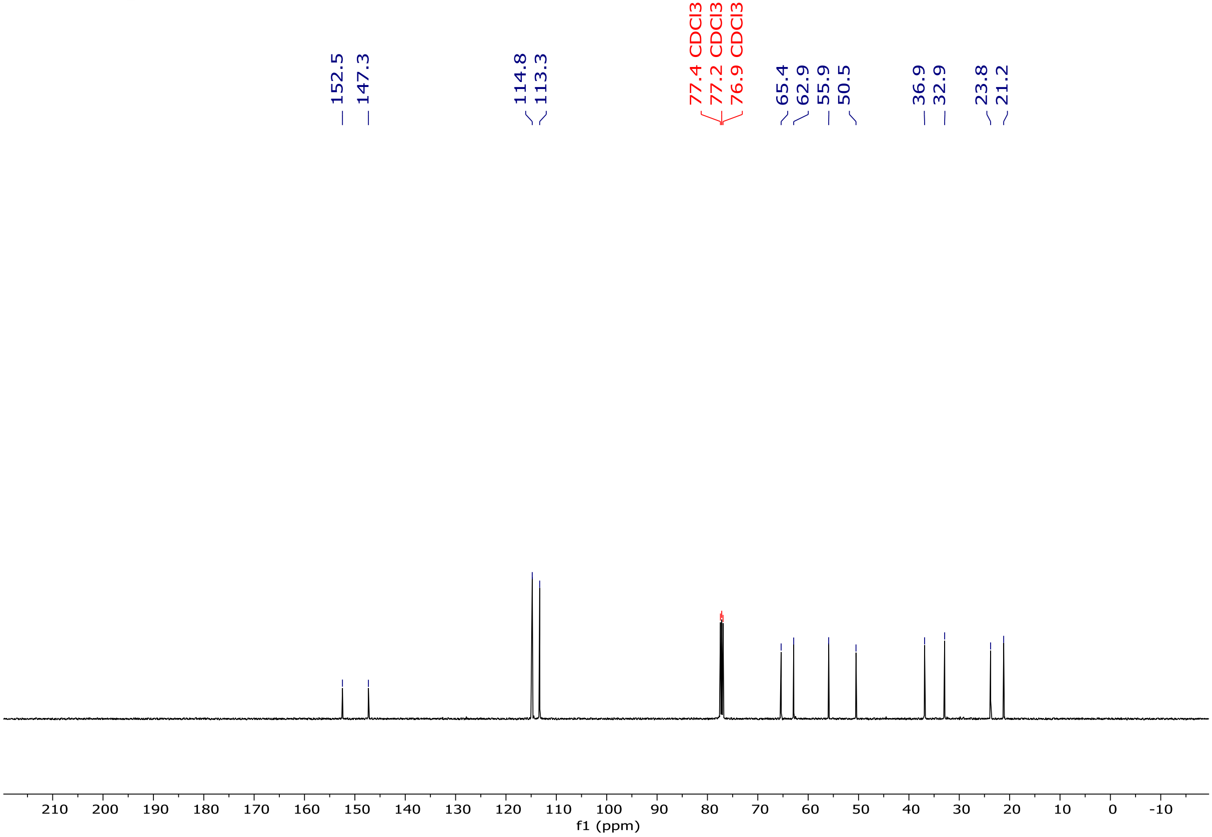
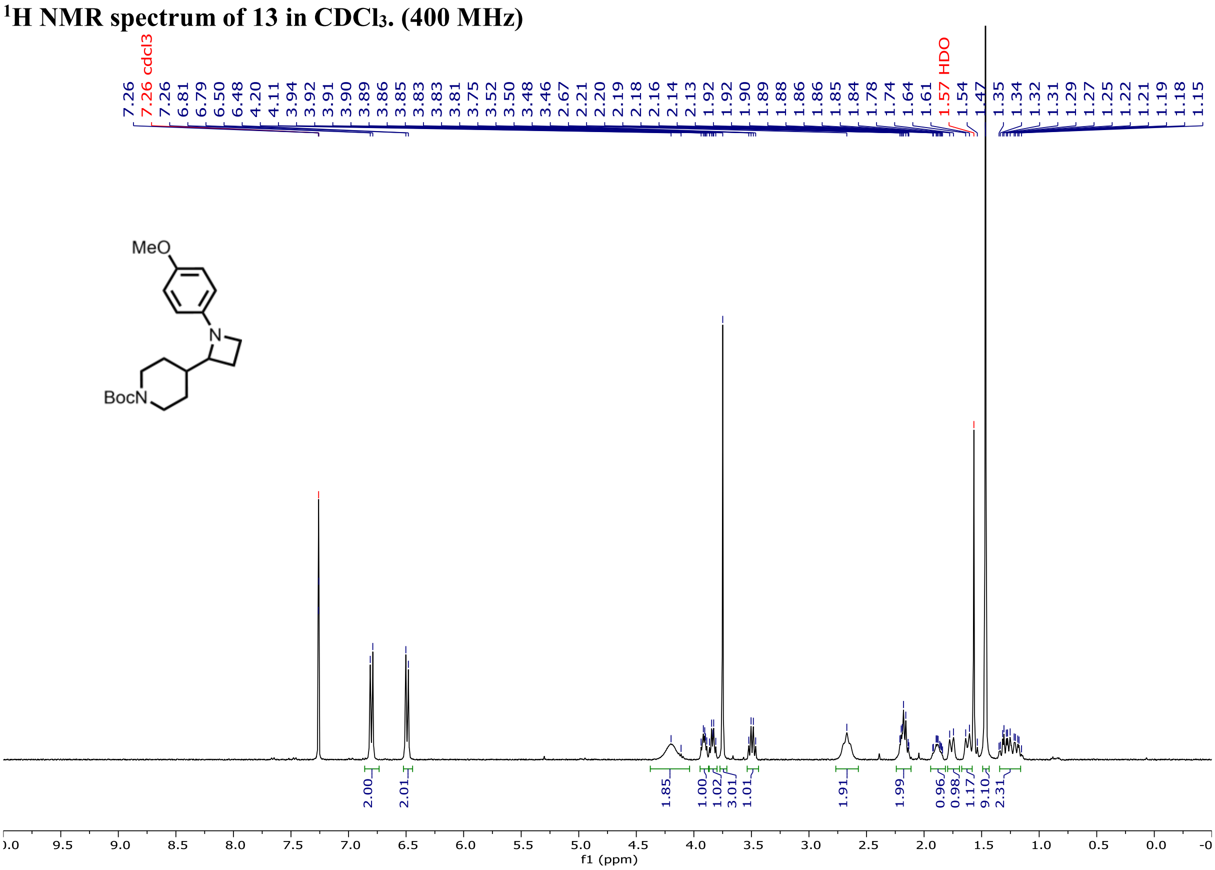
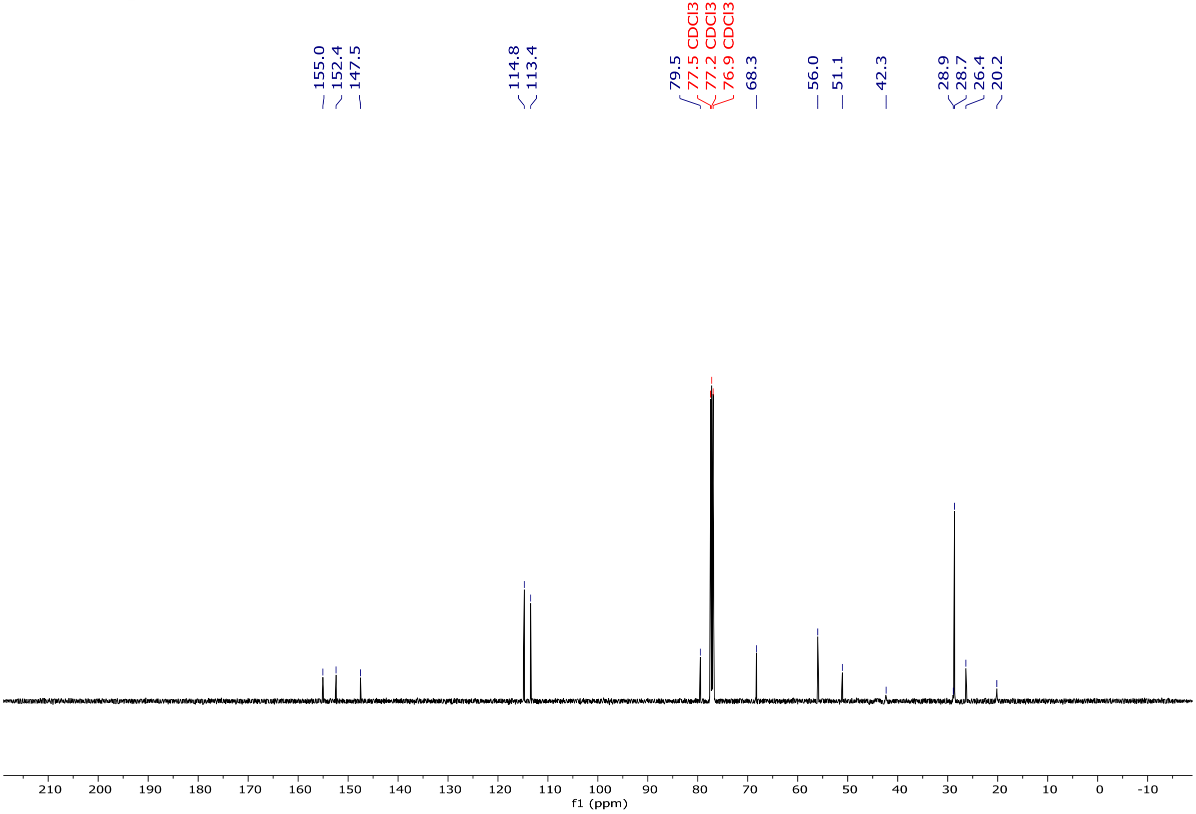


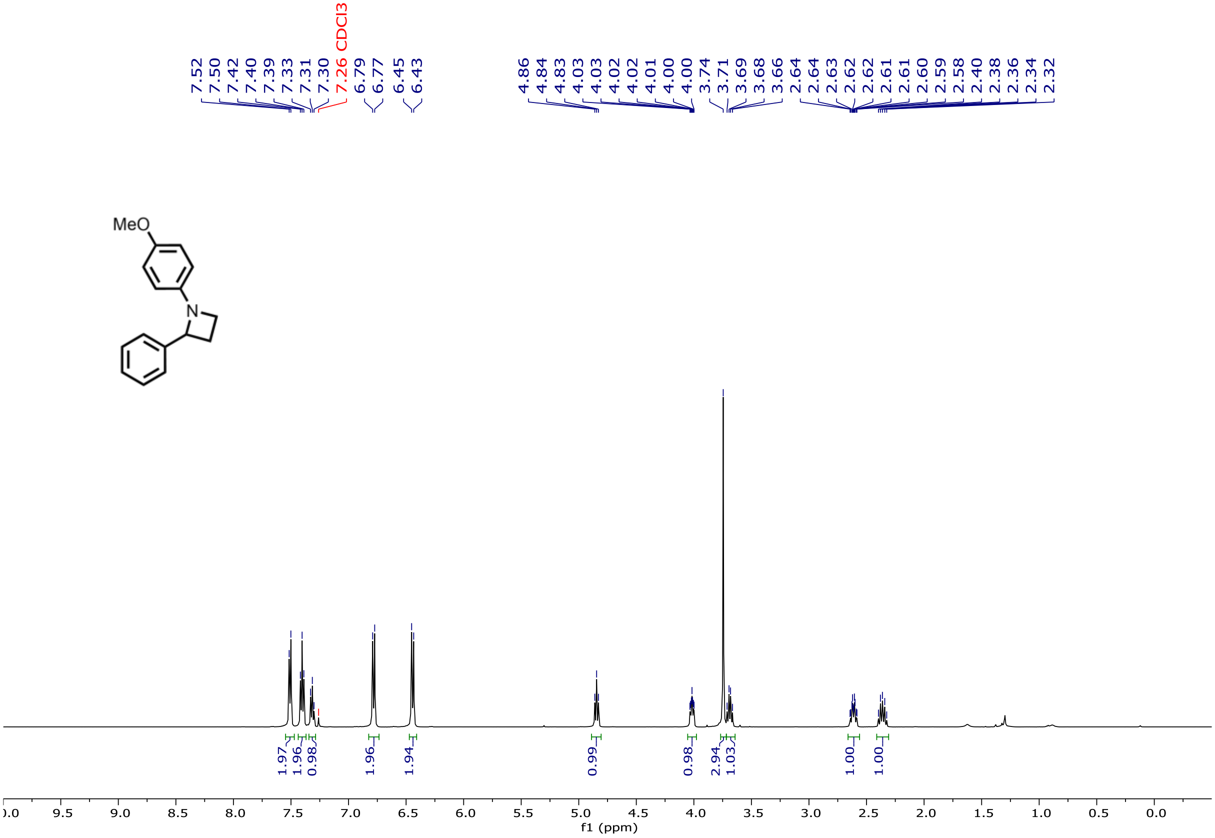
## $^{1}$H NMR spectrum of 13 in CDCl$_3$. (400 MHz)



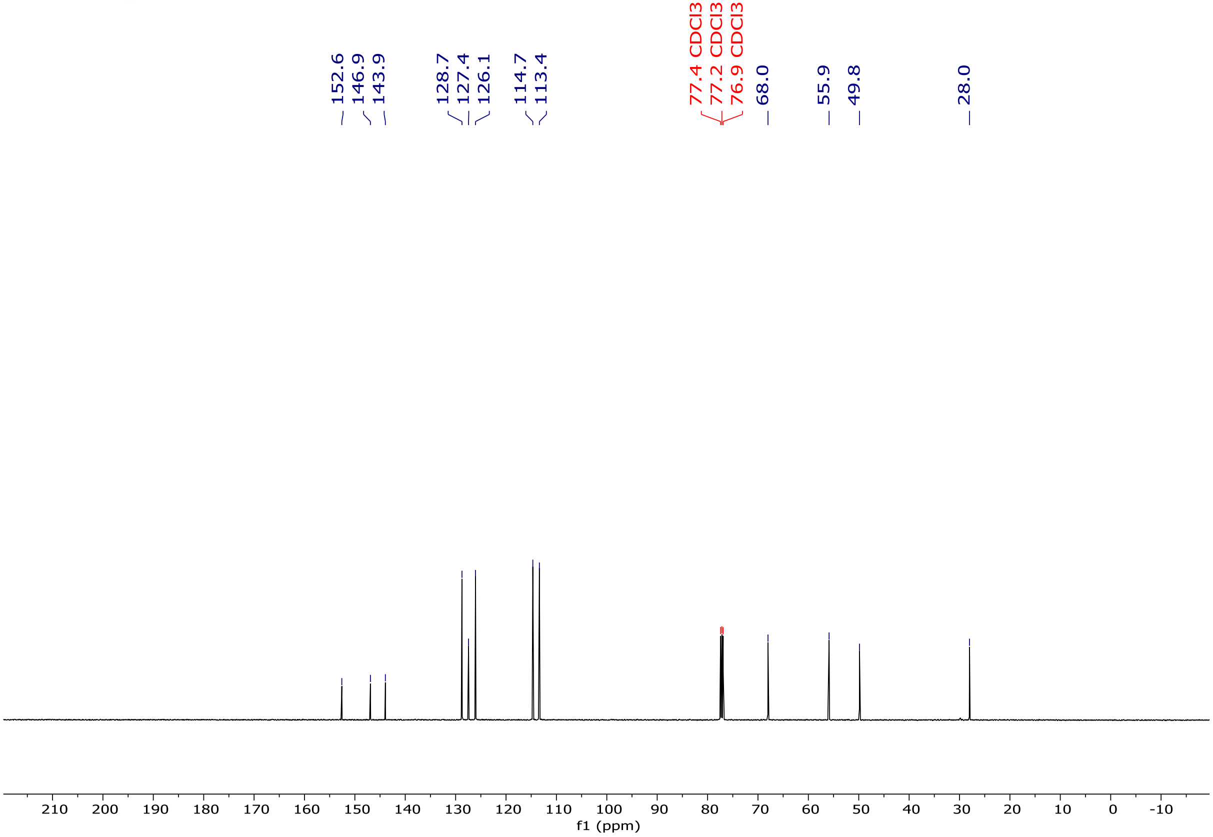
## $^{13}$C NMR spectrum of 13 in CDCl$_3$. (126 MHz)



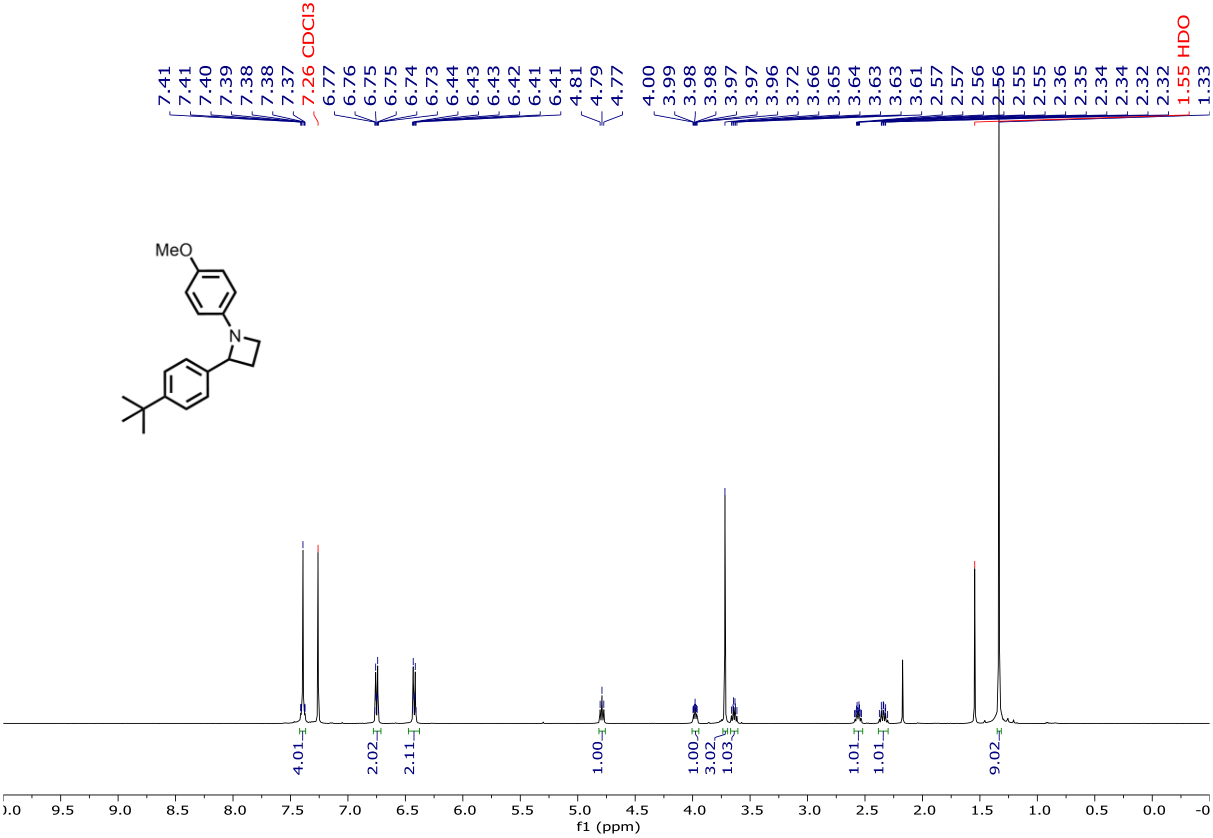
## $^1$H NMR spectrum of 14 in $CDCl_3$. (500 MHz)



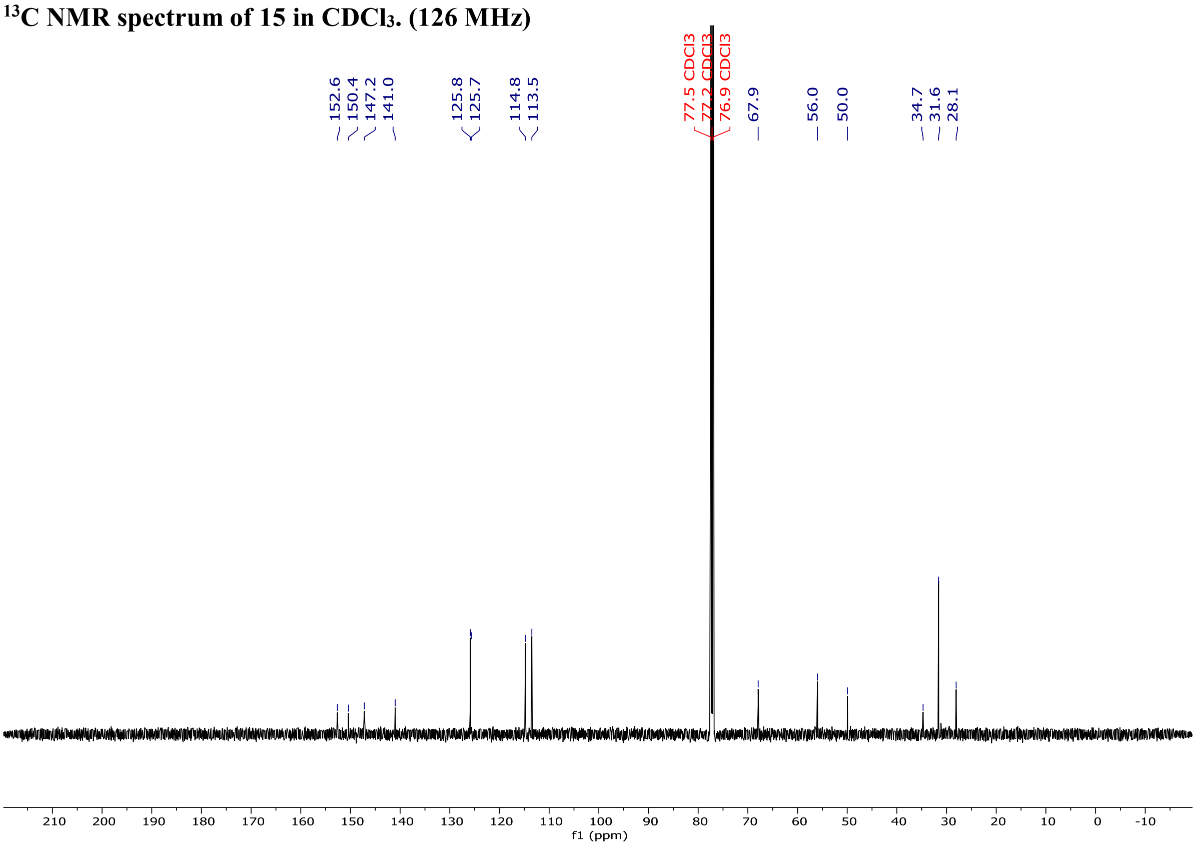
## $^{13}$C NMR spectrum of 14 in $CDCl_3$. (126 MHz)



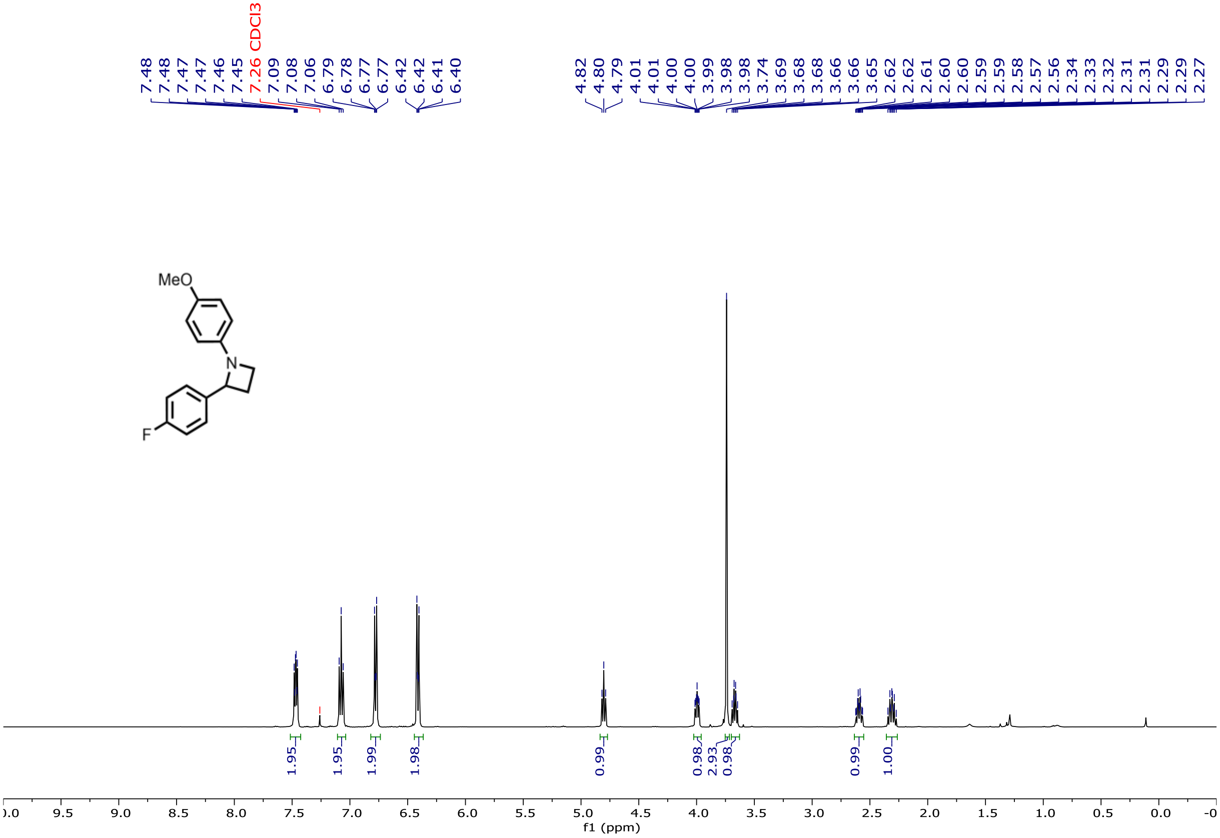
## $^1$H NMR spectrum of 15 in $CDCl_3$. (500 MHz)



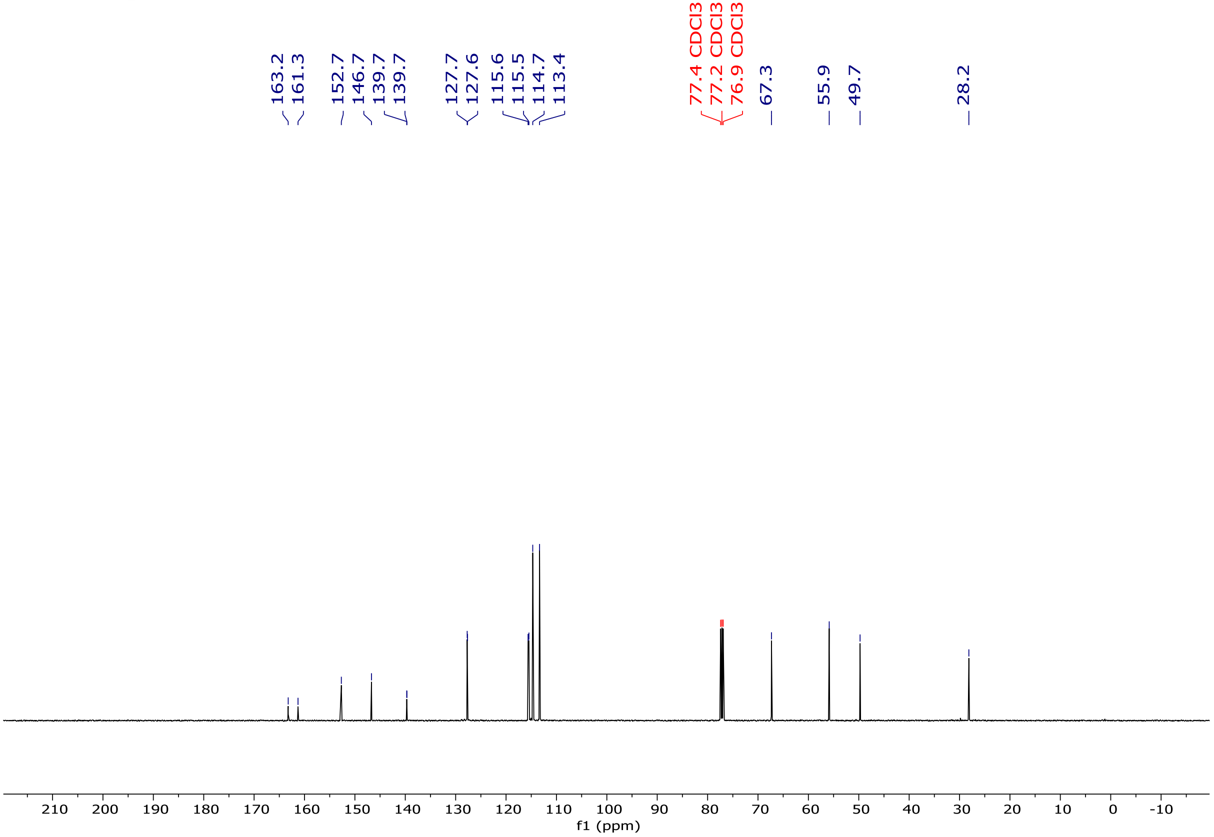
## $^{13}$C NMR spectrum of 15 in $CDCl_3$. (126 MHz)



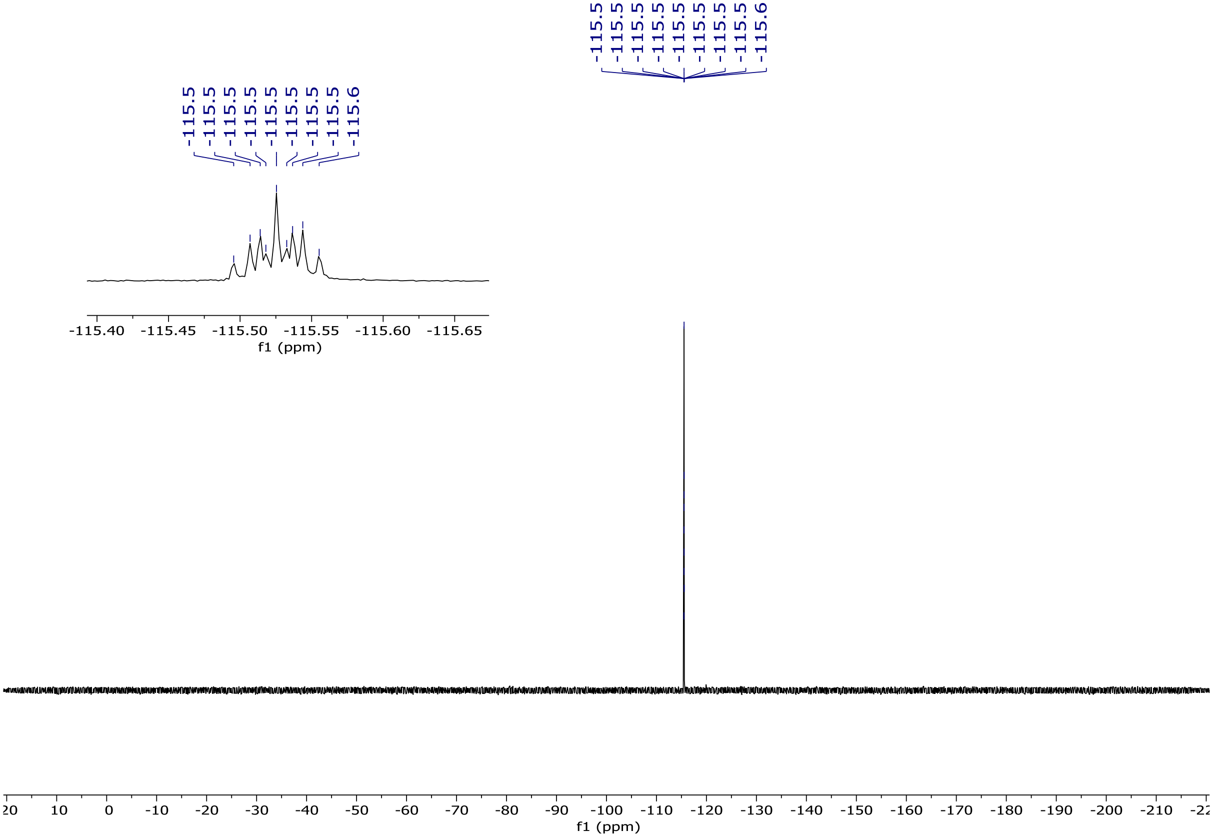
## $^{1}$H NMR spectrum of 16 in $CDCl_3$. (500 MHz)



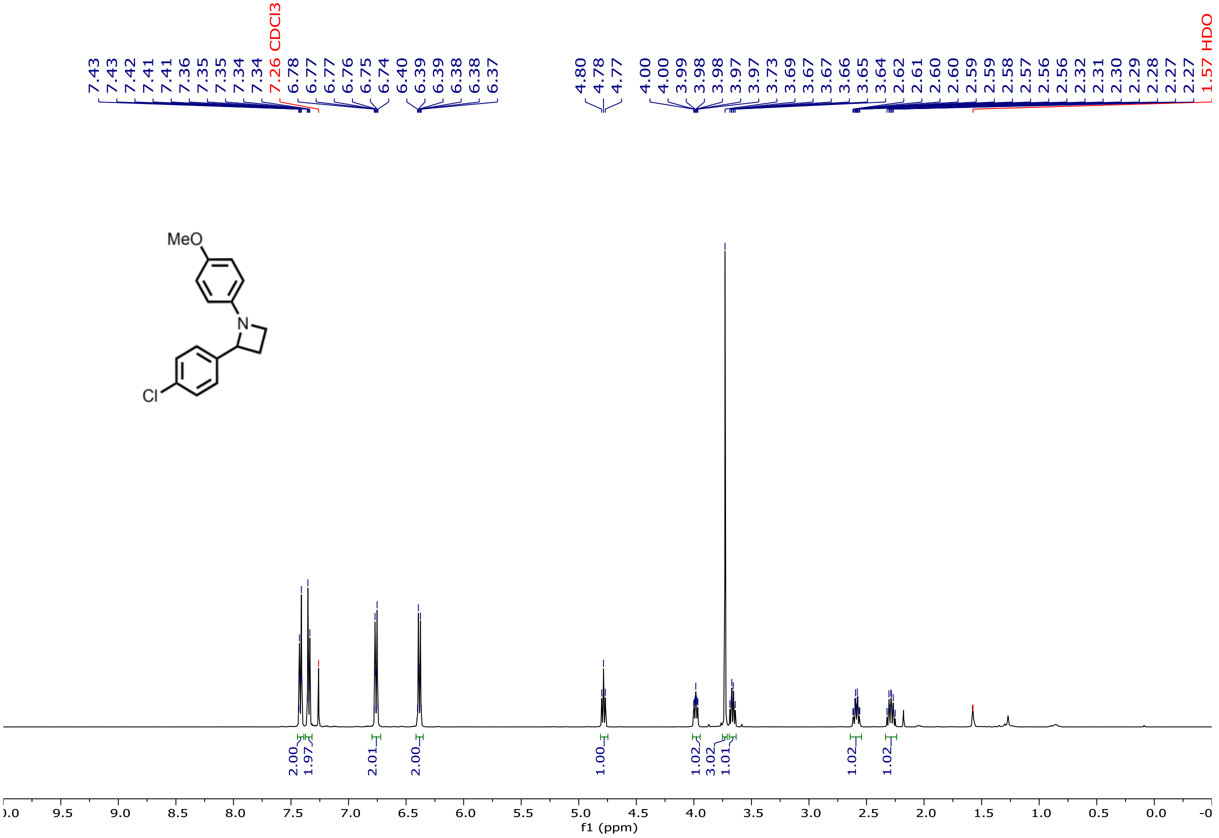
## $^{13}$C NMR spectrum of 16 in $CDCl_3$. (126 MHz)



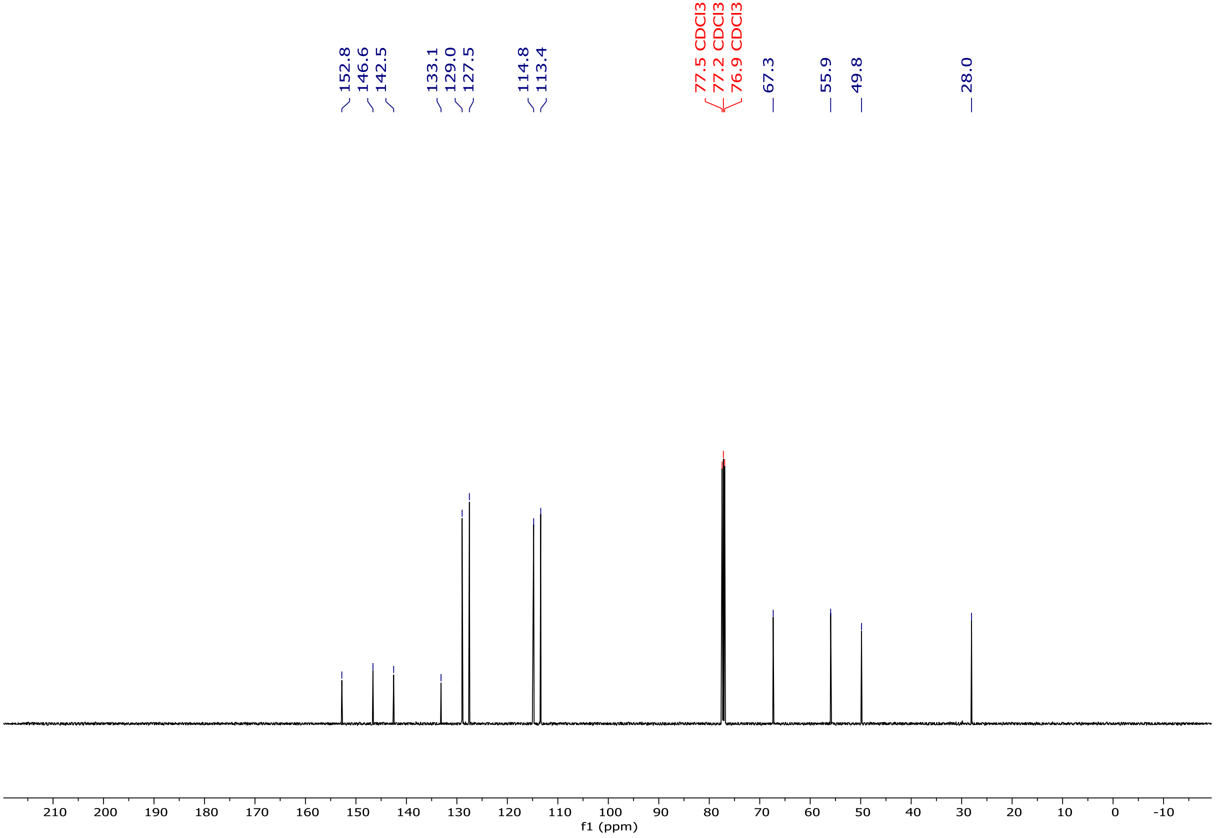
$^{19}$**F NMR spectrum of 16 in CDCl$_3$. (471 MHz)**



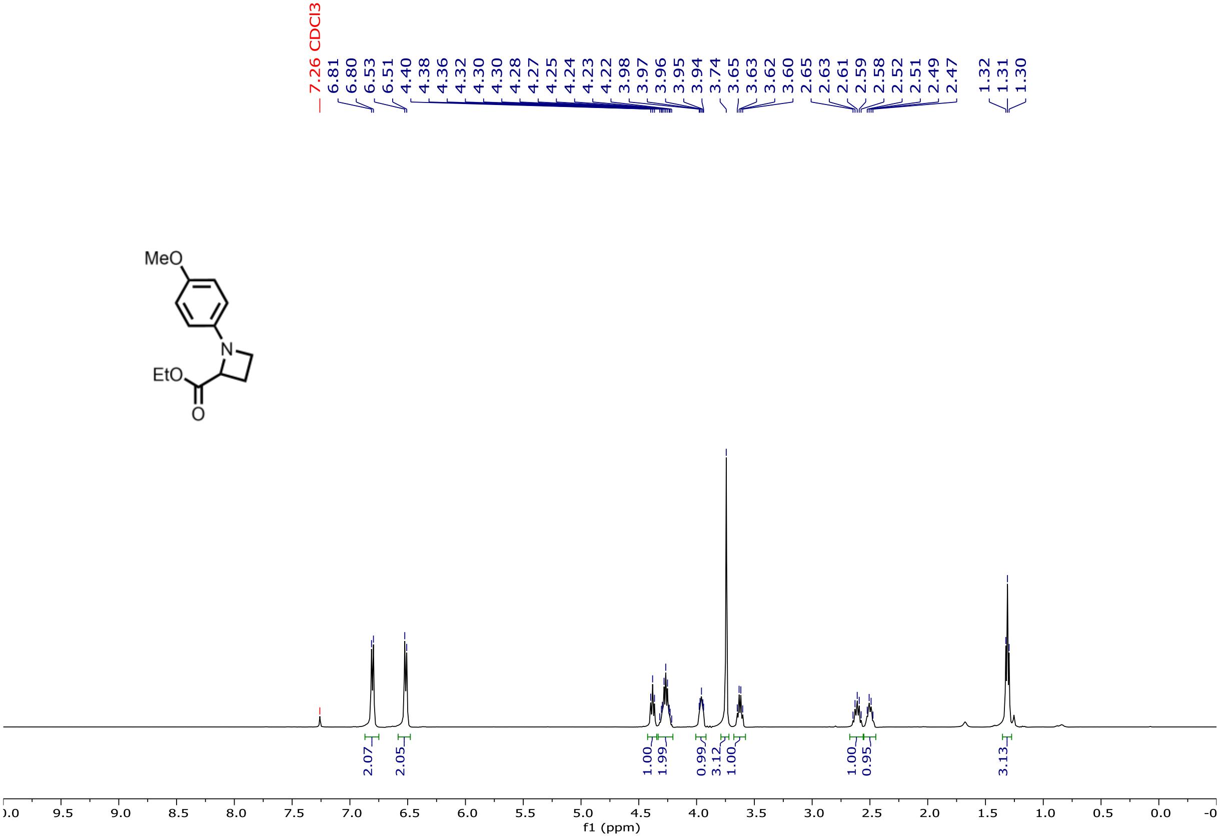
## $^{1}$H NMR spectrum of 17 in $CDCl_3$. (500 MHz)



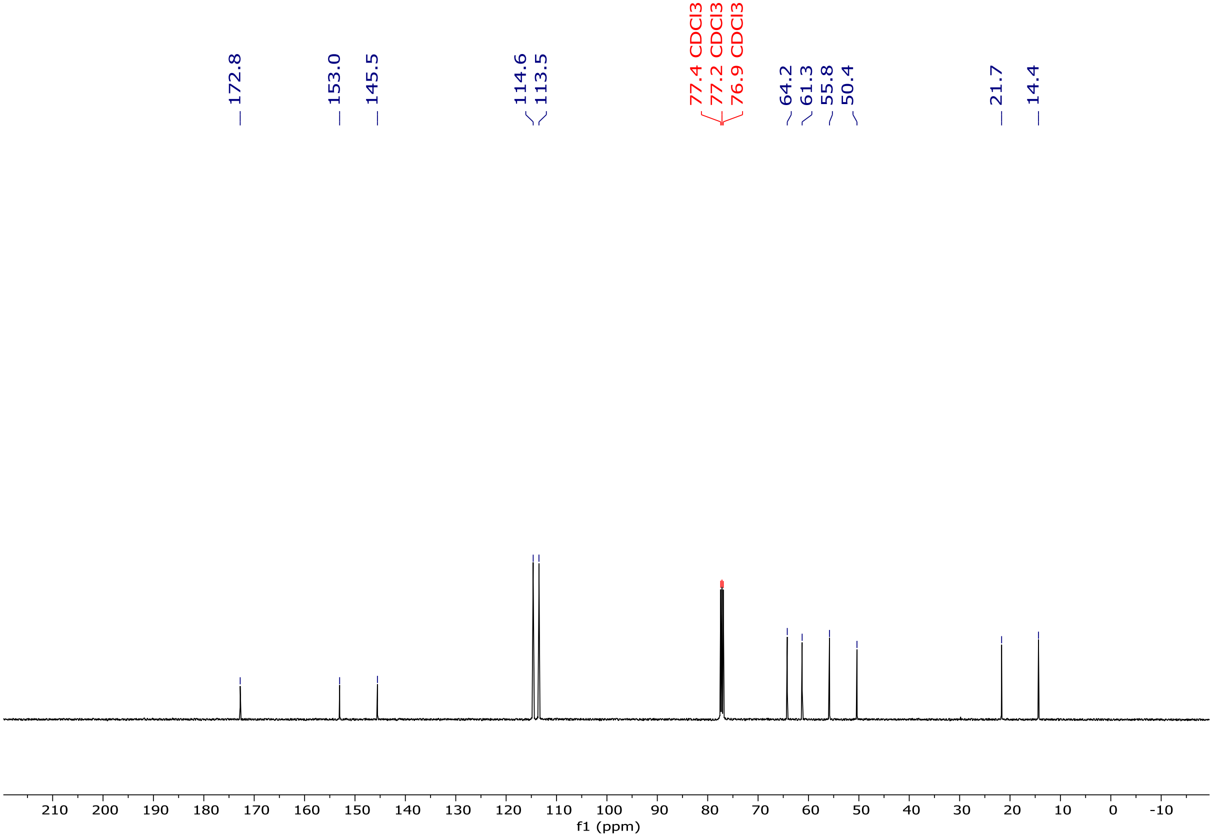
## $^{13}$C NMR spectrum of 17 in $CDCl_3$. (126 MHz)



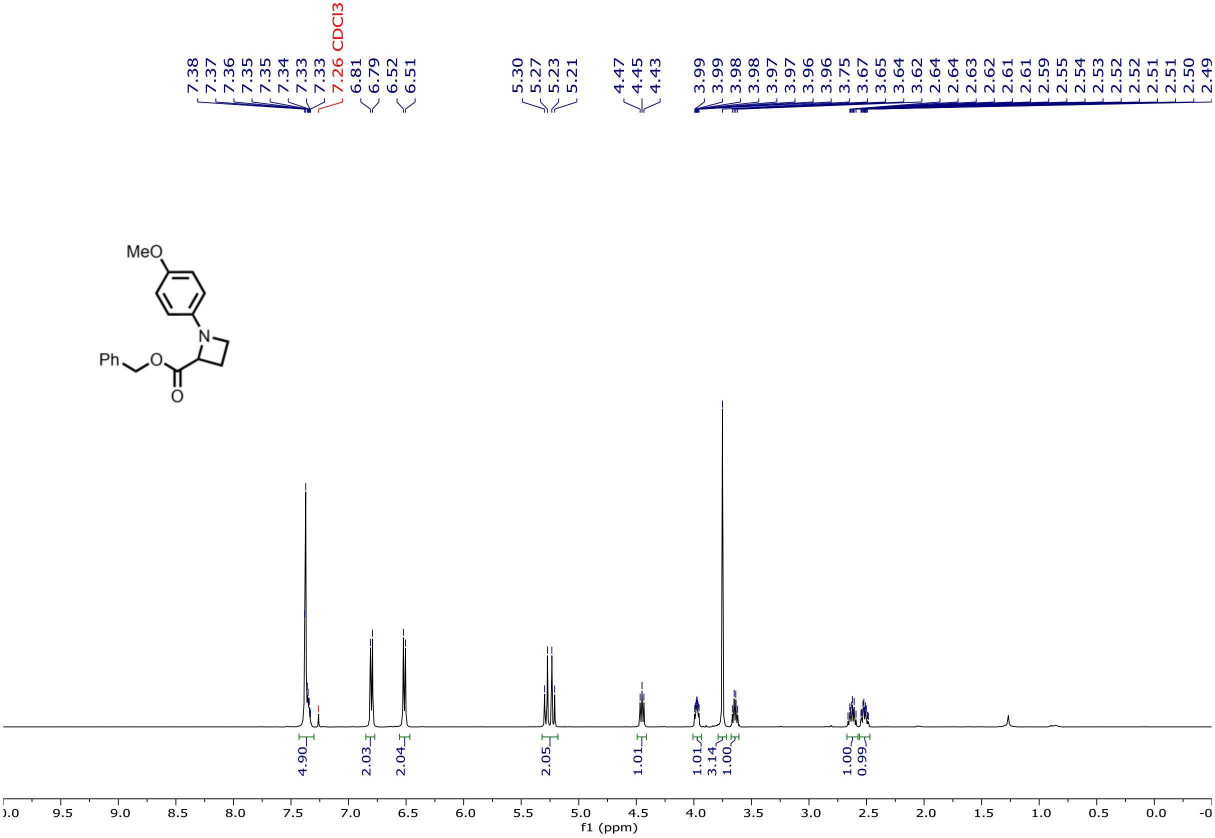
## $^1$H NMR spectrum of 18 in $CDCl_3$. (500 MHz)



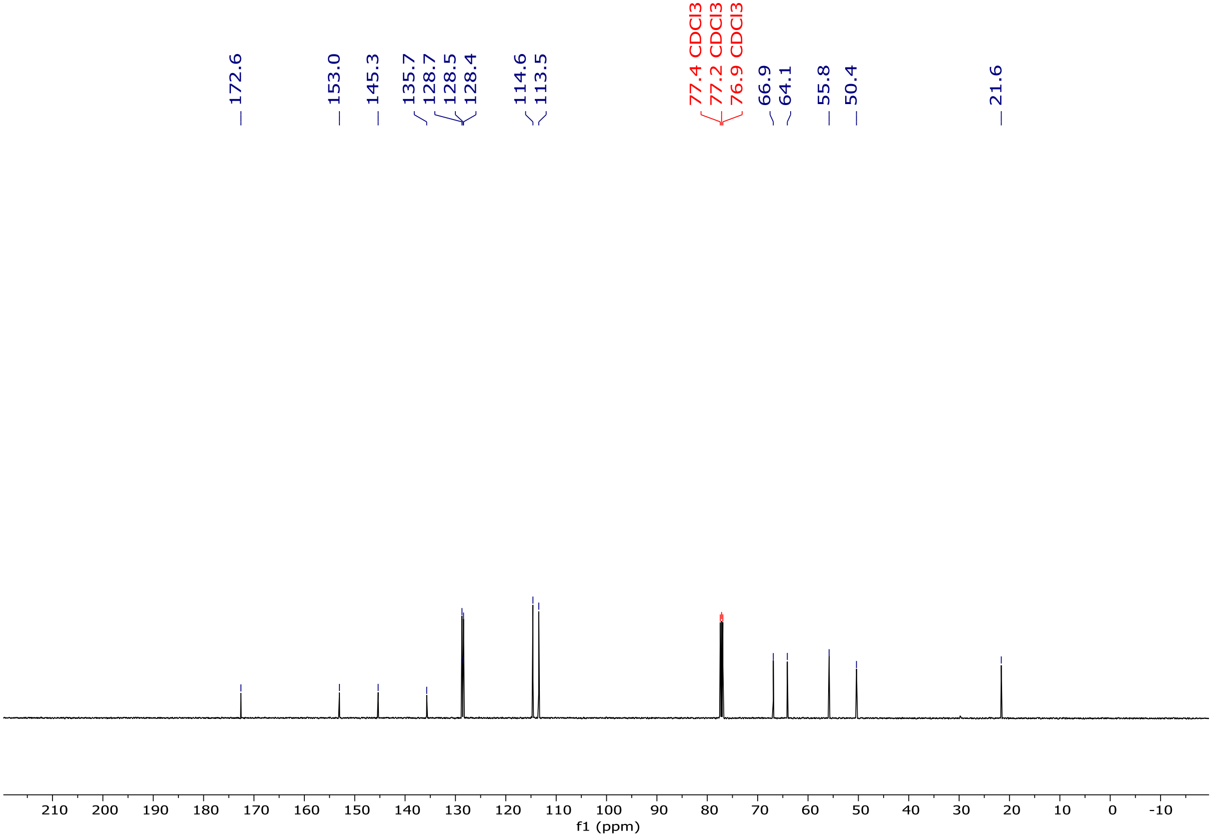
## $^{13}$C NMR spectrum of 18 in $CDCl_3$. (126 MHz)



