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Supplementary Information

Anti-Markovnikov Hydroazidation of Activated Olefins *via* Organic Photoredox Catalysis

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Table of Contents

General Reagent Information: Commercially available reagents were purchased from Sigma-Aldrich, Fischer Scientific or TCI Corporation and were used without further purification. Styrenes containing radical inhibitors were filtered through a small pad of silica gel to remove any inhibitors. Styrenes which appeared impure upon purchase/preparation were also purified by passing them through a short pad of silica. Solvents were used as received unless otherwise noted.

TMS-azide was used as received and stored in a refrigerator.

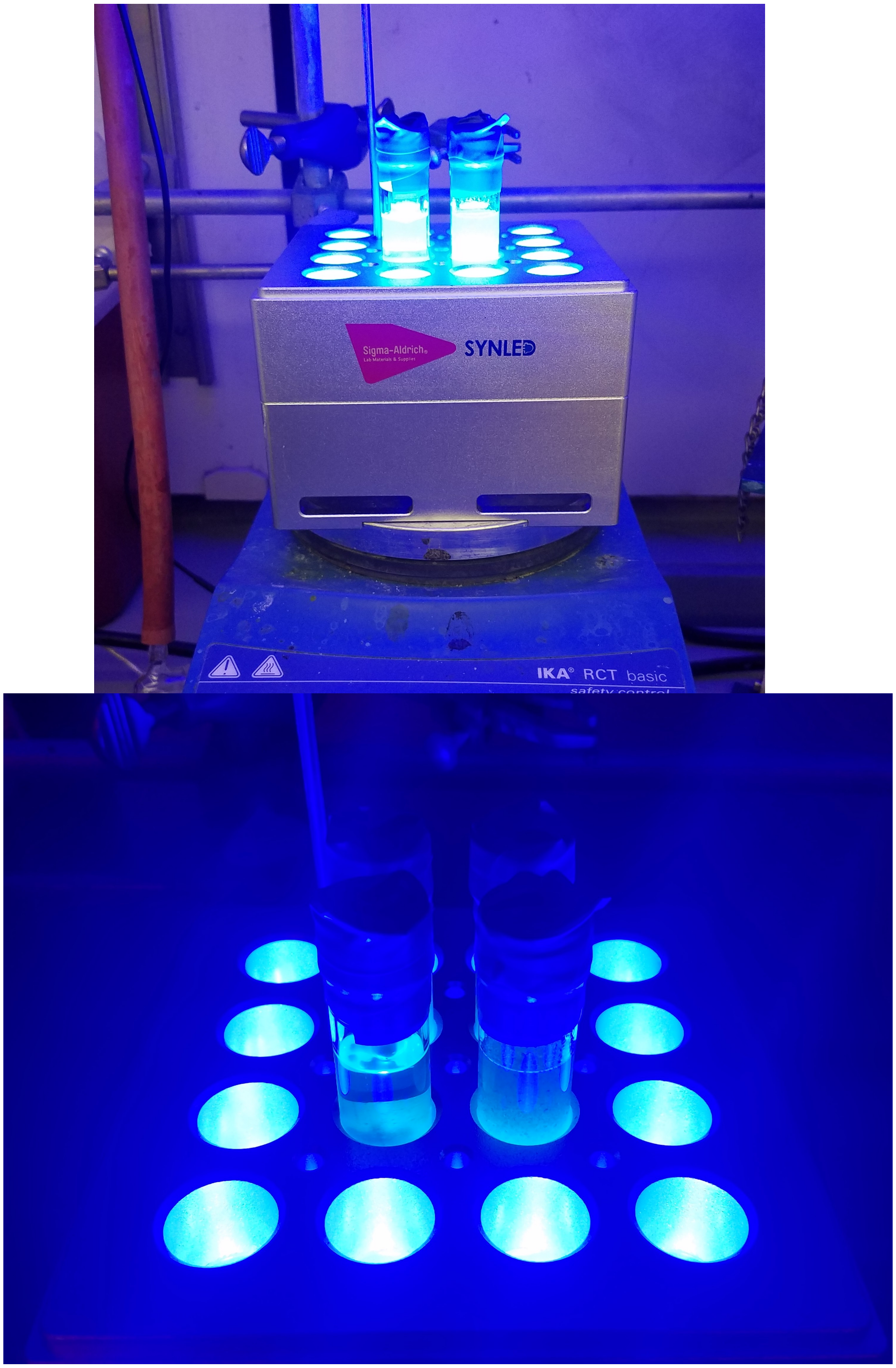
WARNING: TMS-azide is an acutely toxic reagent and should be treated with extreme care. When scaling up reactions, ensure that all waste is kept basic to prevent the formation of hydrazoic acid at any point during work-up. Please familiarize yourself with the handling of this hazardous reagent before attempting any of the reactions disclosed within.

General Analytical Information:_Proton and carbon (^{1}H and ^{13}C) magnetic resonance spectra were collected on a Bruker AVANCE III 600 CryoProbe (^{1} H NMR at 600 MHz and ^{13}C NMR at 151 MHz) spectrometer or Bruker AVANCE III 500 (^{1} H NMR at 500 MHz and ^{13}C NMR at 126 MHz) spectrometer. Unless otherwise noted, spectra are referenced to Chloroform-d (^{1} H NMR at 7.26 ppm and ^{13}C at 77.16 ppm) and reported as parts per million. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, ddddd = doublet of doublets of doublets of doublets of doublets, dt = doublet of triplets, ddt = doublet of doublets of triplets, td = triplet of doublets, tt = triplet of triplets, m = multiplet, q = quartet), coupling constants (Hz), and integration

High Resolution Mass Spectra (HRMS) were obtained via direct infusion using a Thermo LTQ FT mass spectrometer with positive mode electrospray ionization or APCI. Low resolution mass spectra were obtained using an Agilent Technologies 5977E MSD GC/MS unit with electron impact (EI) ionization.

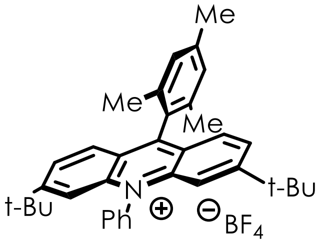
Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle.

General Photoreactor Configuration: All photochemical reactions were conducted using a SynLED Parallel Photoreactor, available for purchase from Sigma-Aldrich (item number: Z742680). The unit has bottom-lit LEDS (465-470 nm) with 130-140 lm intensity and a built-in cooling fan. The measured temperature range was 35 - 40°C. The reactor was fit to an IKA magnetic stirrer with round plate (item number: Z645052). Small stir bars are sometimes required for efficient stirring when using 2 dram vials.

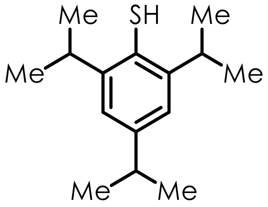


General Procedure for Photochemical Reactions: A flame-