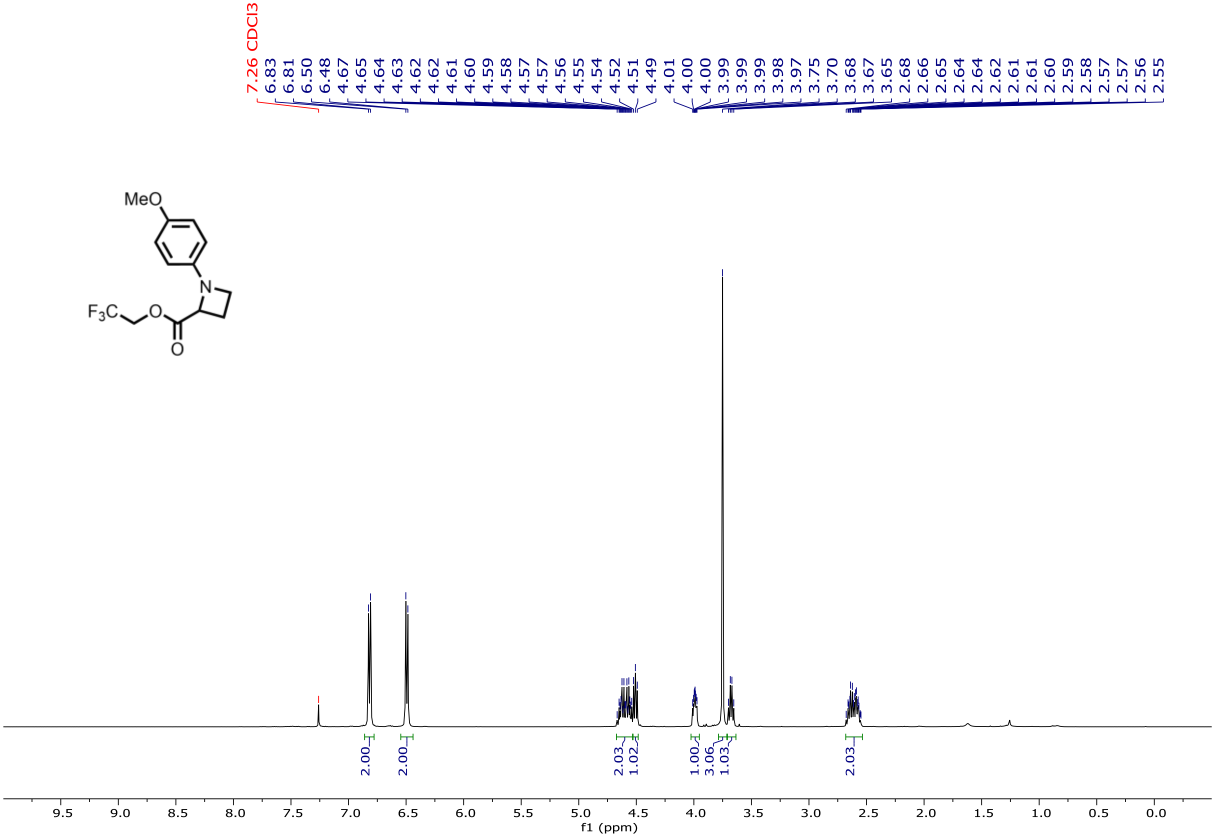
### $^1$H NMR spectrum of 19 in $CDCl_3$. (500 MHz)



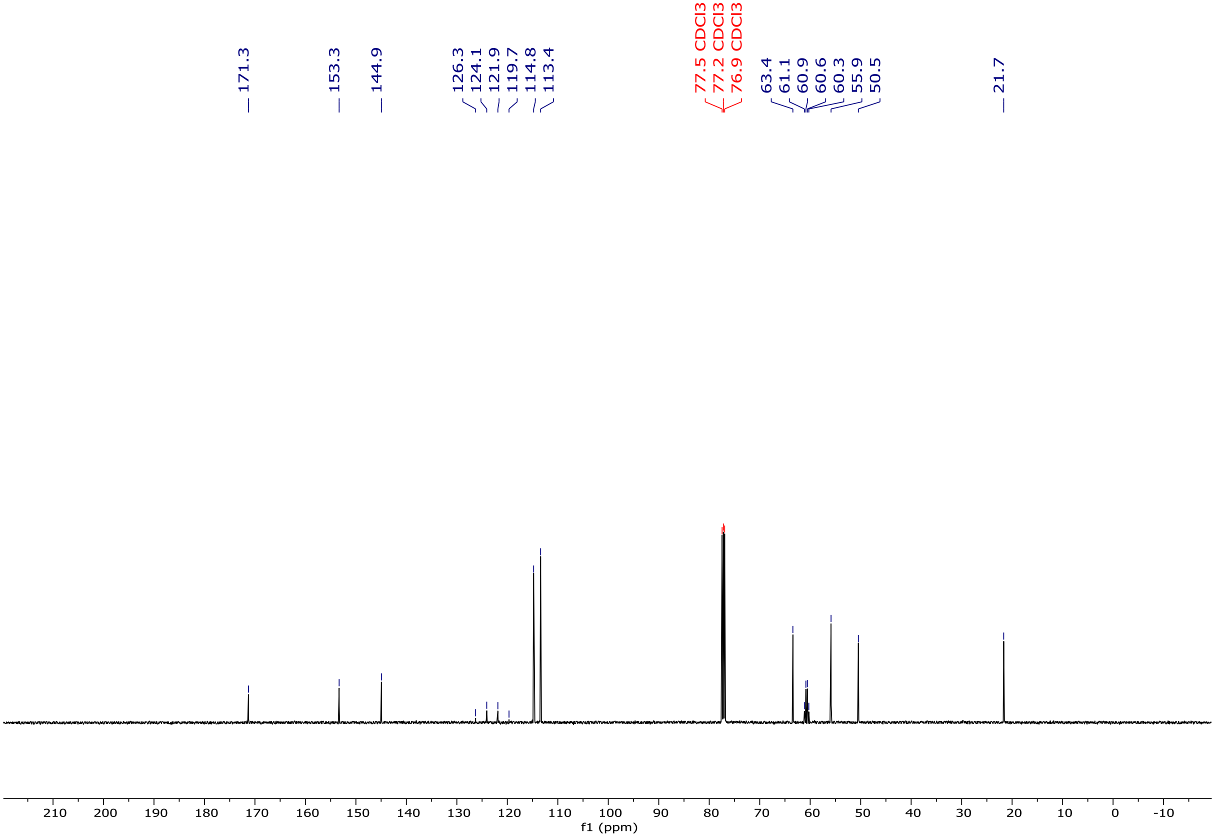
### $^{13}$C NMR spectrum of 19 in $CDCl_3$. (126 MHz)



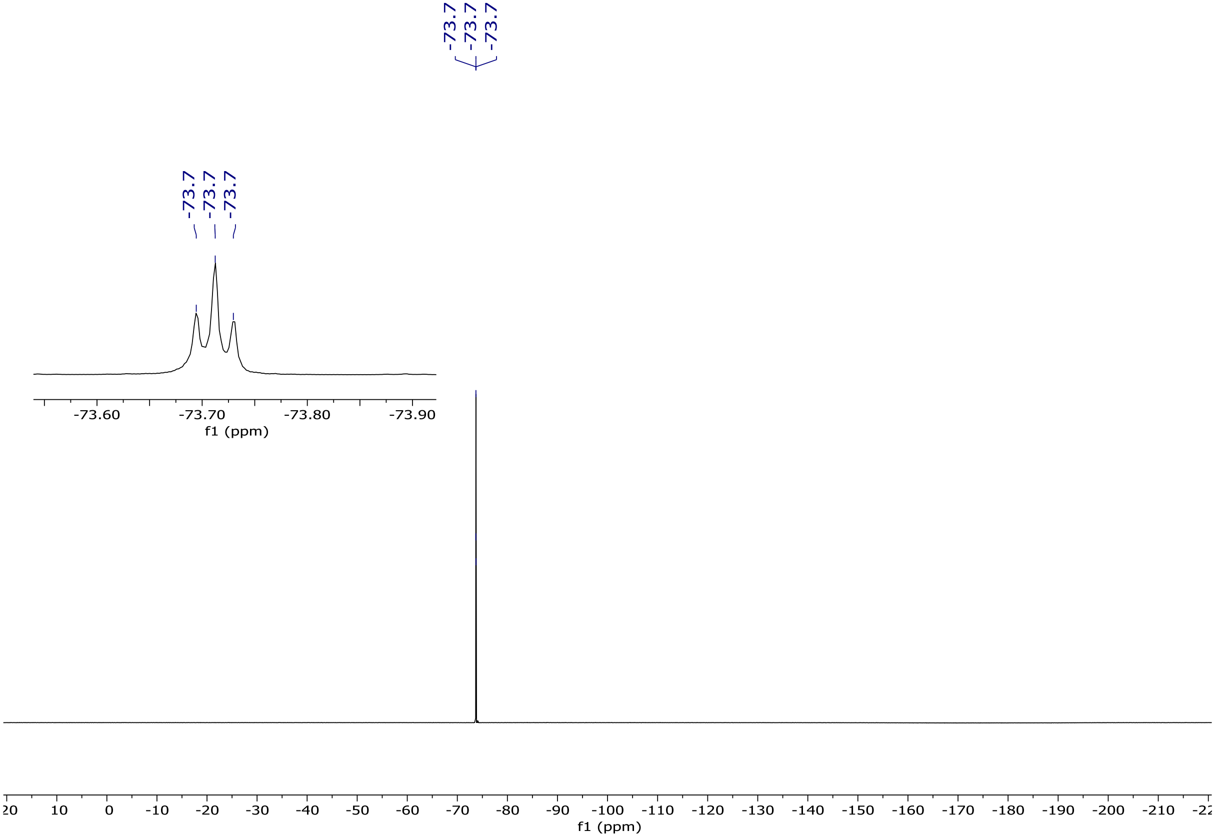
### $^1$H NMR spectrum of 20 in CDCl$_3$. (500 MHz)



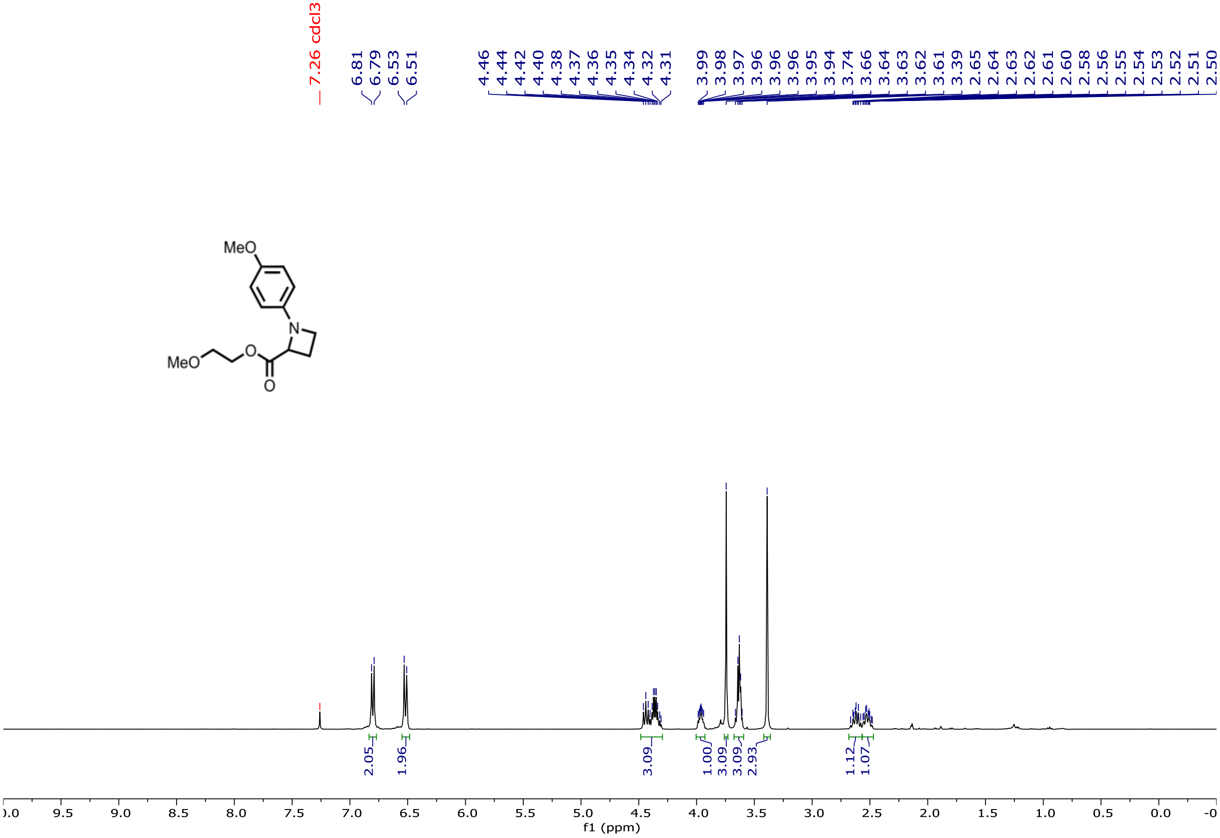
### $^{13}$C NMR spectrum of 20 in CDCl$_3$. (126 MHz)



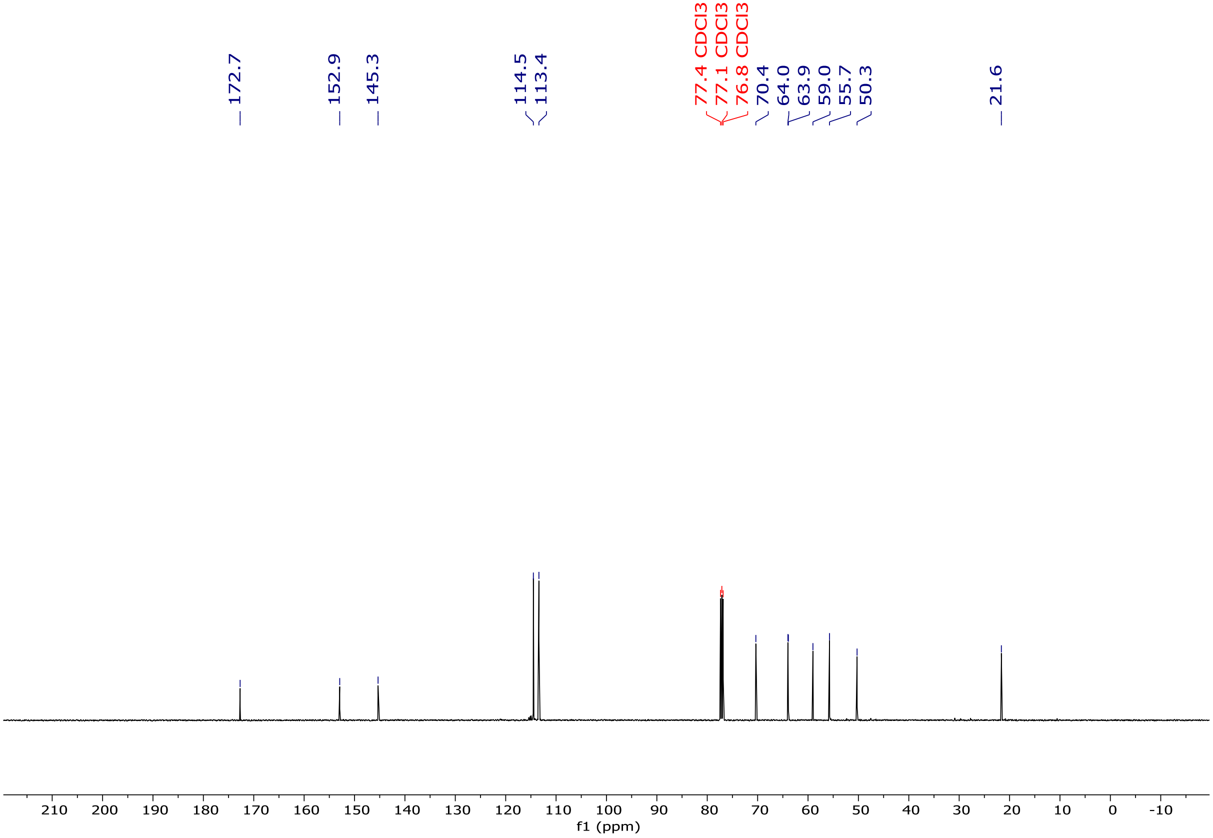
**$^{19}$F NMR spectrum of 20 in CDCl$_3$. (471 MHz)**



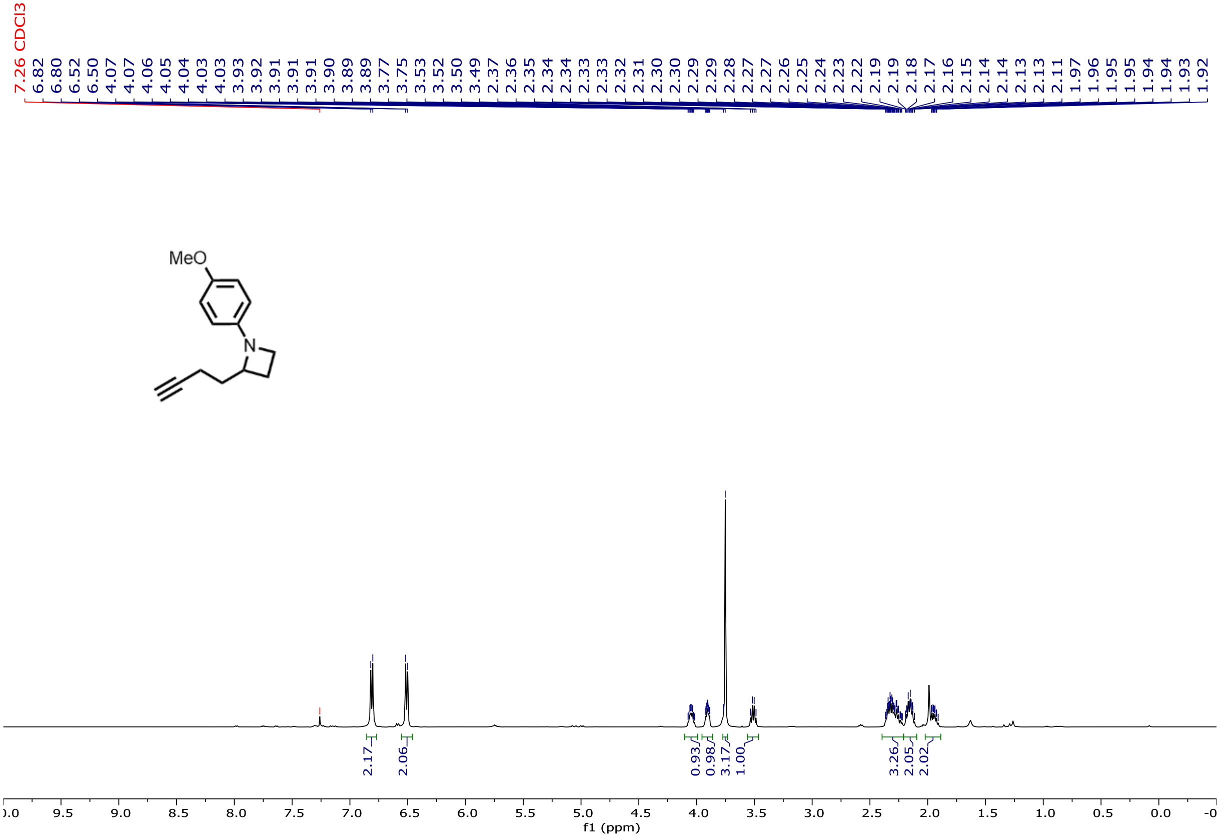
## $^1$H NMR spectrum of 21 in $CDCl_3$. (400 MHz)



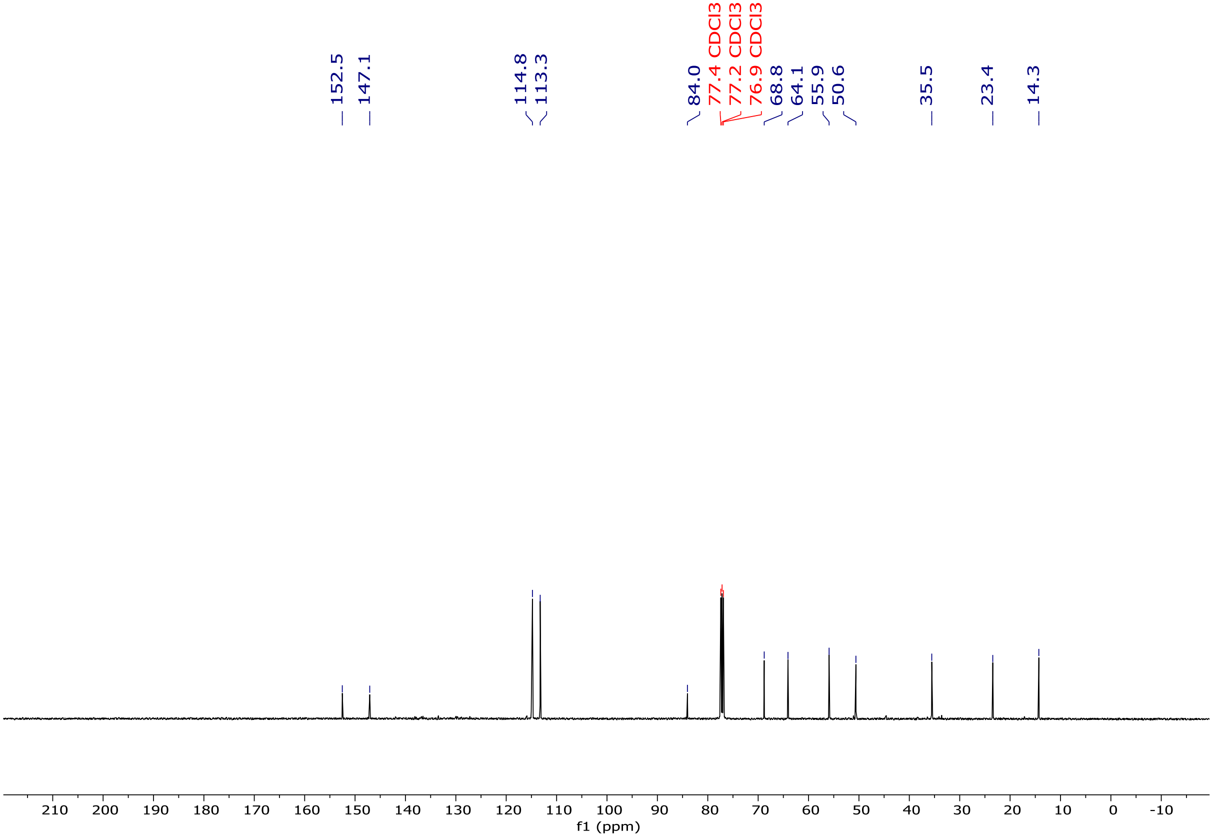
## $^{13}$C NMR spectrum of 21 in $CDCl_3$. (126 MHz)



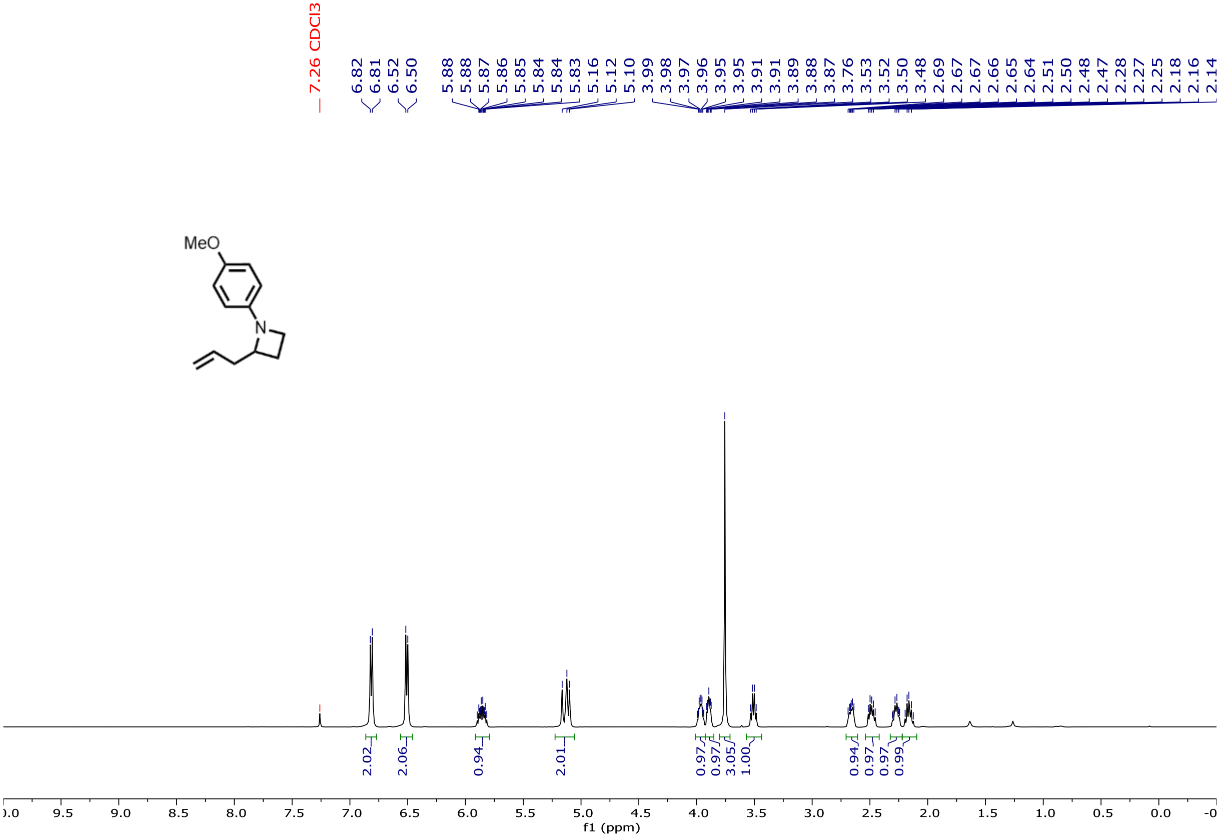
### $^1$H NMR spectrum of 22 in $CDCl_3$. (500 MHz)



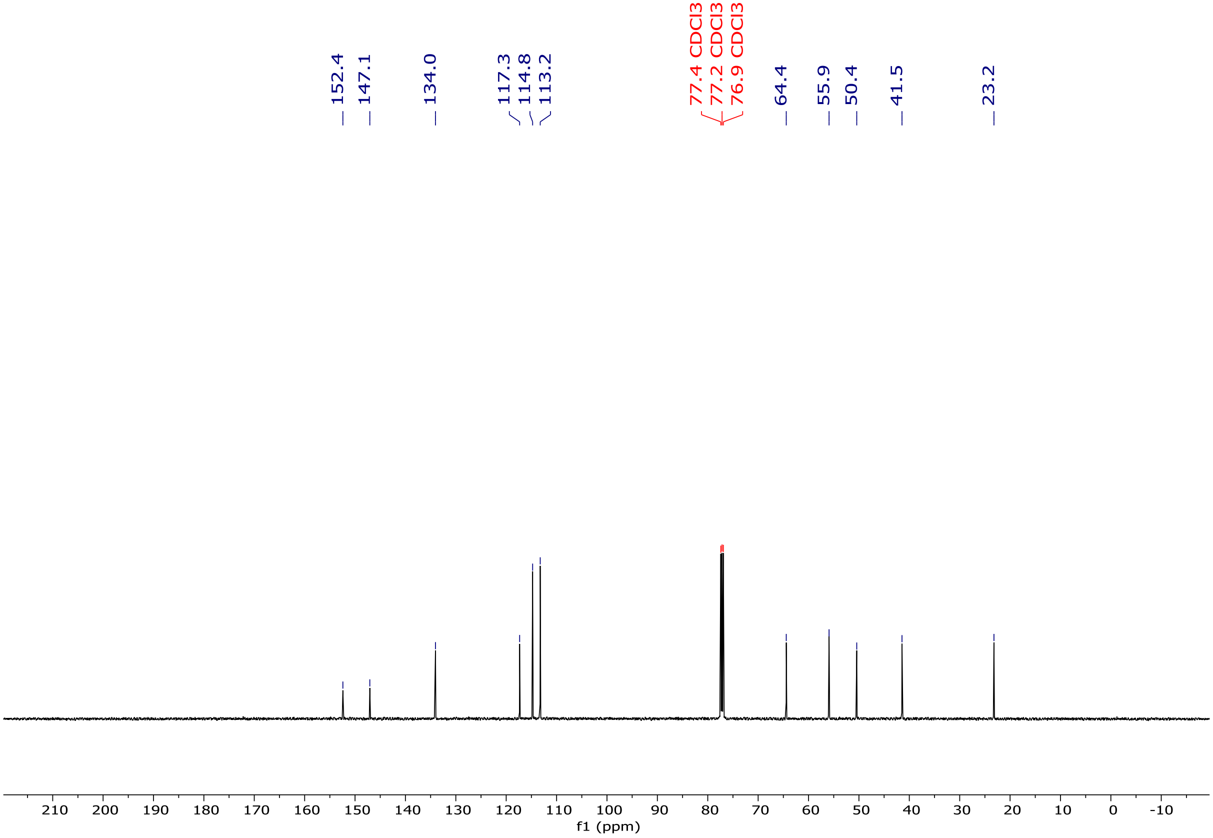
### $^{13}$C NMR spectrum of 22 in $CDCl_3$. (126 MHz)



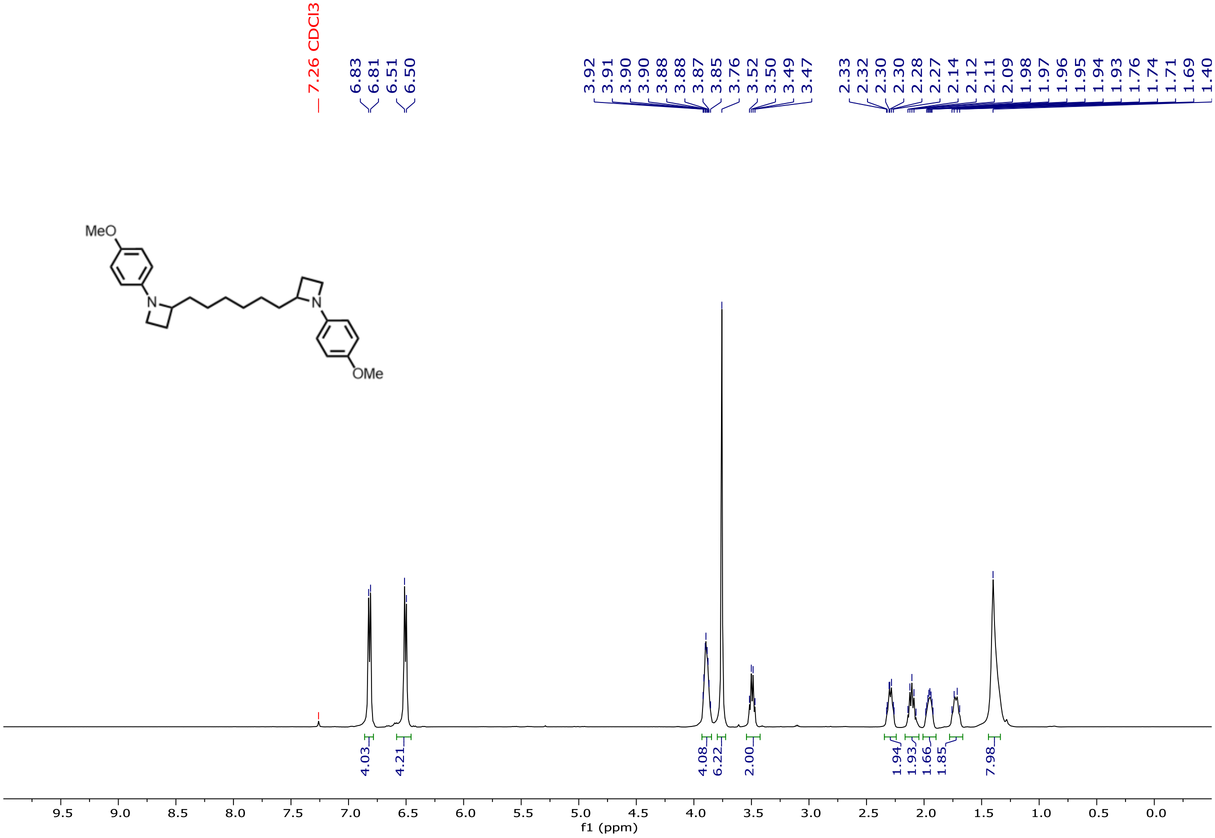
## $^1$H NMR spectrum of 23 in CDCl$_3$. (500 MHz)



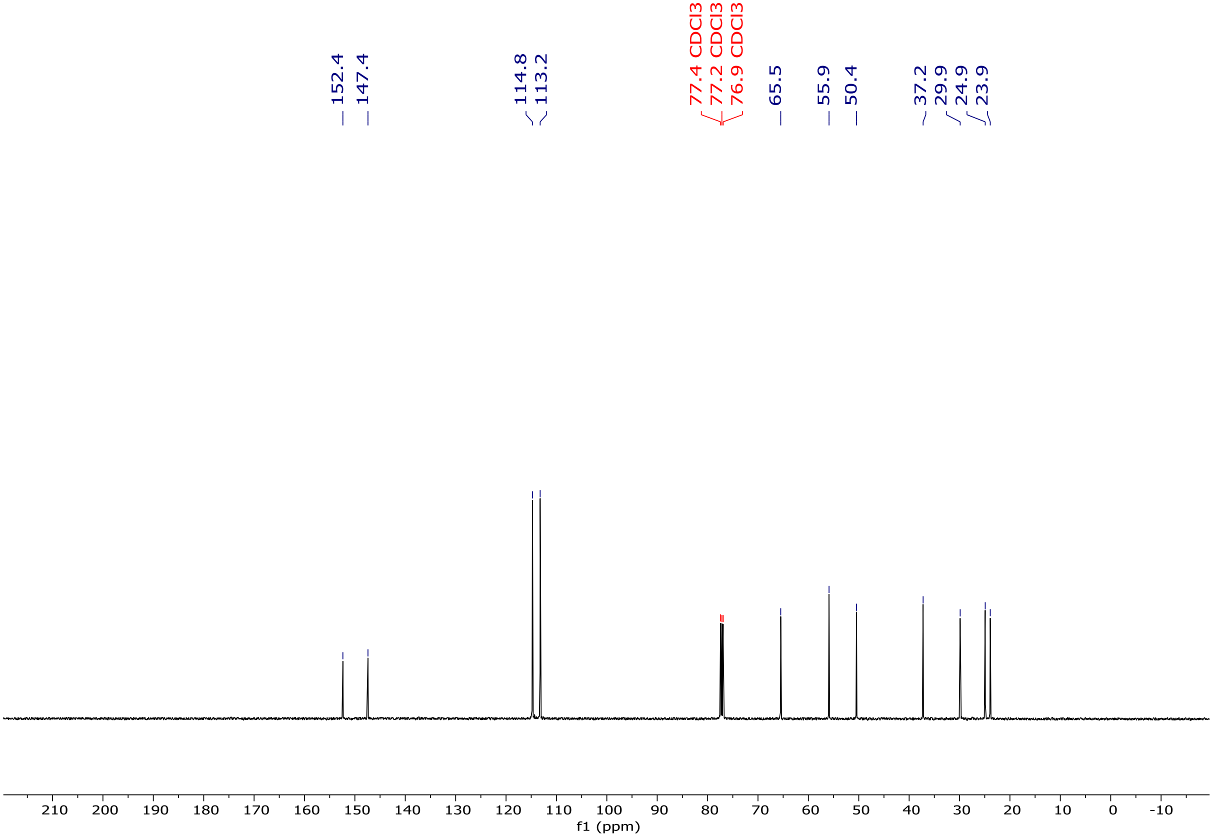
## $^{13}$C NMR spectrum of 23 in CDCl$_3$. (126 MHz)



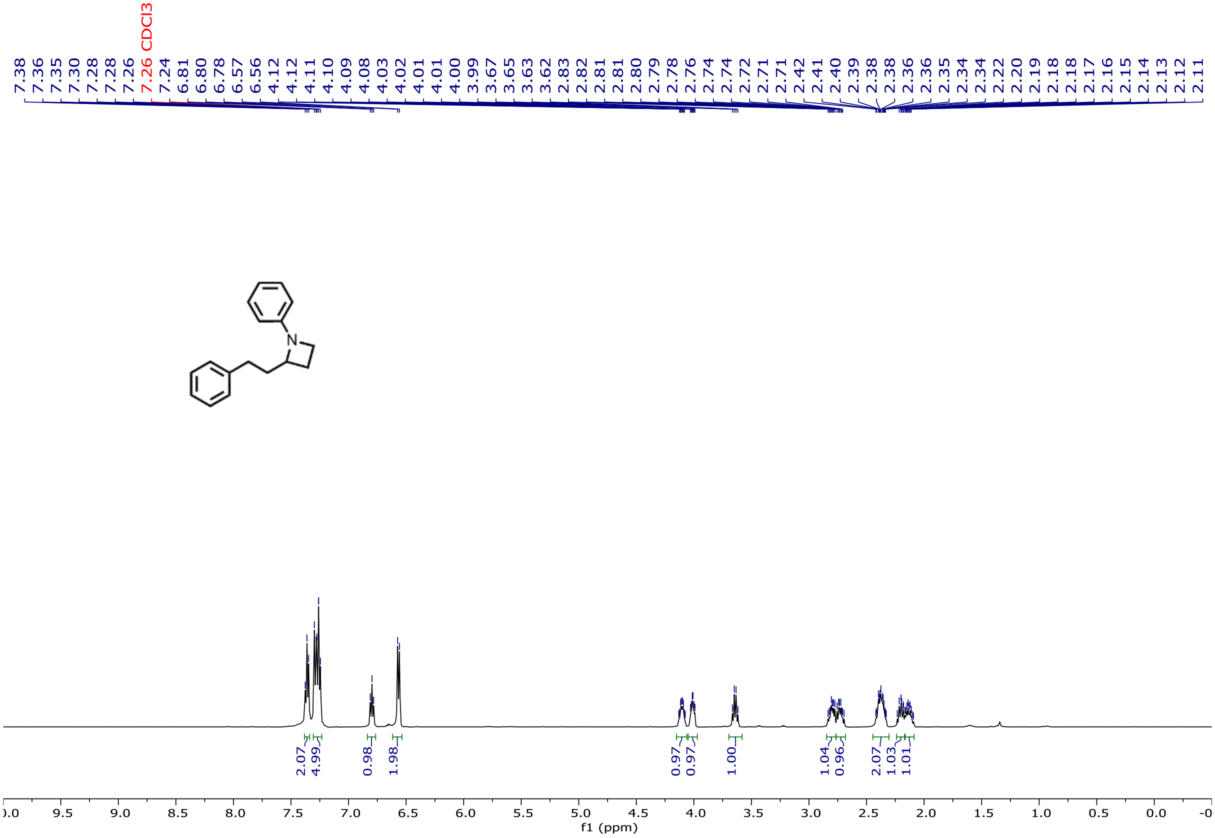
## $^1$H NMR spectrum of 24 in $CDCl_3$. (500 MHz)



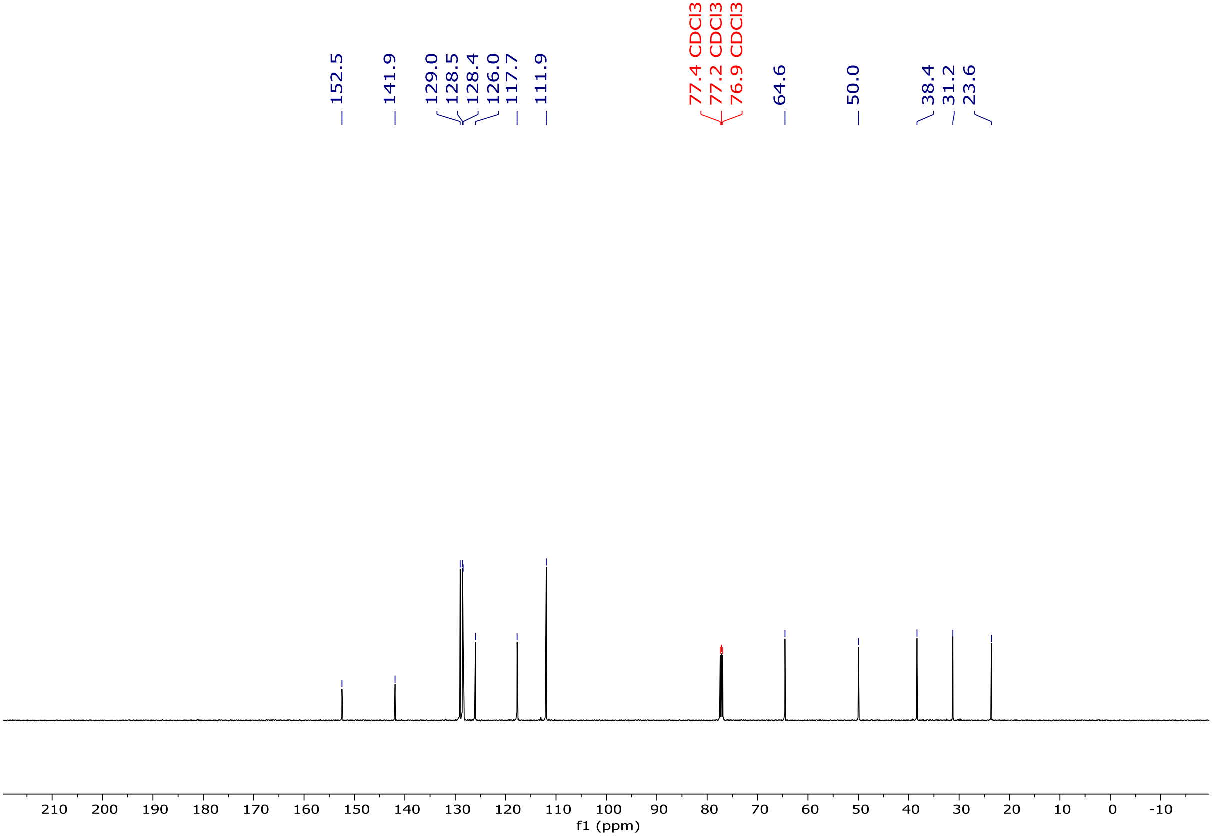
## $^{13}$C NMR spectrum of 24 in $CDCl_3$. (126 MHz)



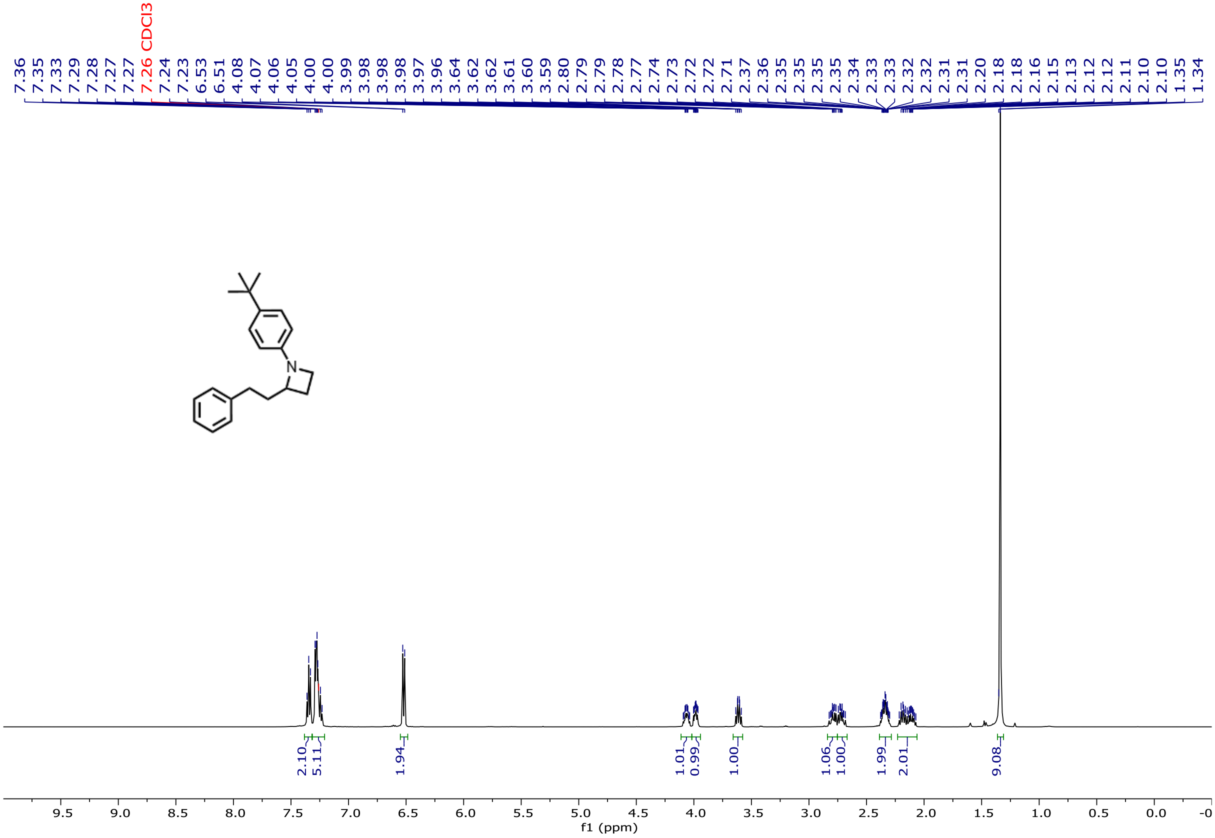
## $^1$H NMR spectrum of 25 in $CDCl_3$. (500 MHz)



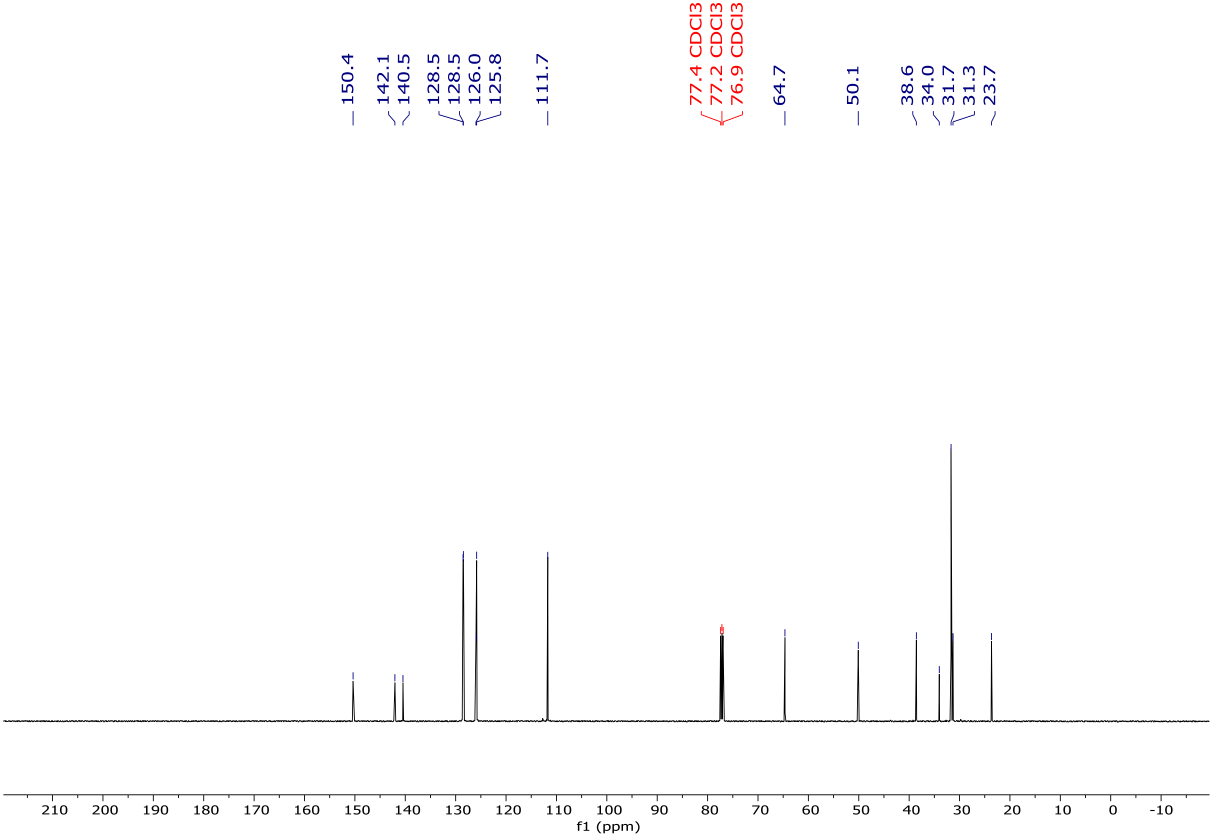
## $^{13}$C NMR spectrum of 25 in $CDCl_3$. (126 MHz)



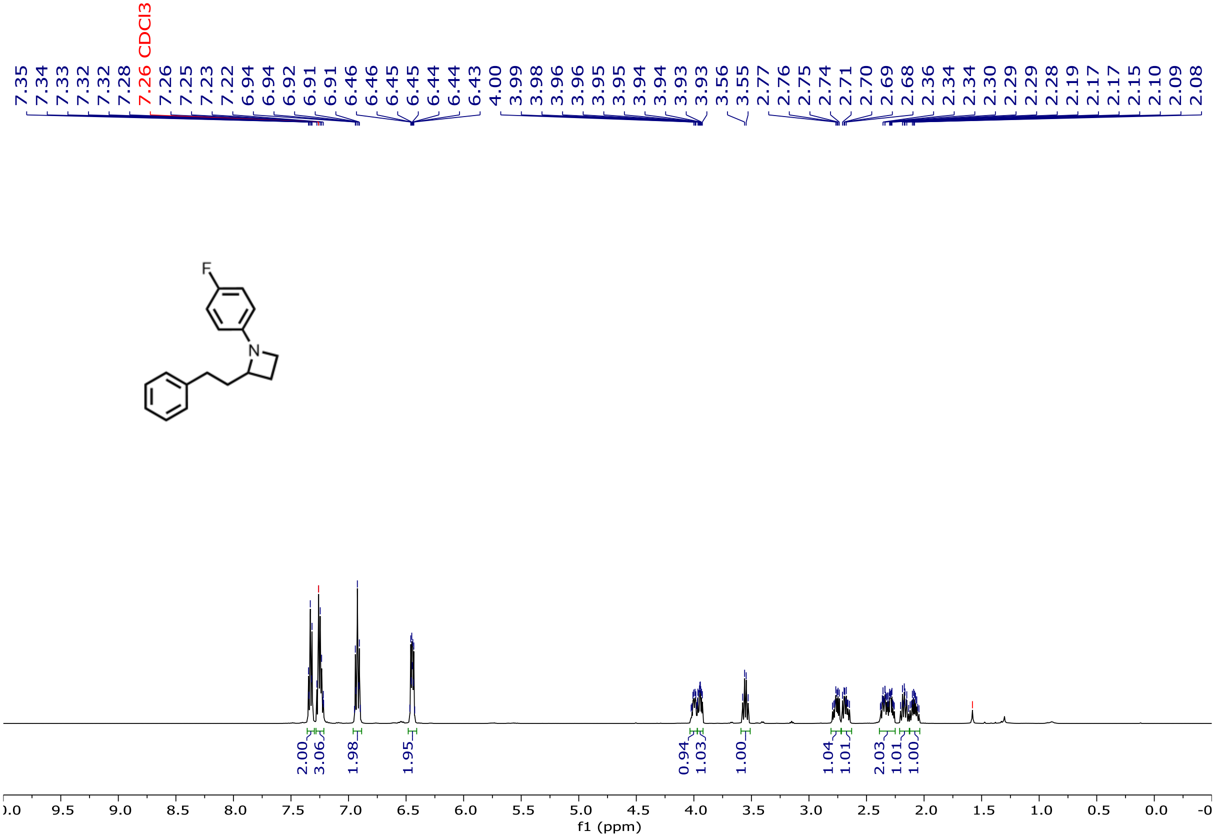
**$^1$H NMR spectrum of 26 in $CDCl_3$. (500 MHz)**



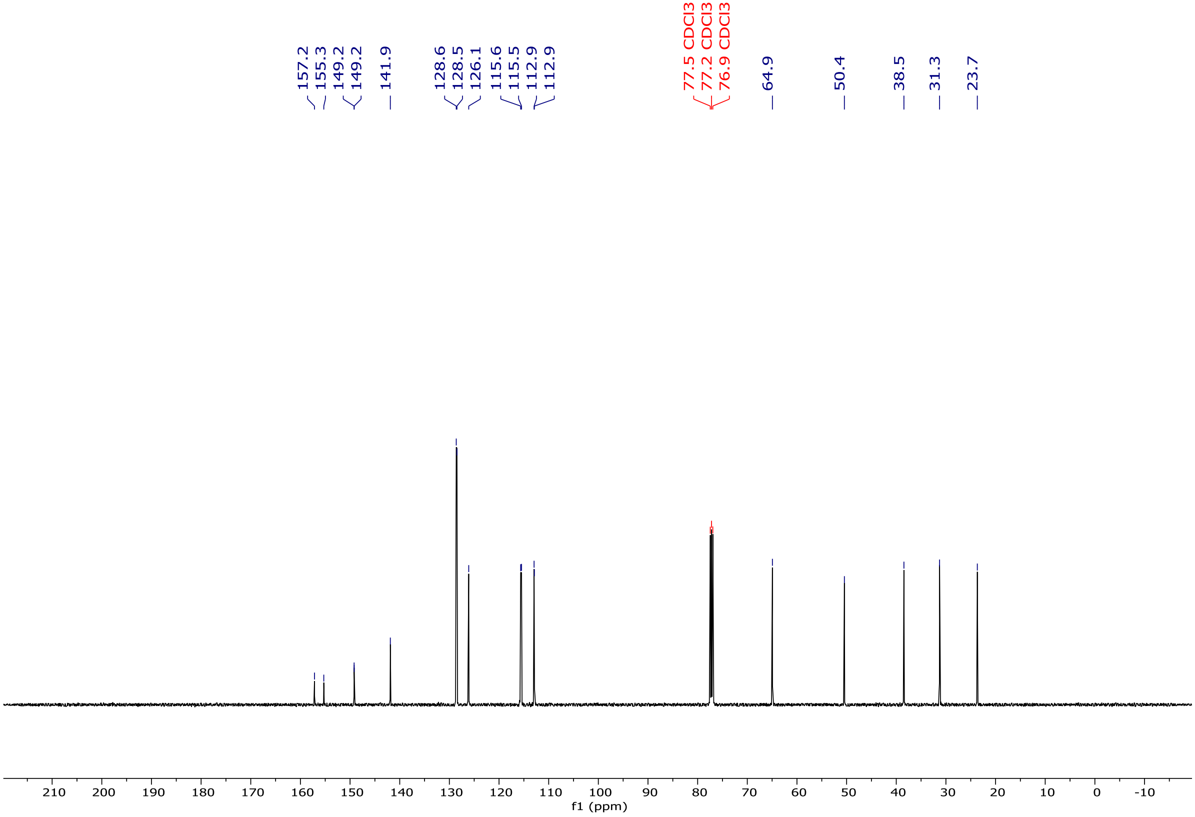
**$^{13}$C NMR spectrum of 26 in $CDCl_3$. (126 MHz)**



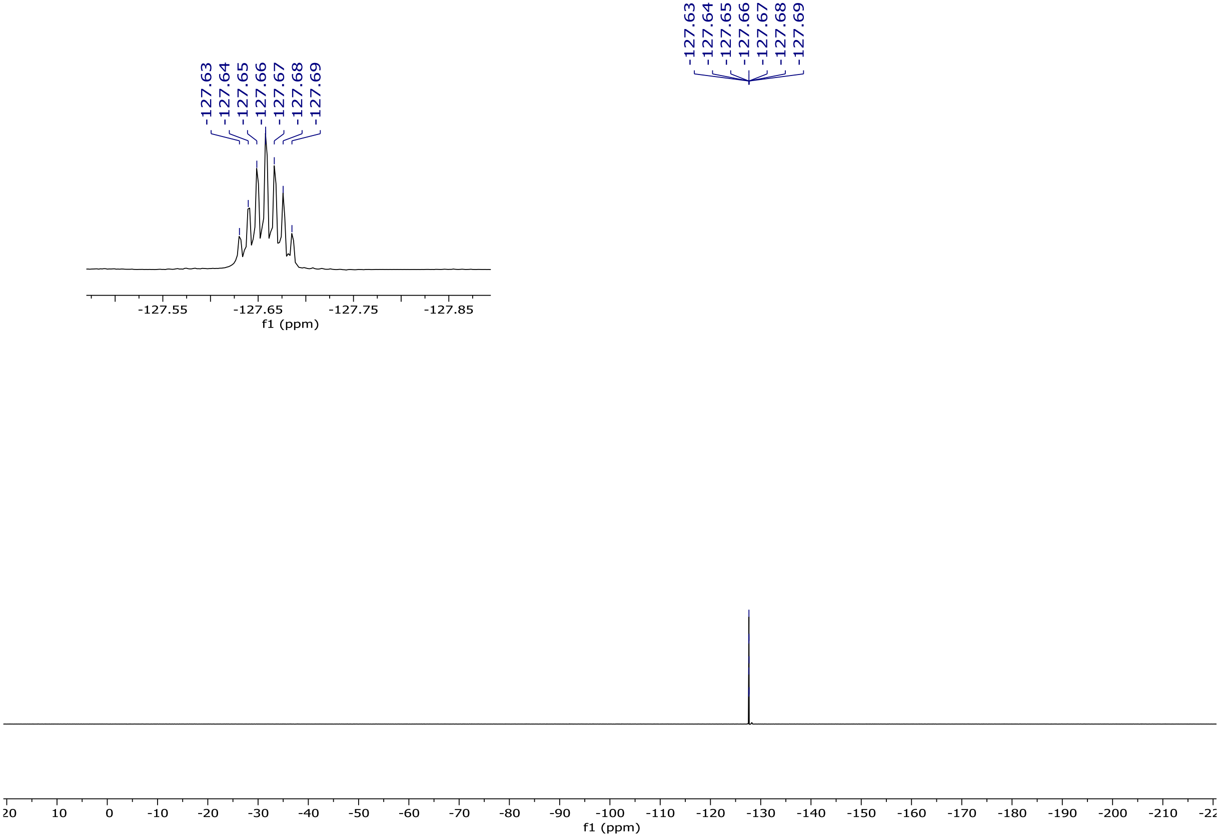
## $^{1}$H NMR spectrum of 27 in $CDCl_3$. (500 MHz)



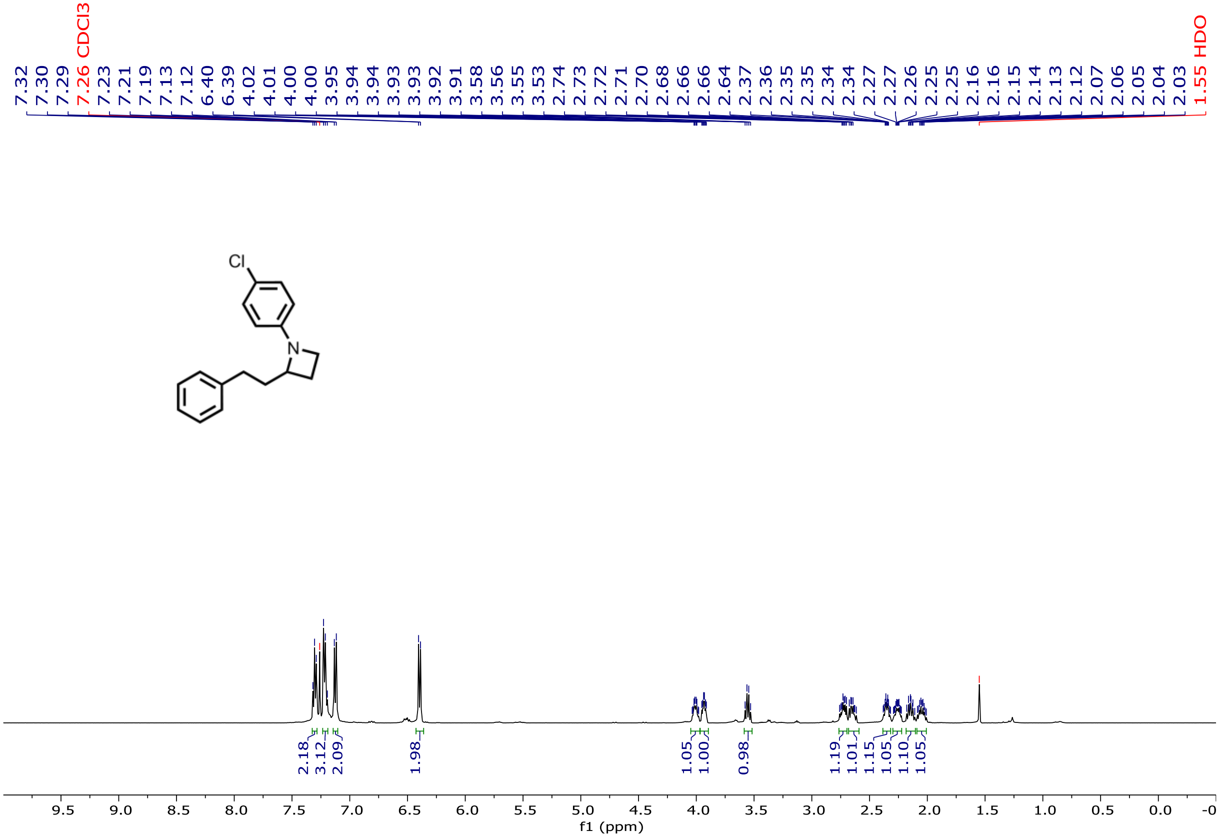
## $^{13}$C NMR spectrum of 27 in $CDCl_3$. (126 MHz)



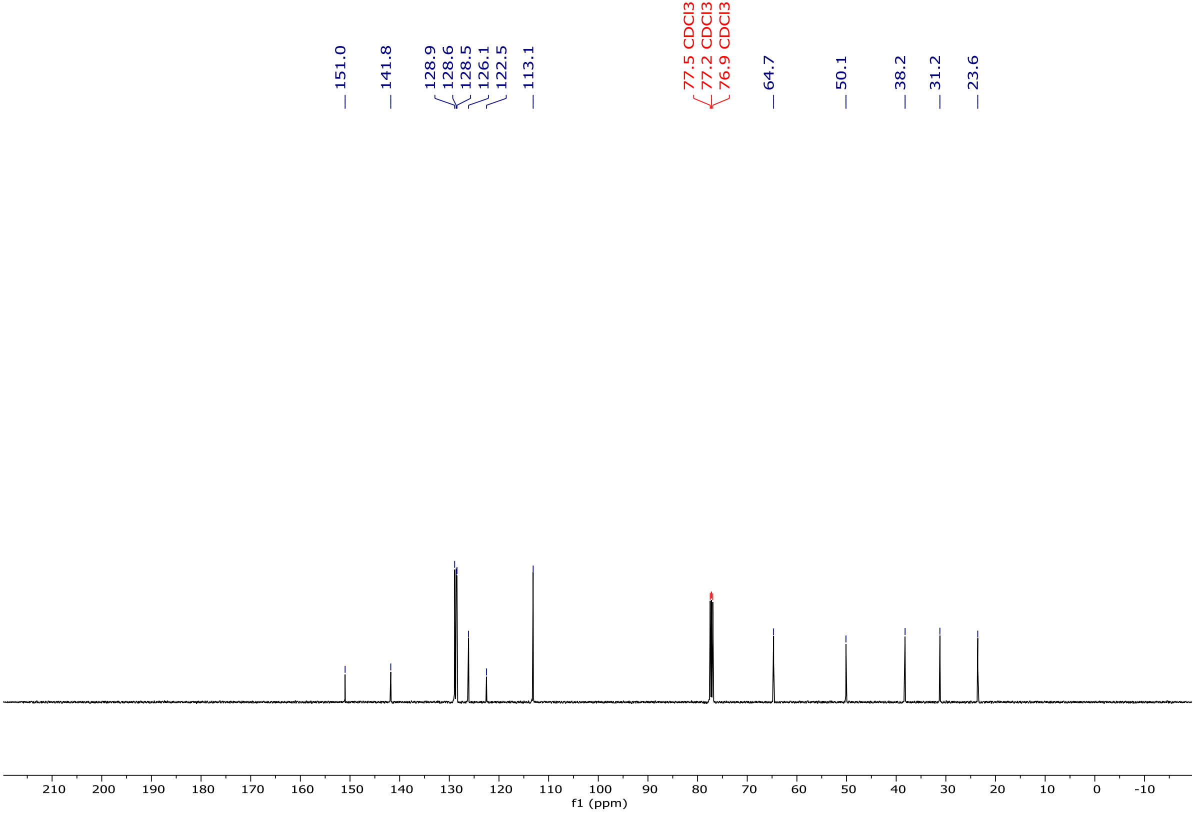
**$^{19}$F NMR spectrum of 27 in $CDCl_3$. (471 MHz)**



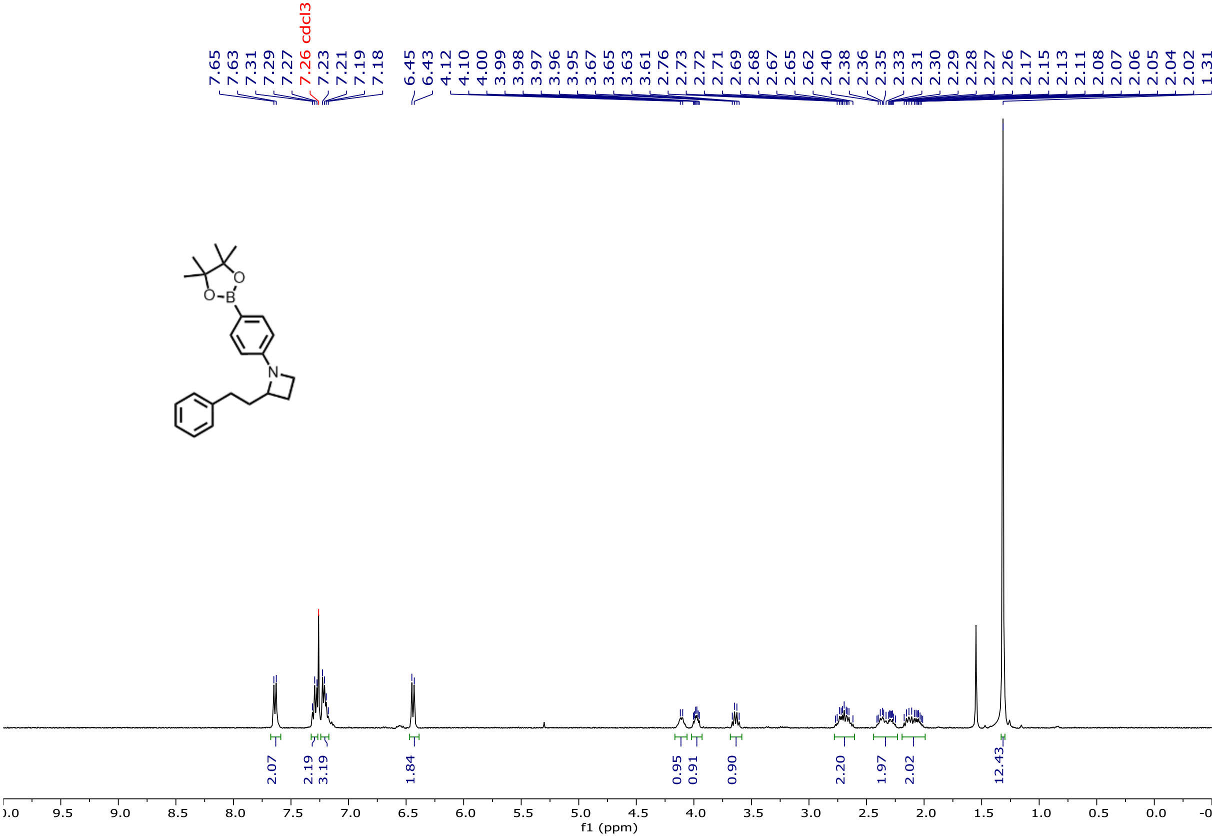
## $^1$H NMR spectrum of 28 in $CDCl_3$. (500 MHz)



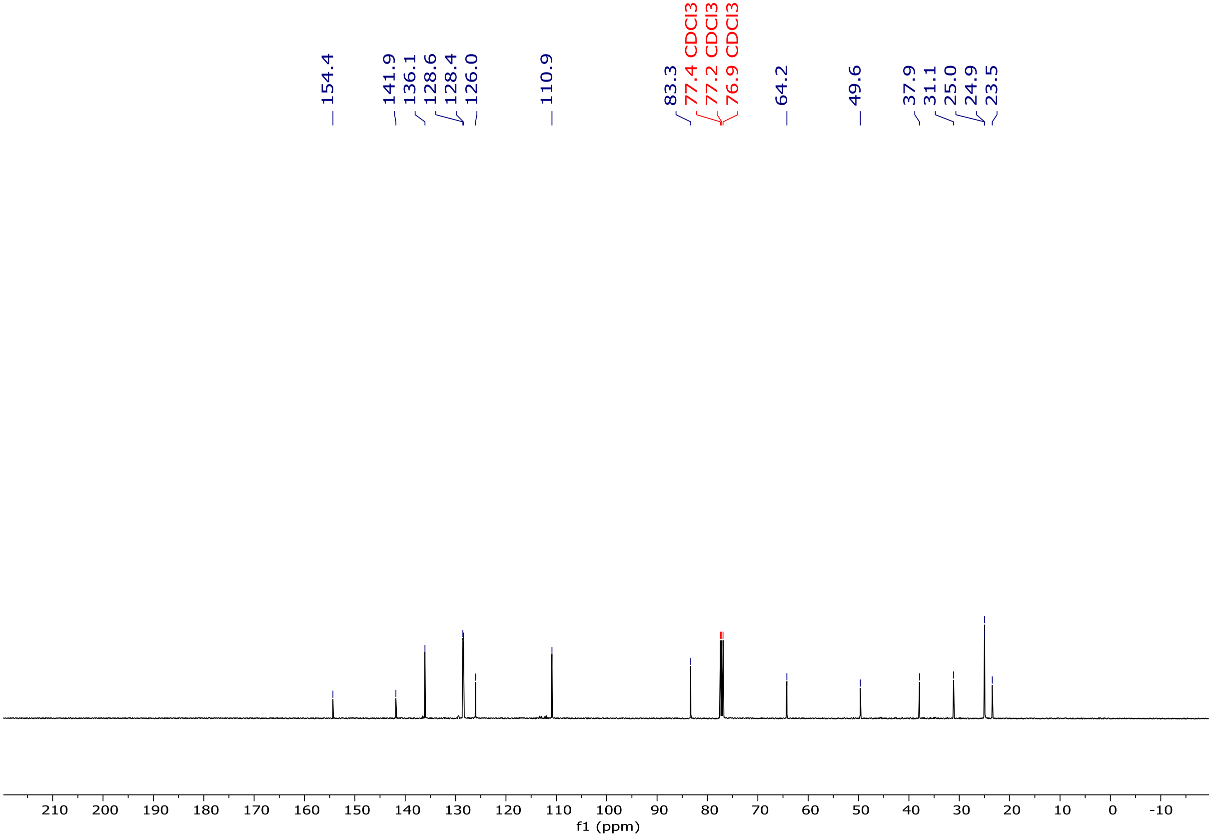
## $^{13}$C NMR spectrum of 28 in $CDCl_3$. (126 MHz)



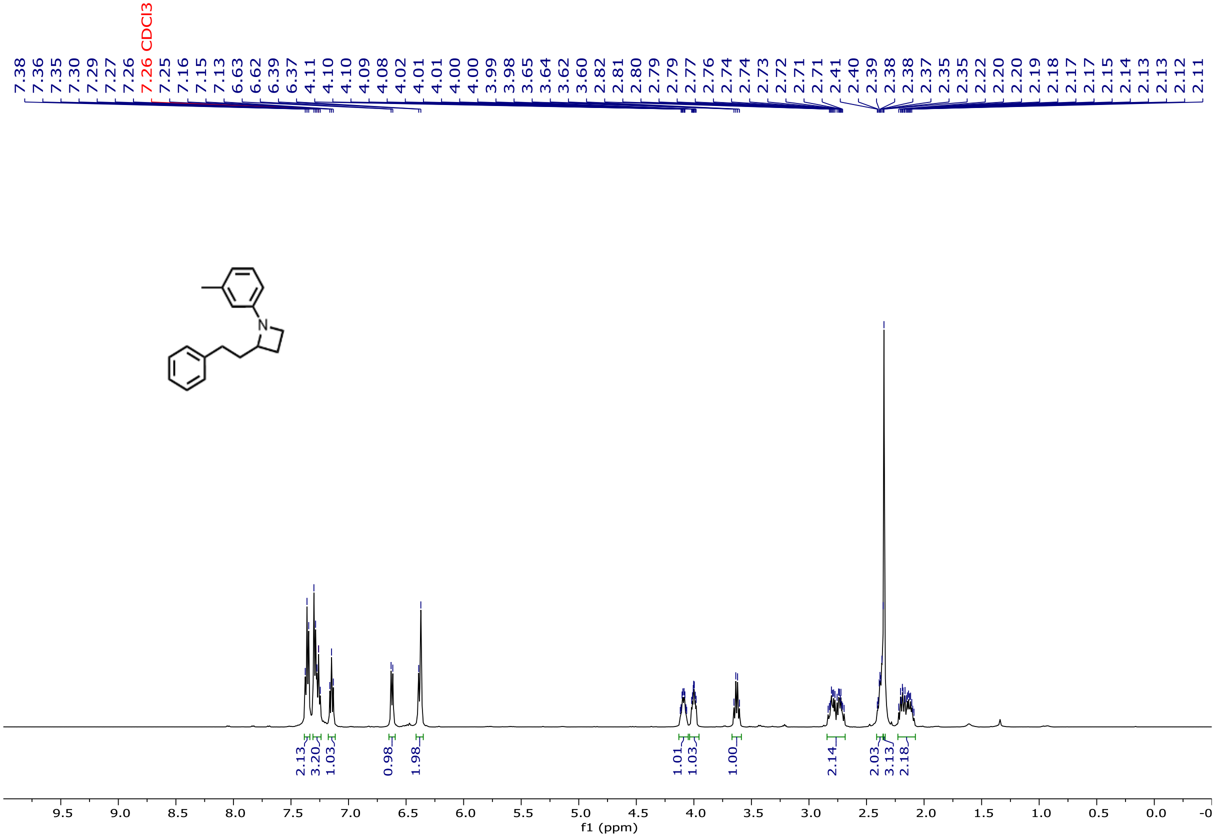
## $^{1}H$ NMR spectrum of 29 in $CDCl_3$. (400 MHz)



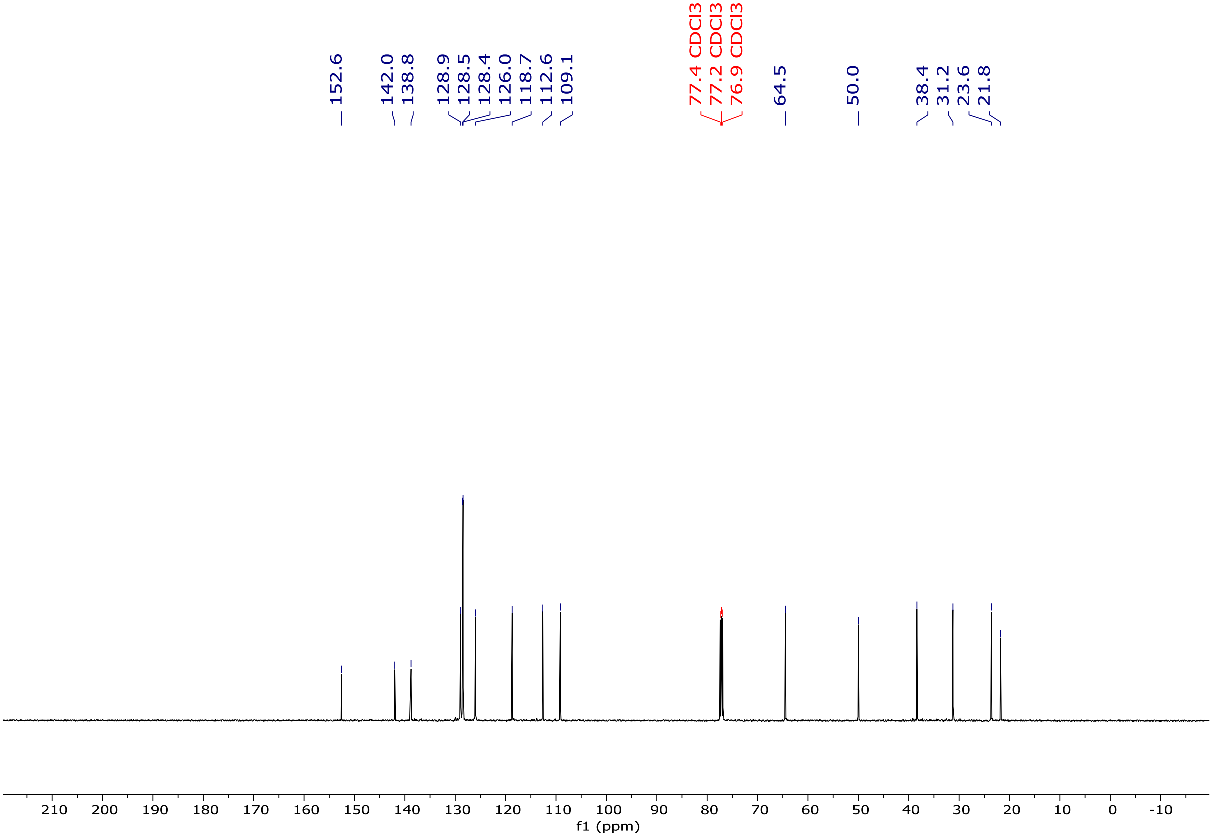
## $^{13}C$ NMR spectrum of 29 in $CDCl_3$. (126 MHz)



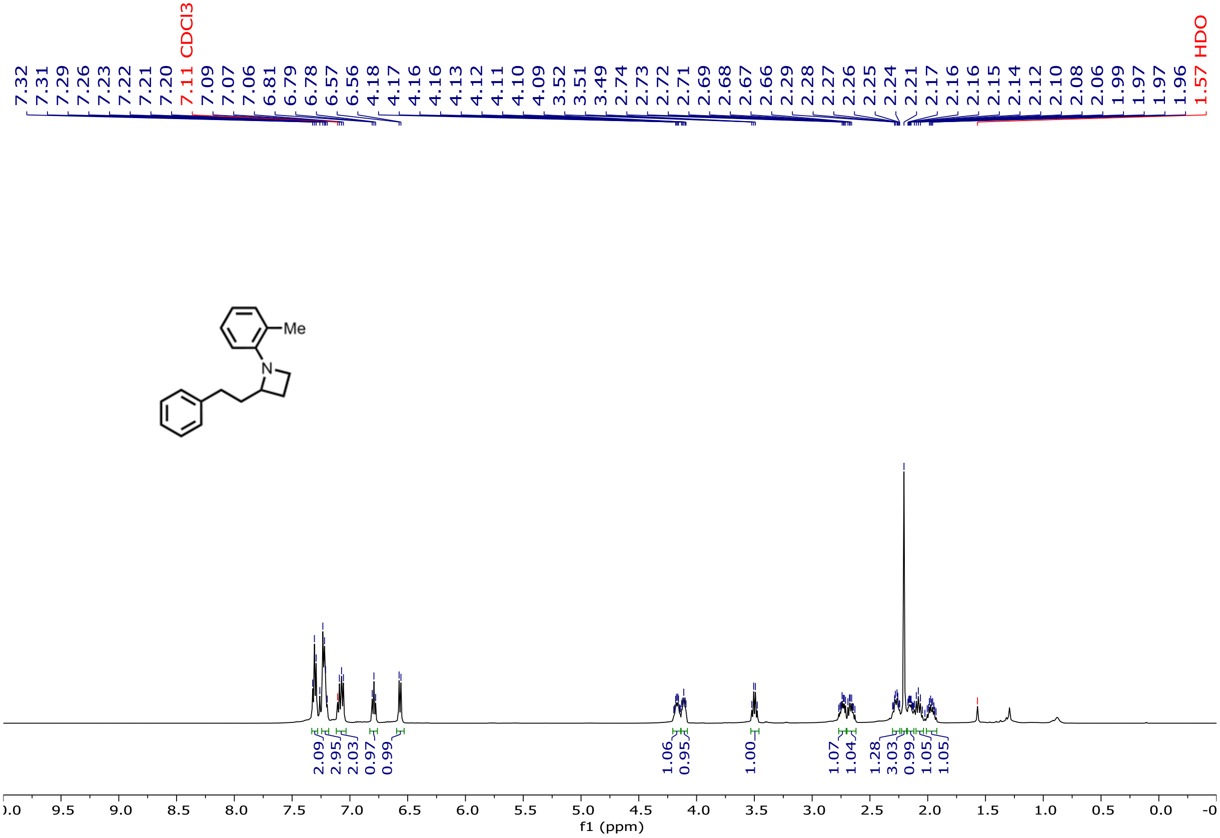
## $^1$H NMR spectrum of 30 in $CDCl_3$. (500 MHz)



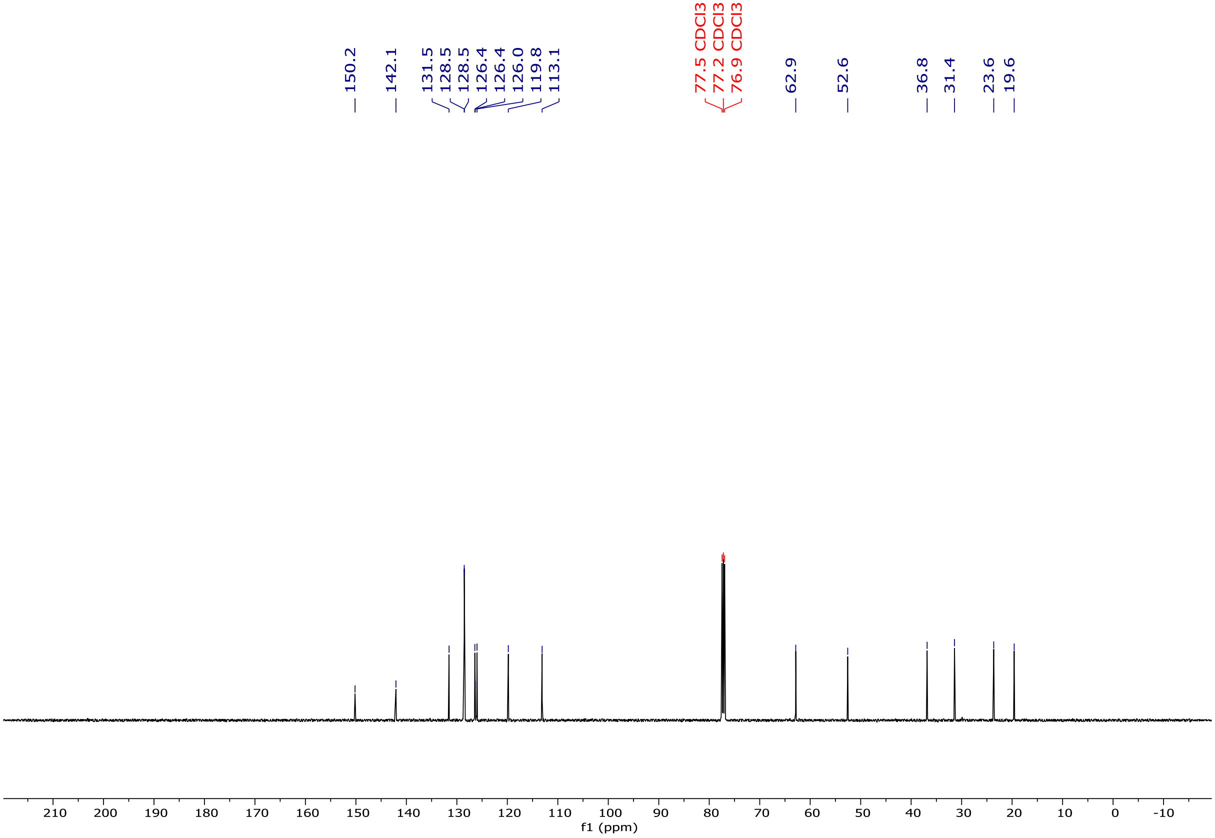
## $^{13}$C NMR spectrum of 30 in $CDCl_3$. (126 MHz)



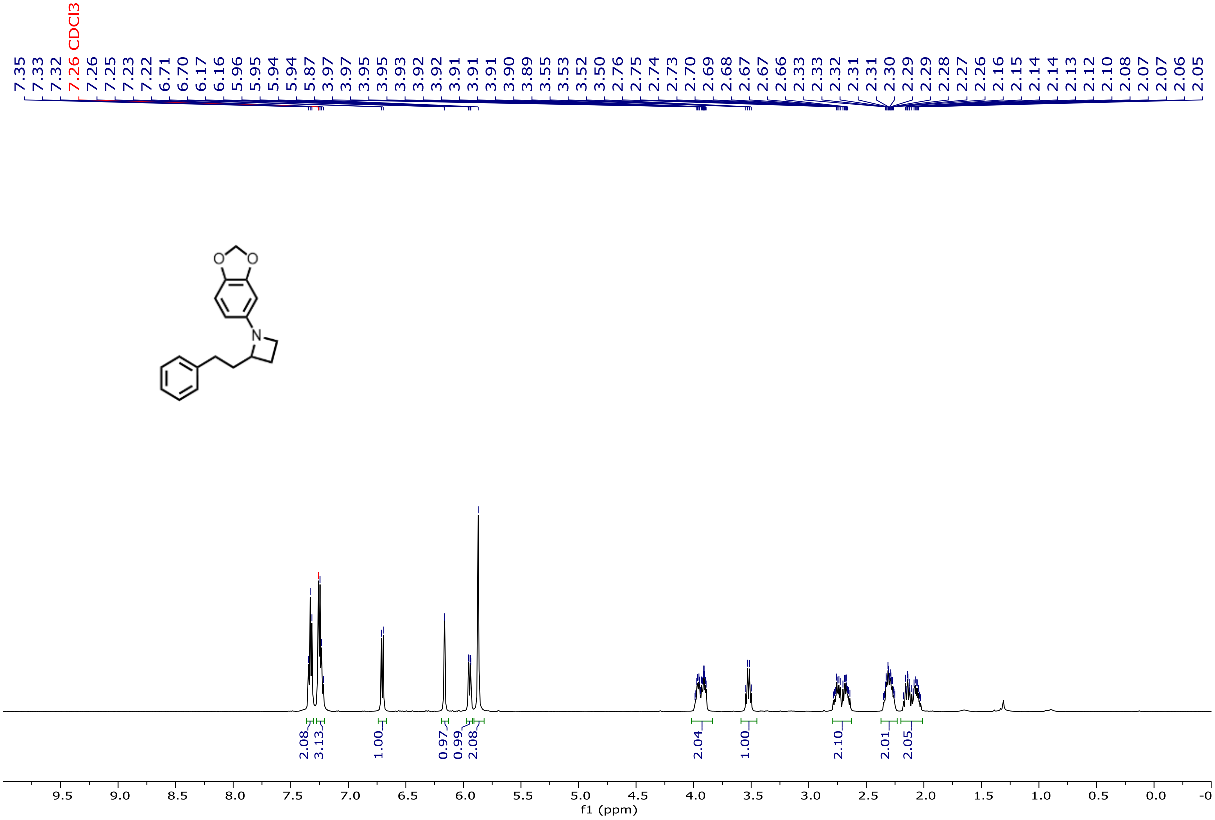
## $^1$H NMR spectrum of 31 in CDCl$_3$. (500 MHz)



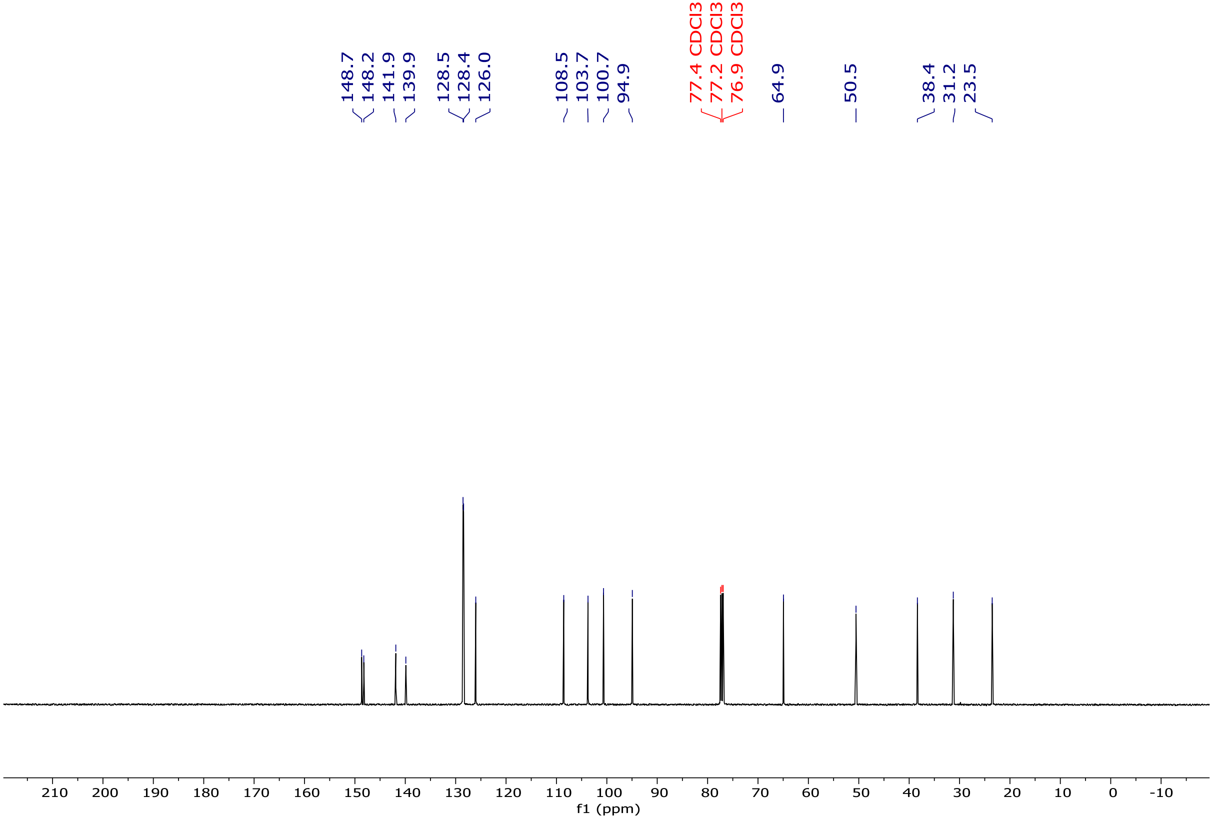
## $^{13}$C NMR spectrum of 31 in CDCl$_3$. (126 MHz)



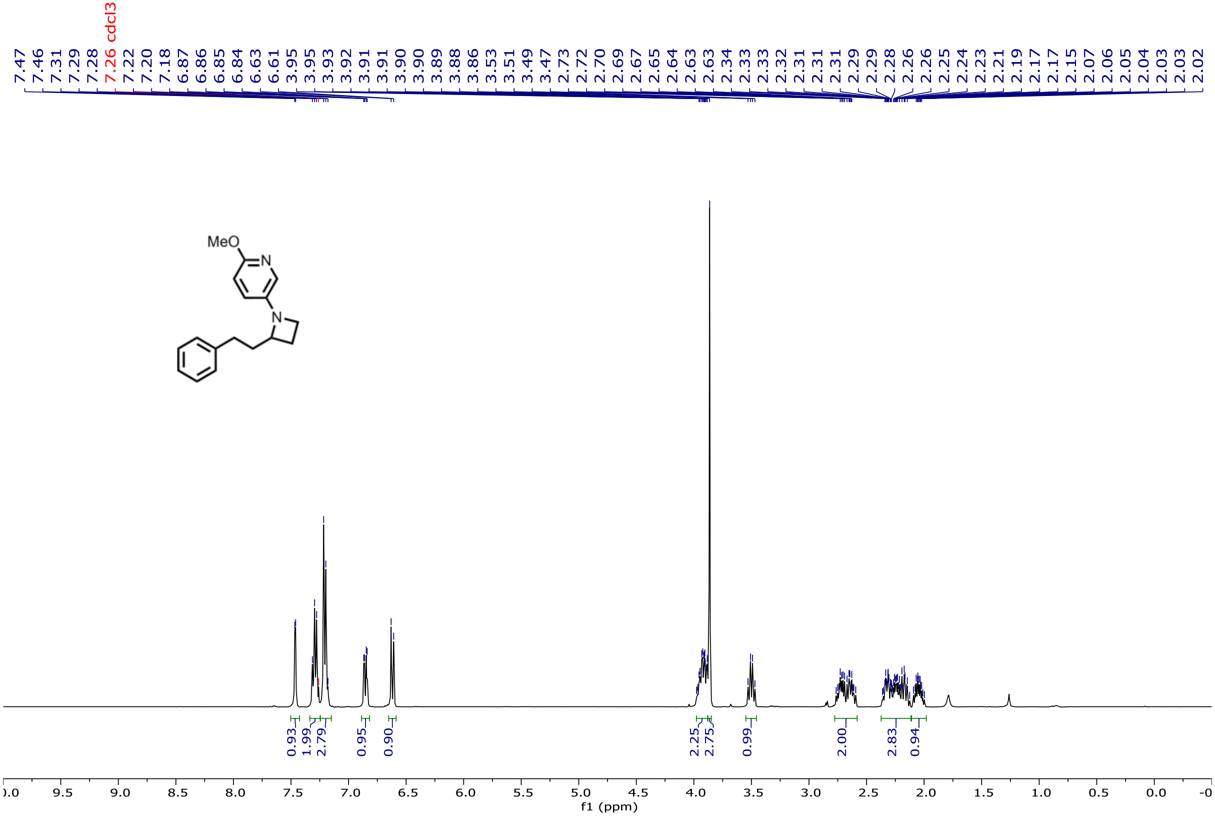
## $^1$H NMR spectrum of 32 in $CDCl_3$. (500 MHz)



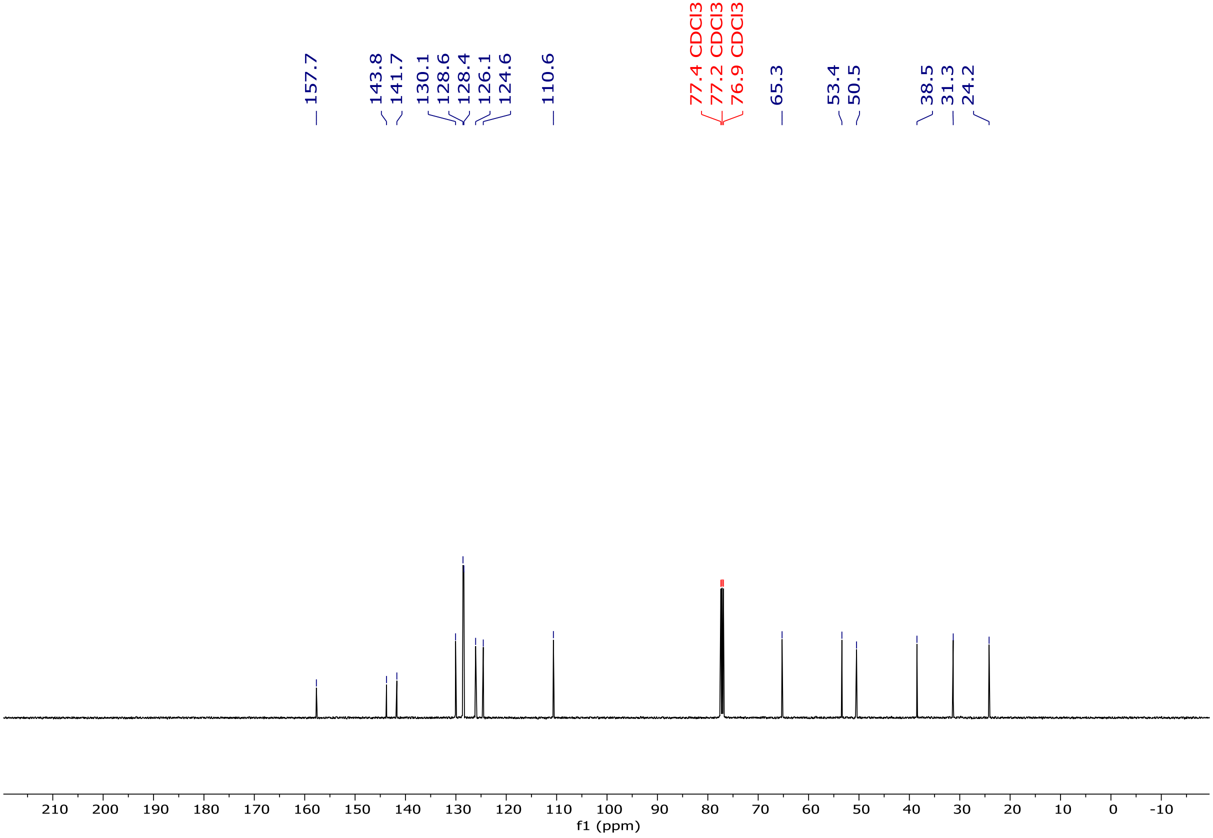
## $^{13}$C NMR spectrum of 32 in $CDCl_3$. (126 MHz)



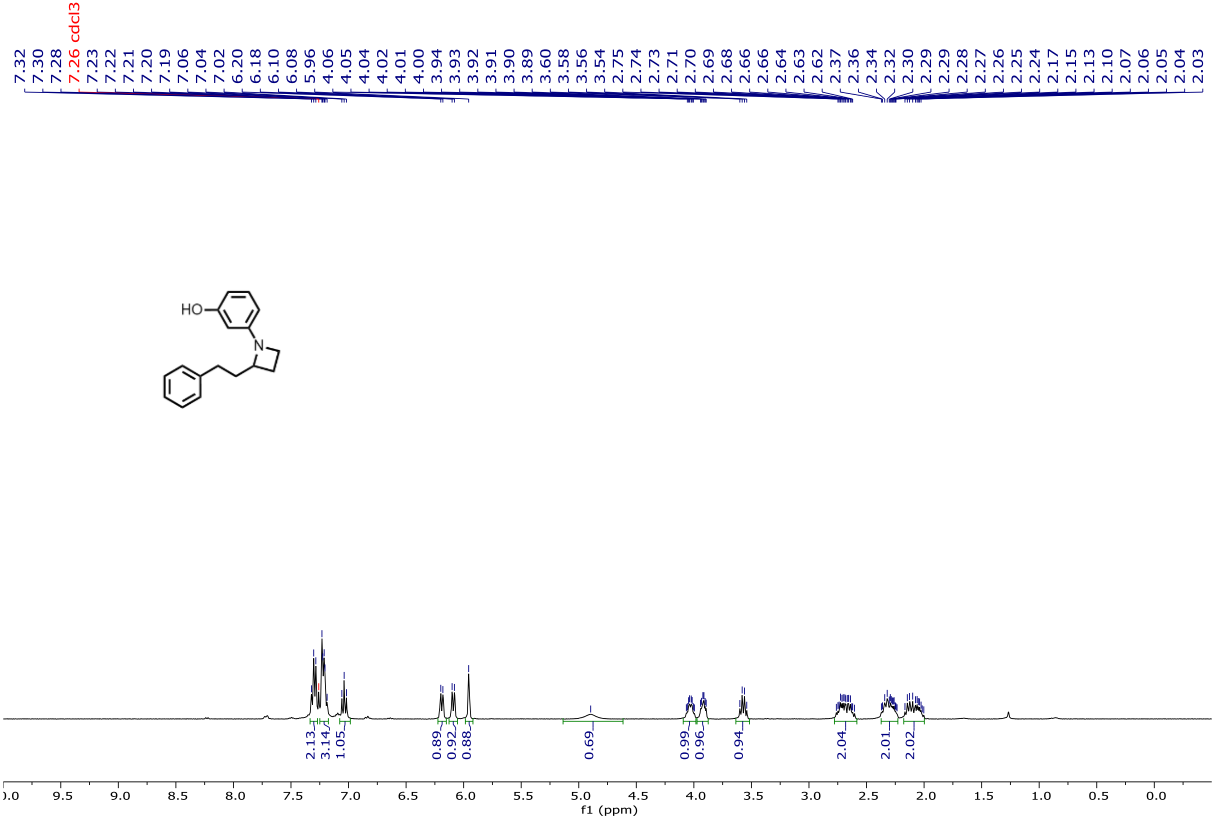
## $^1$H NMR spectrum of 33 in $CDCl_3$. (400 MHz)



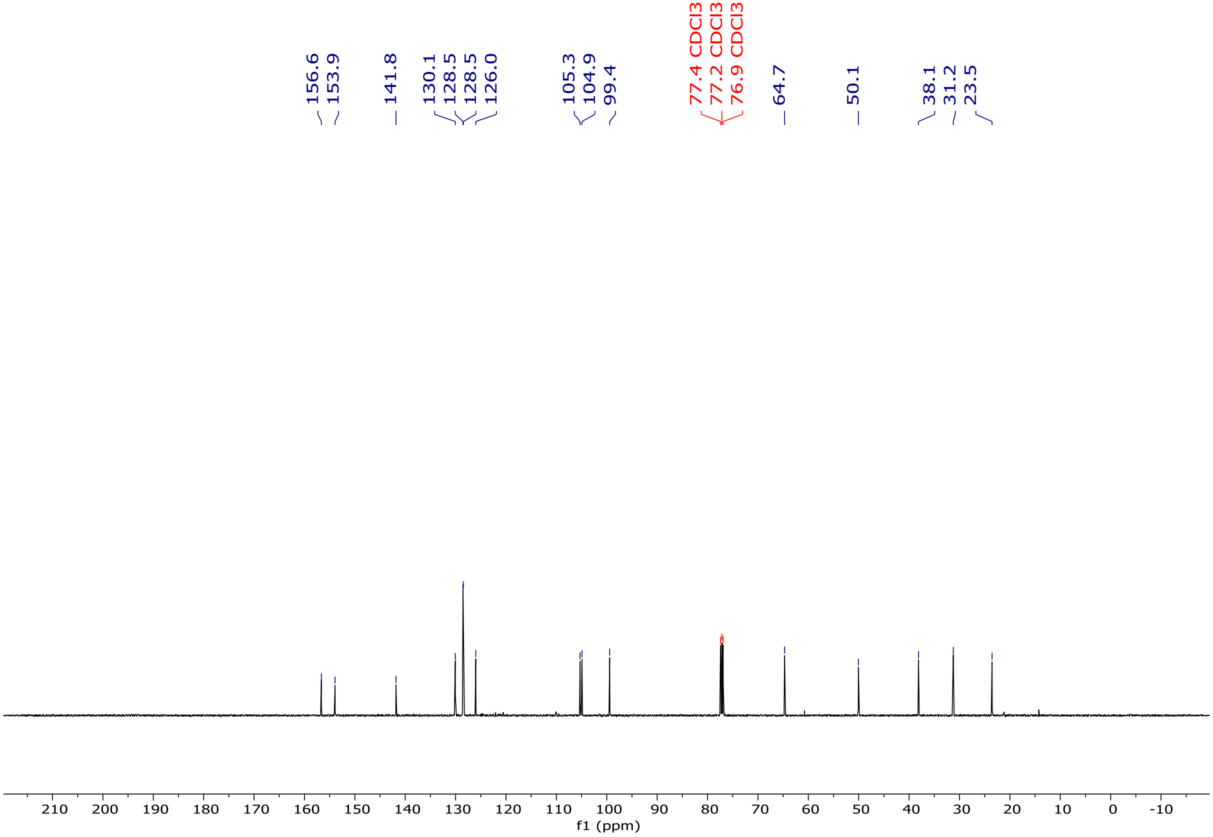
## $^{13}$C NMR spectrum of 33 in $CDCl_3$. (126 MHz)



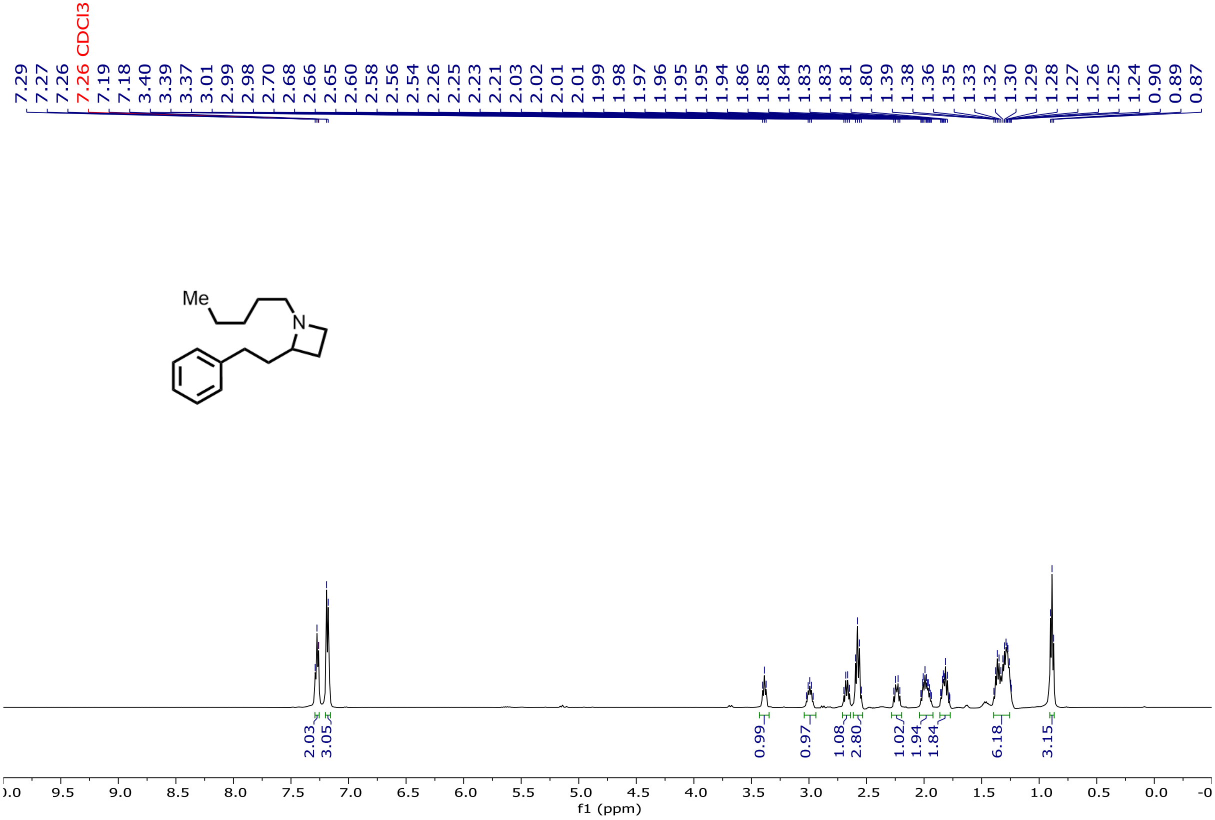
## $^{1}$H NMR spectrum of 34 in $CDCl_3$. (400 MHz)



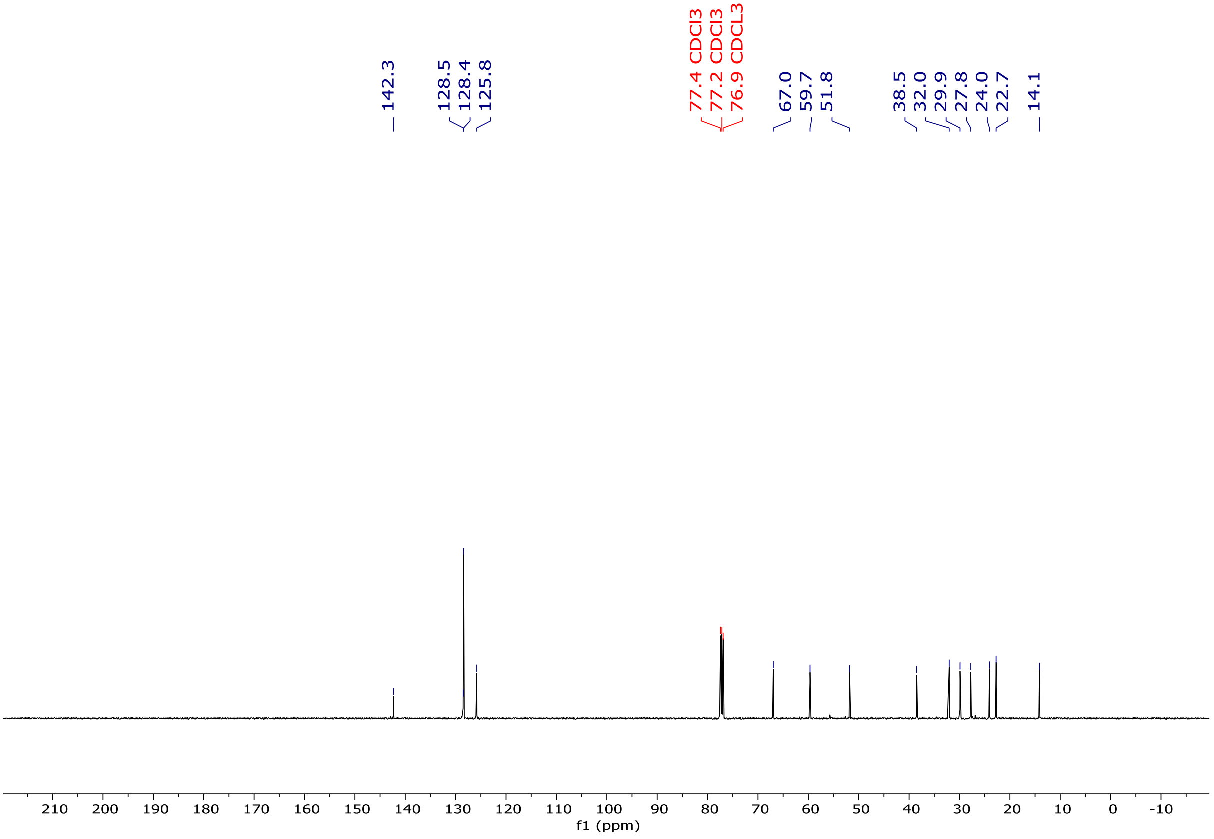
## $^{13}$C NMR spectrum of 34 in $CDCl_3$. (126 MHz)



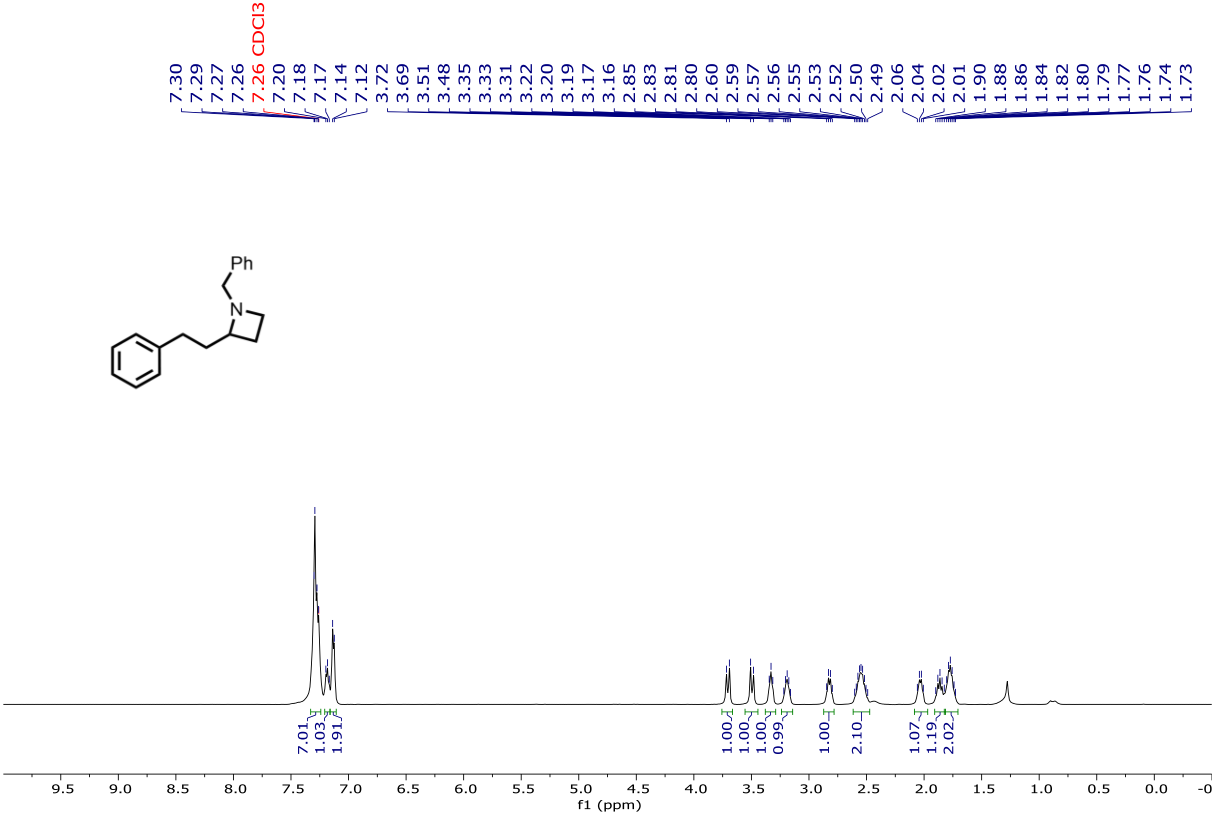
$^{1}$H NMR spectrum of 35 in CDCl$_3$. (500 MHz)



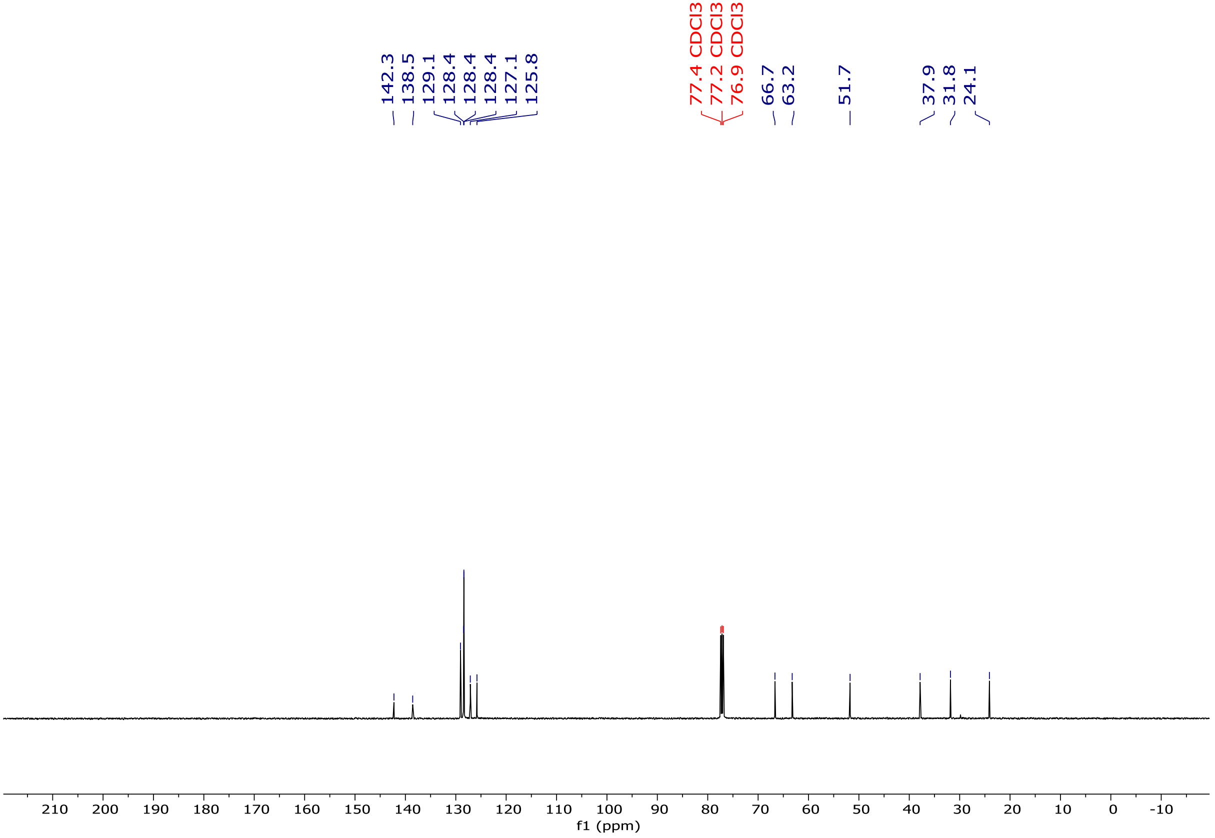
$^{13}$C NMR spectrum of 35 in CDCl$_3$. (126 MHz)



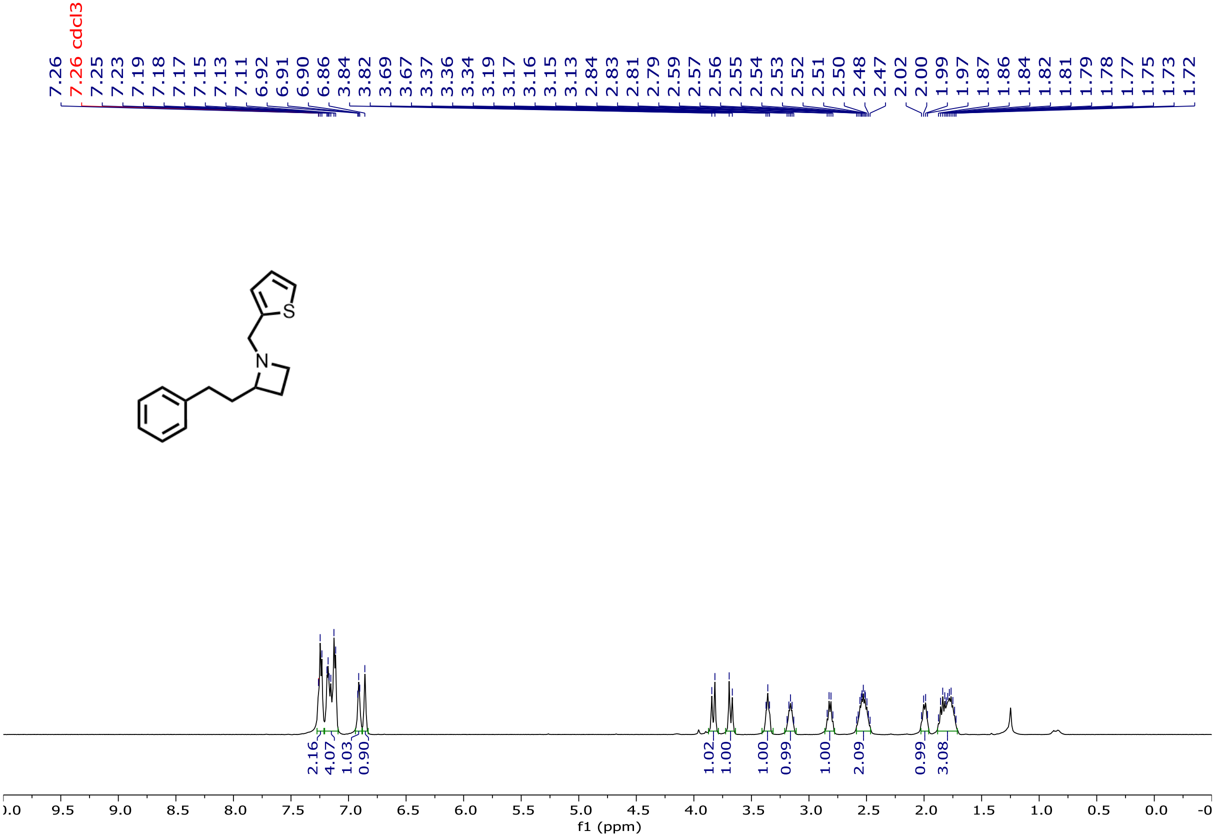
**$^1$H NMR spectrum of 36 in CDCl$_3$. (500 MHz)**



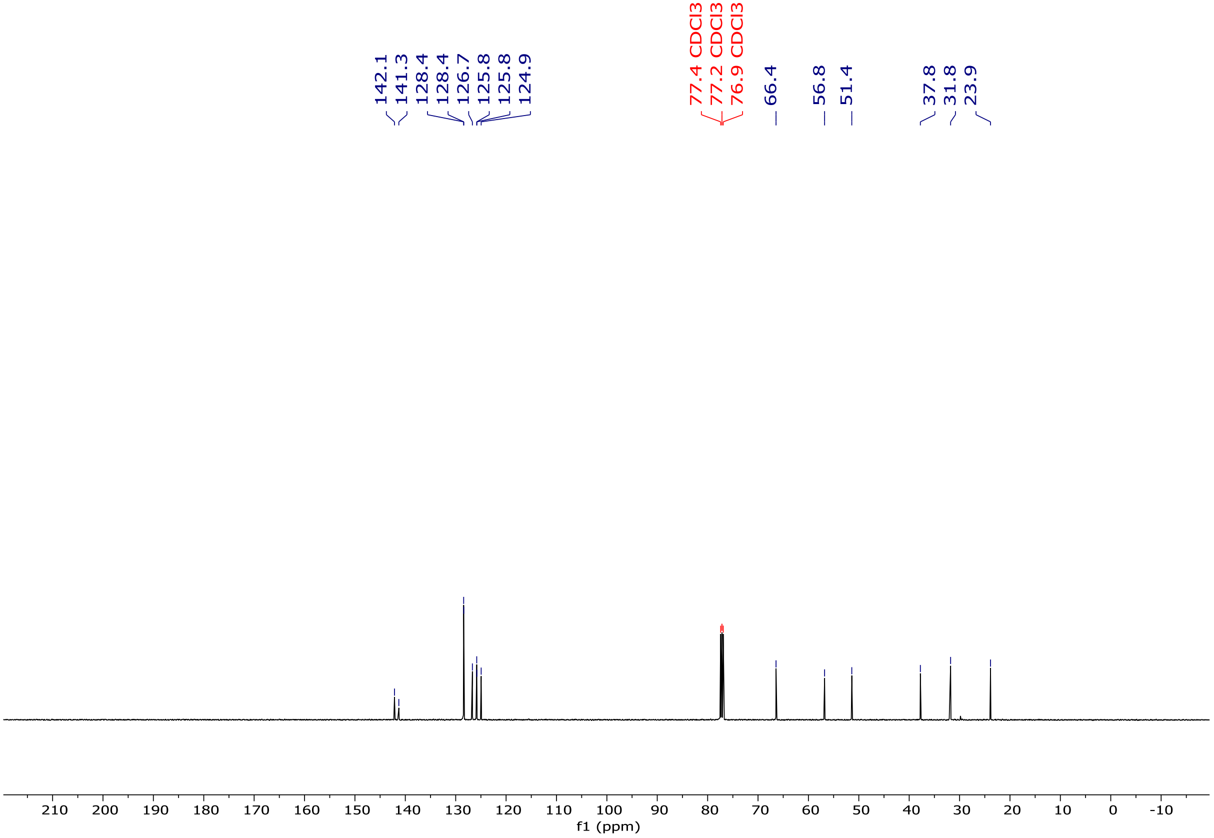
**$^{13}$C NMR spectrum of 36 in CDCl$_3$. (126 MHz)**



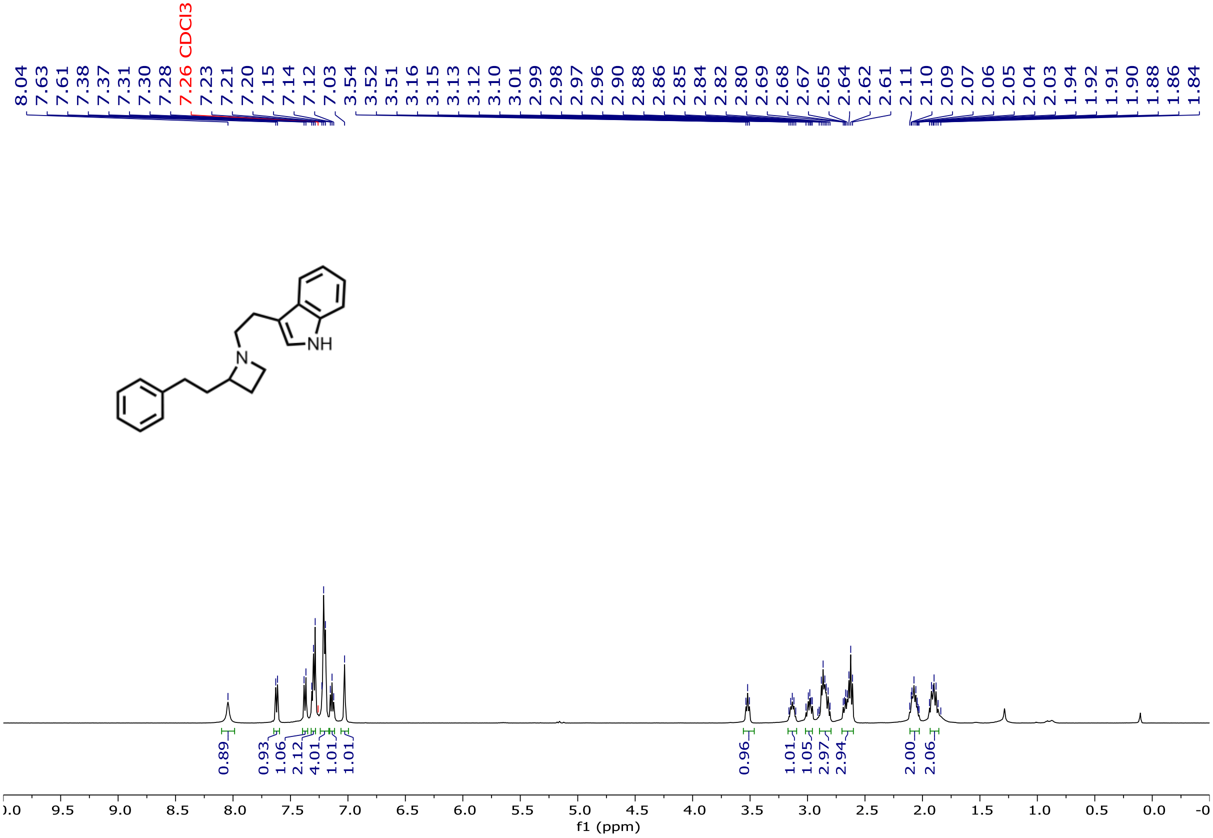
## $^{1}$H NMR spectrum of 37 in CDCl$_3$. (500 MHz)



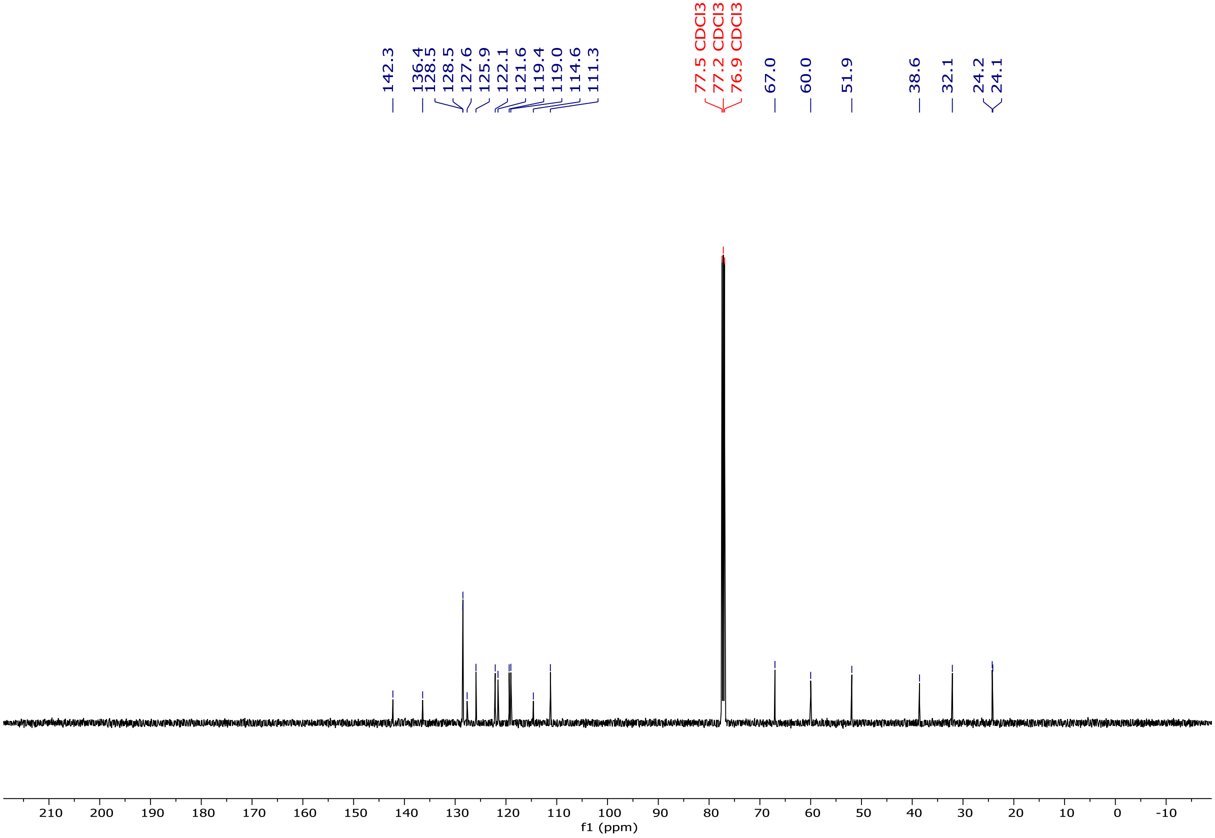
## $^{13}$C NMR spectrum of 37 in CDCl$_3$. (126 MHz)



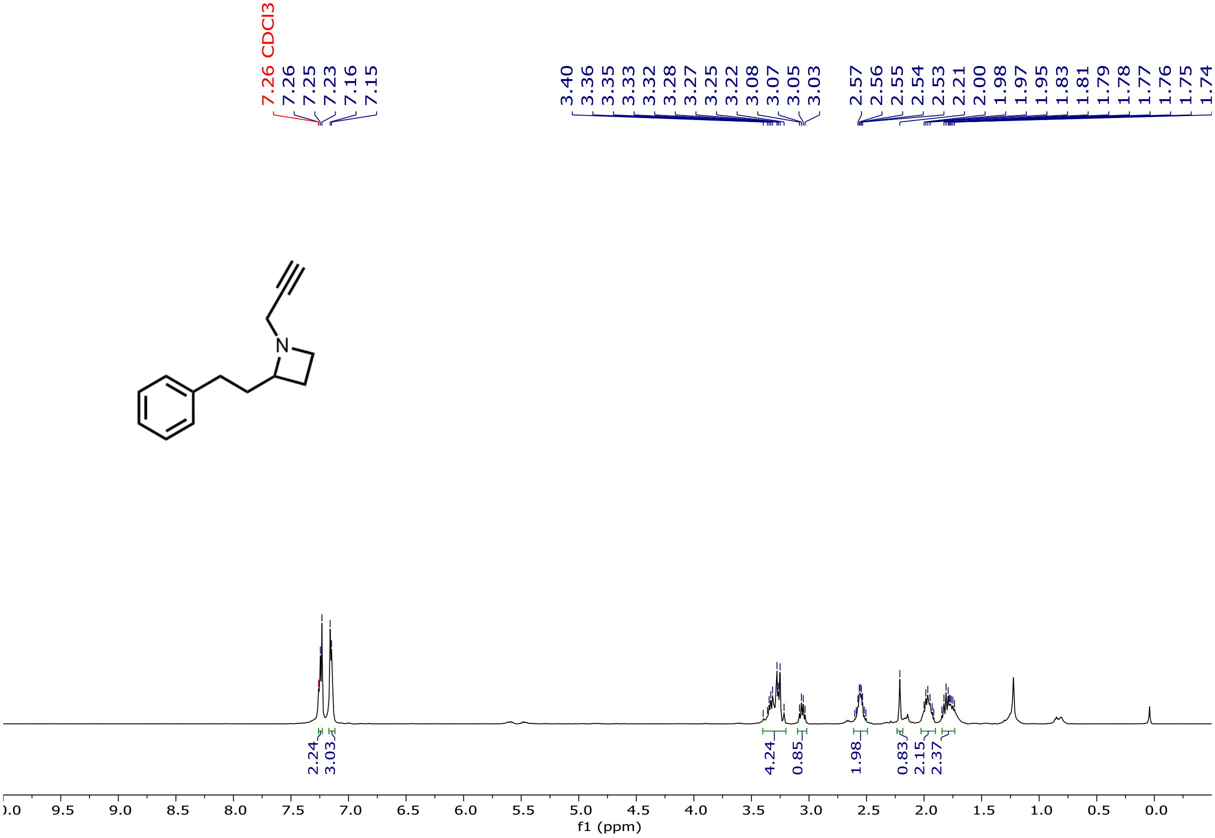
## $^1$H NMR spectrum of 38 in CDCl$_3$. (500 MHz)



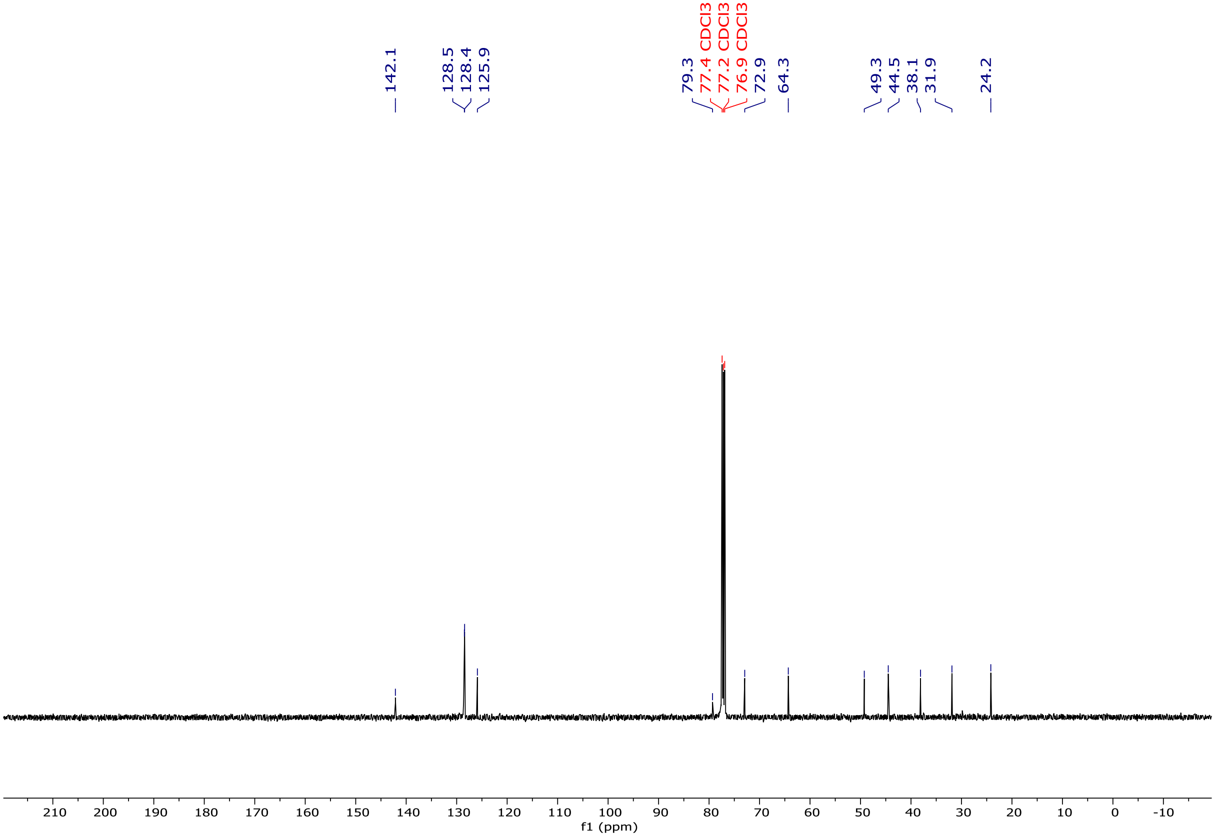
## $^{13}$C NMR spectrum of 38 in CDCl$_3$. (126 MHz)



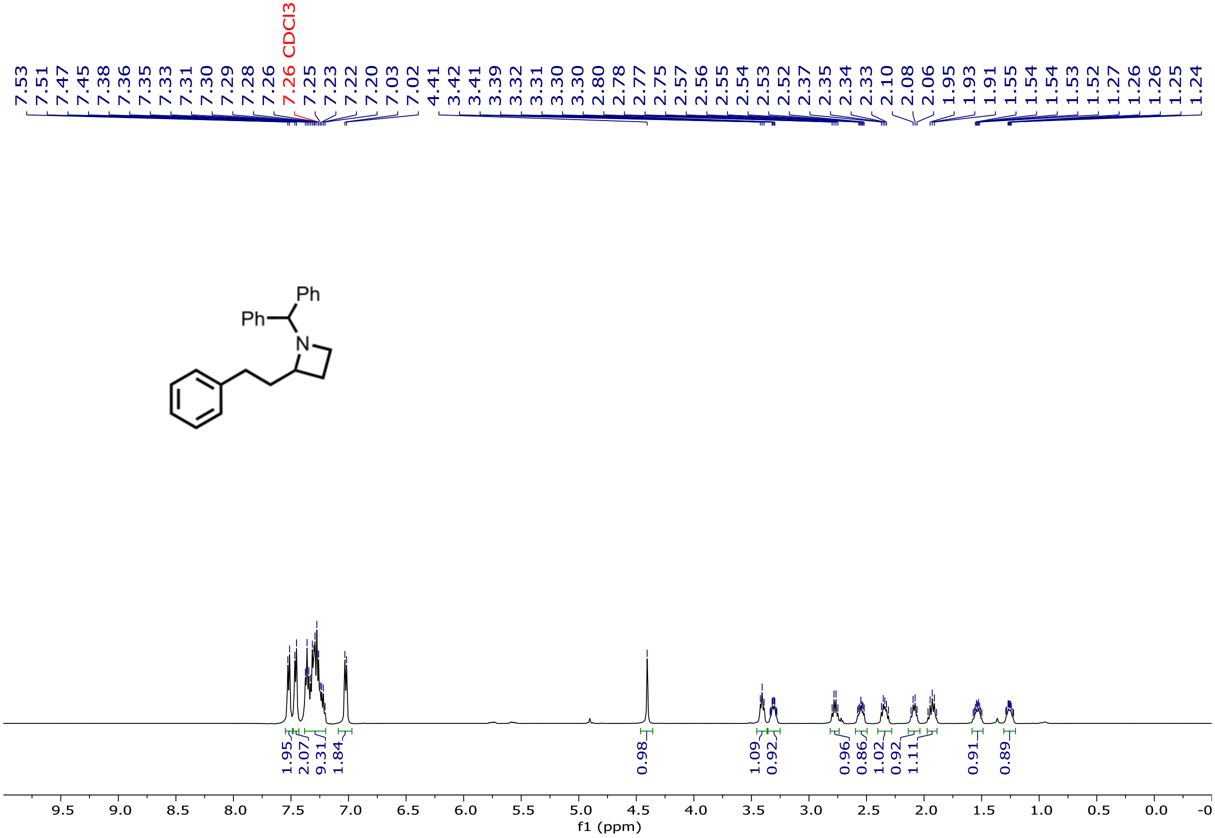
## $^{1}H$ NMR spectrum of 39 in $CDCl_3$. (500 MHz)



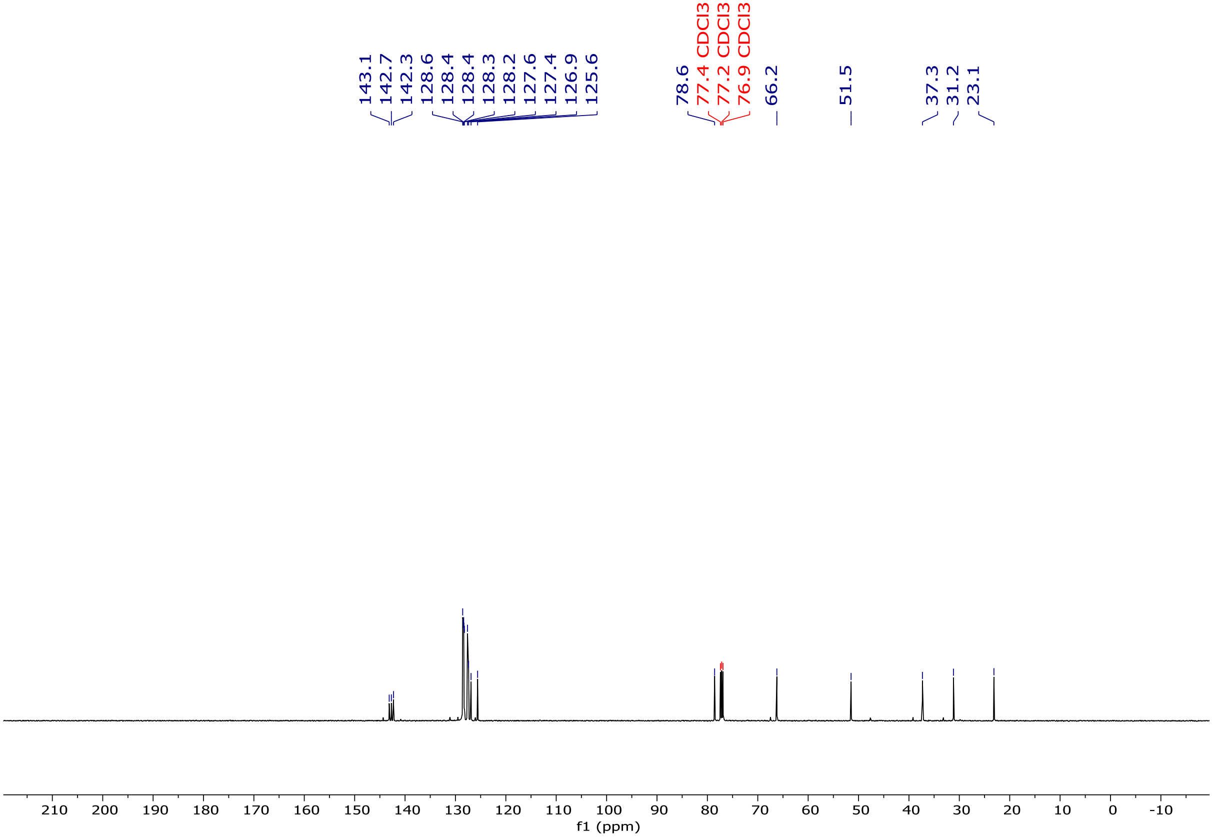
## $^{13}C$ NMR spectrum of 39 in $CDCl_3$. (126 MHz)



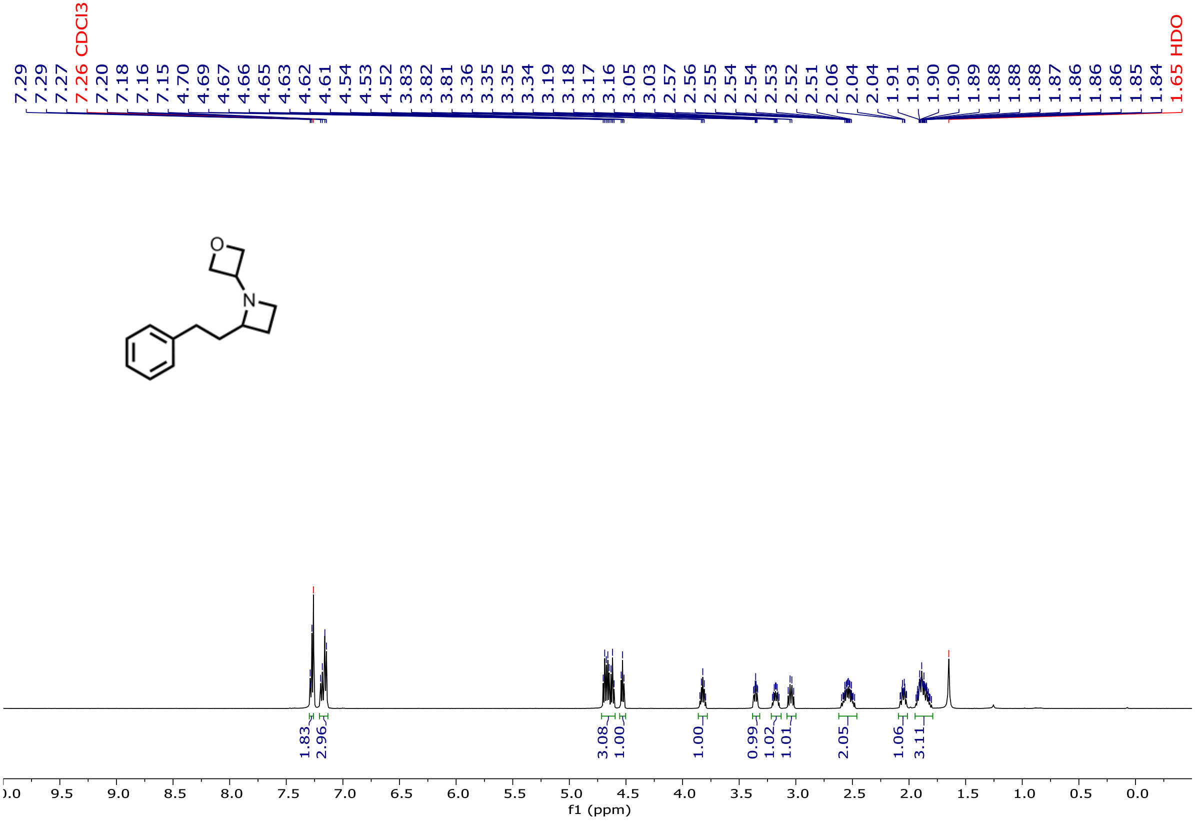
### $^{1}$H NMR spectrum of 40 in CDCl$_3$. (500 MHz)



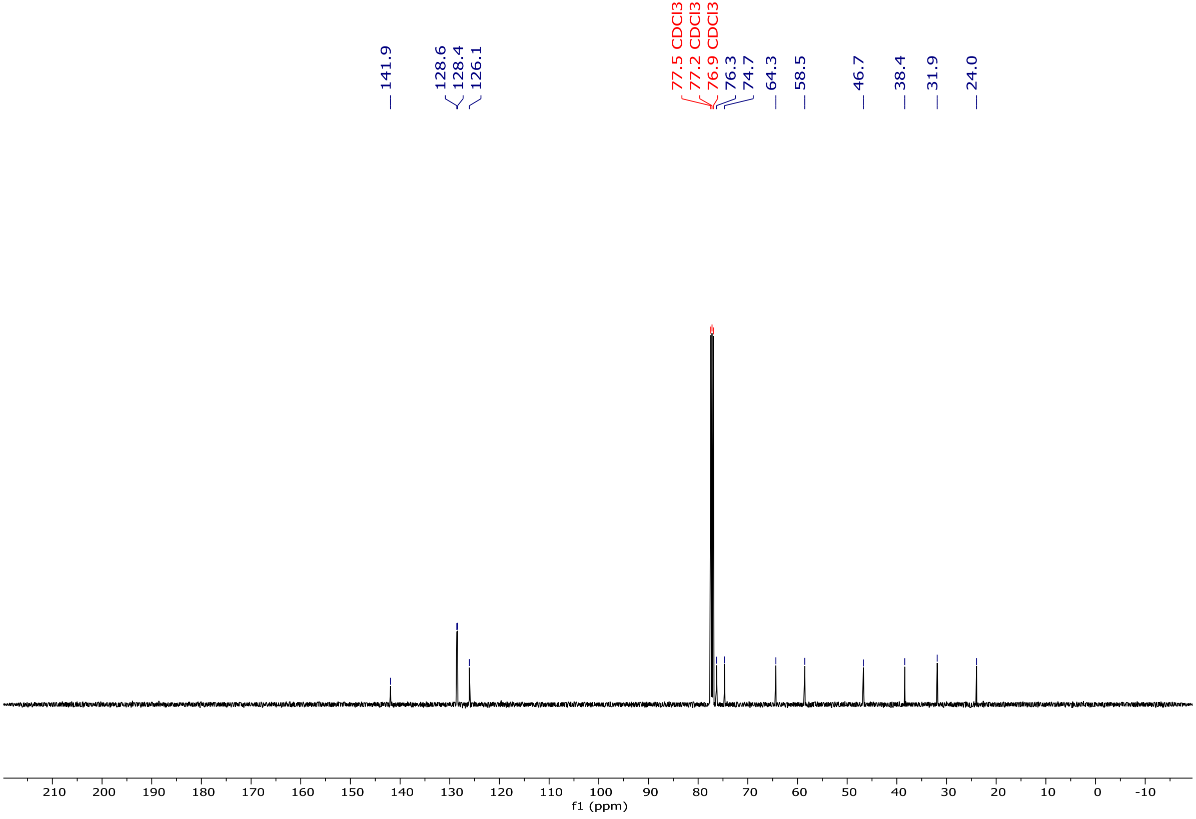
### $^{13}$C NMR spectrum of 40 in CDCl$_3$. (126 MHz)



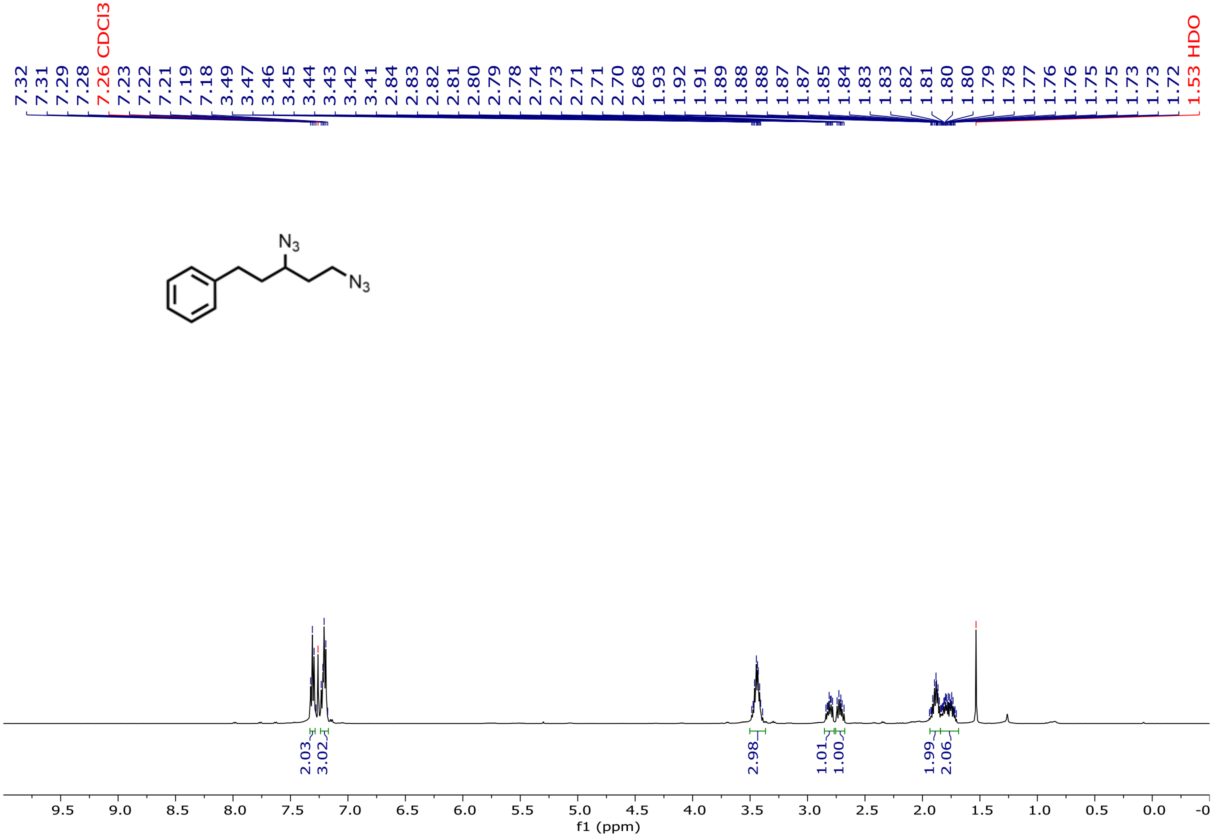
$^1$H NMR spectrum of 41 in CDCl$_3$. (500 MHz)



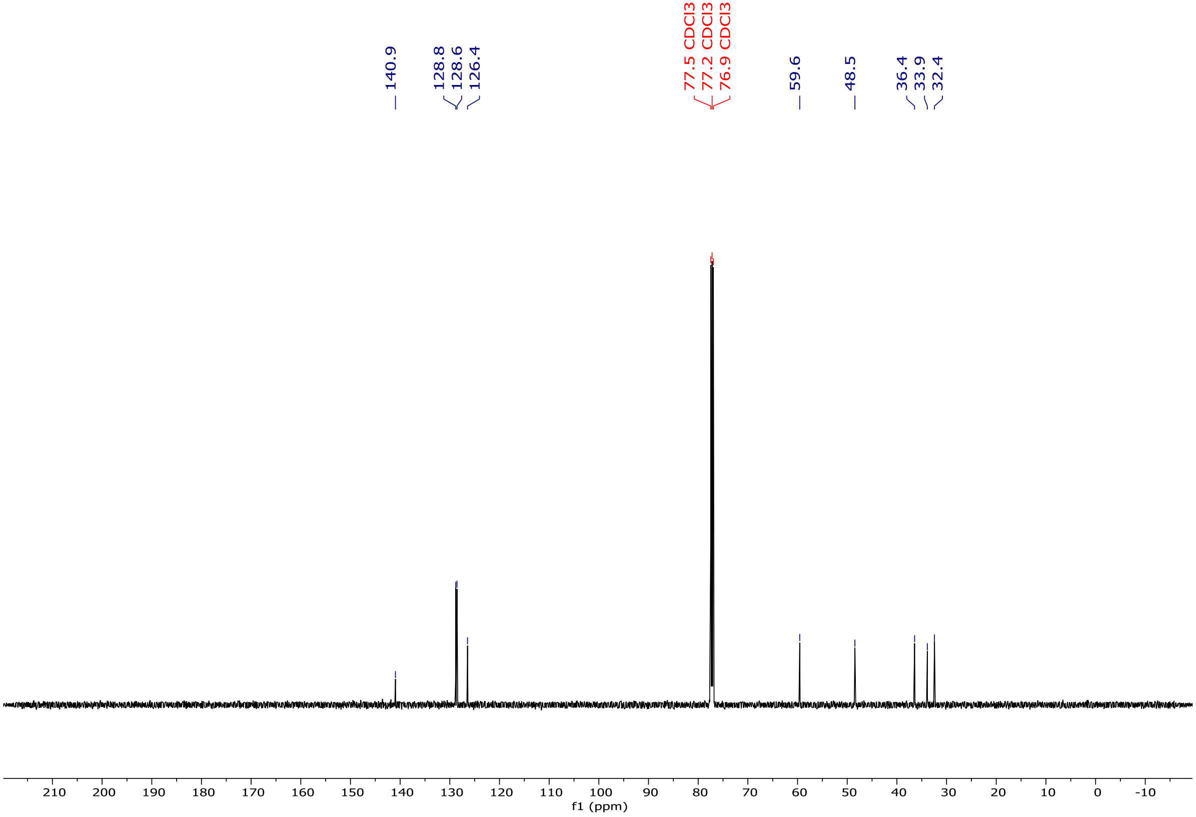
$^{13}$C NMR spectrum of 41 in CDCl$_3$. (126 MHz)



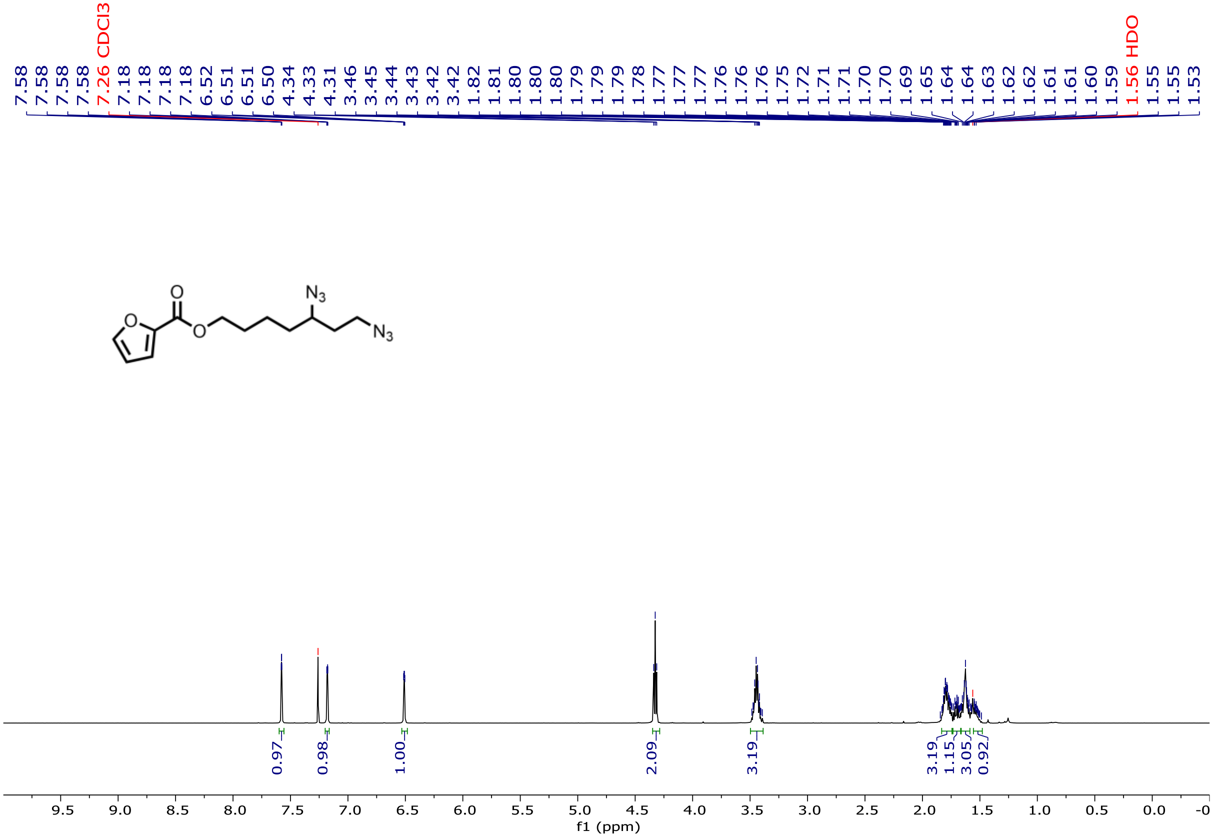
### $^1$H NMR spectrum of 42 in $CDCl_3$. (500 MHz)



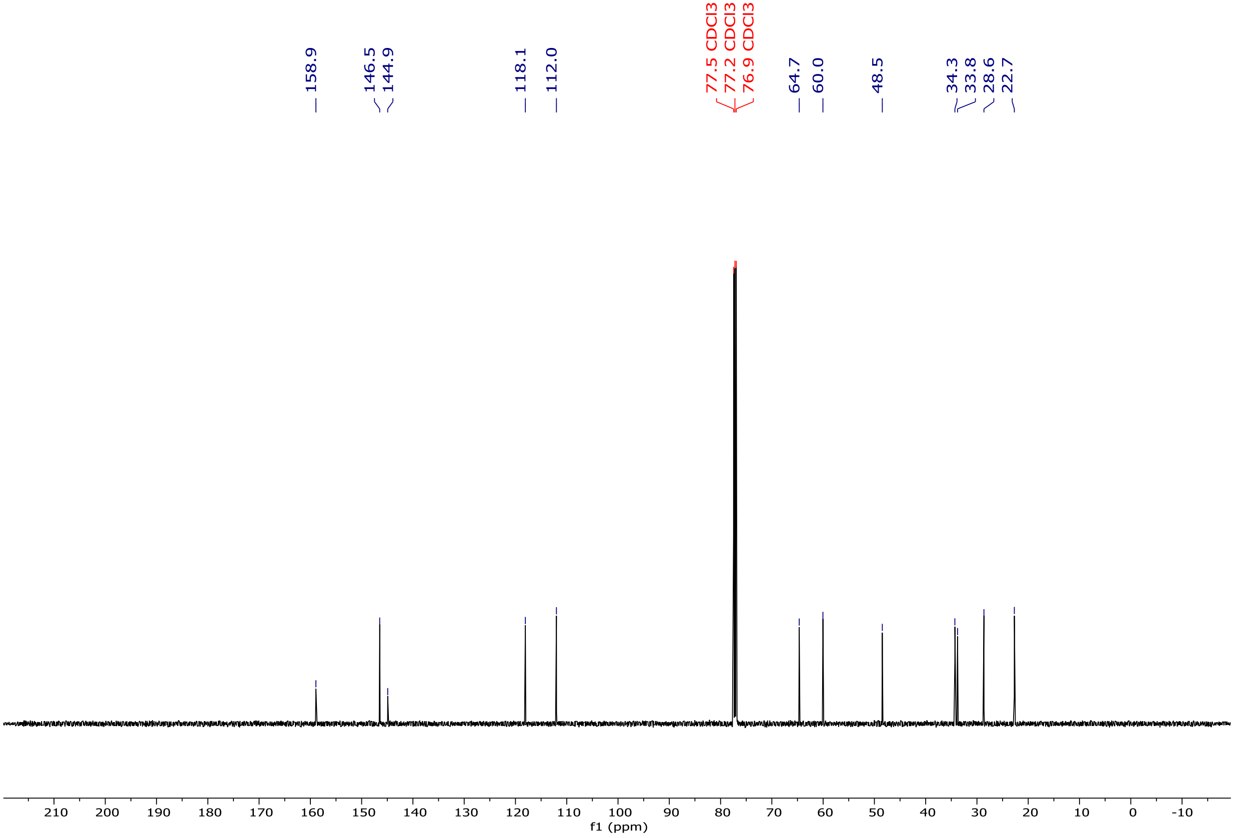
### $^{13}$C NMR spectrum of 42 in $CDCl_3$. (126 MHz)



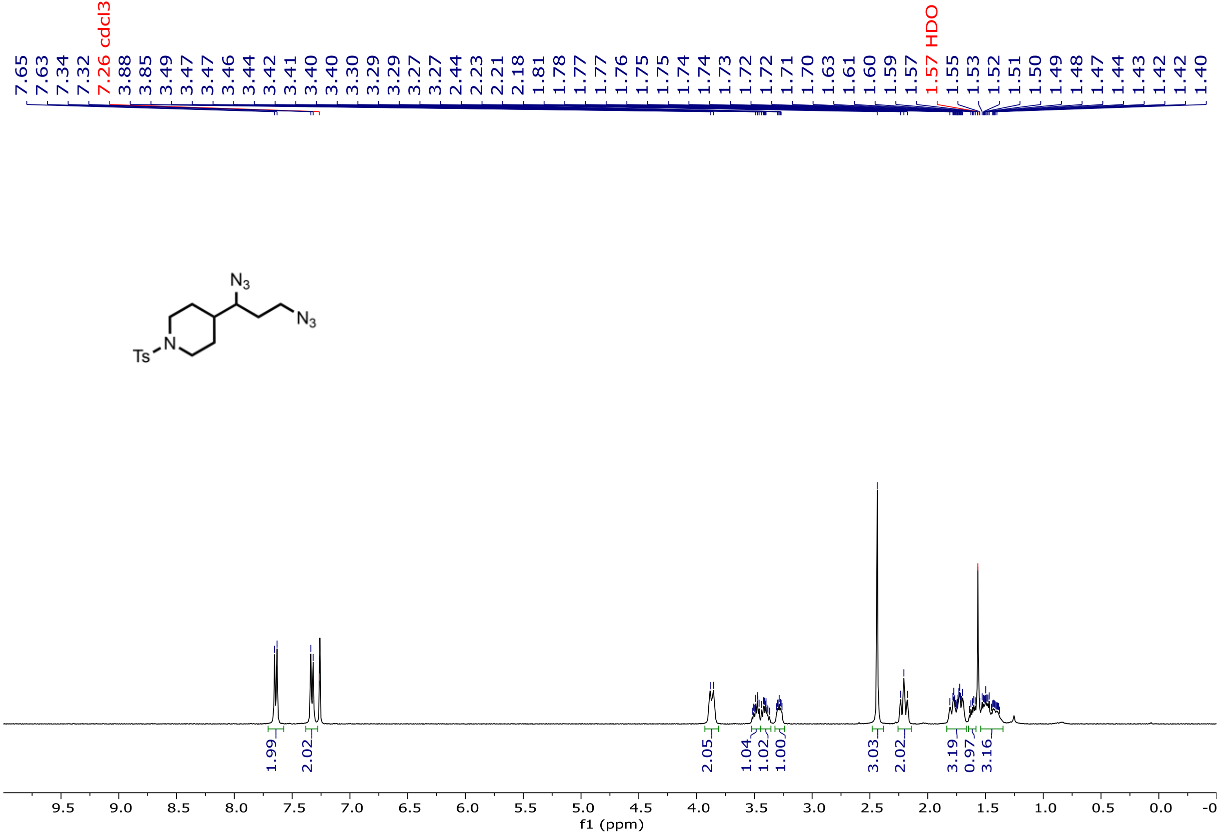
## $^{1}$H NMR spectrum of 43 in CDCl$_3$. (500 MHz)



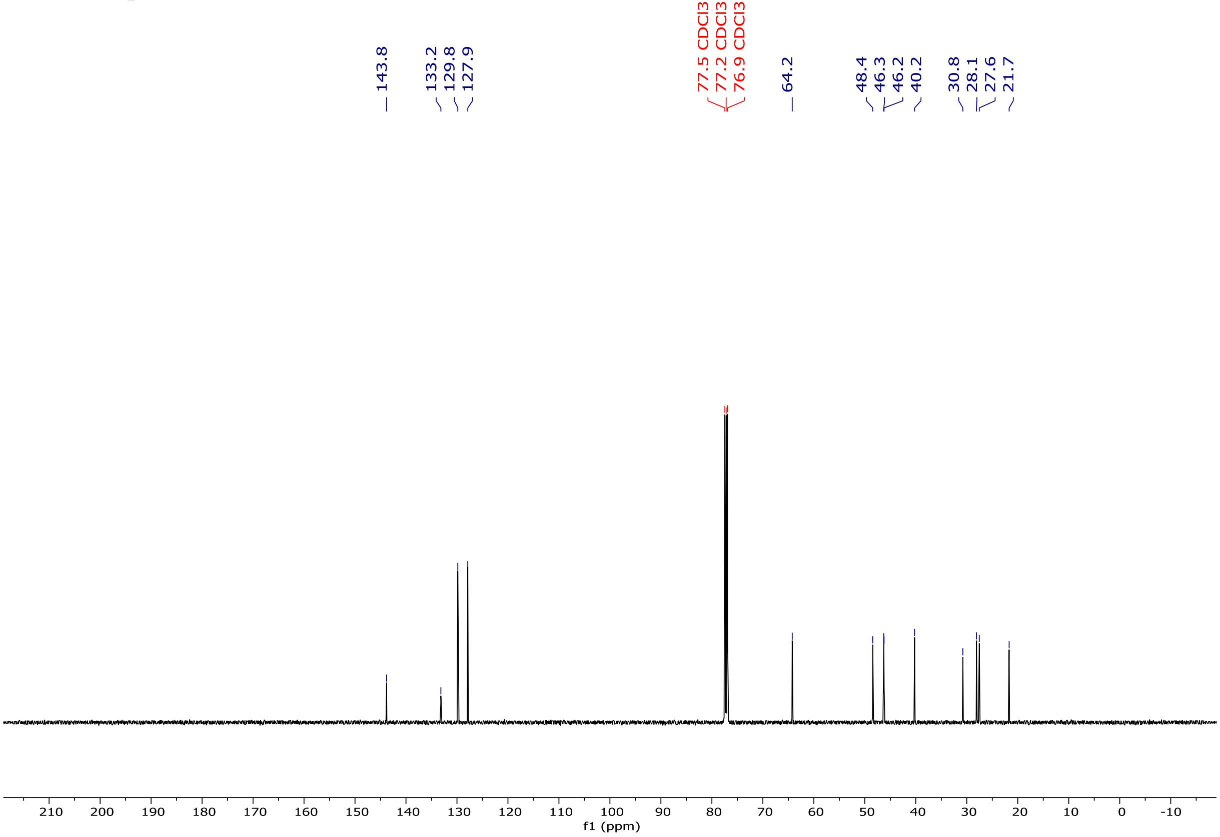
## $^{13}$C NMR spectrum of 43 in CDCl$_3$. (126 MHz)



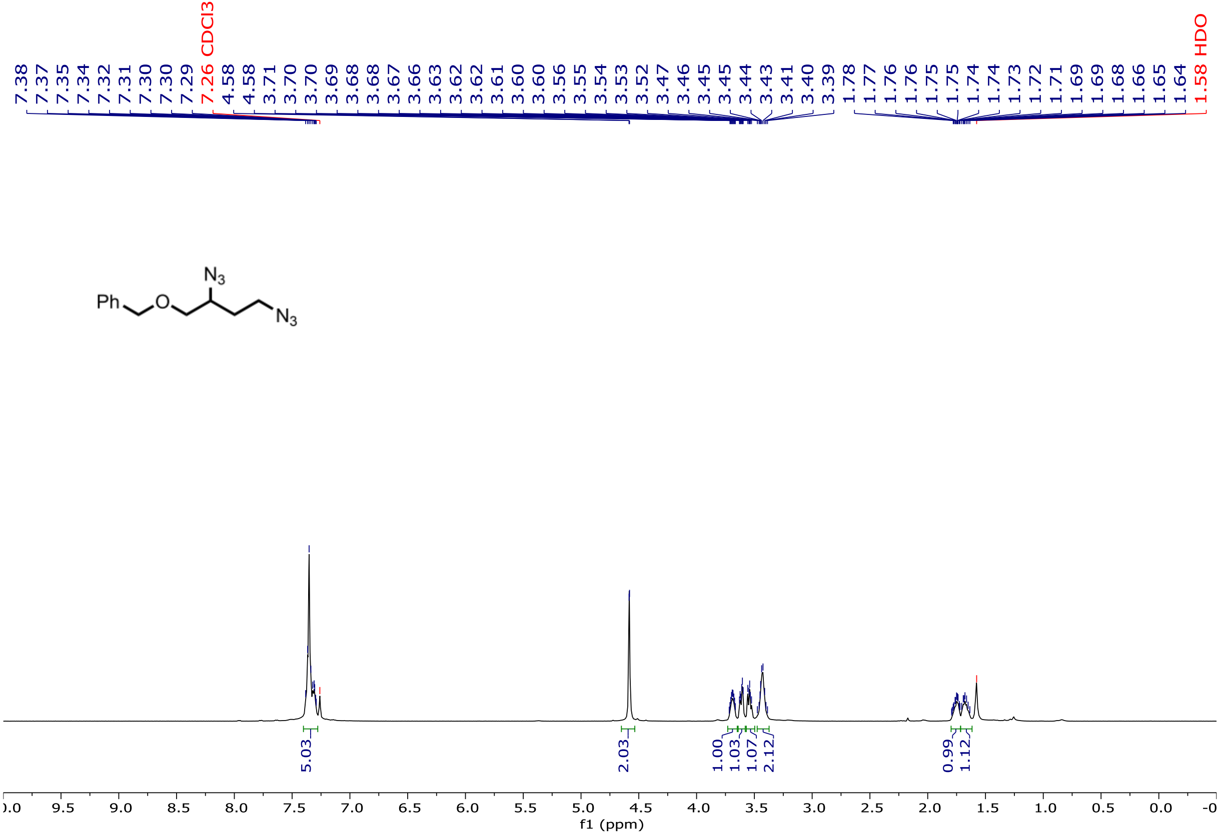
## $^1$H NMR spectrum of 44 in $CDCl_3$. (400 MHz)



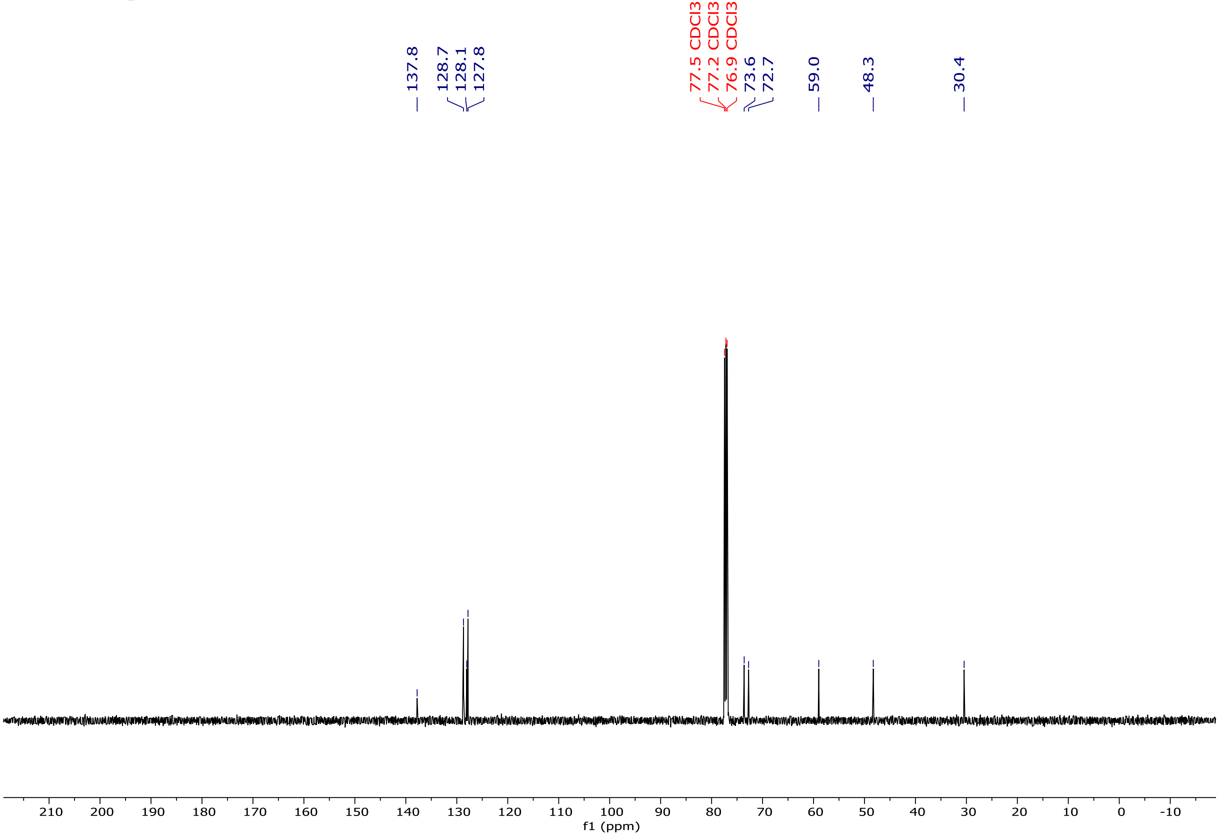
## $^{13}$C NMR spectrum of 44 in $CDCl_3$. (126 MHz)



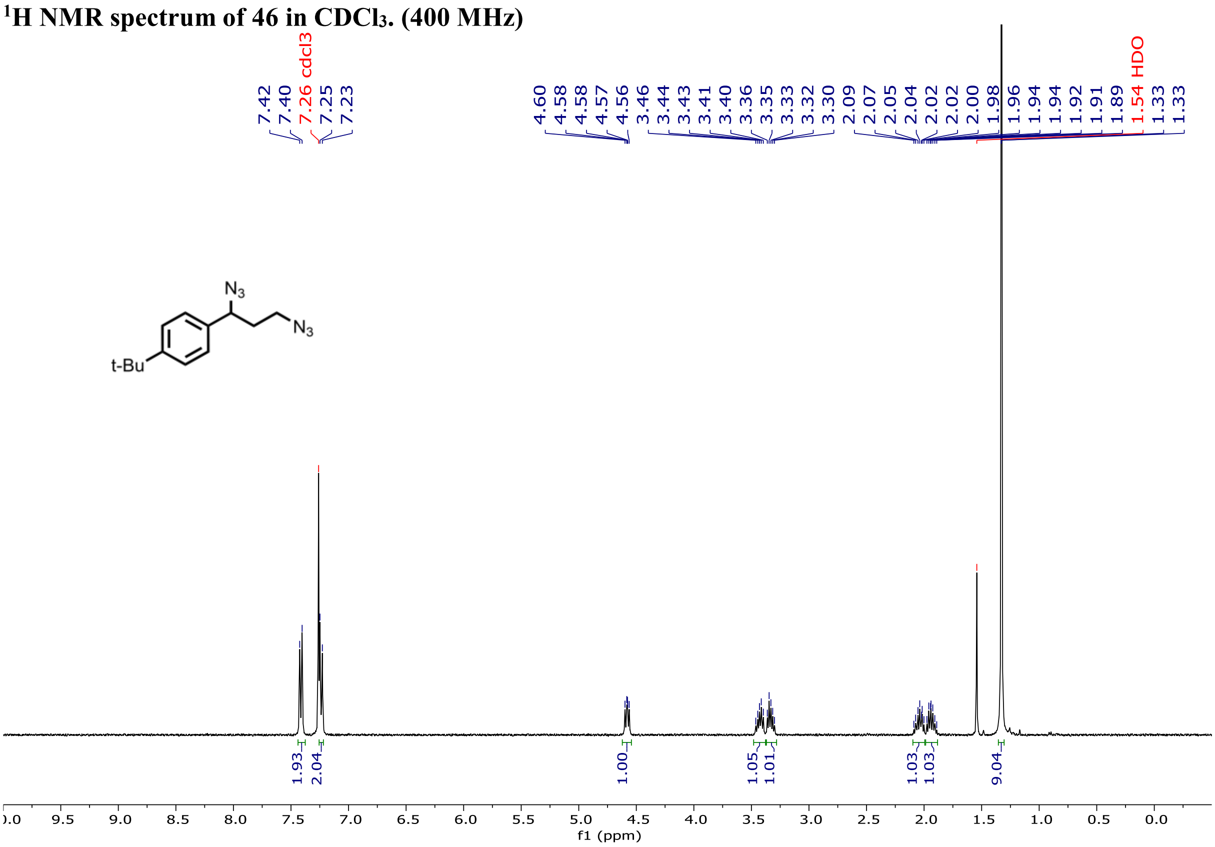
### $^{1}$H NMR spectrum of 45 in CDCl$_3$. (500 MHz)



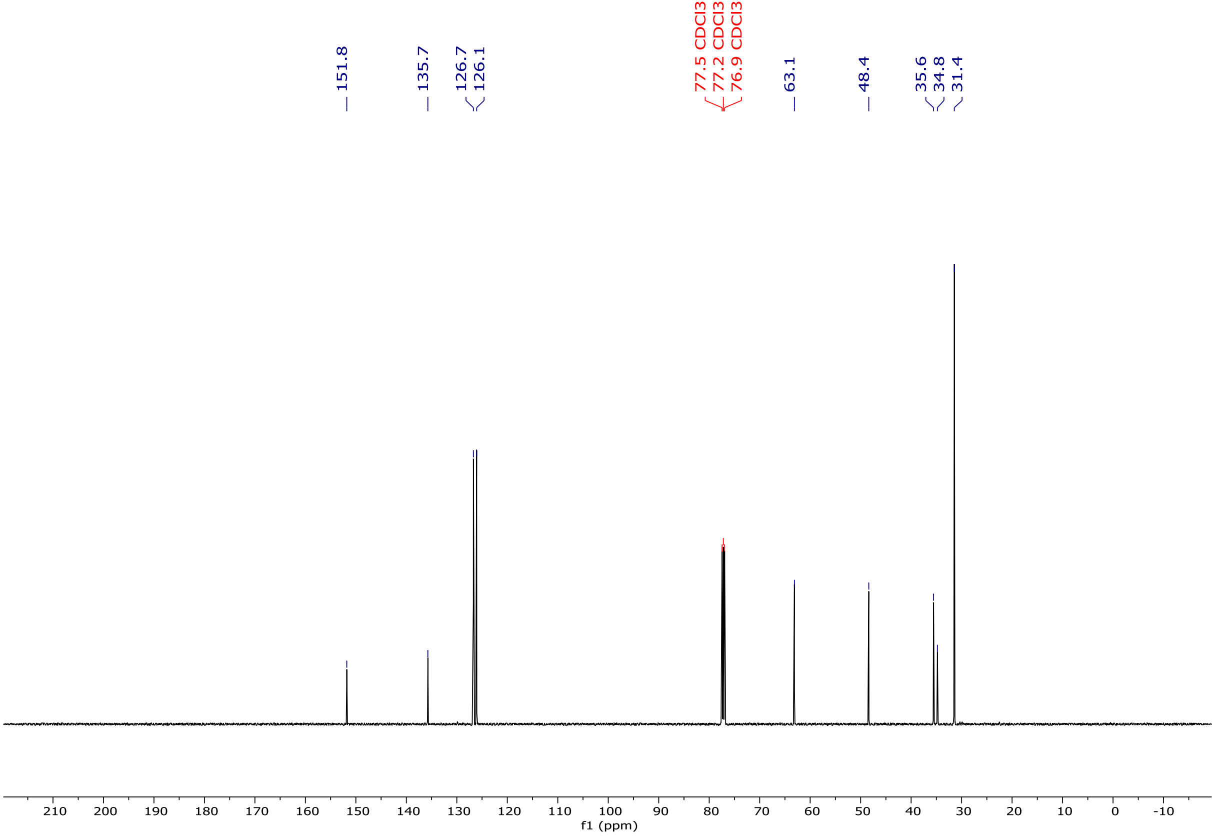
### $^{13}$C NMR spectrum of 45 in CDCl$_3$. (126 MHz)



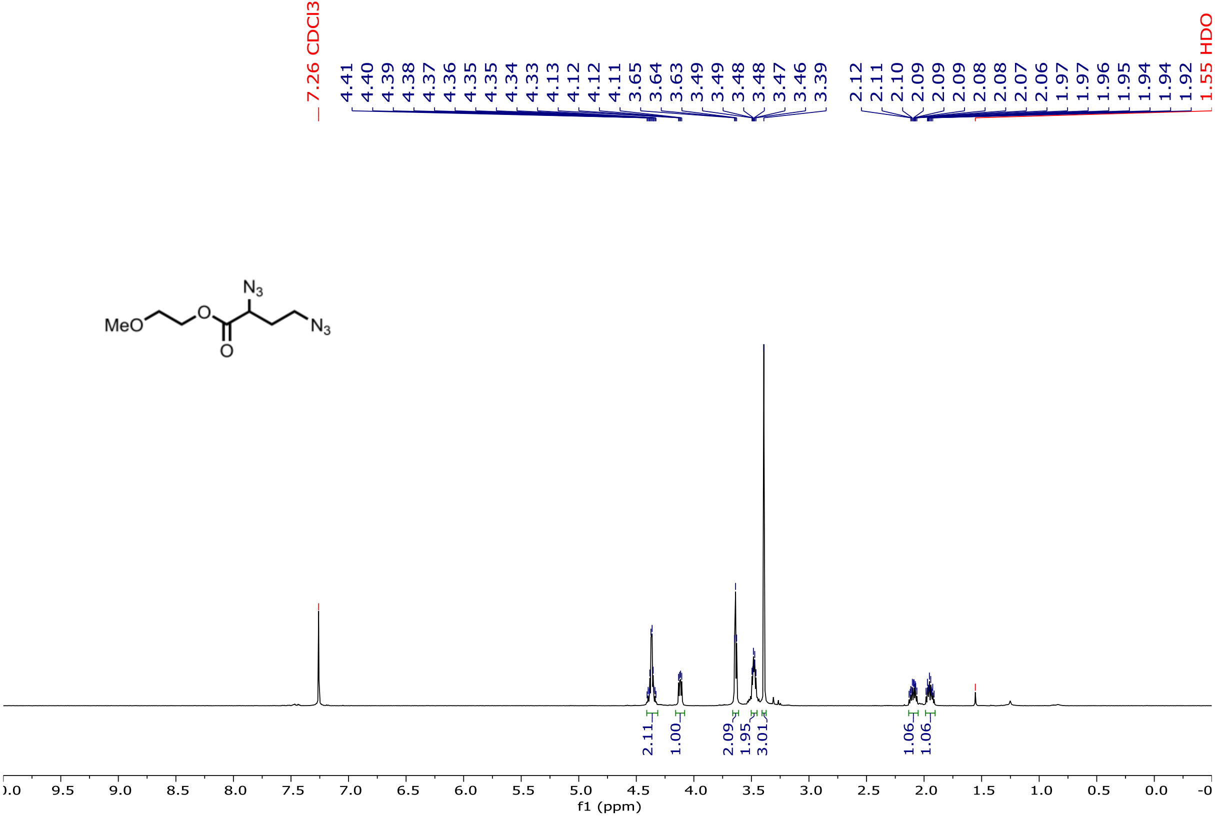
**$^1$H NMR spectrum of 46 in CDCl$_3$. (400 MHz)**



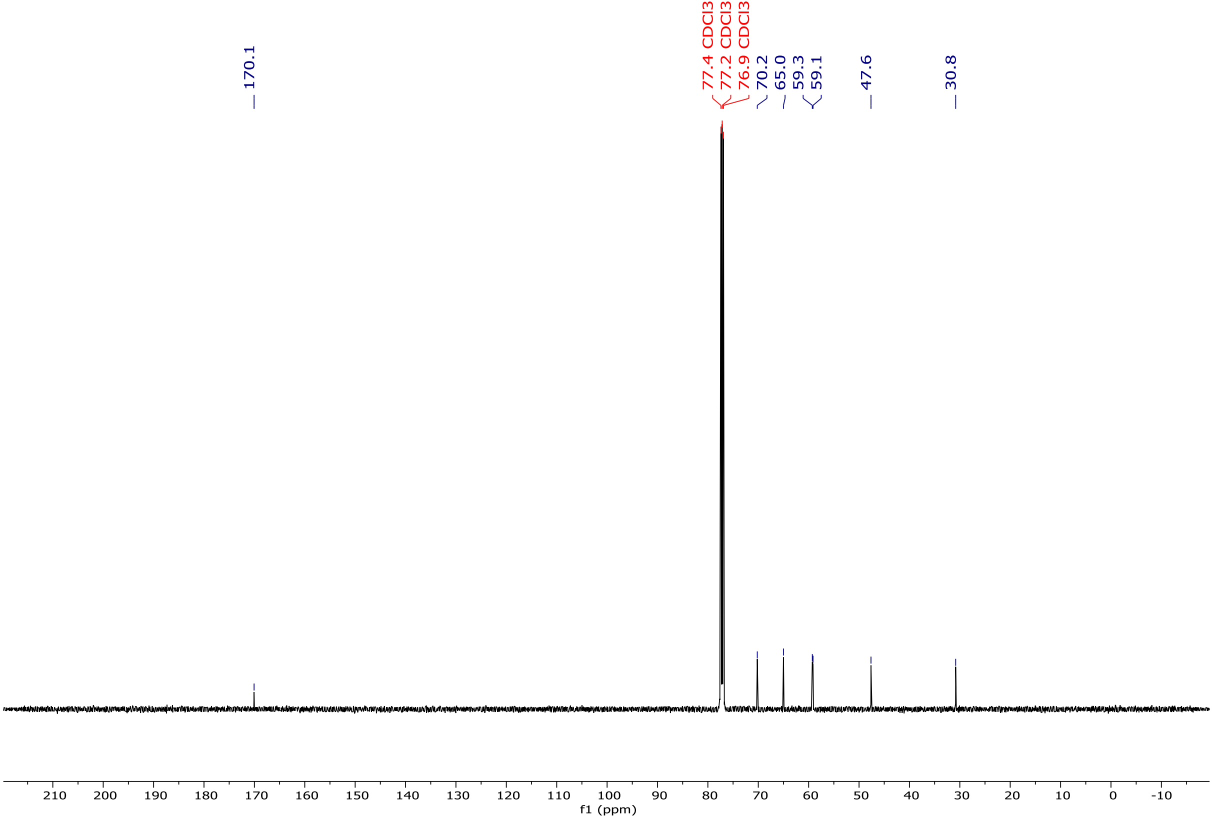
**$^{13}$C NMR spectrum of 46 in CDCl$_3$. (126 MHz)**



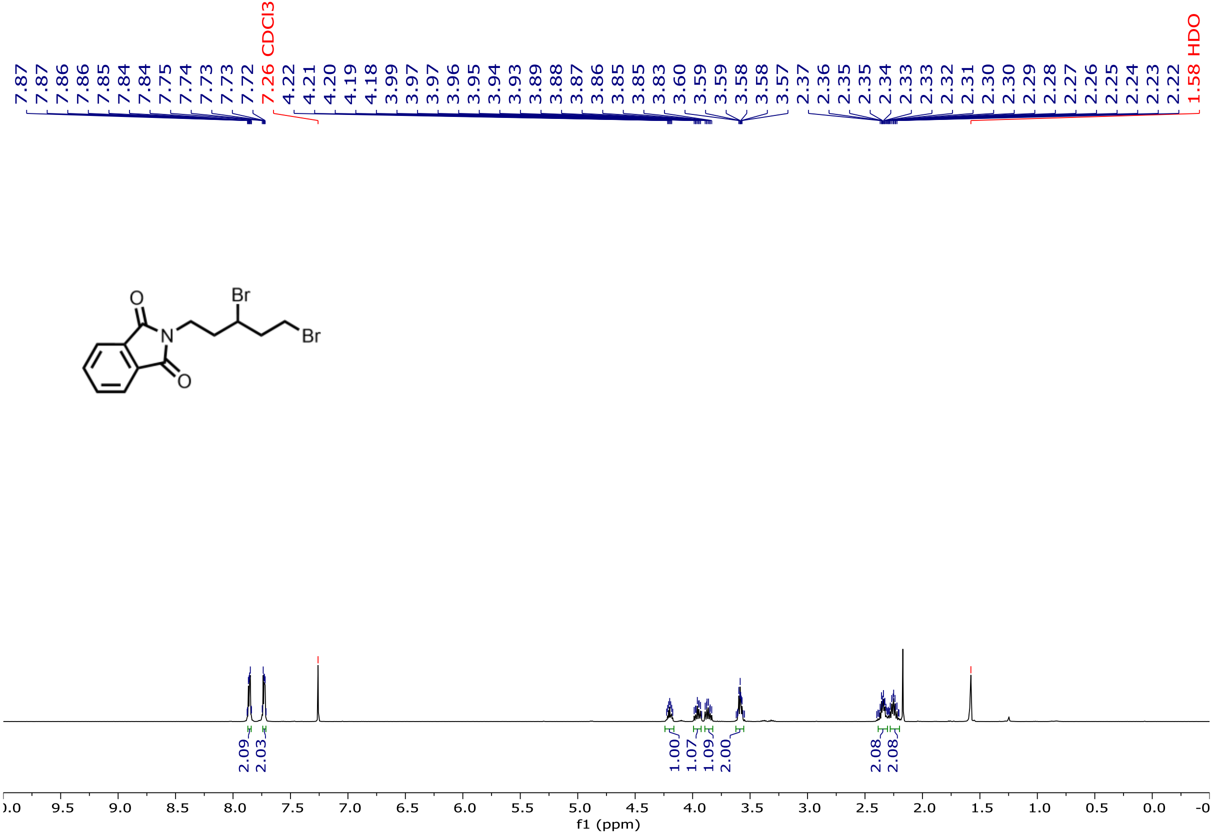
$^{1}$H NMR spectrum of 47 in $CDCl_3$. (500 MHz)



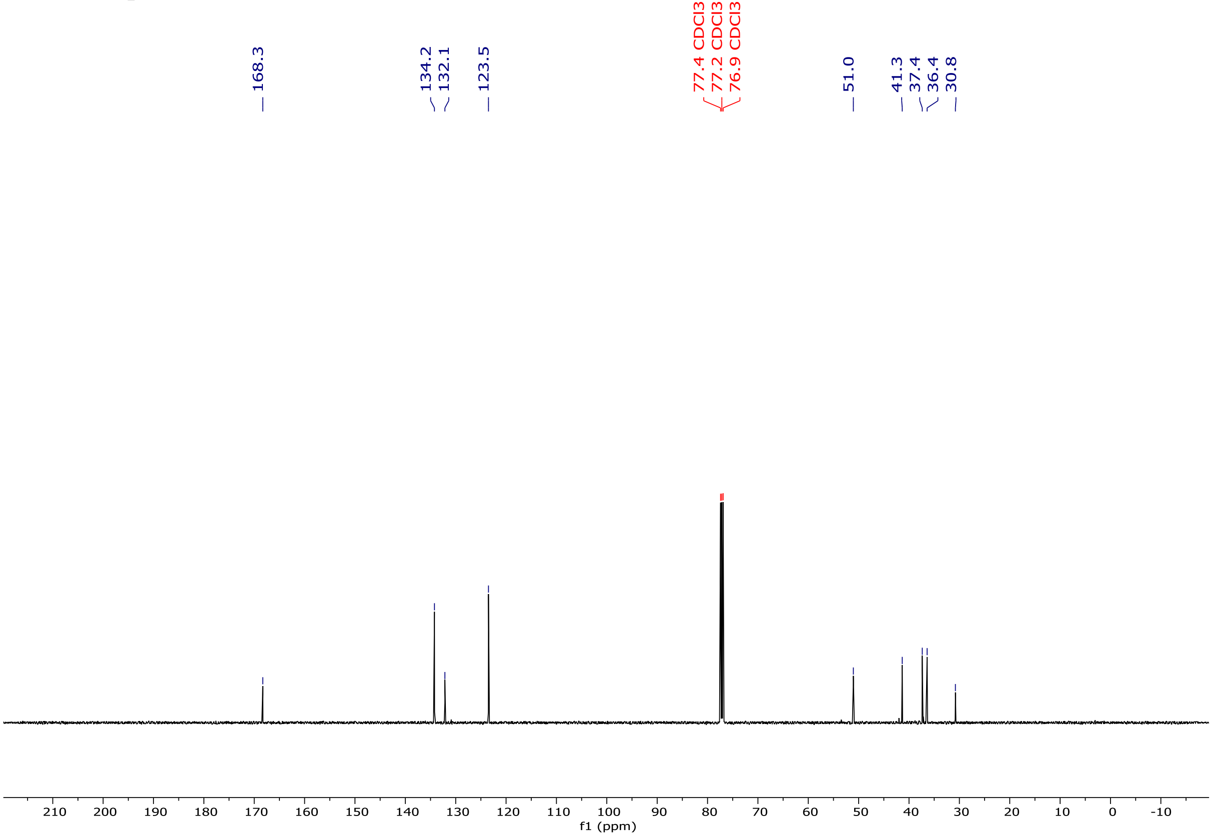
$^{13}$C NMR spectrum of 47 in $CDCl_3$. (500 MHz)



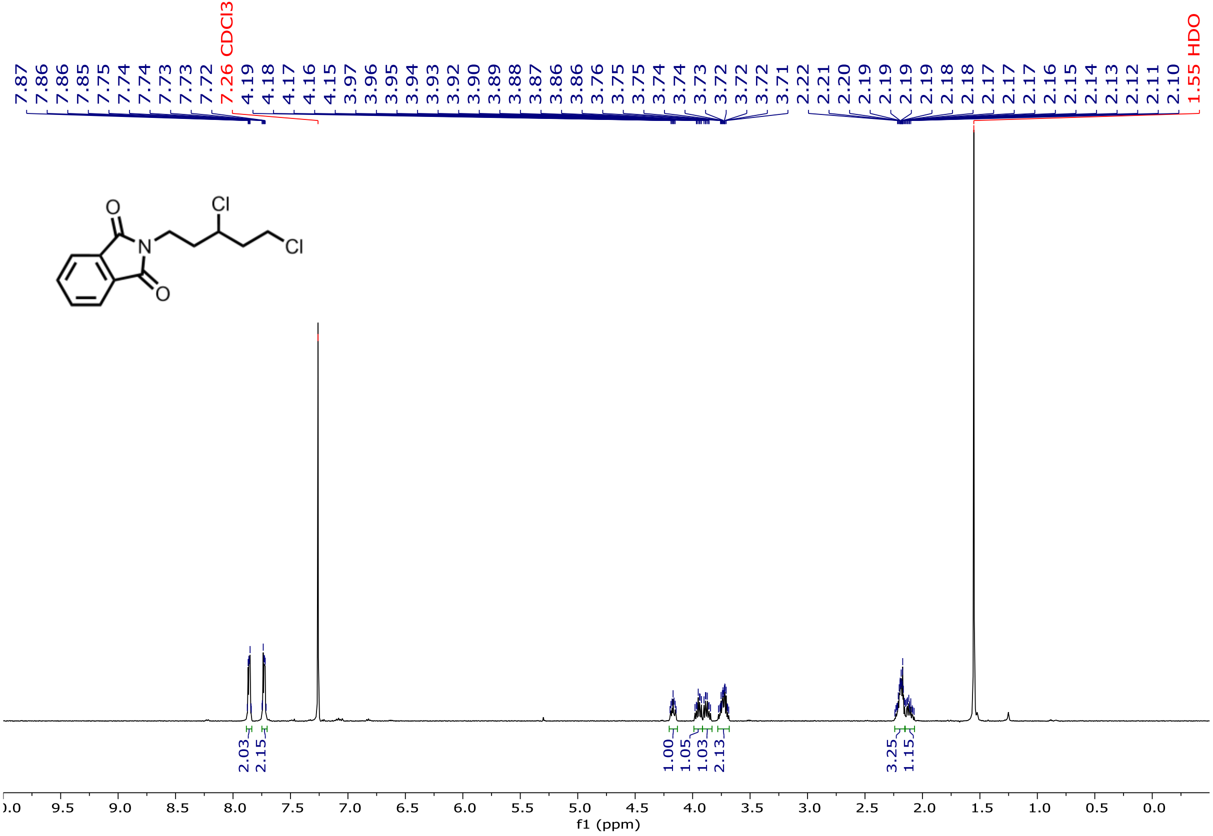
## $^1$H NMR spectrum of 48 in $CDCl_3$. (500 MHz)



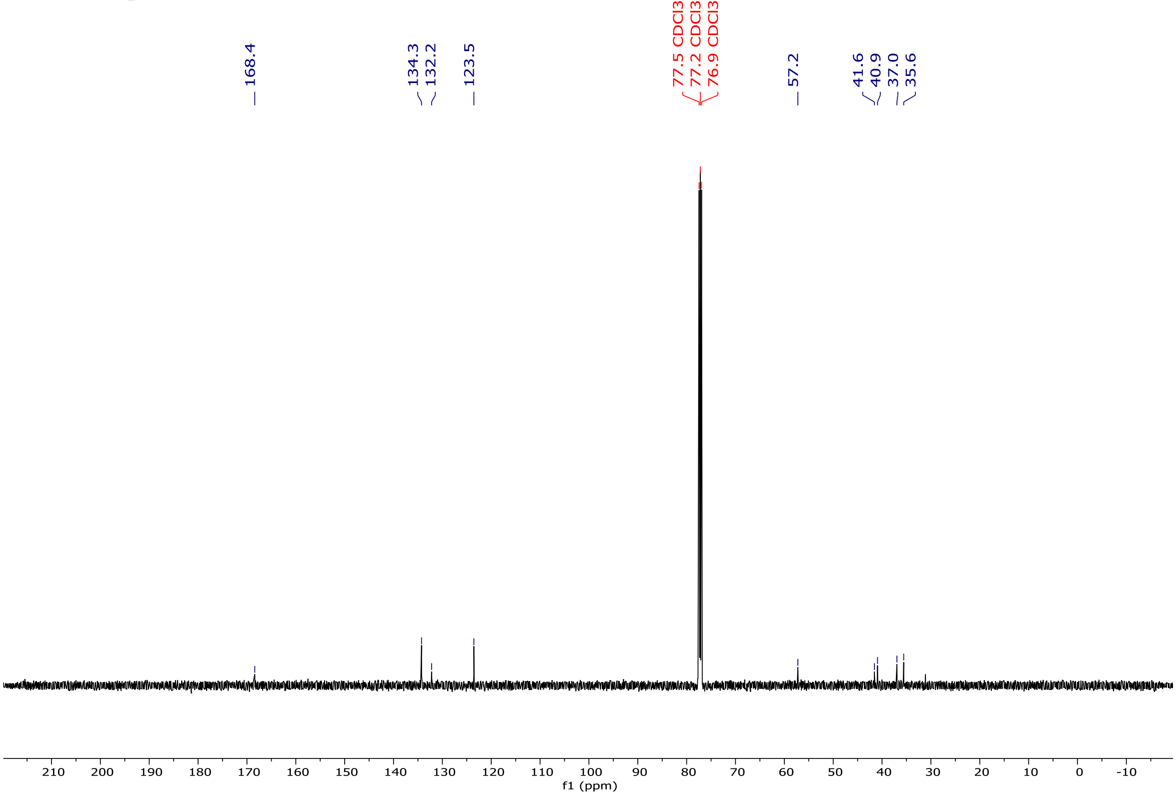
## $^{13}$C NMR spectrum of 48 in $CDCl_3$. (126 MHz)



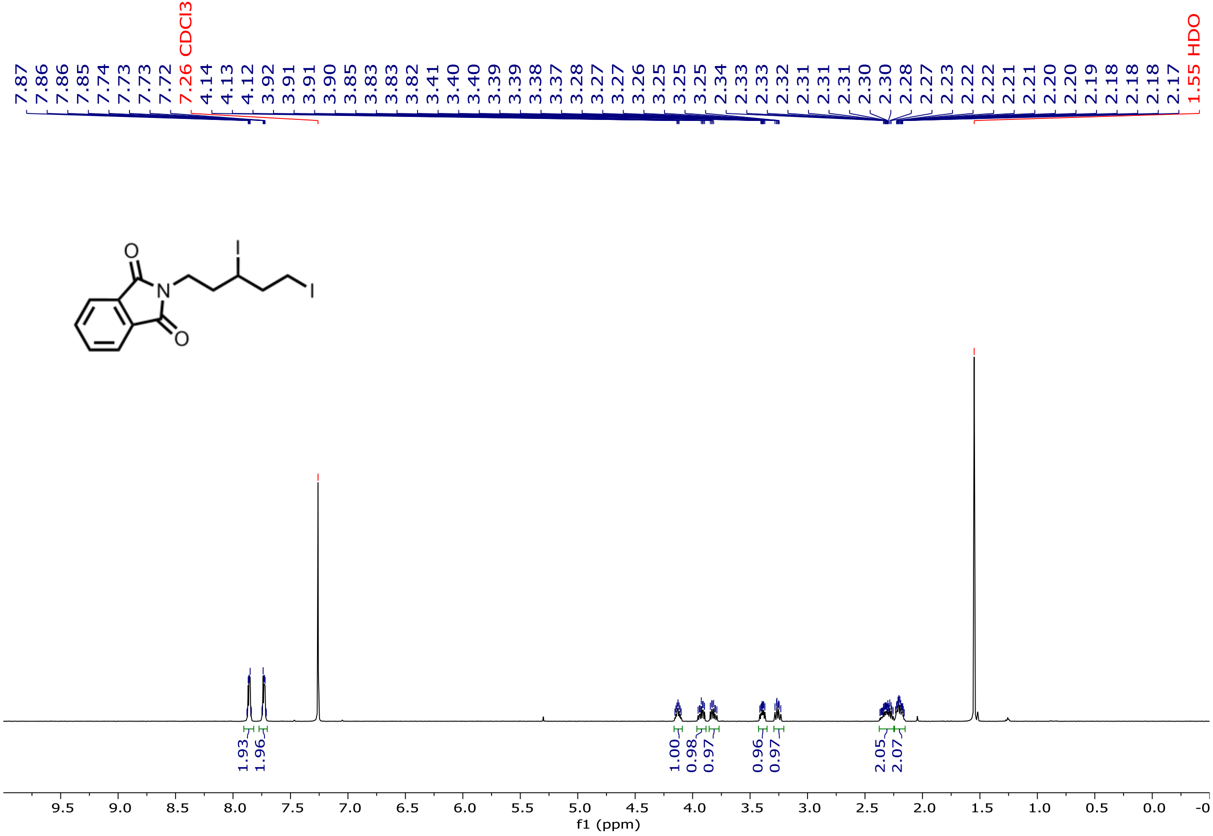
$^{1}$H NMR spectrum of 49 in CDCl$_3$. (500 MHz)



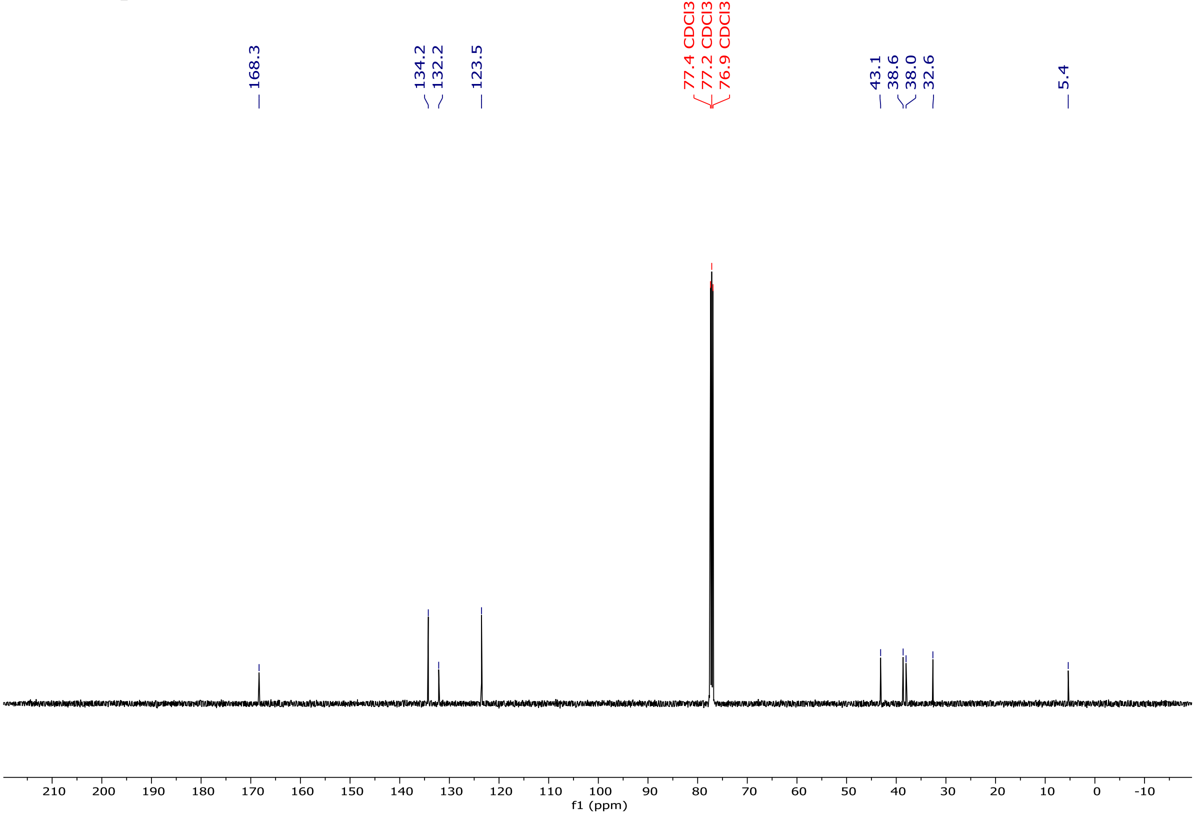
$^{13}$C NMR spectrum of 49 in CDCl$_3$. (126 MHz)



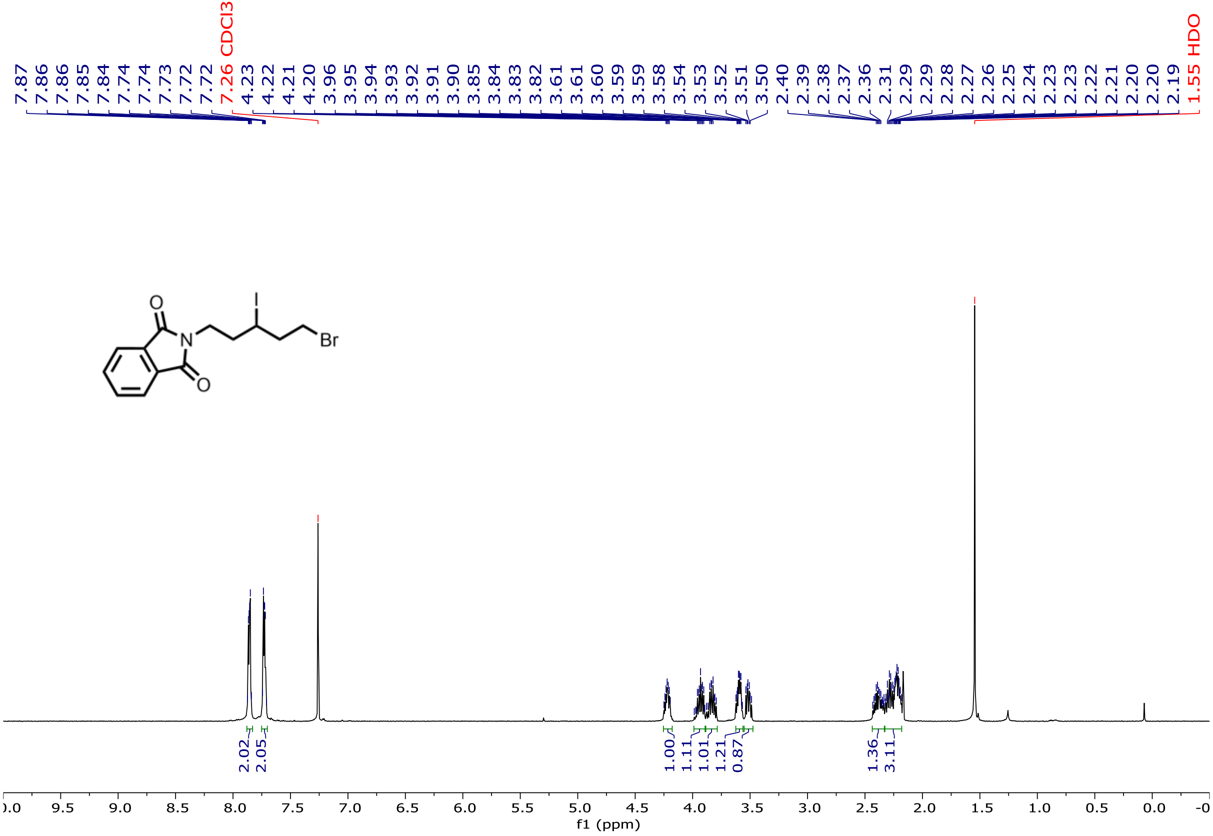
## $^1$H NMR spectrum of 50 in CDCl$_3$. (500 MHz)



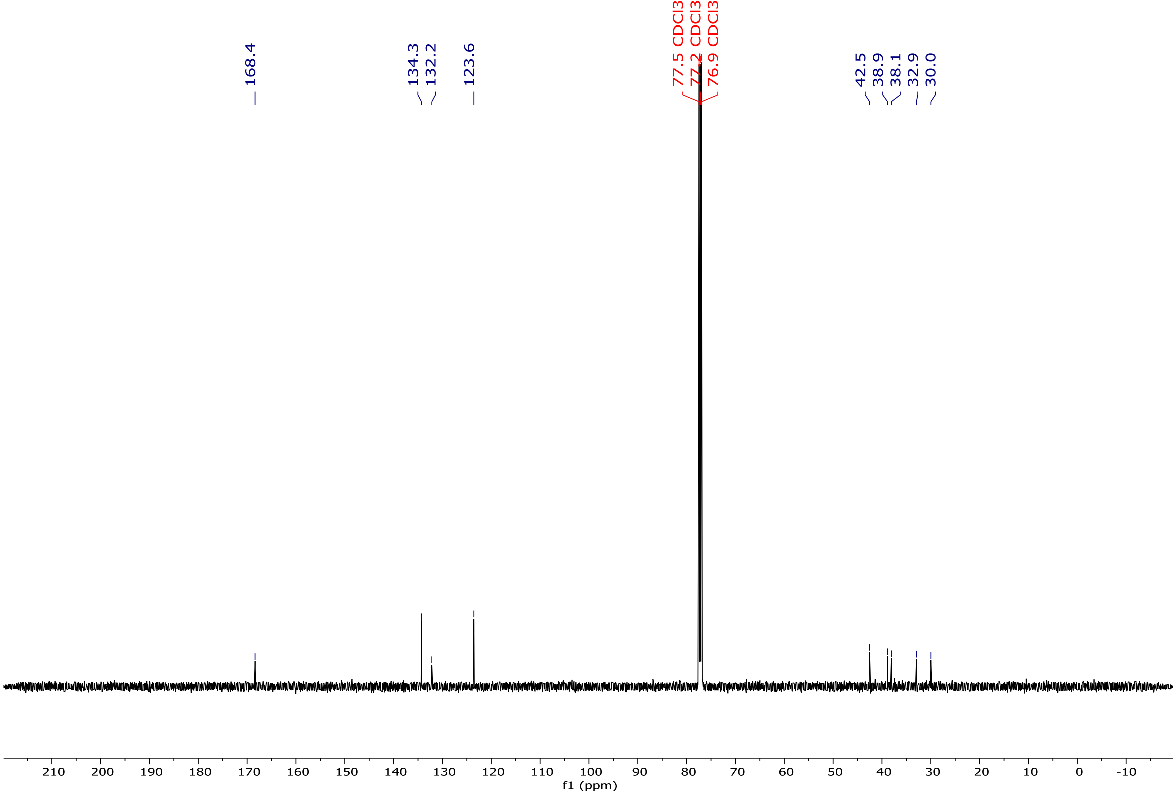
## $^1$H NMR spectrum of 50 in CDCl$_3$. (126 MHz)



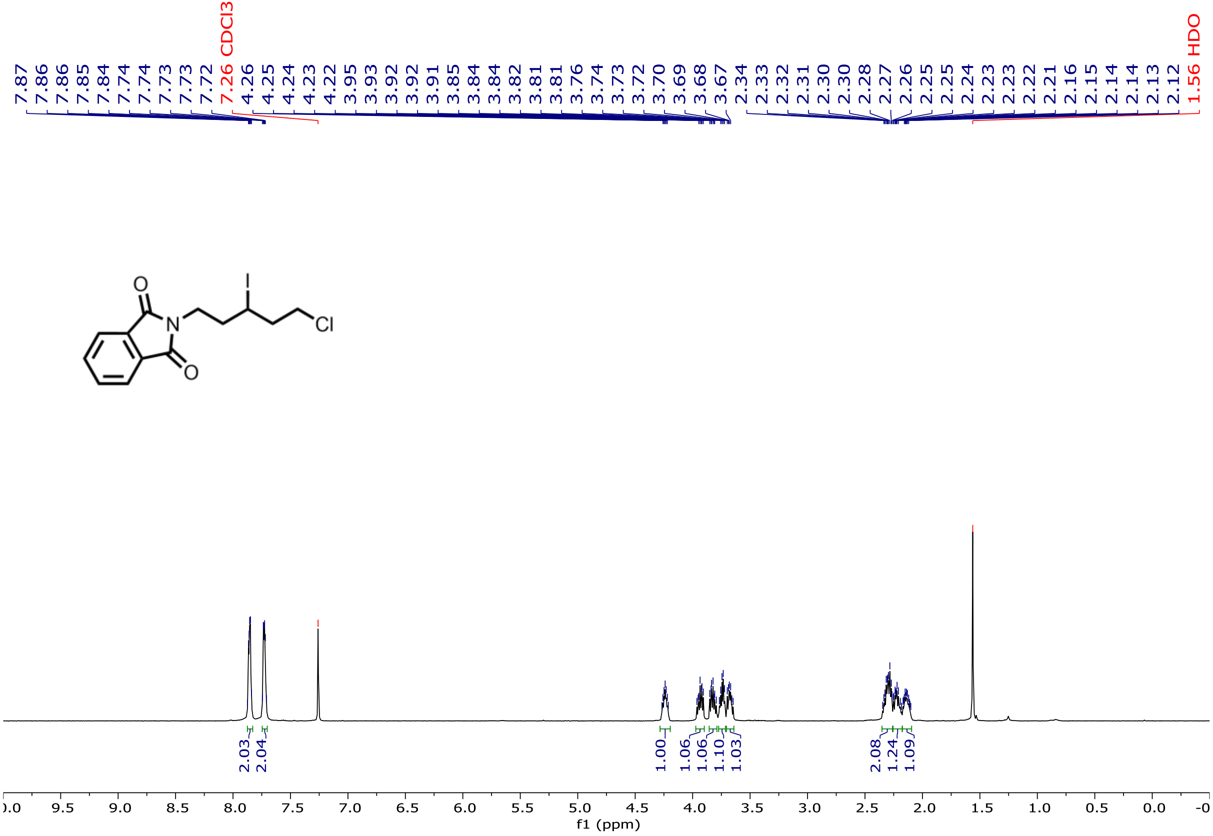
## $^1$H NMR spectrum of 51 in CDCl$_3$. (500 MHz)



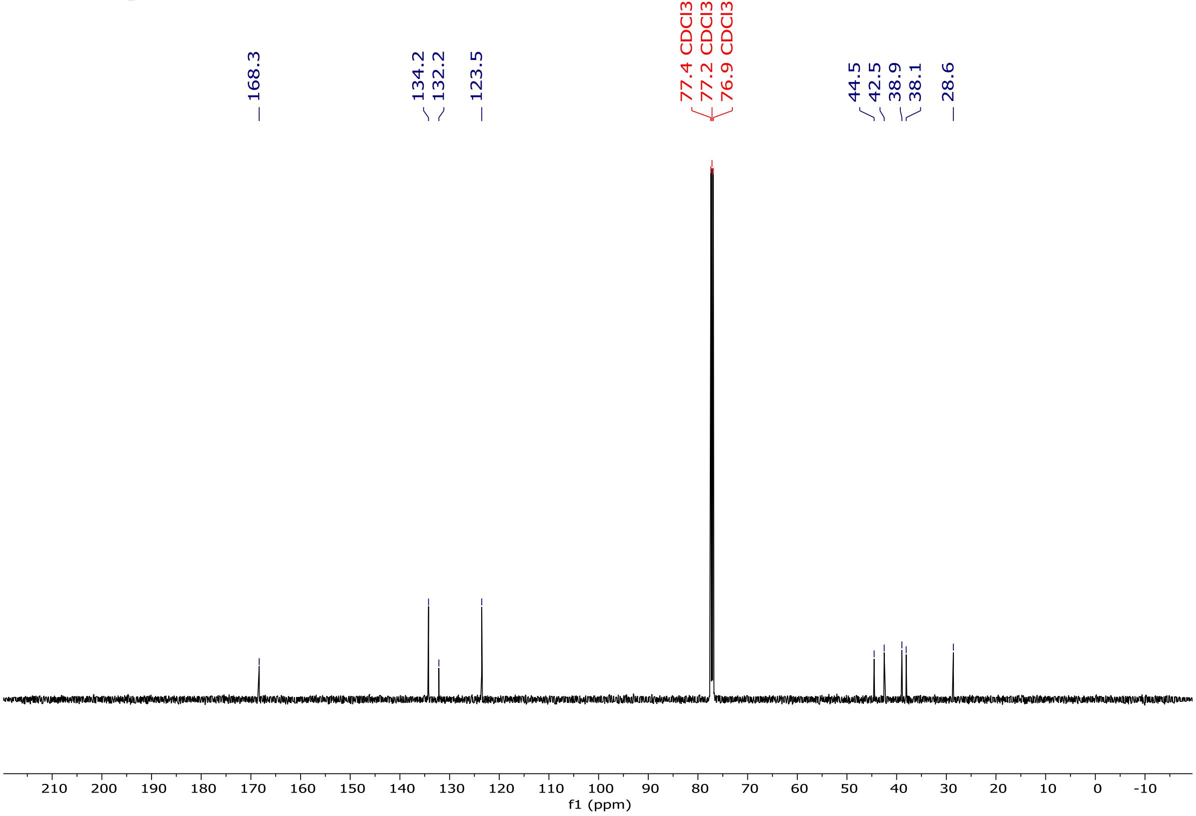
## $^1$H NMR spectrum of 51 in CDCl$_3$. (126 MHz)



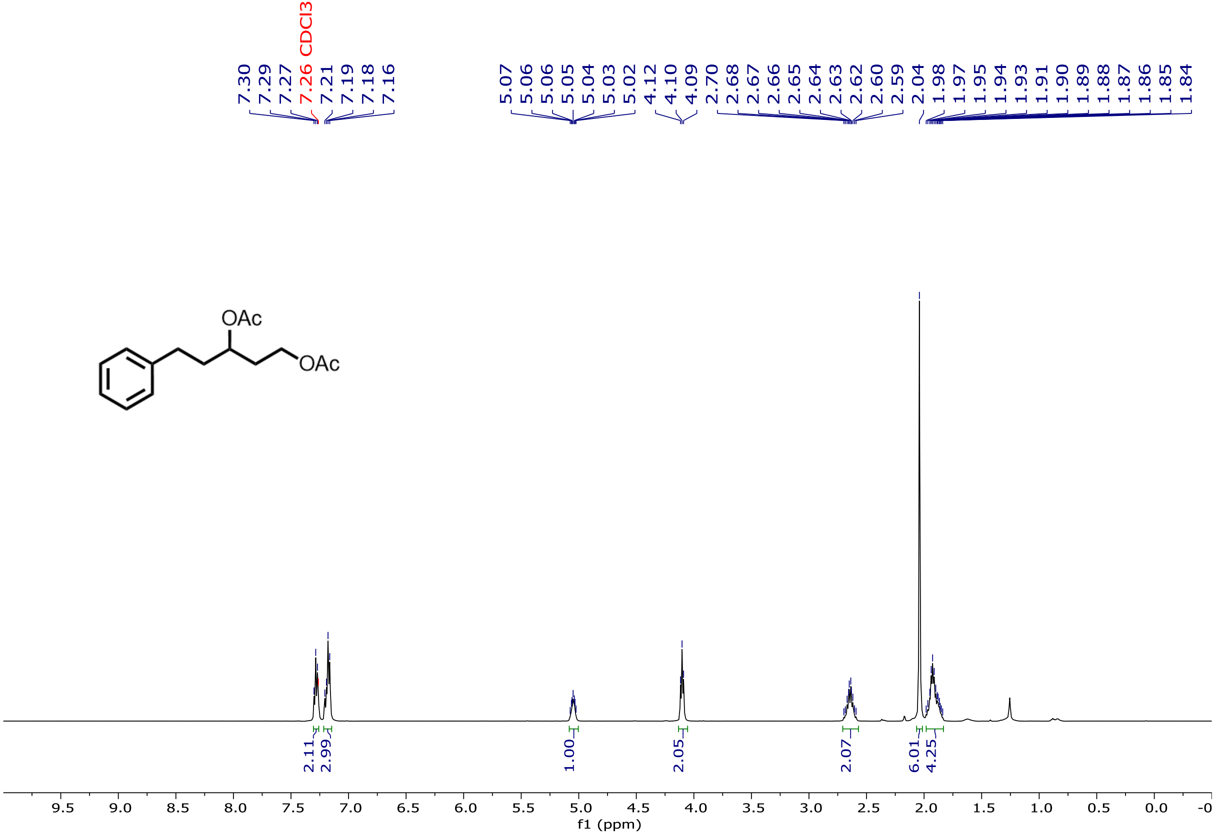
## $^1$H NMR spectrum of 52 in $CDCl_3$. (500 MHz)



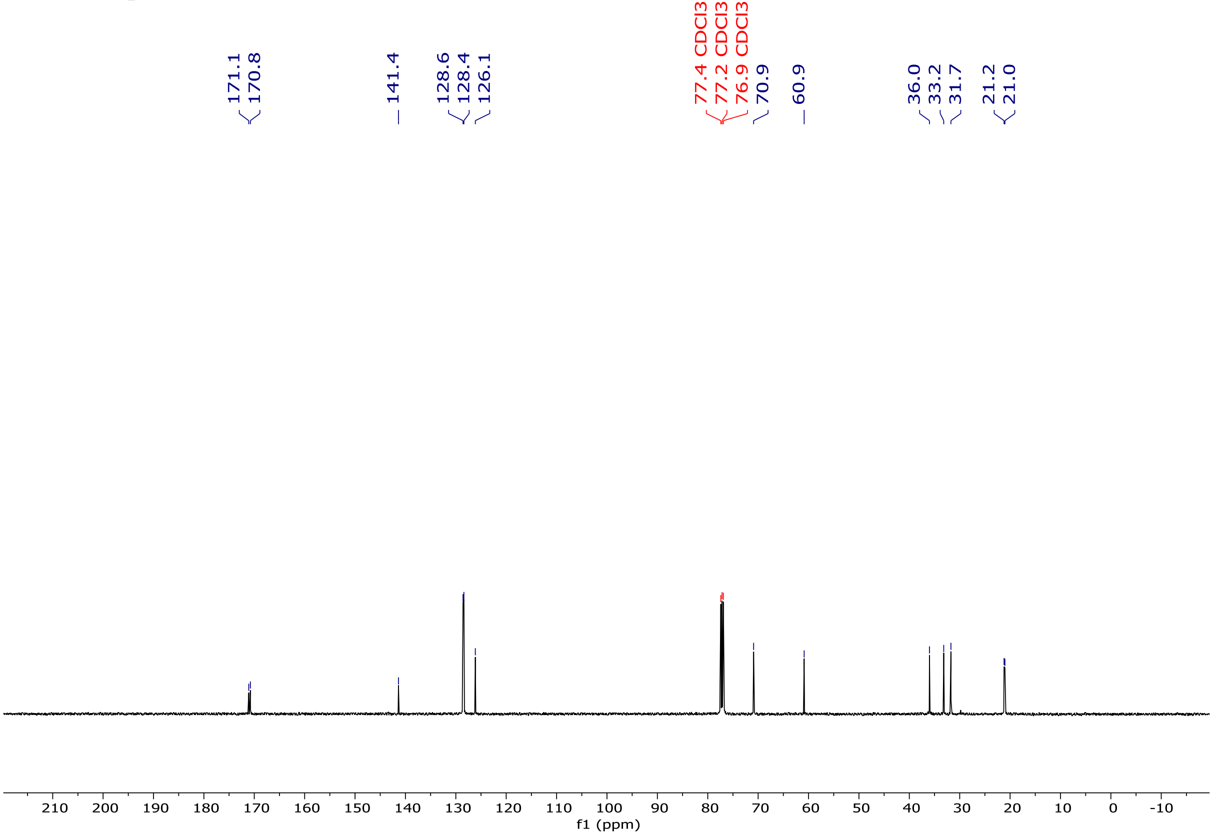
## $^{13}$C NMR spectrum of 52 in $CDCl_3$. (126 MHz)



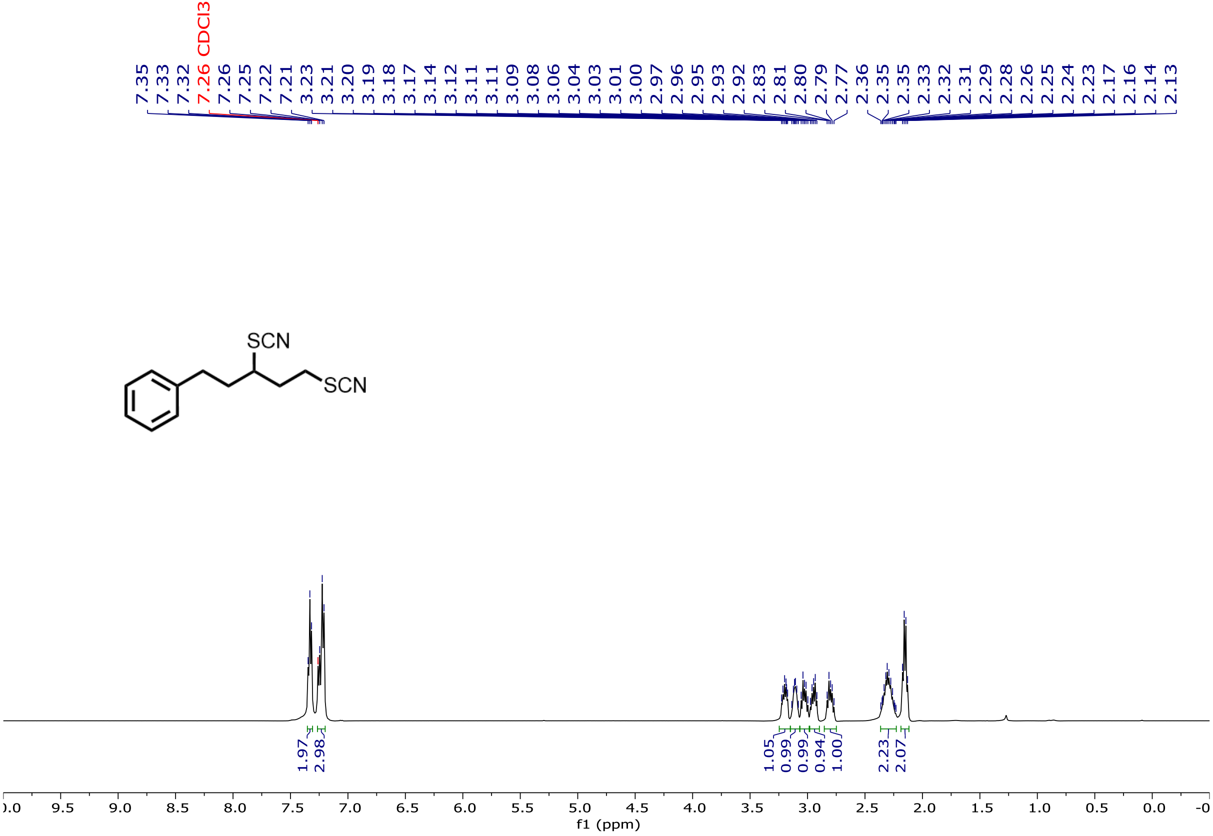
## $^{1}H$ NMR spectrum of 53 in $CDCl_3$. (500 MHz)



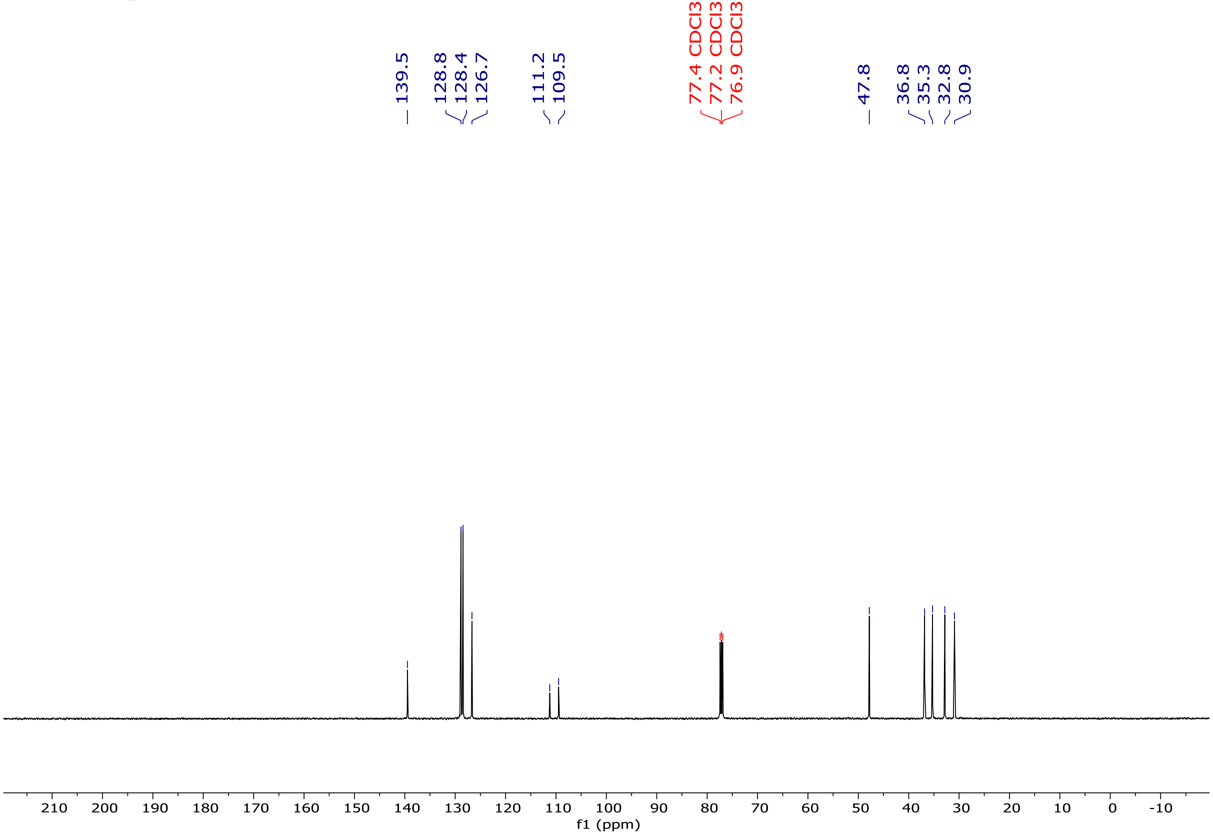
## $^{13}C$ NMR spectrum of 53 in $CDCl_3$. (126 MHz)



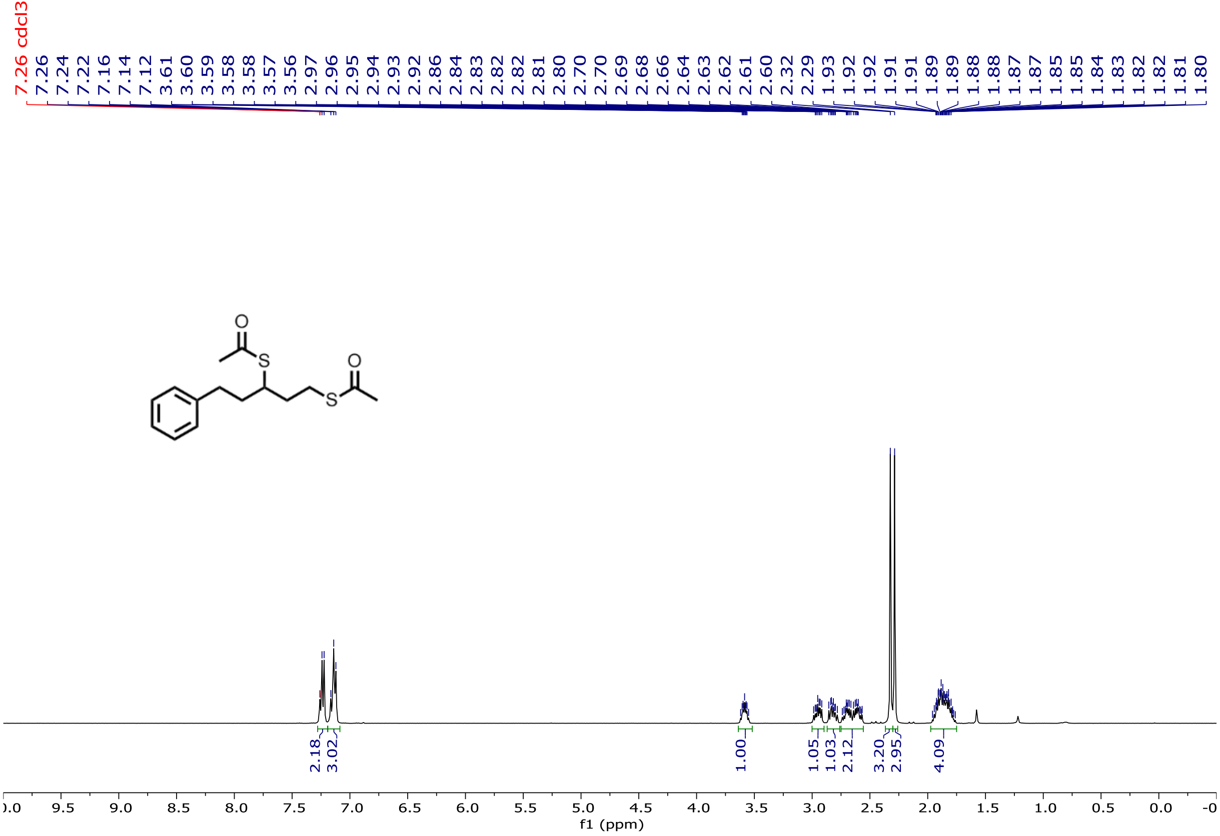
## $^{1}$H NMR spectrum of 54 in $CDCl_3$. (500 MHz)



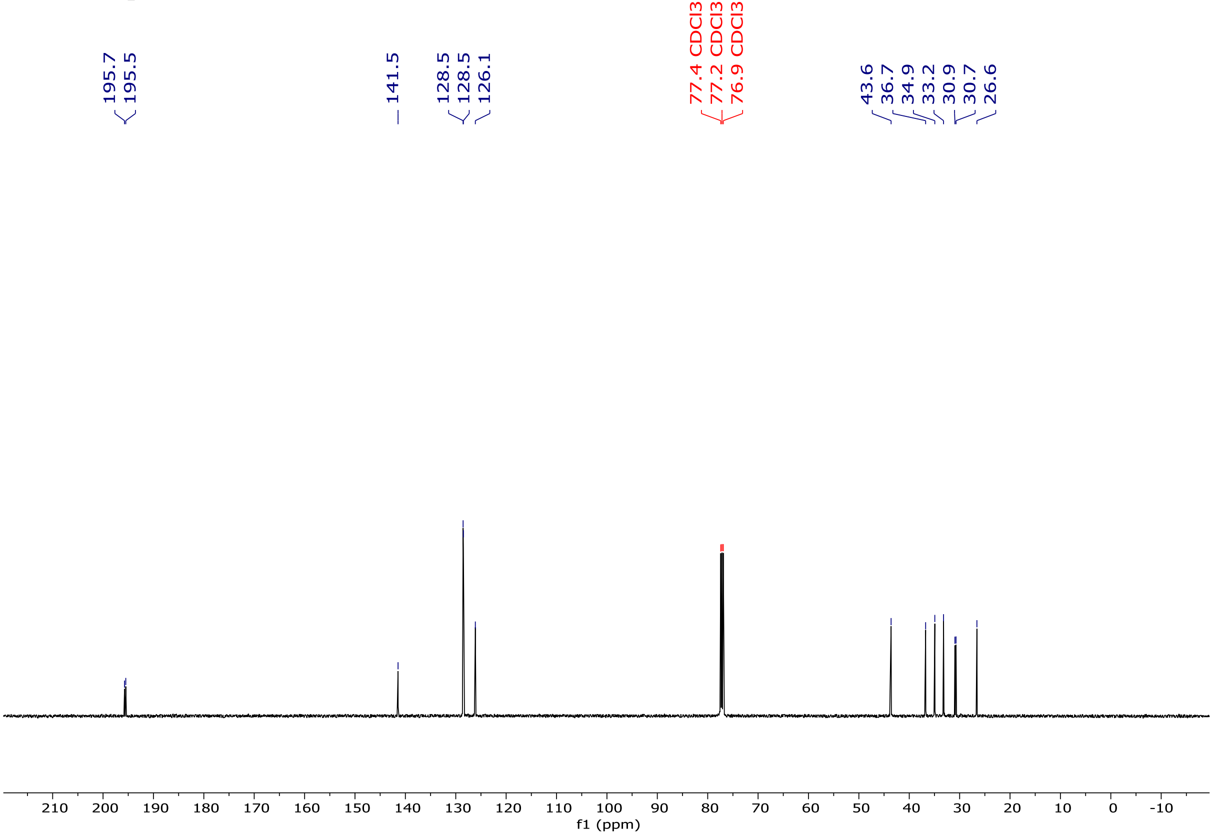
## $^{13}$C NMR spectrum of 54 in $CDCl_3$. (126 MHz)



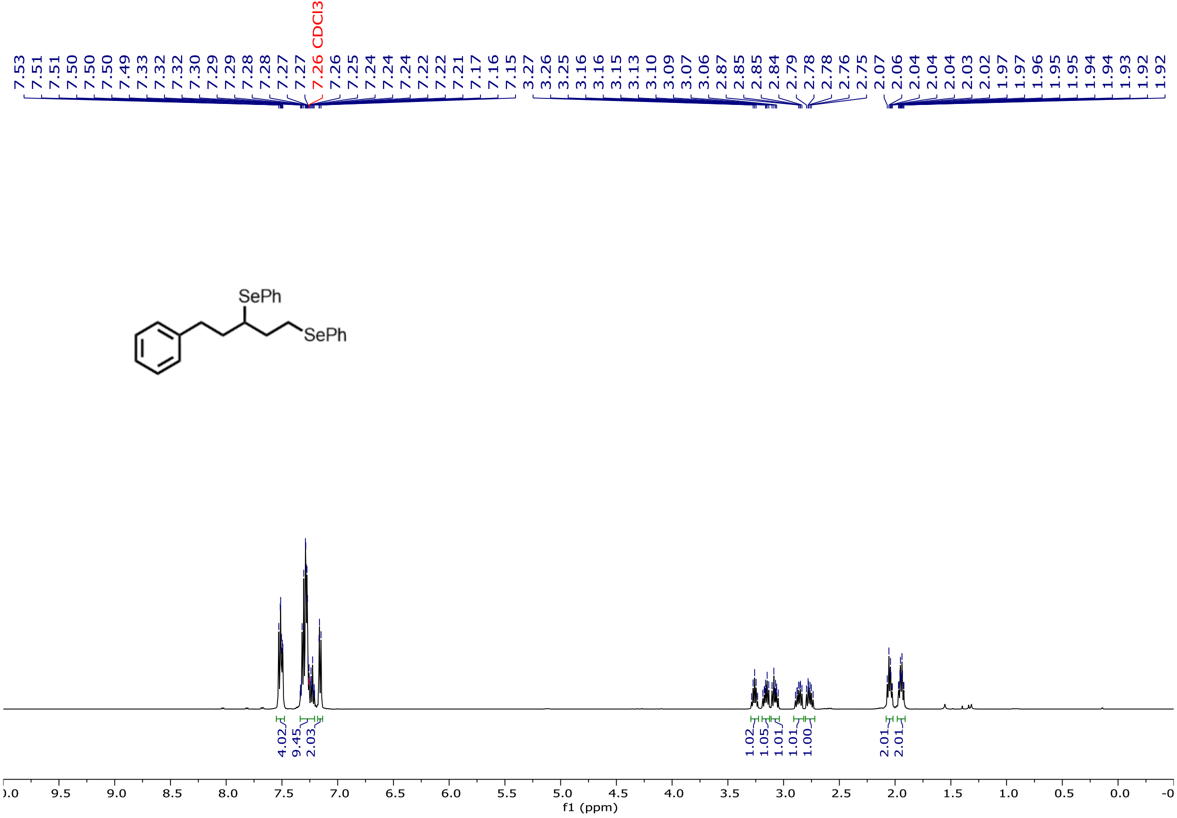
## $^{1}$H NMR spectrum of 55 in $CDCl_3$. (400 MHz)



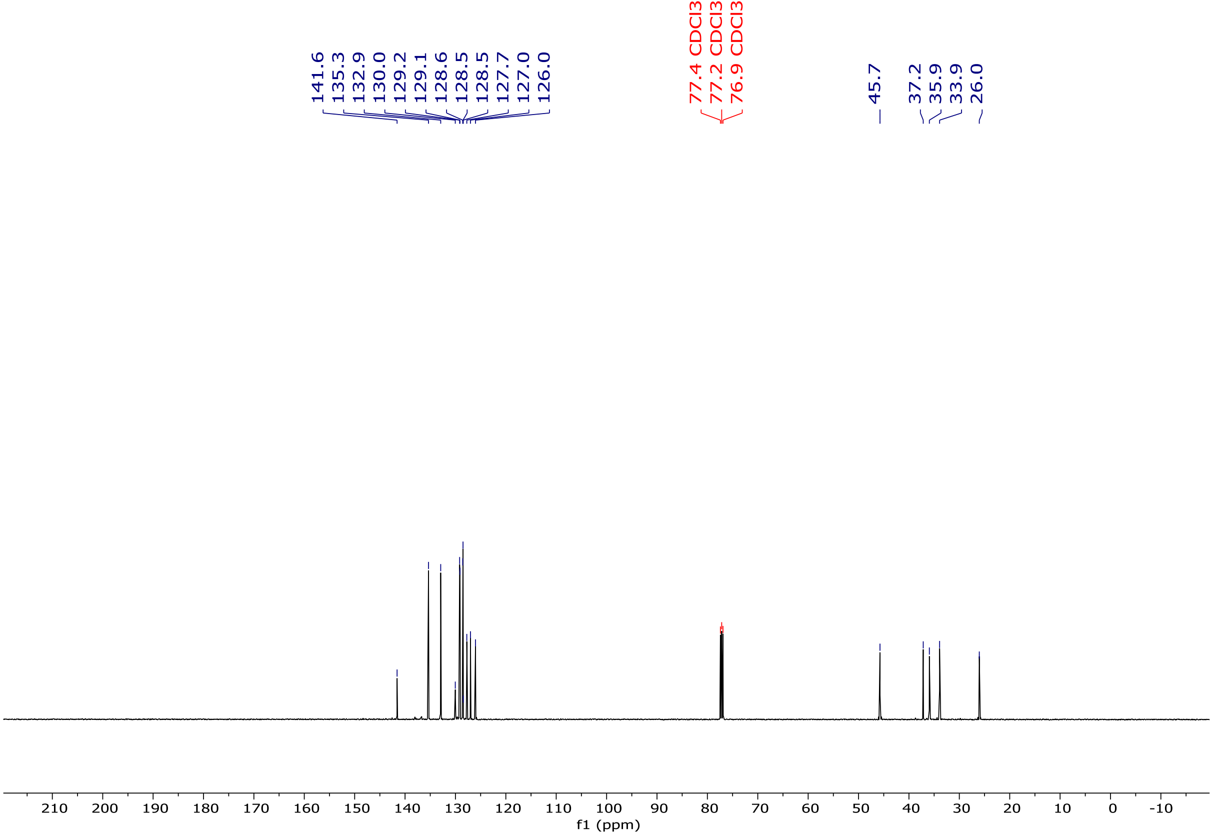
## $^{13}$C NMR spectrum of 55 in $CDCl_3$. (126 MHz)



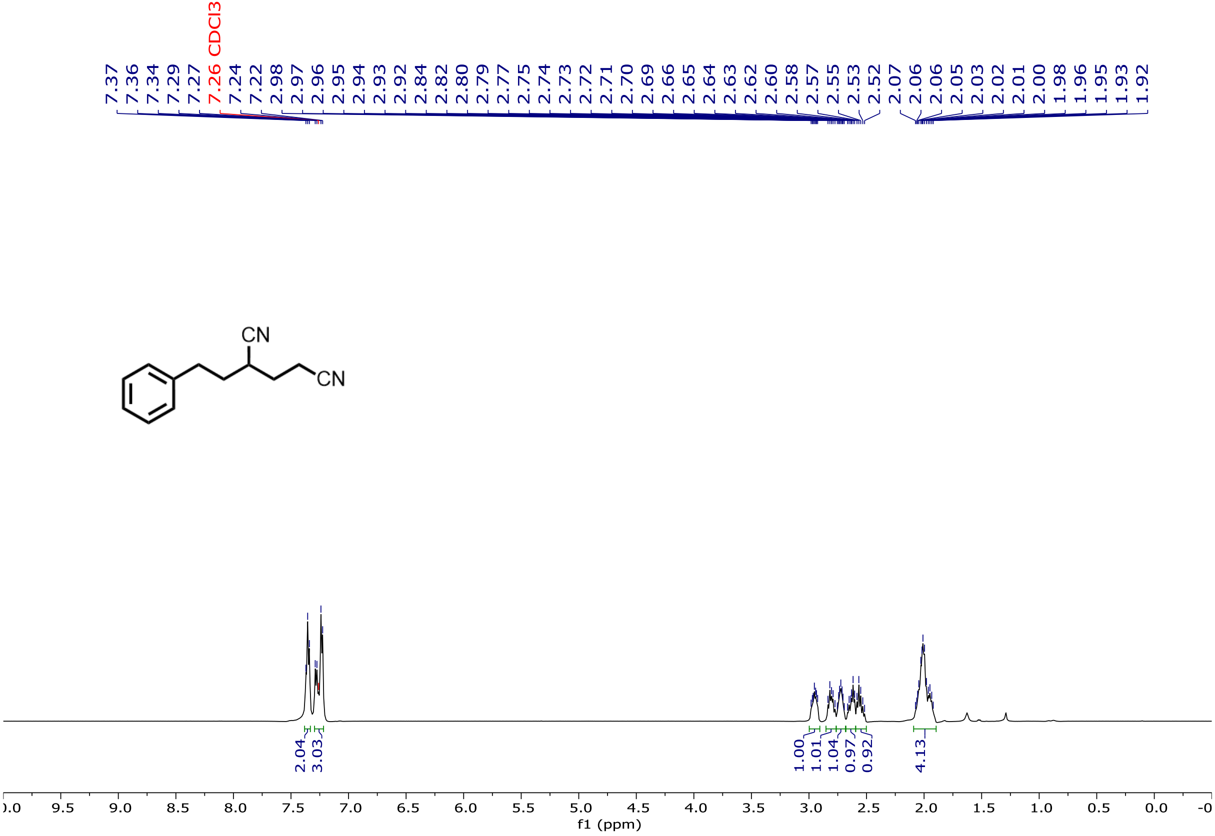
**$^{1}$H NMR spectrum of 56 in CDCl$_3$. (500 MHz)**



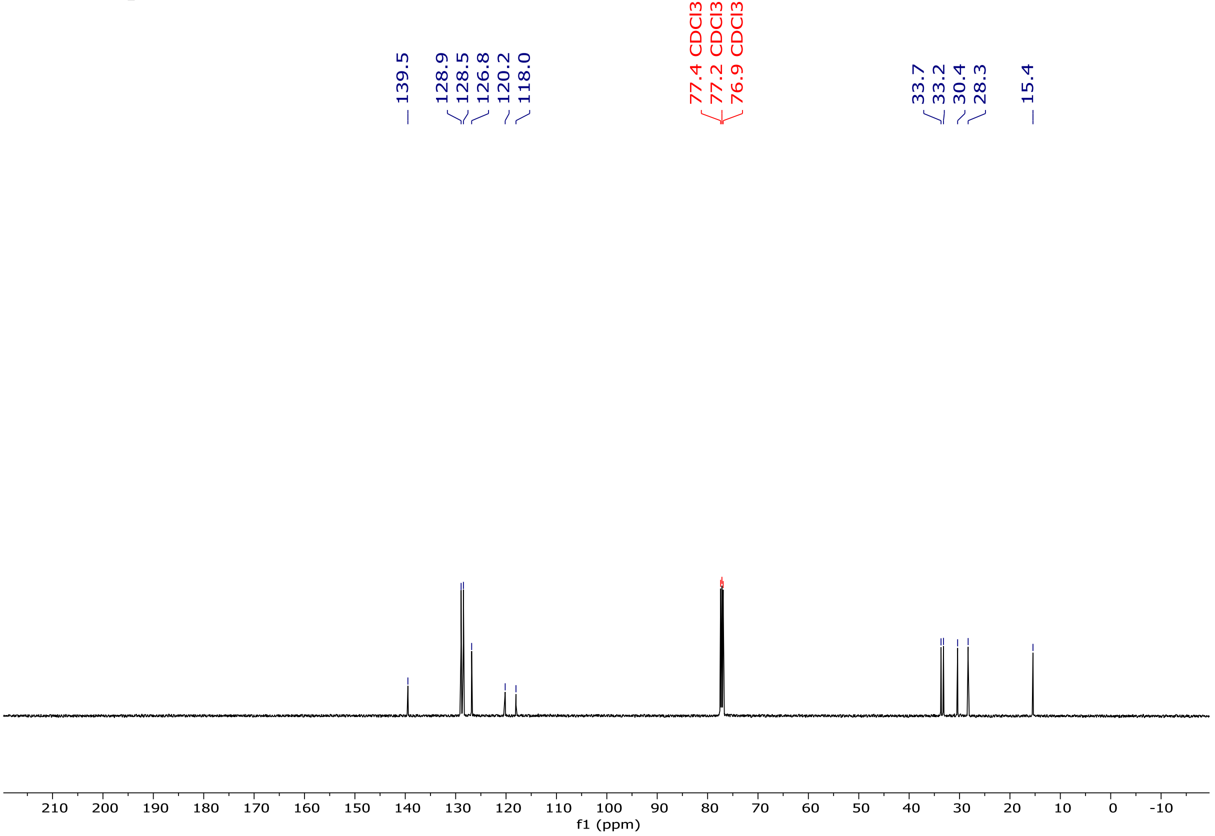
**$^{13}$C NMR spectrum of 56 in CDCl$_3$. (126 MHz)**



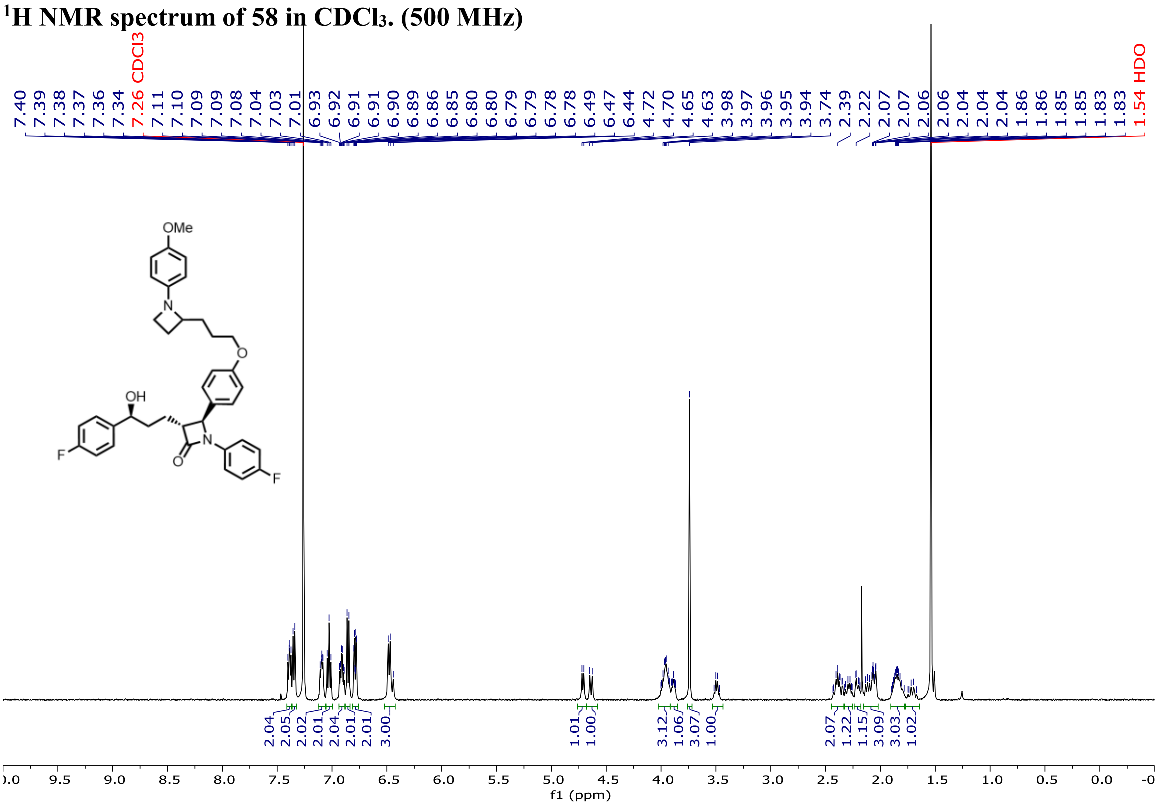
## $^1$H NMR spectrum of 57 in $CDCl_3$. (500 MHz)



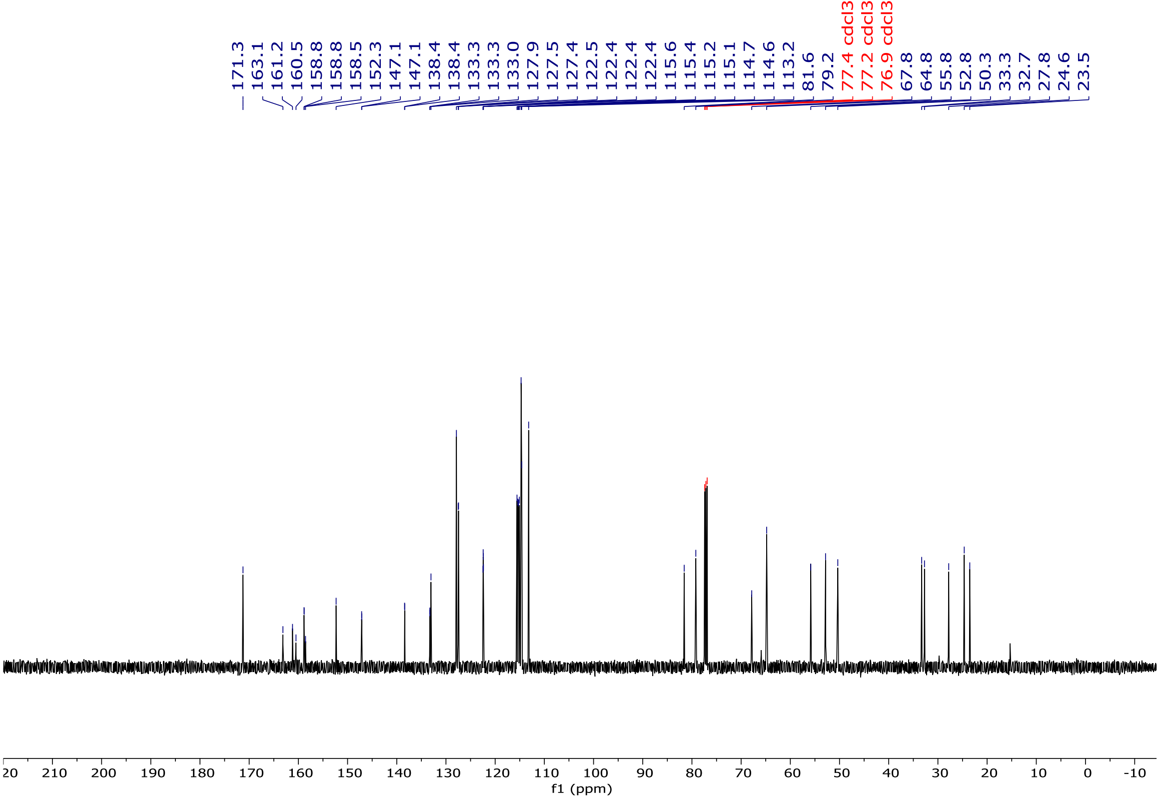
## $^{13}$C NMR spectrum of 57 in $CDCl_3$. (126 MHz)



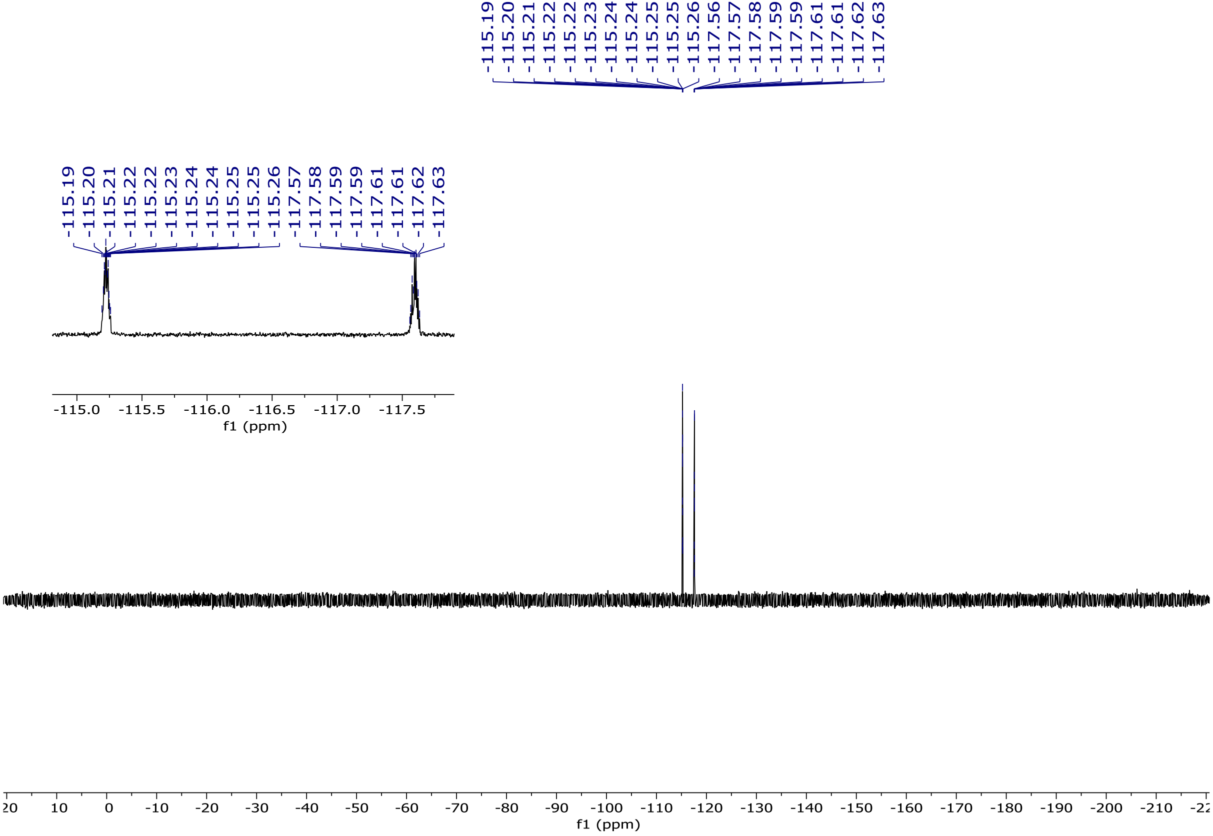
### $^{1}$H NMR spectrum of 58 in $CDCl_3$. (500 MHz)



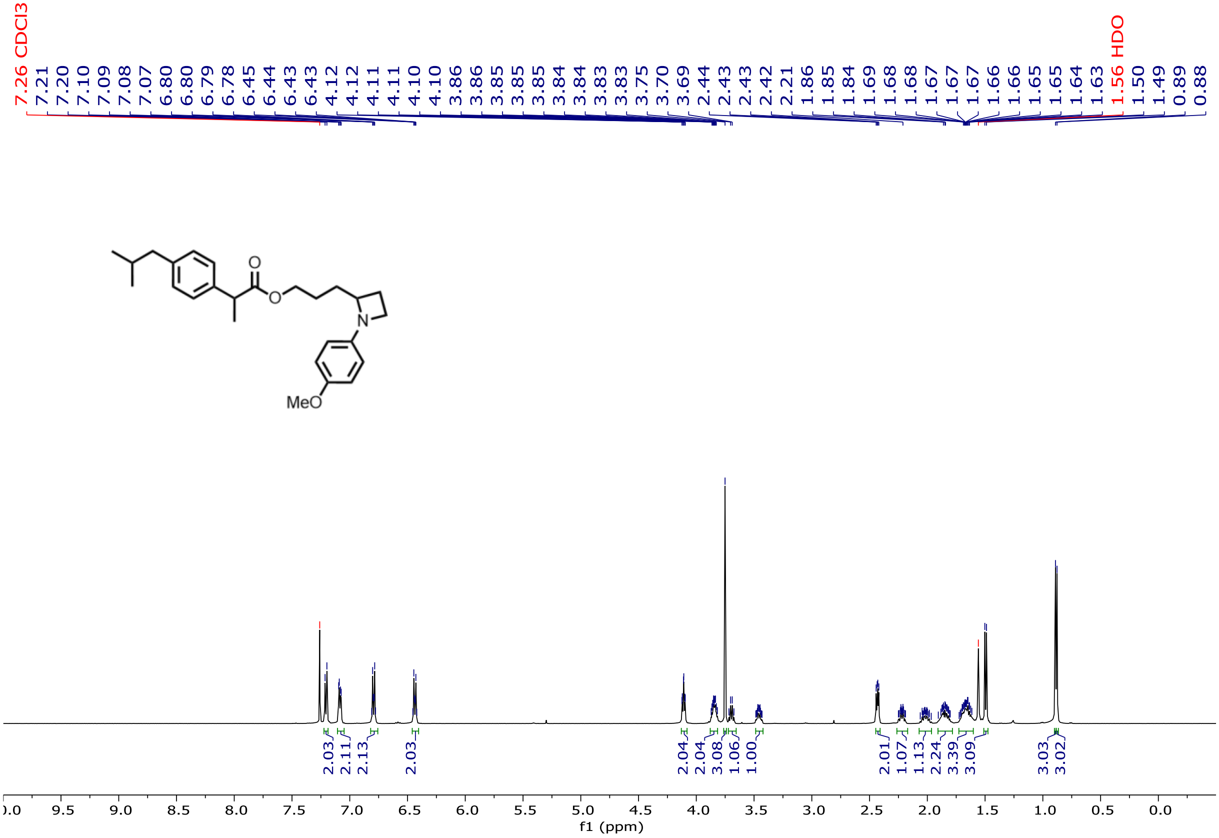
### $^{13}$C NMR spectrum of 58 in $CDCl_3$. (126 MHz)



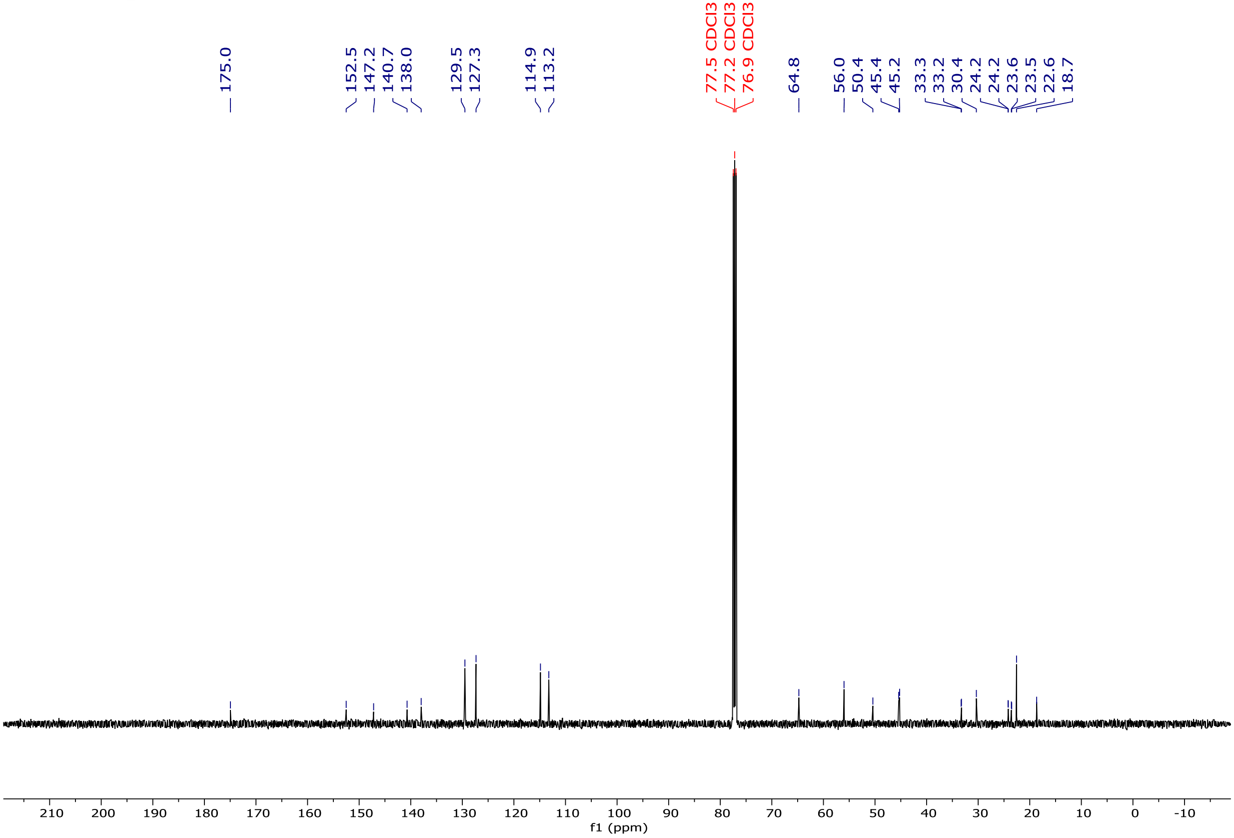
**$^{19}$F NMR spectrum of 58 in CDCl$_3$. (471 MHz)**



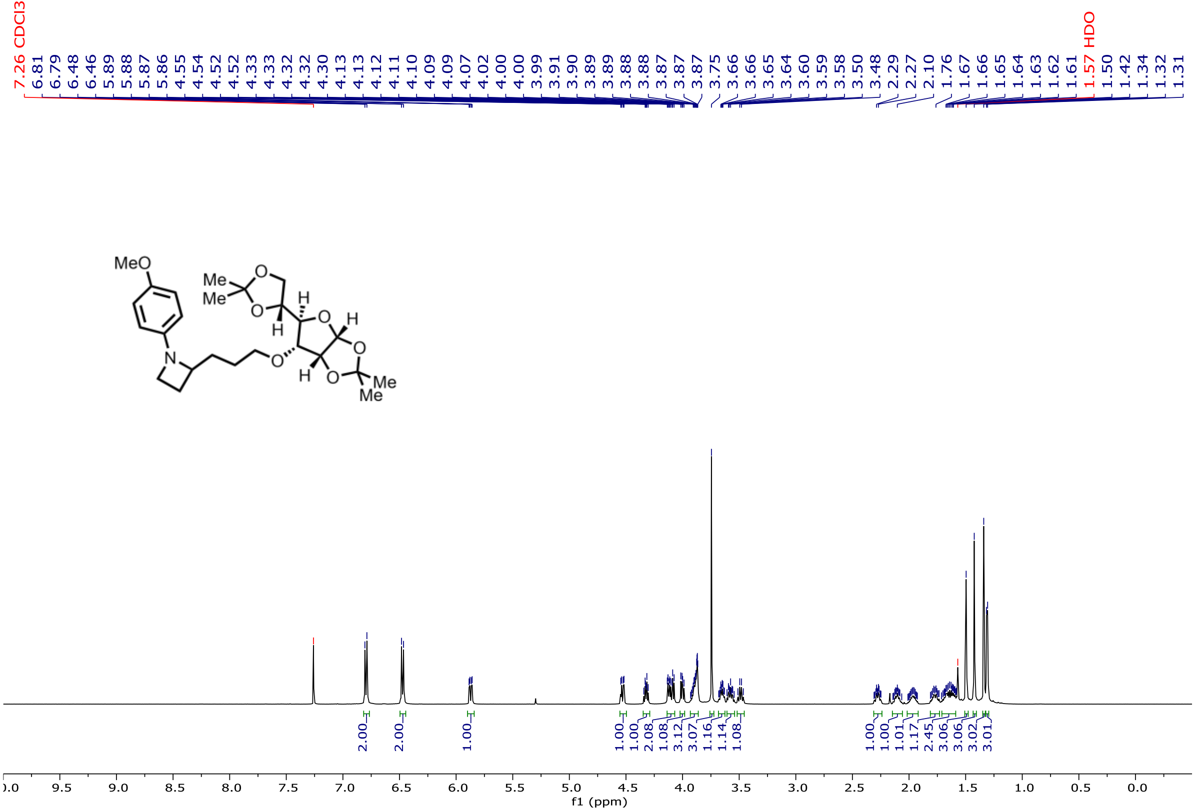
## $^1$H NMR spectrum of 59 in CDCl$_3$. (500 MHz)



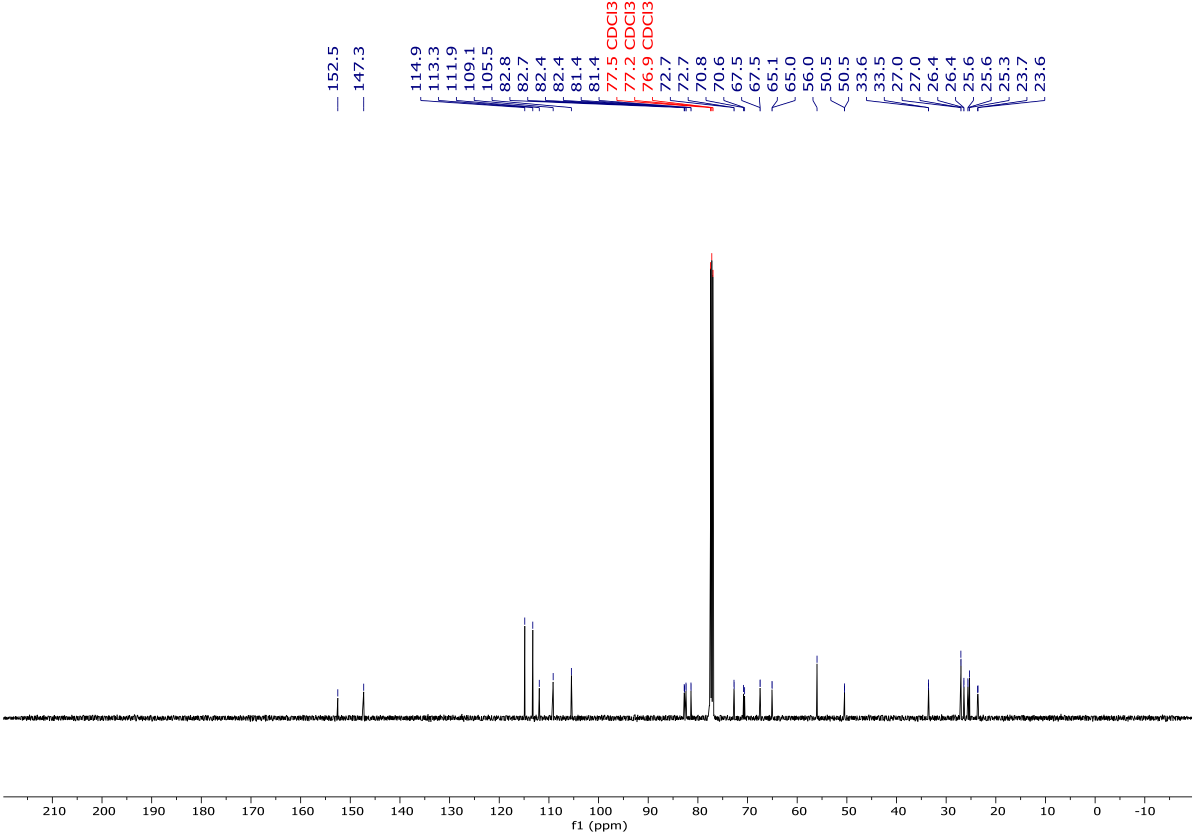
## $^{13}$C NMR spectrum of 59 in CDCl$_3$. (126 MHz)



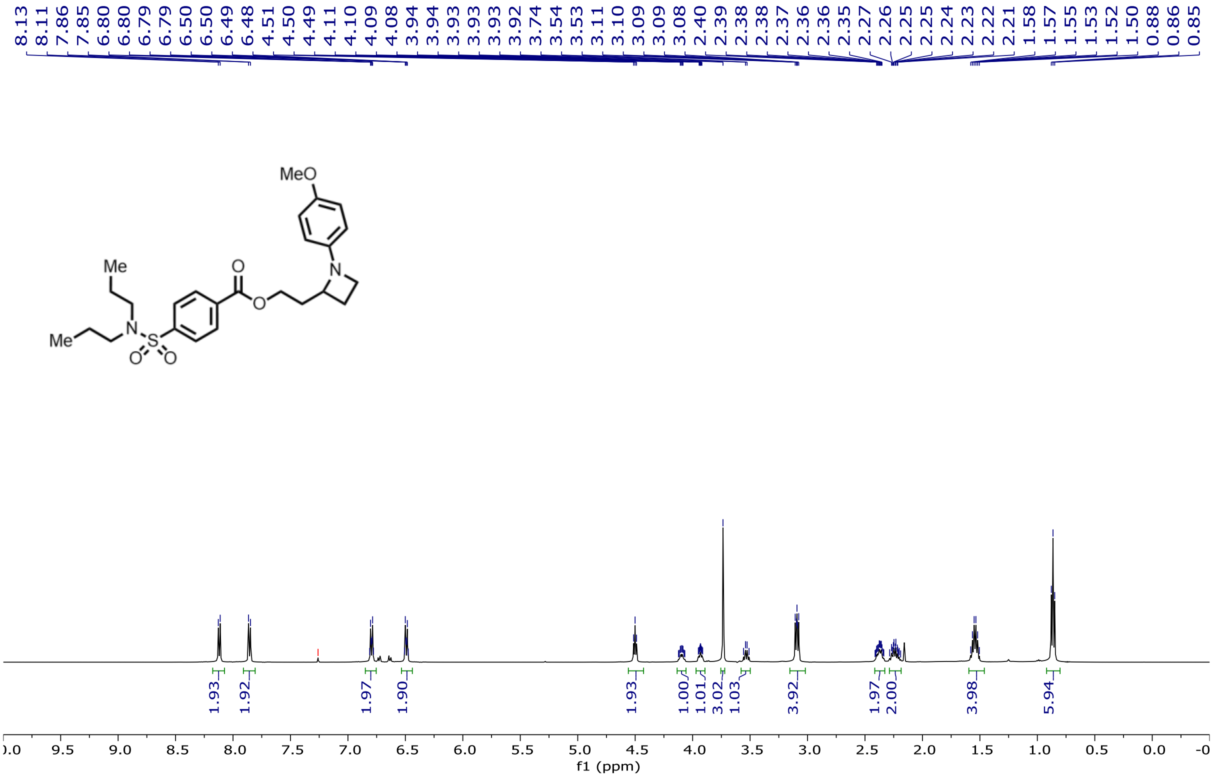
## $^{1}$H NMR spectrum of 60 in CDCl$_3$. (500 MHz)



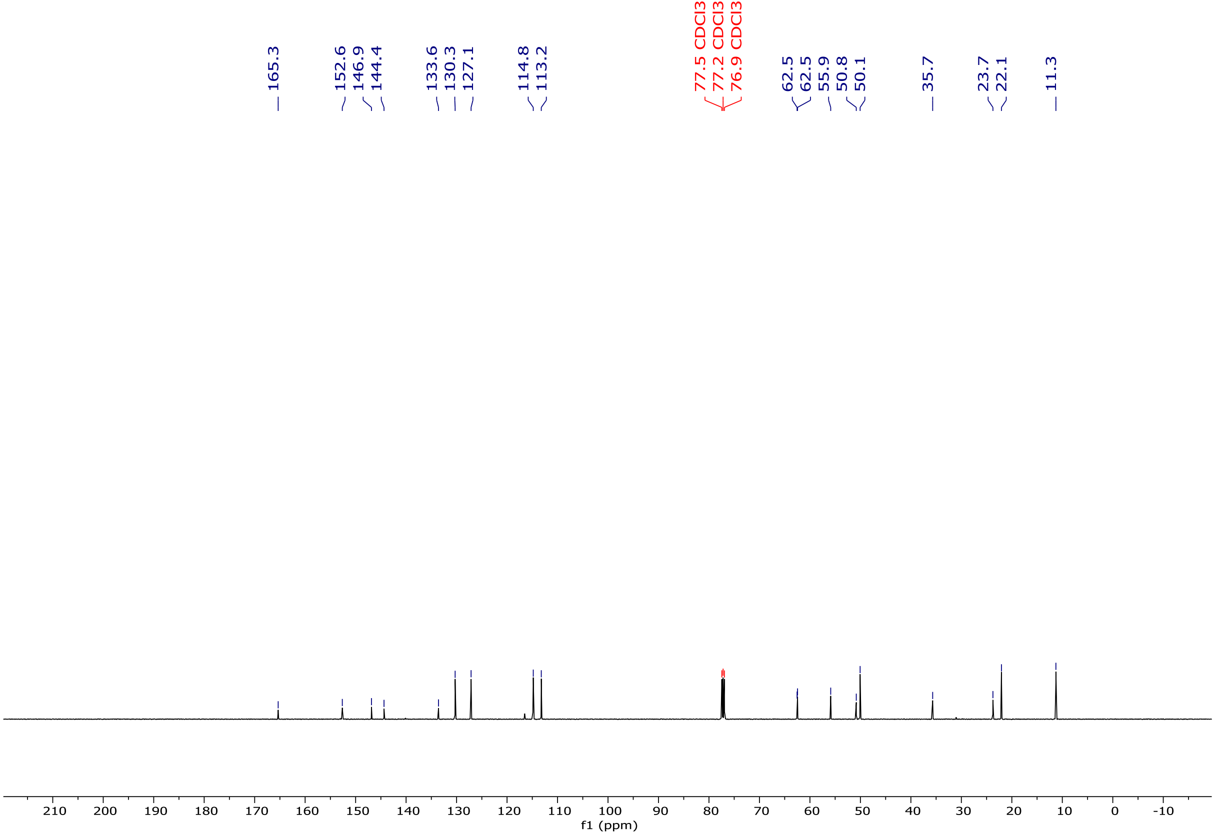
## $^{13}$C NMR spectrum of 60 in CDCl$_3$. (126 MHz)



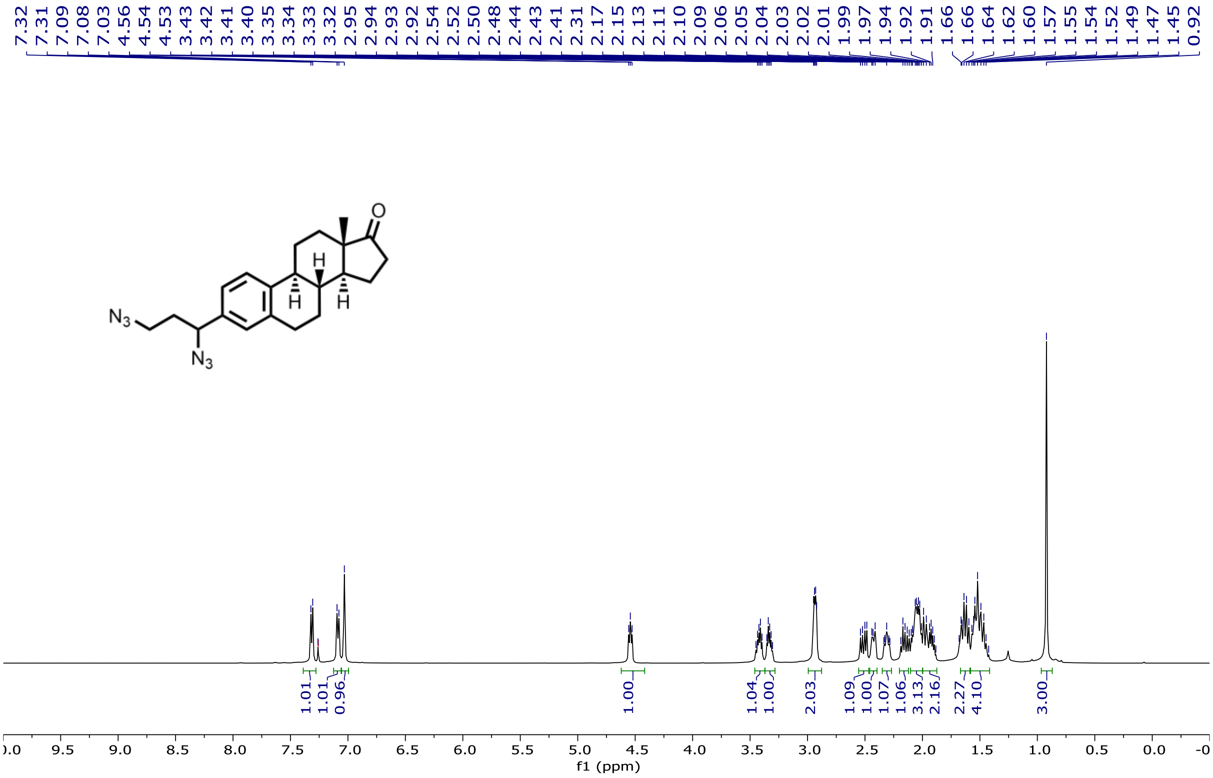
## $^1$H NMR spectrum of 61 in $CDCl_3$. (500 MHz)



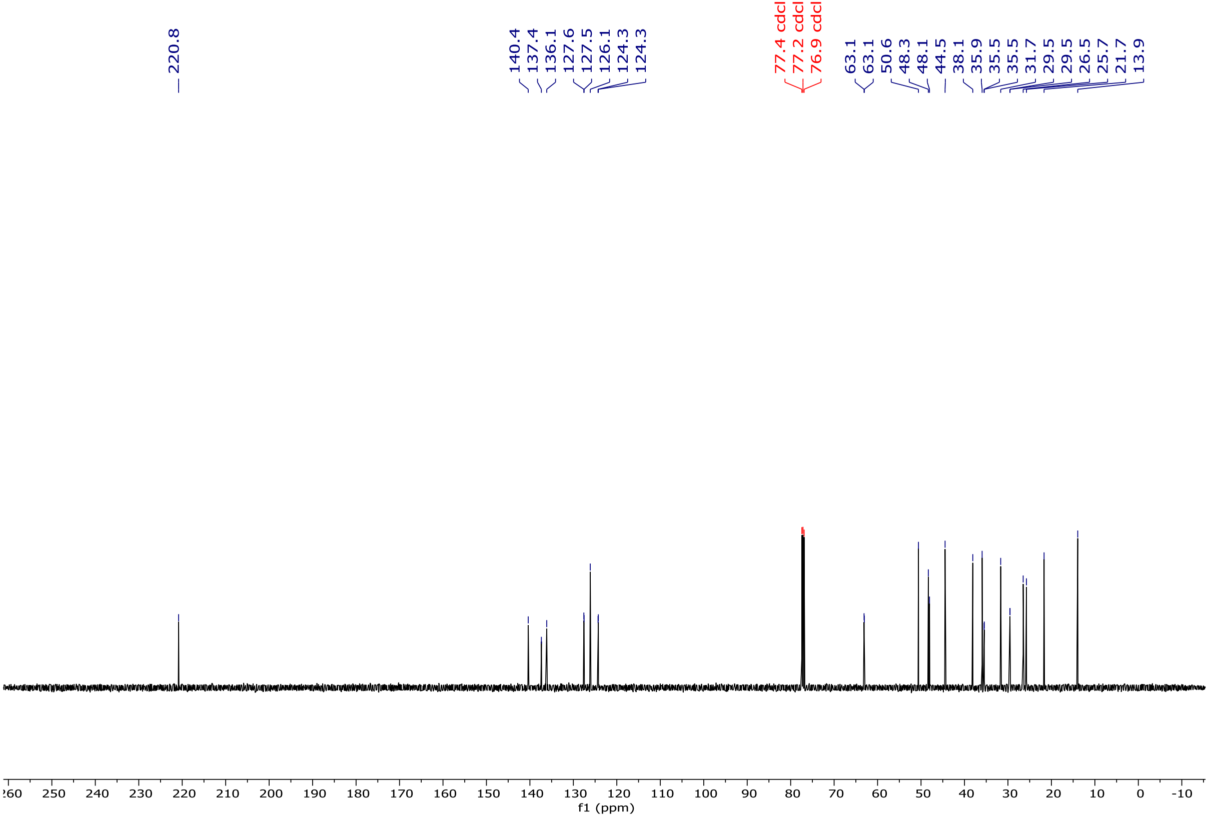
## $^{13}$C NMR spectrum of 61 in $CDCl_3$. (126 MHz)



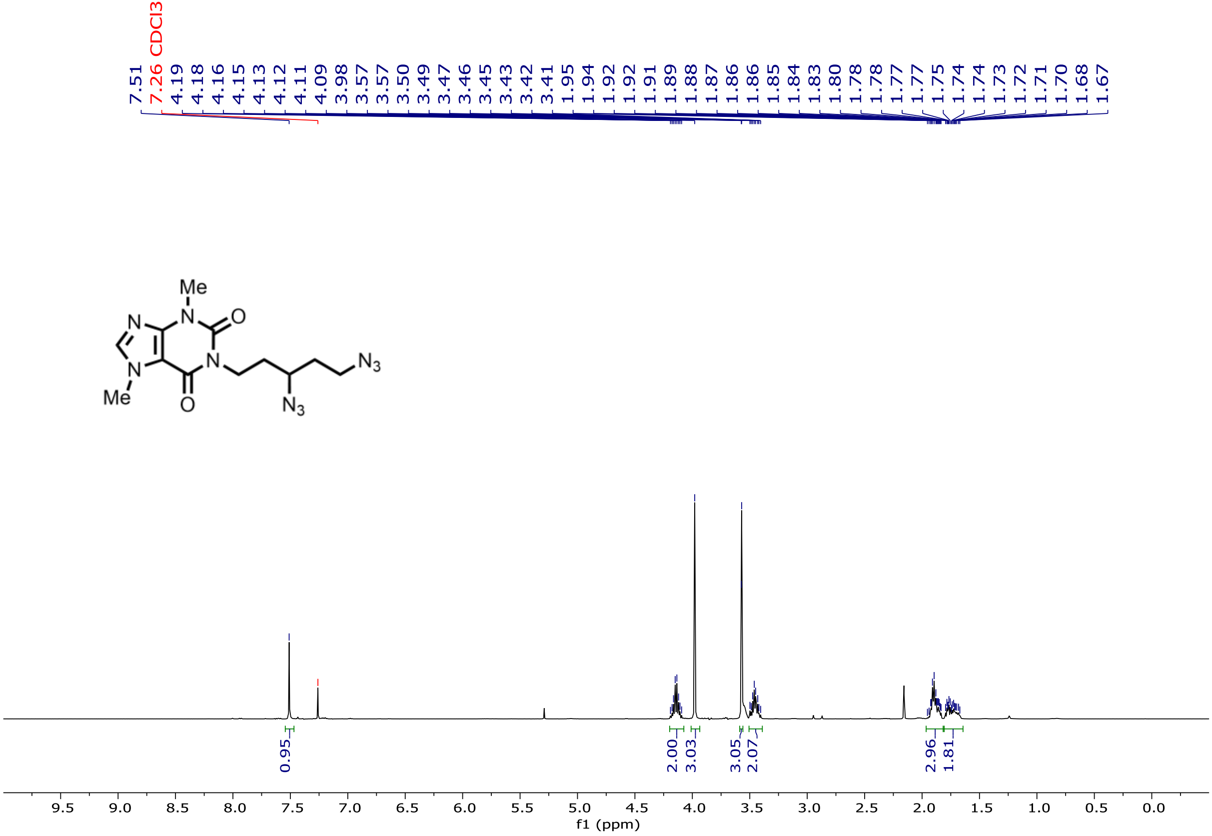
## $^{1}H$ NMR spectrum of 62 in $CDCl_3$. (500 MHz)



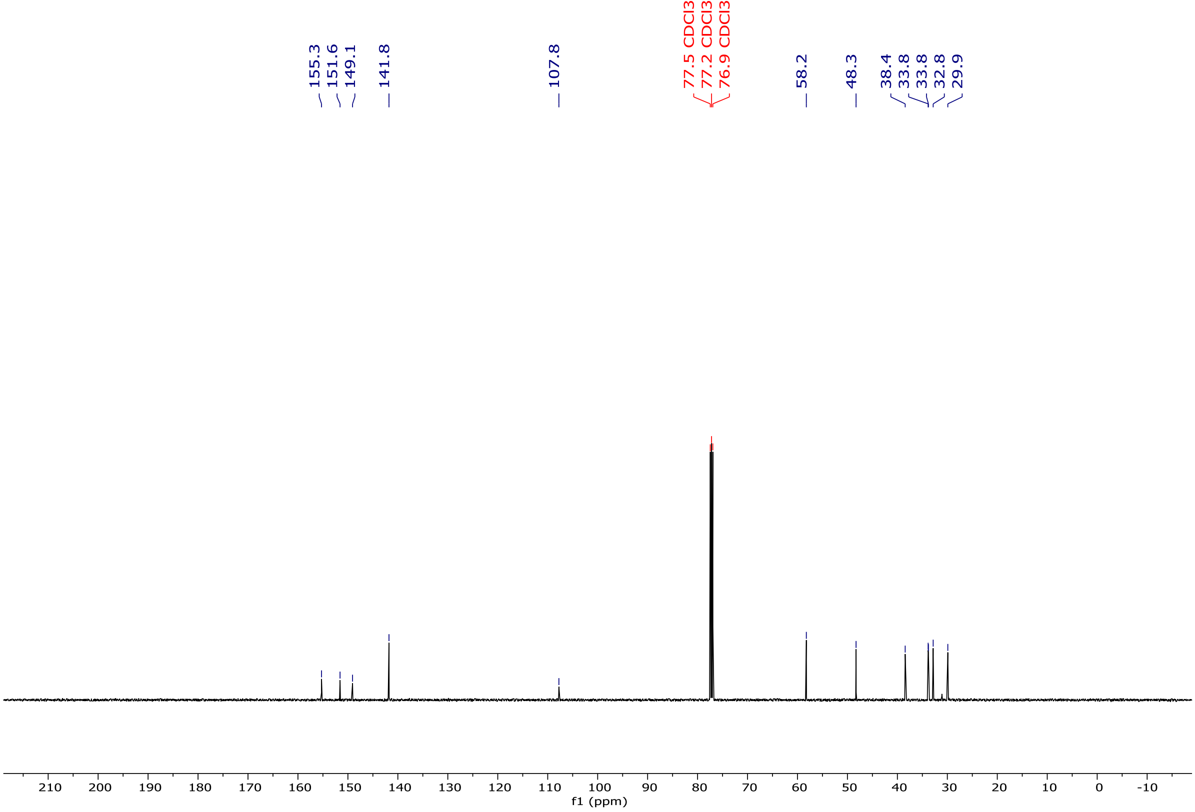
## $^{13}C$ NMR spectrum of 62 in $CDCl_3$. (126 MHz)



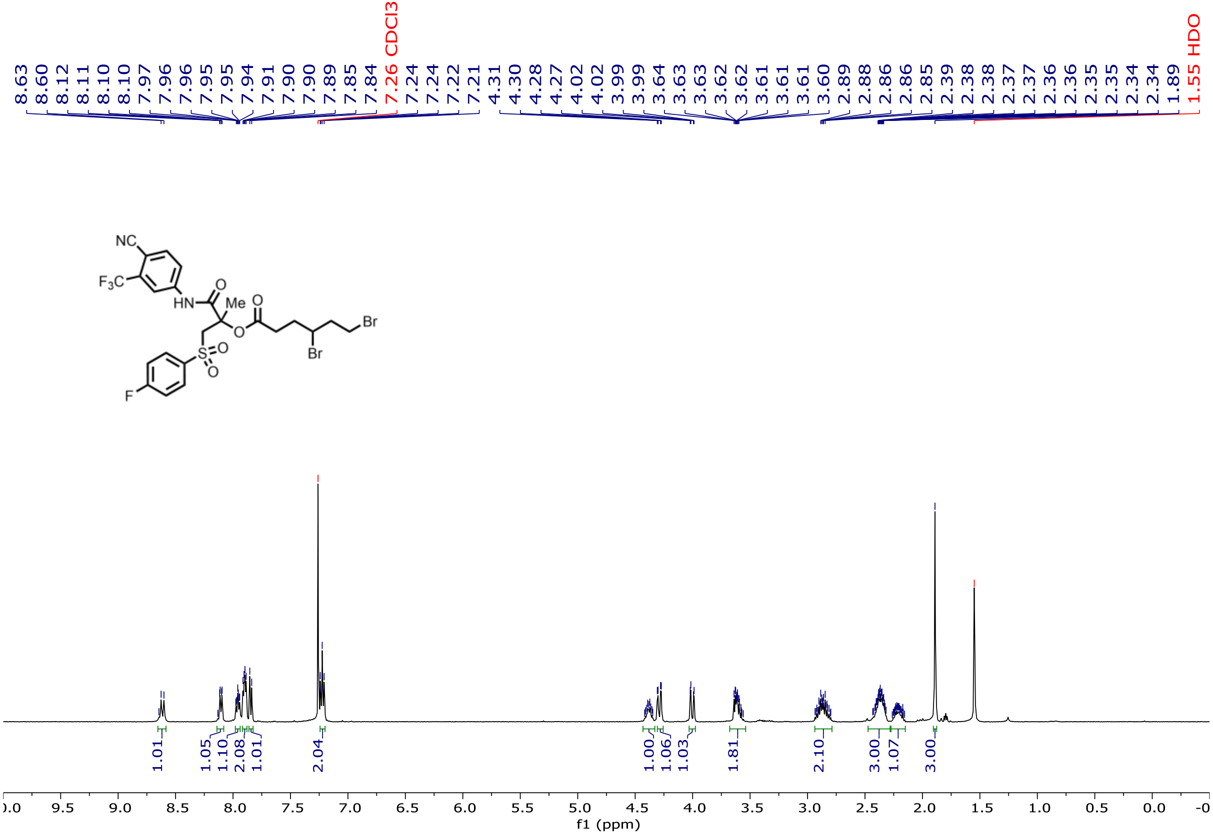
## $^{1}$H NMR spectrum of 63 in CDCl$_3$. (500 MHz)



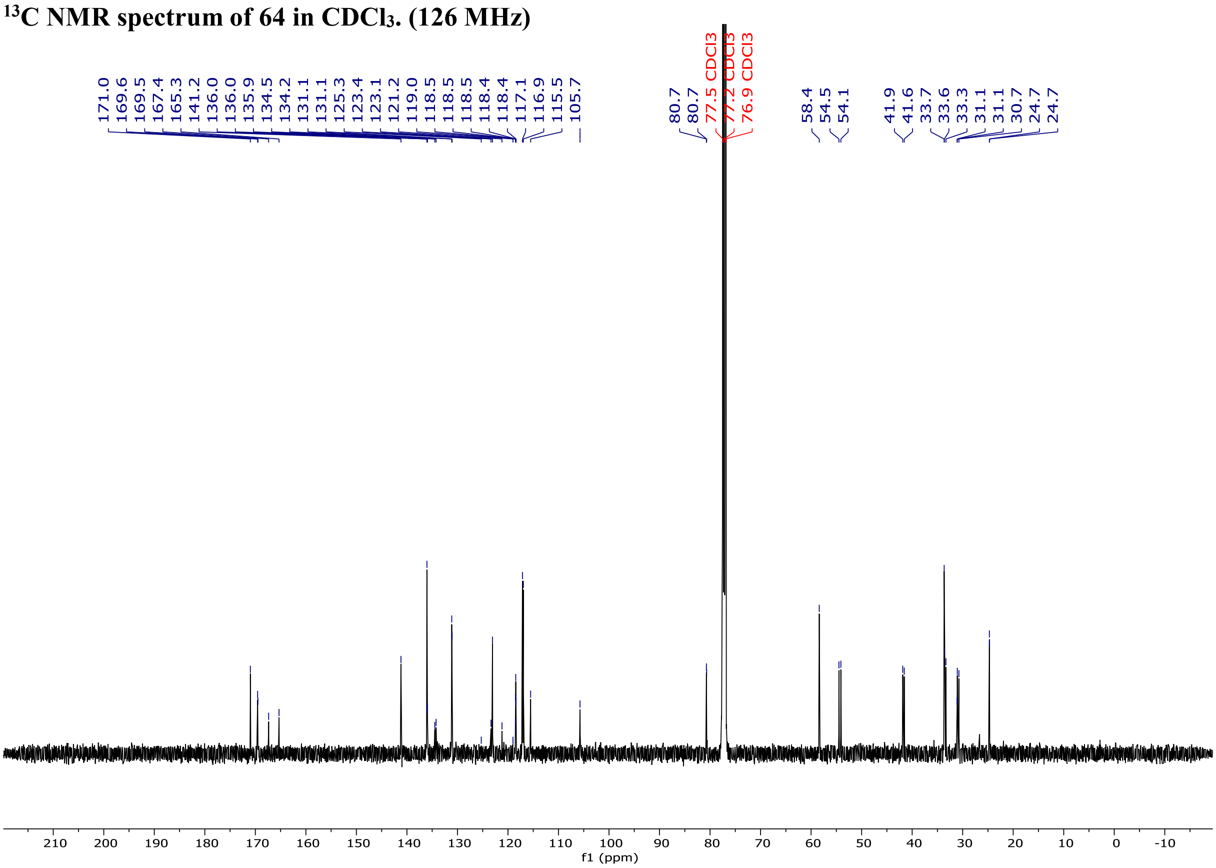
## $^{13}$C NMR spectrum of 63 in CDCl$_3$. (126 MHz)



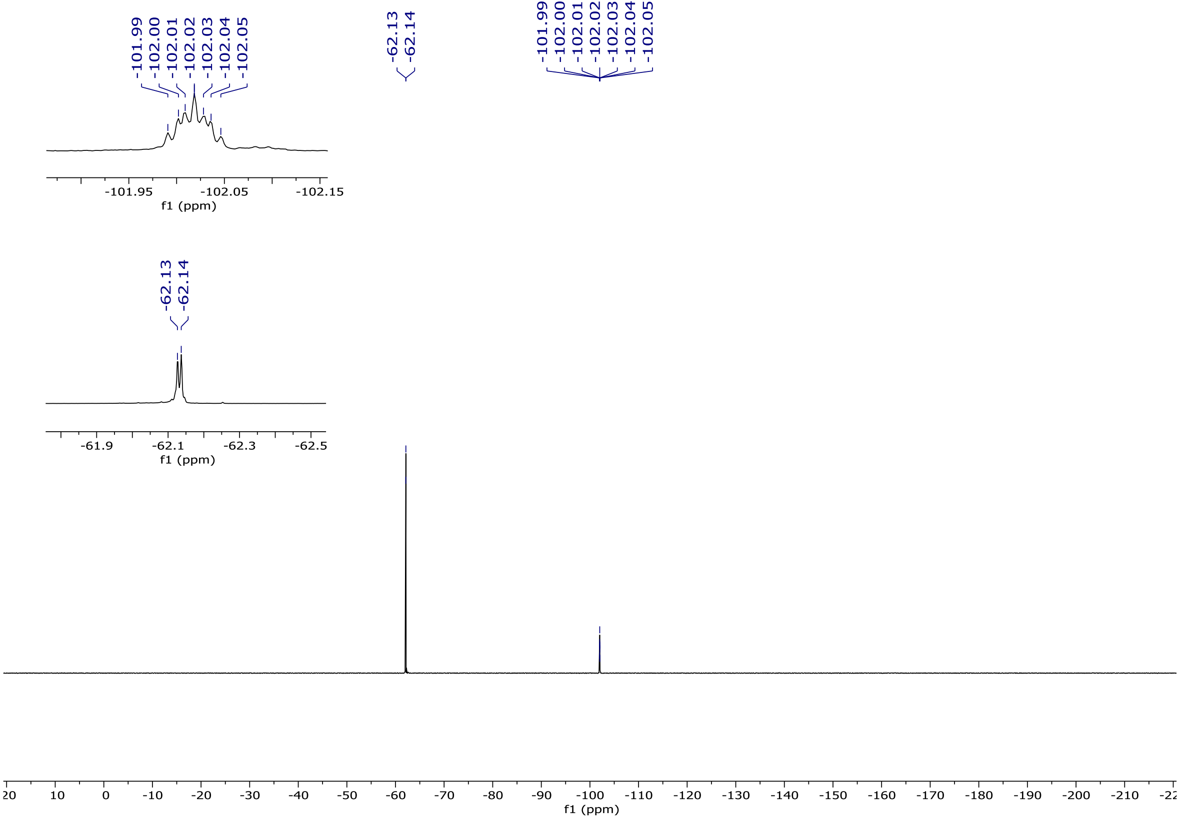
## $^{1}$H NMR spectrum of 64 in CDCl$_3$. (500 MHz)



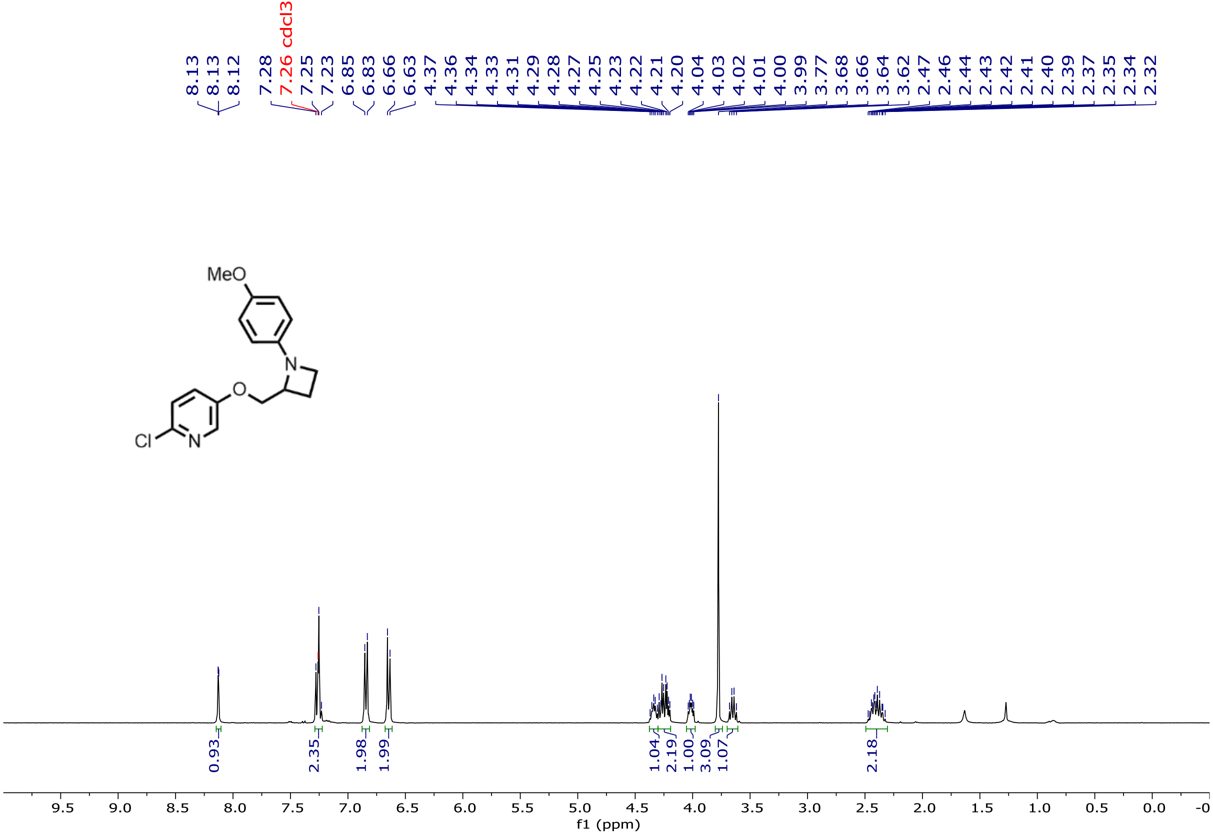
## $^{13}$C NMR spectrum of 64 in CDCl$_3$. (126 MHz)



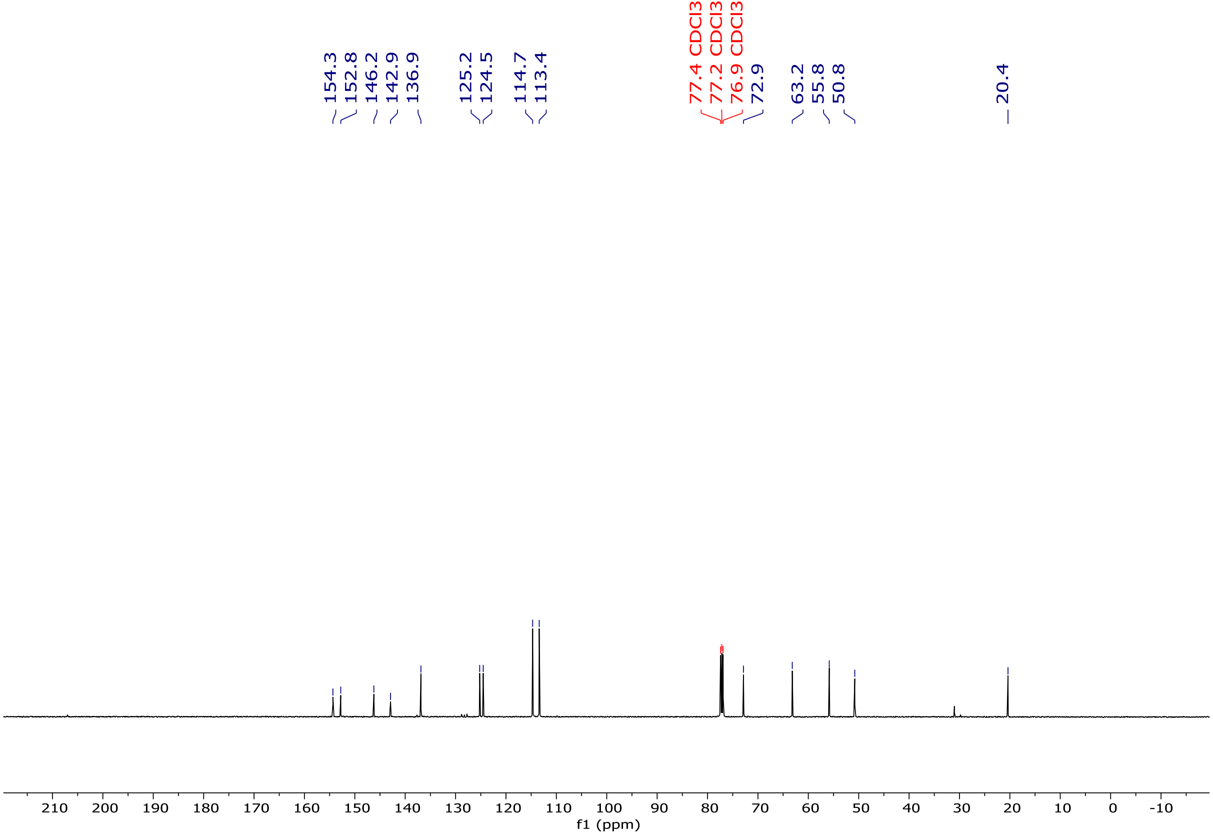
**$^{19}$F NMR spectrum of 64 in CDCl$_3$. (471 MHz)**



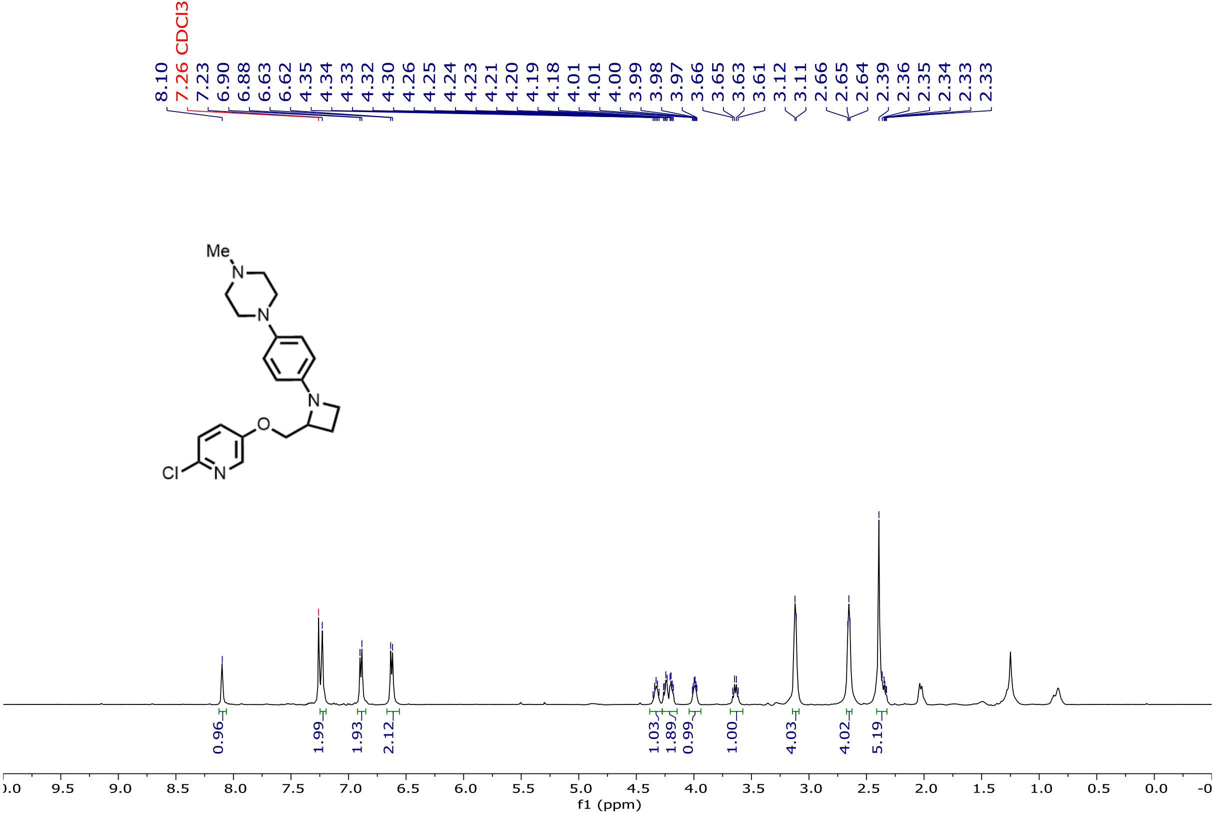
**$^{1}$H NMR spectrum of 66 in CDCl$_3$. (400 MHz)**



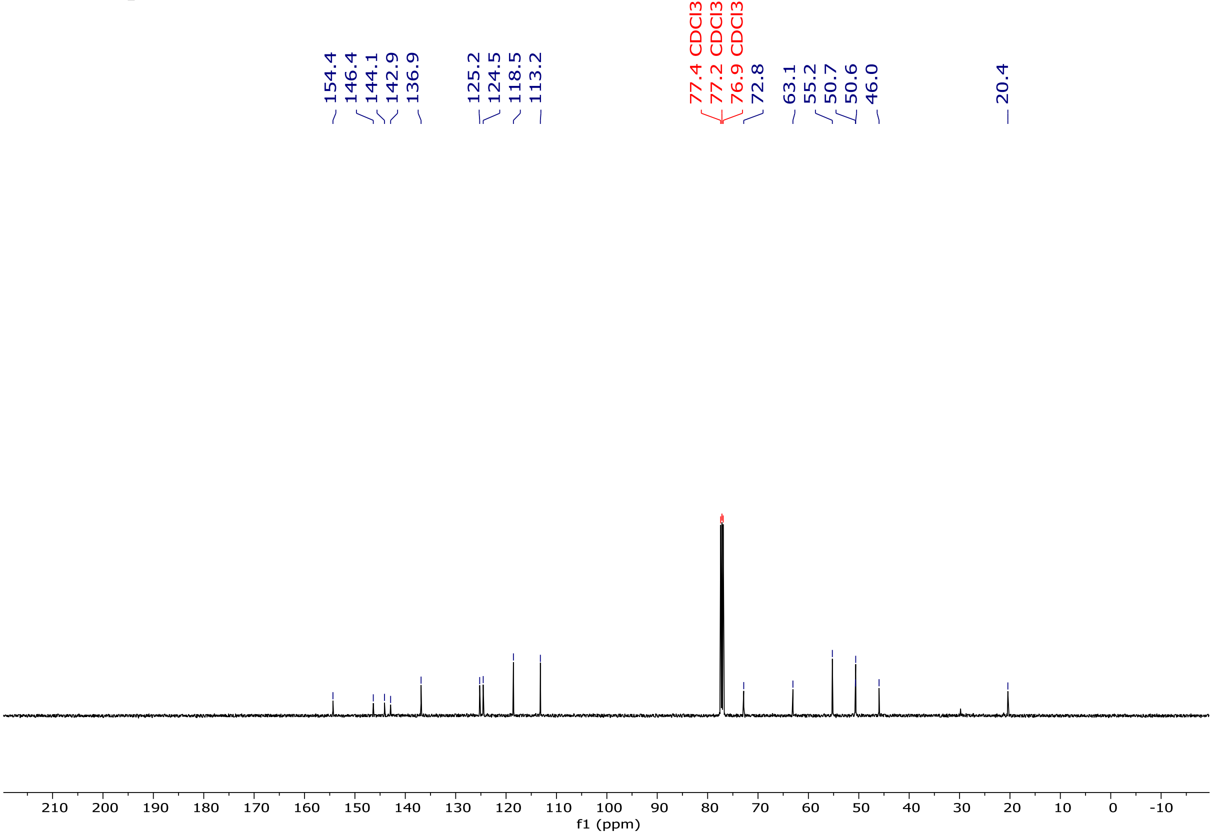
**$^{13}$C NMR spectrum of 66 in CDCl$_3$. (126 MHz)**



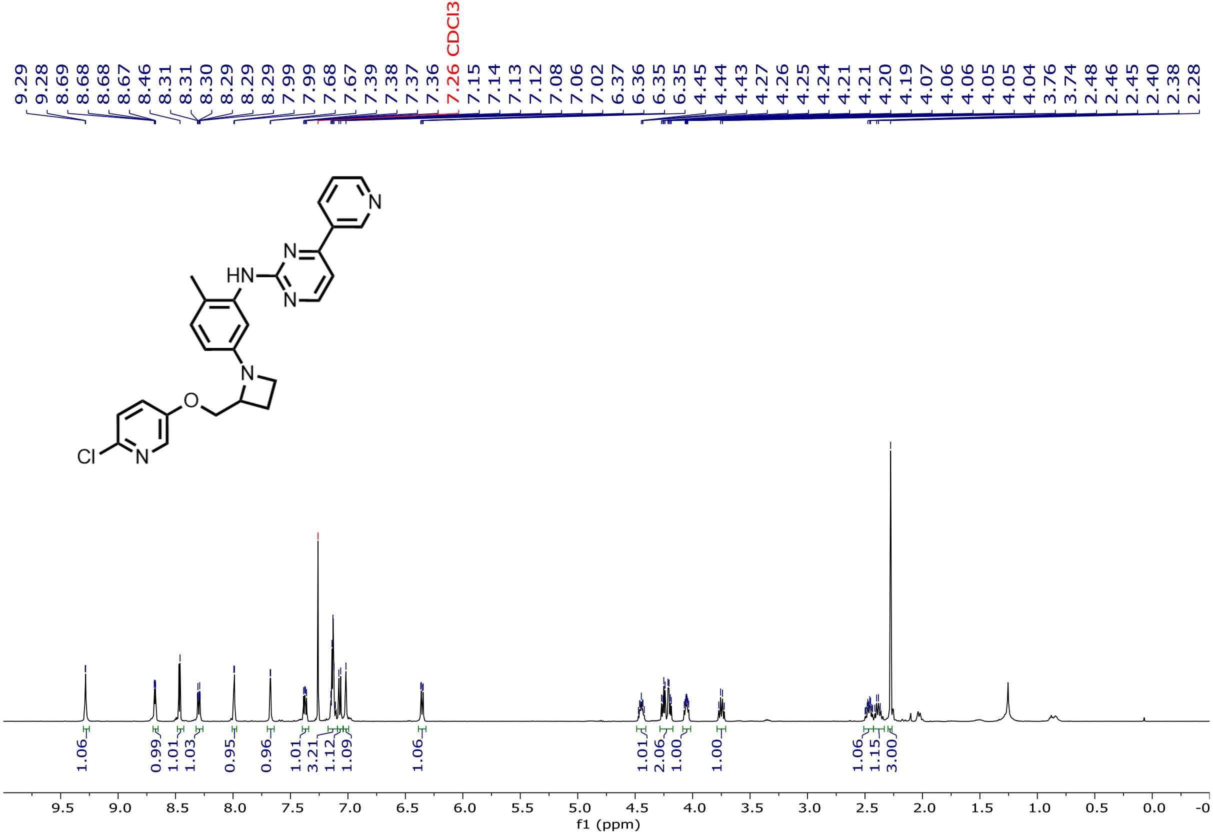
### $^1$H NMR spectrum of 67 in CDCl$_3$. (500 MHz)



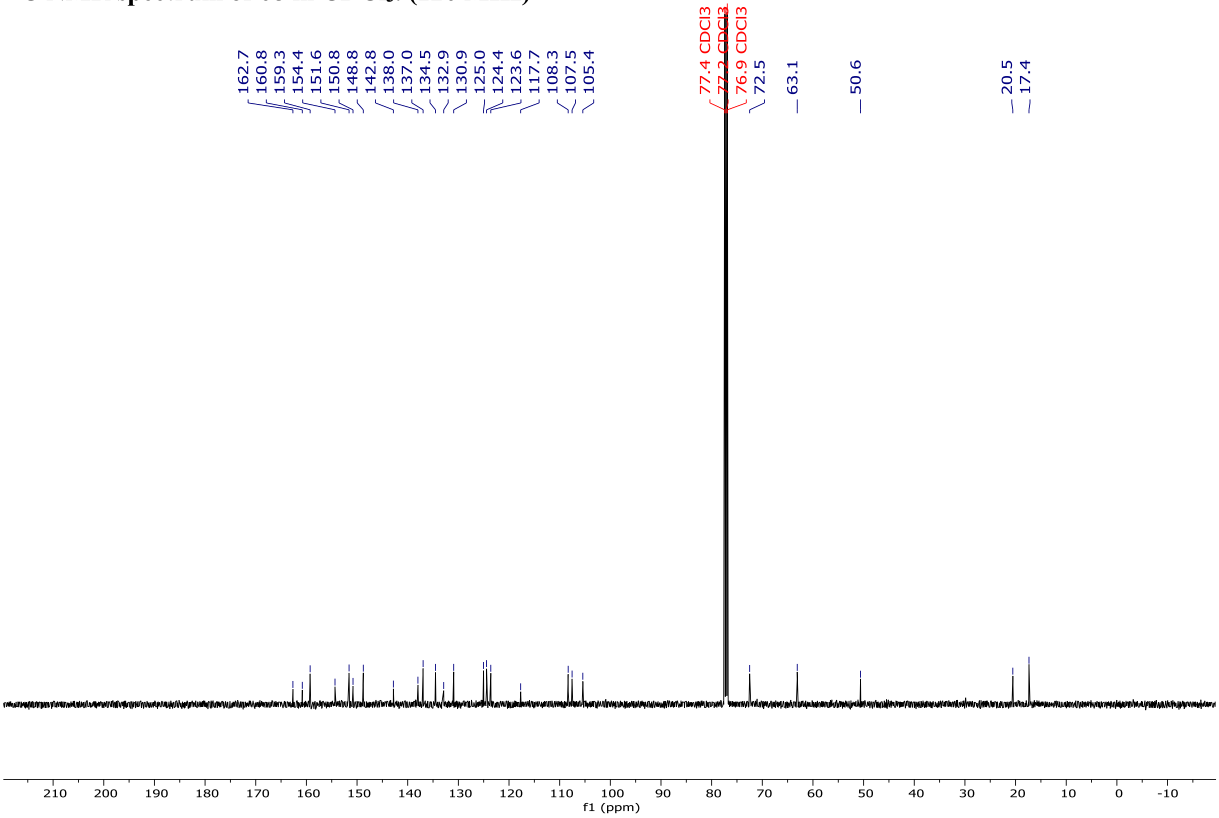
### $^{13}$C NMR spectrum of 67 in CDCl$_3$. (126 MHz)



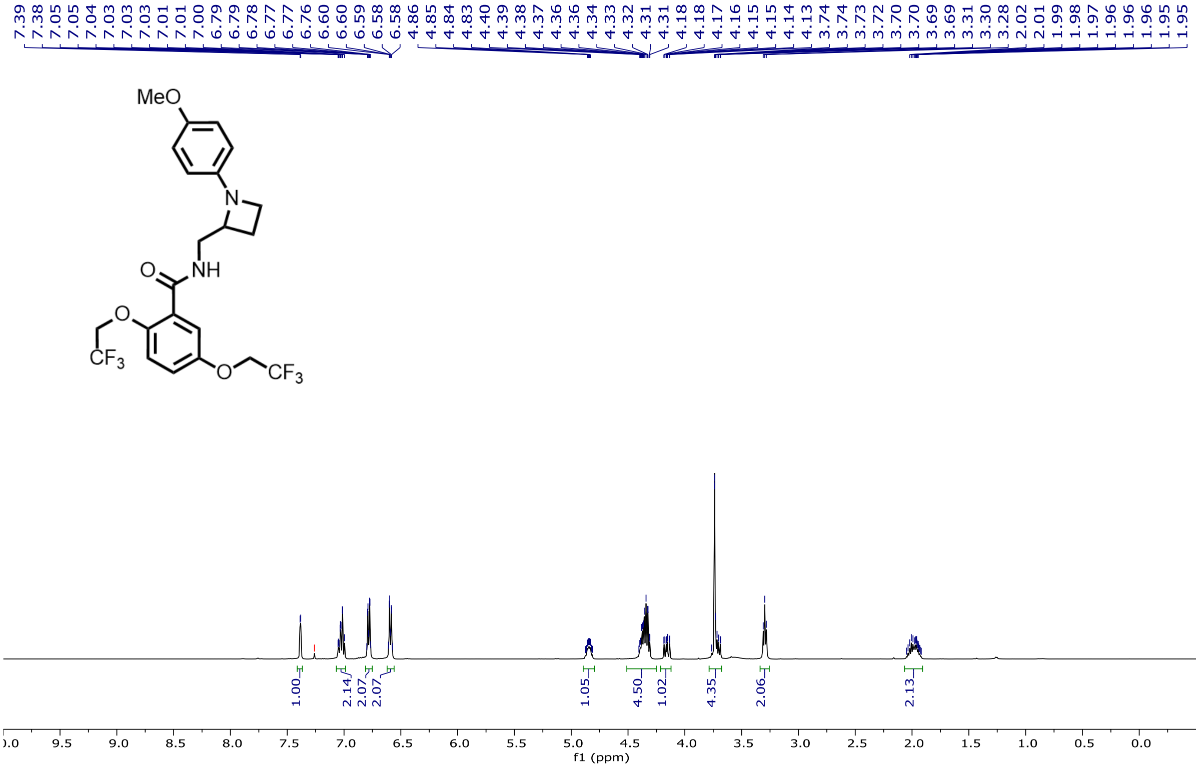
## $^1$H NMR spectrum of 68 in $CDCl_3$. (500 MHz)



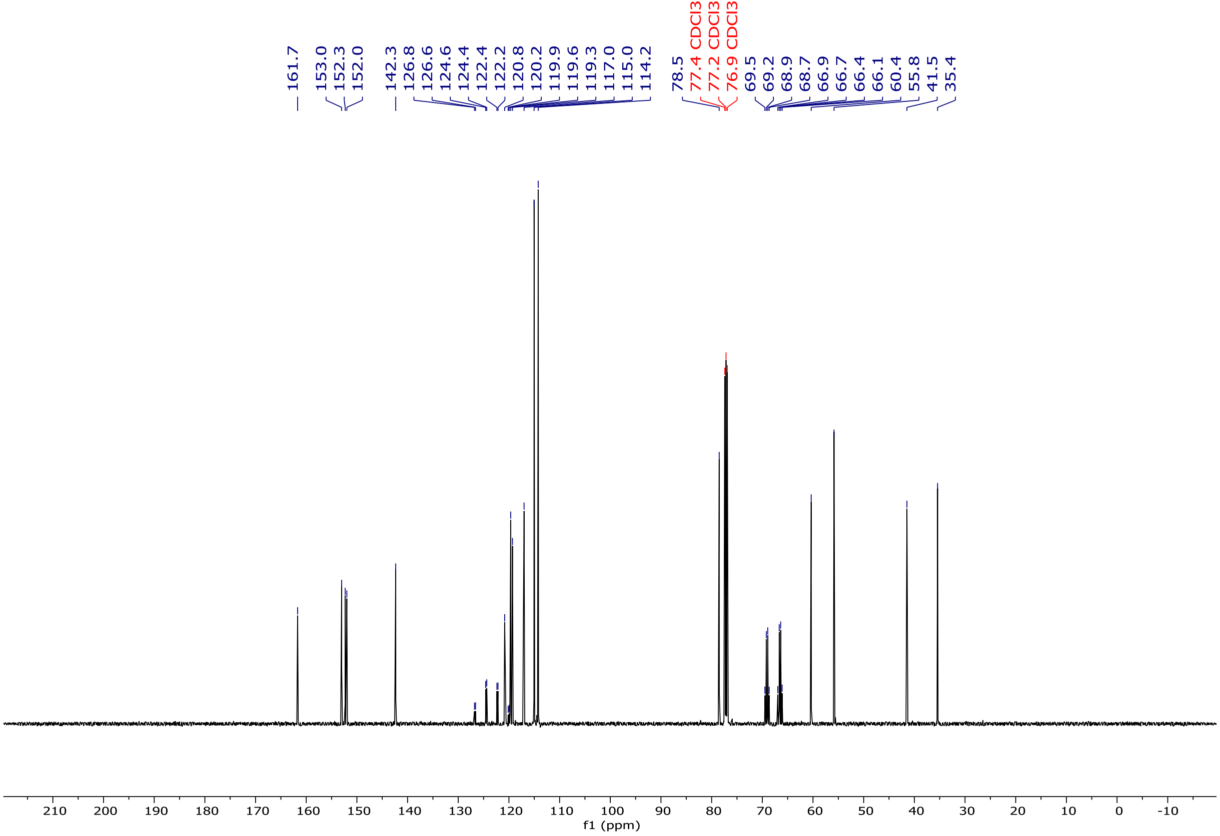
## $^{13}$C NMR spectrum of 68 in $CDCl_3$. (126 MHz)



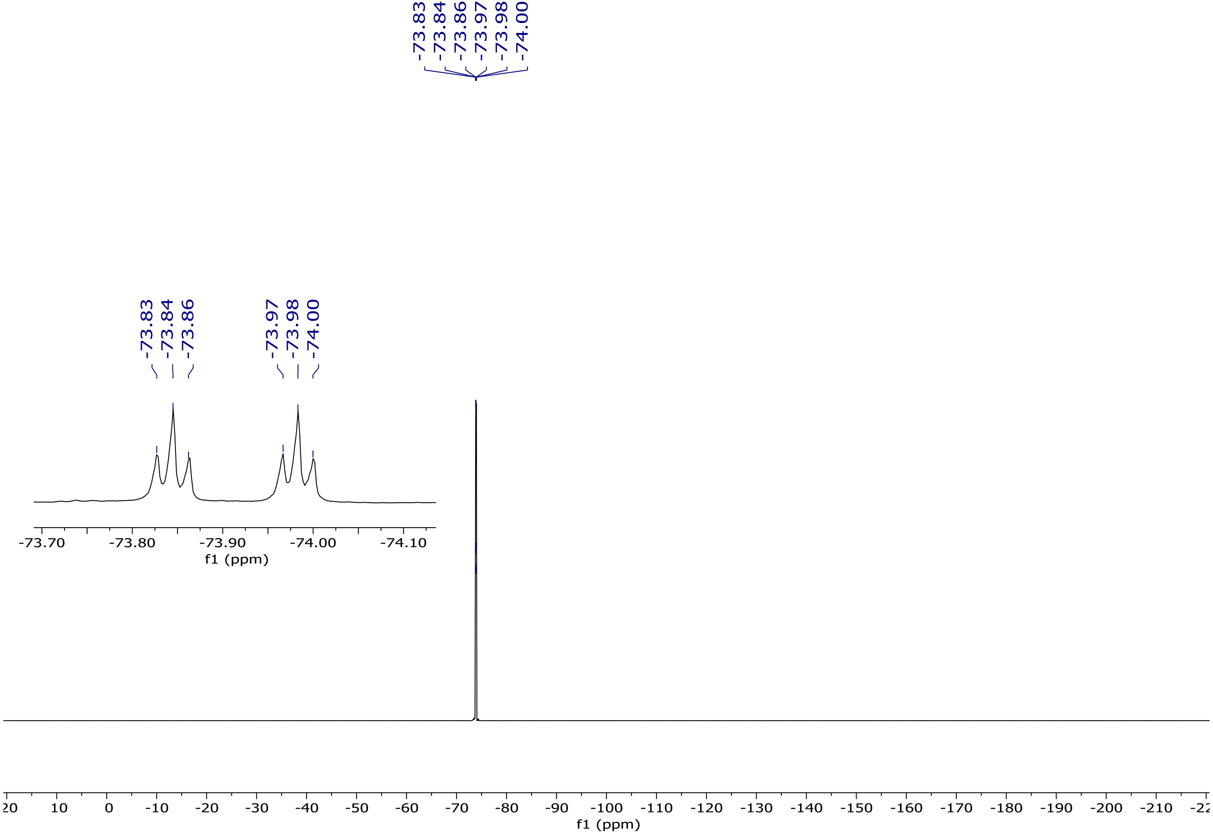
## $^{1}H$ NMR spectrum of 70 in $CDCl_3$. (500 MHz)



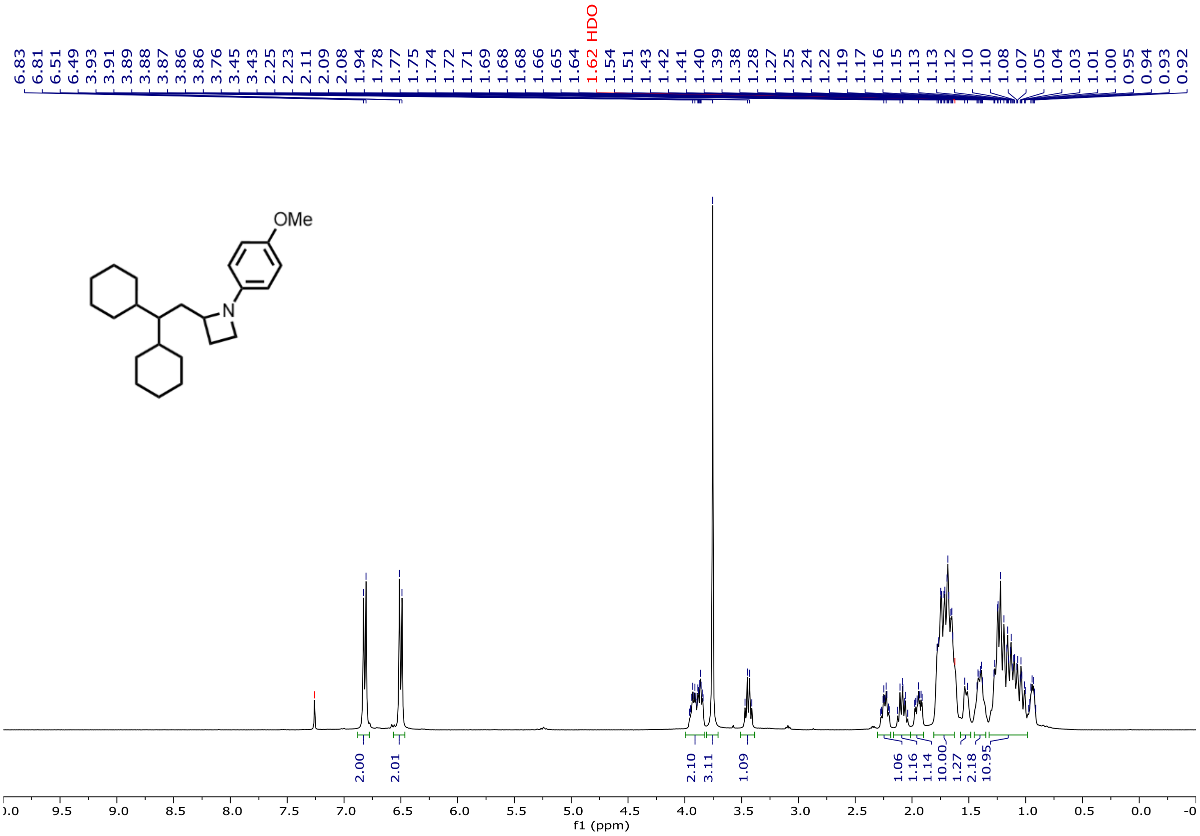
## $^{13}C$ NMR spectrum of 70 in $CDCl_3$. (126 MHz)



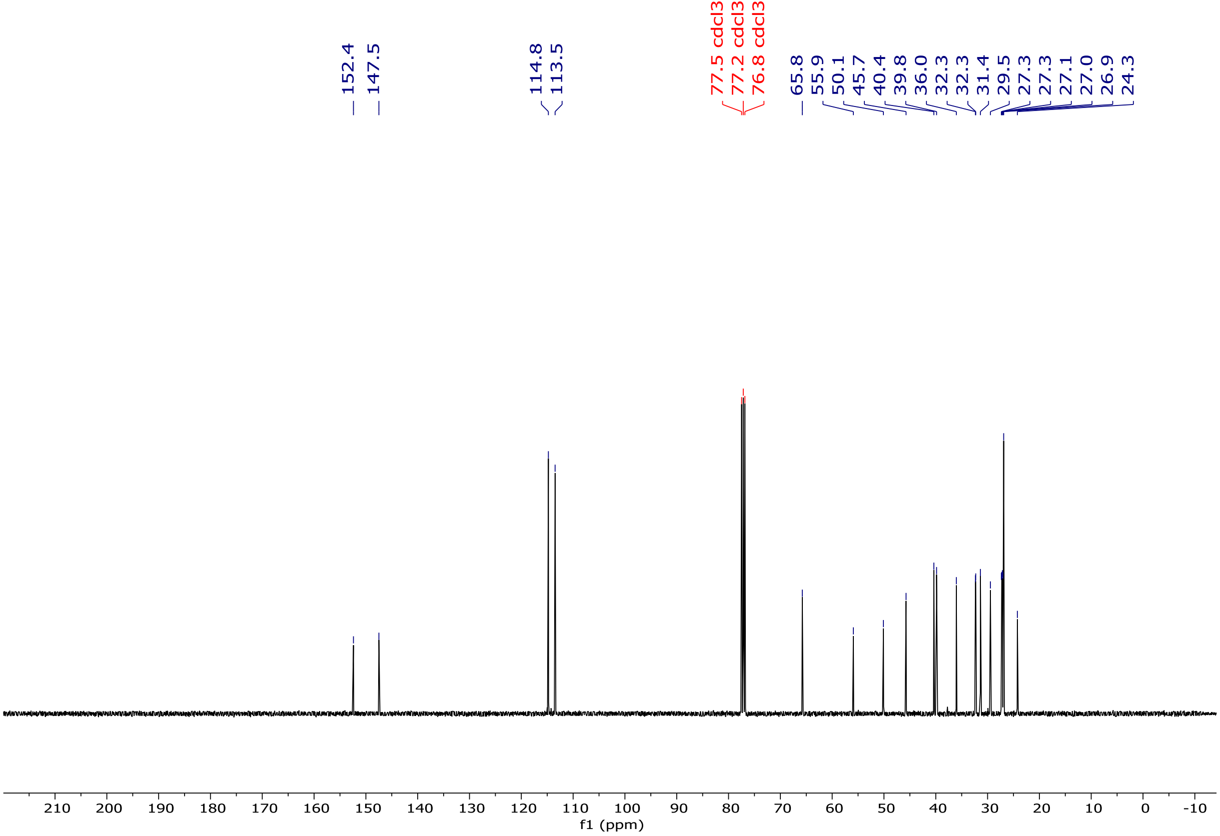
### $^{19}$F NMR spectrum of 70 in $CDCl_3$. (471 MHz)



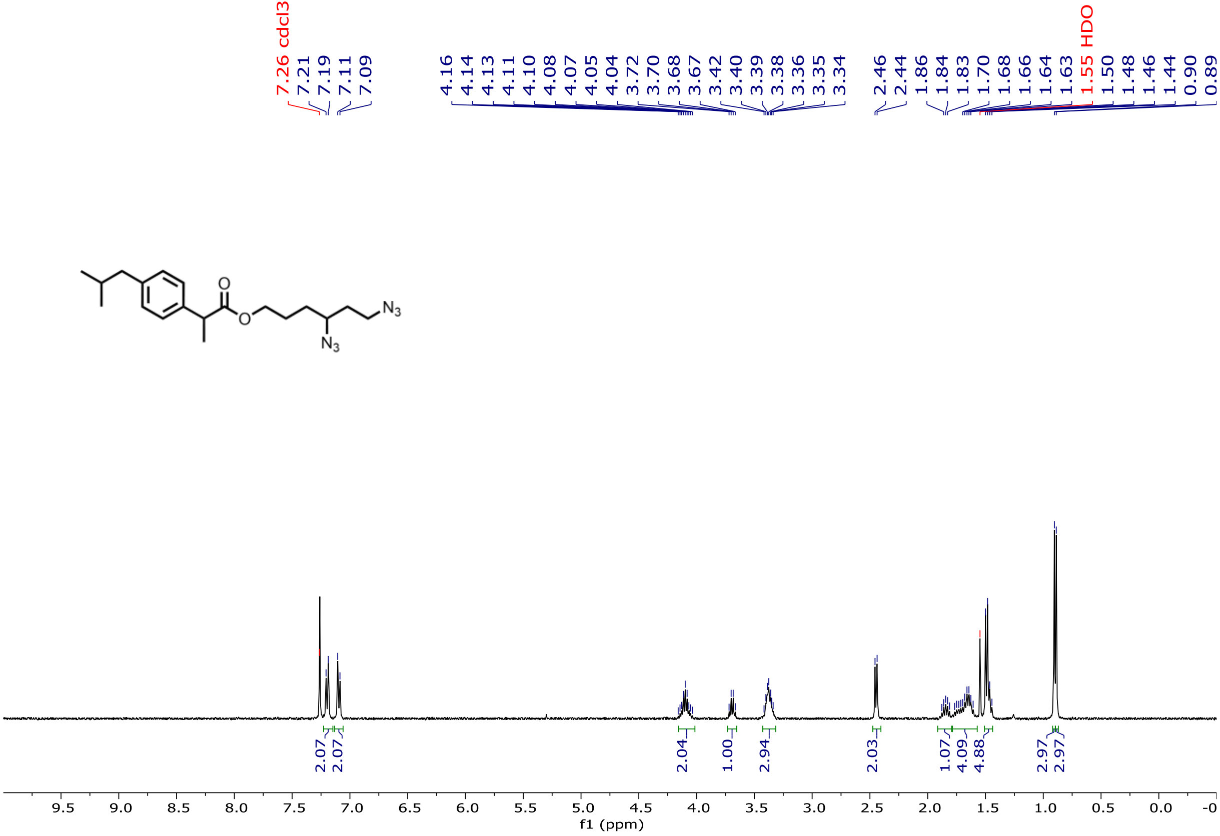
$^{1}$H NMR spectrum of 72 in CDCl$_3$. (400 MHz)



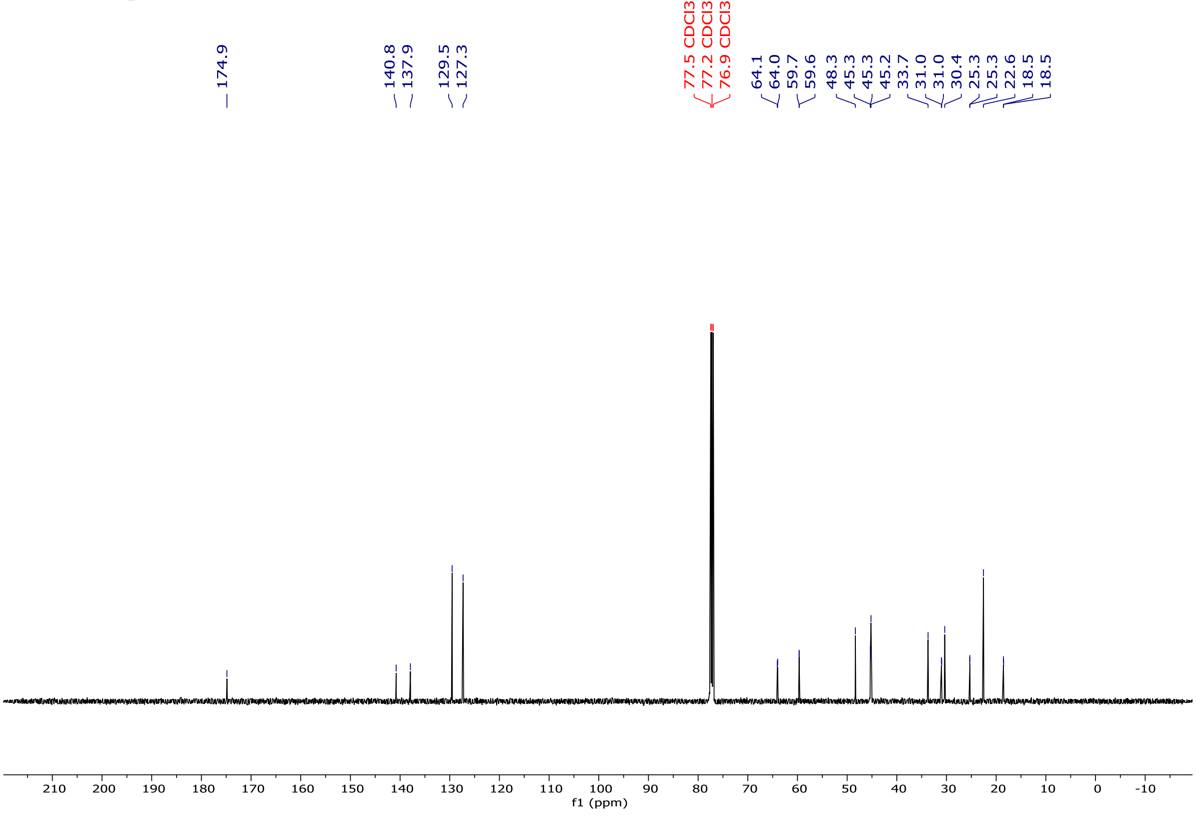
$^{13}$C NMR spectrum of 72 in CDCl$_3$. (101 MHz)



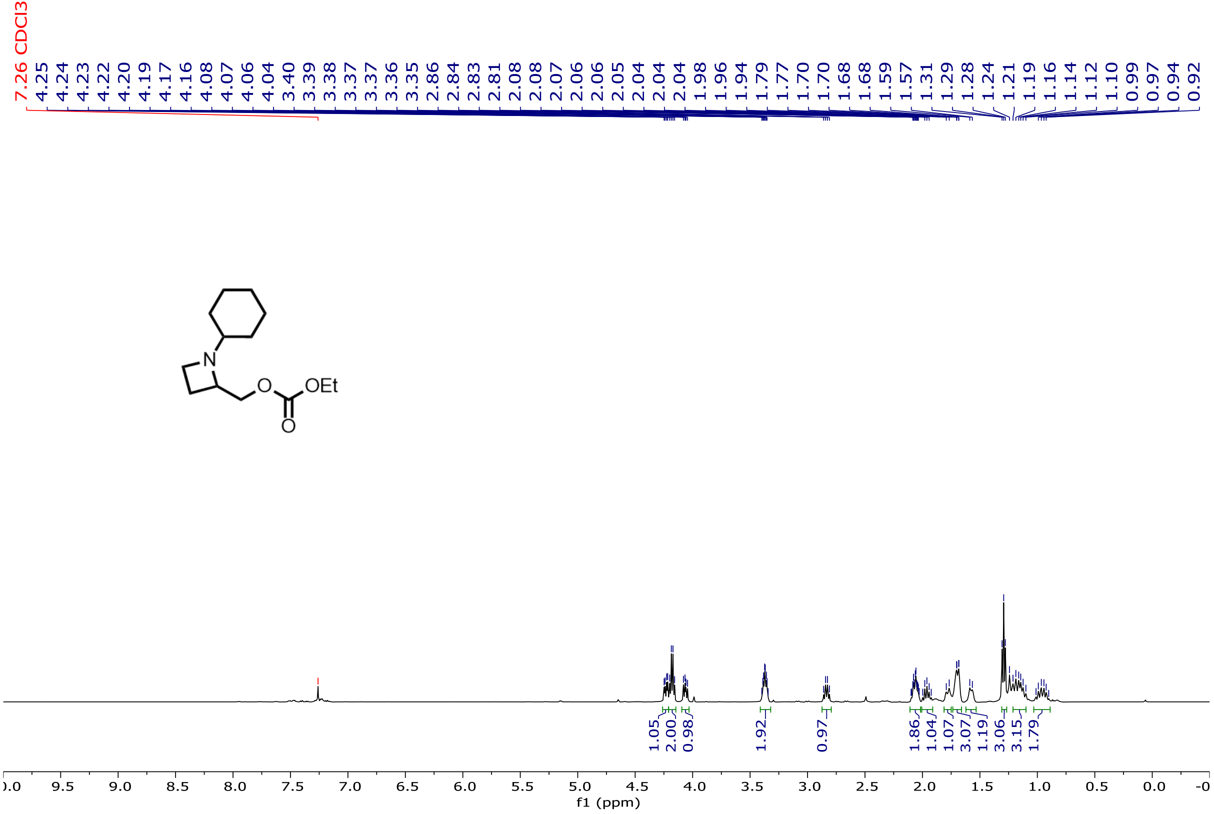
## $^1$H NMR spectrum of 75 in $CDCl_3$. (400 MHz)



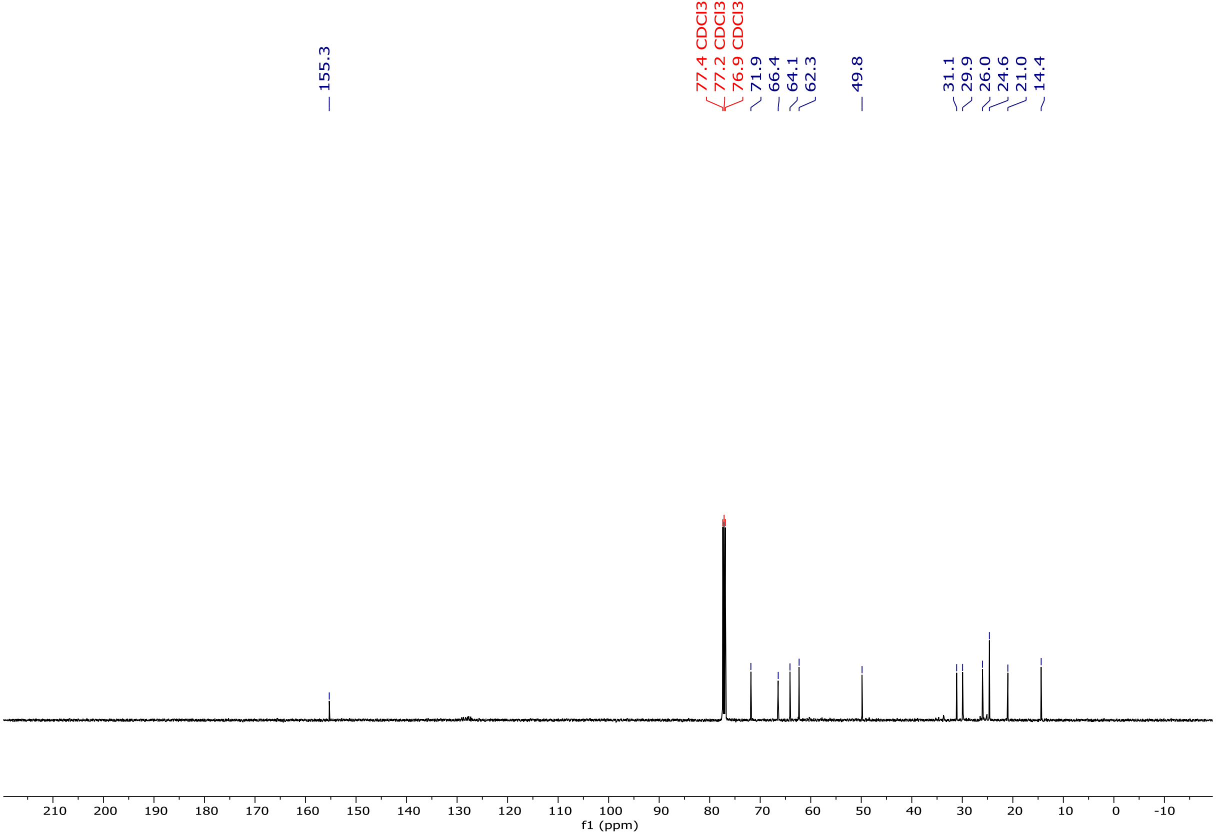
## $^{13}$C NMR spectrum of 75 in $CDCl_3$. (126 MHz)



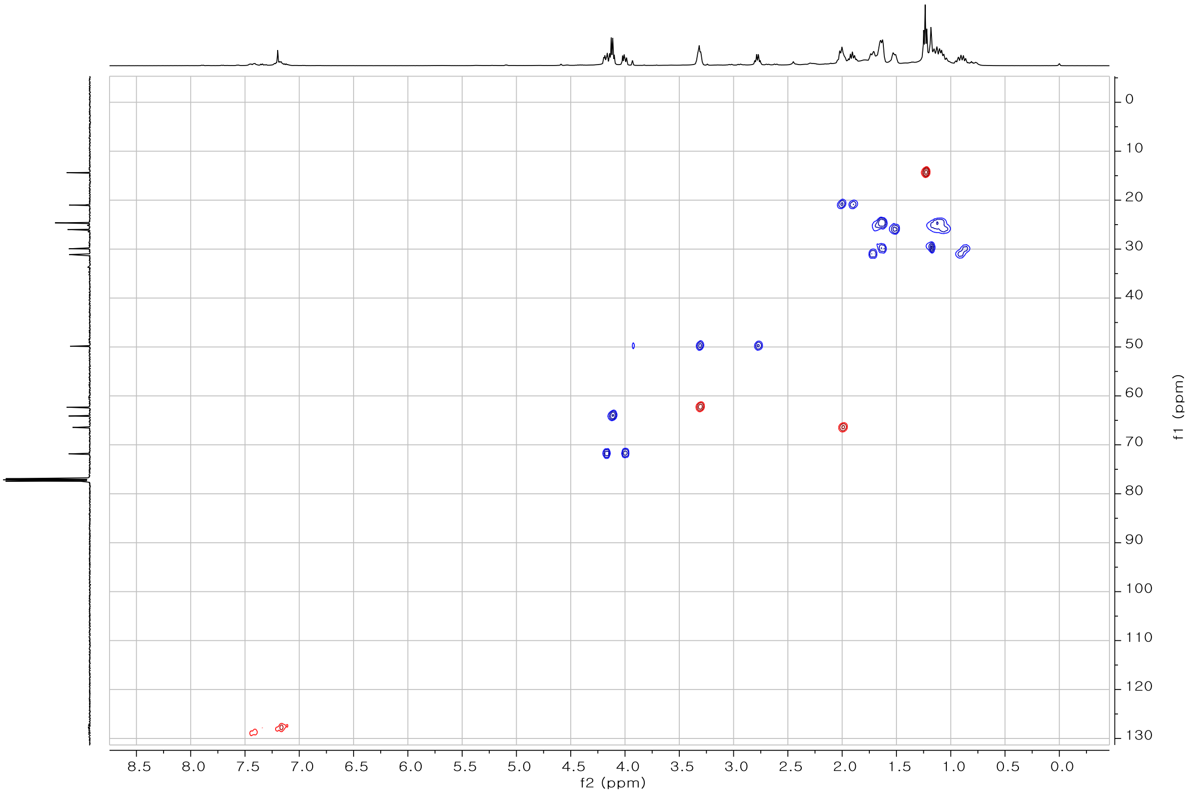
## $^{1}$H NMR spectrum of 79 in CDCl$_3$. (500 MHz)



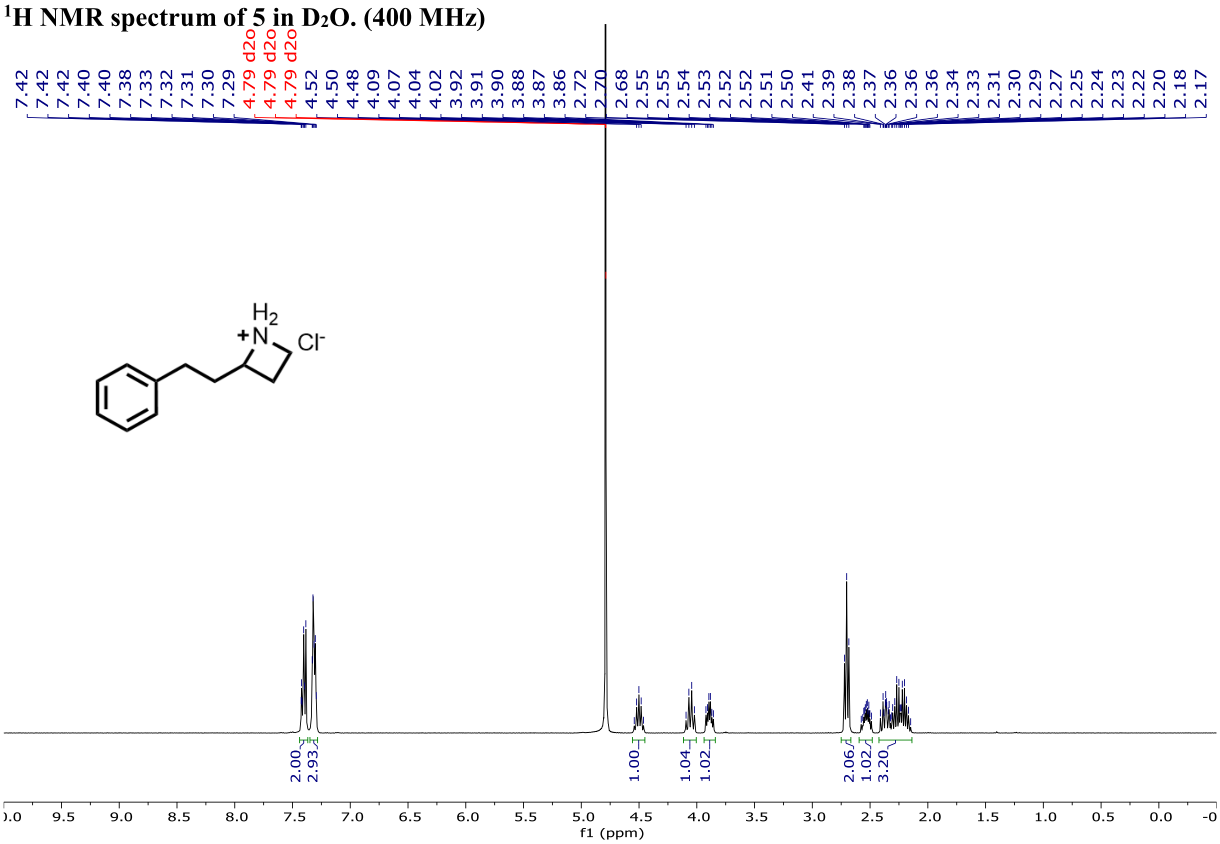
## $^{13}$C NMR spectrum of 79 in CDCl$_3$. (126 MHz)



**HSQC spectrum of 79 in CDCl₃. ($^1$H NMR at 500 MHz, $^{13}$C NMR at 126 MHz)**



$^1$H NMR spectrum of 5 in $D_2O$. (400 MHz)



$^{13}$C NMR spectrum of 5 in $D_2O$. (126 MHz)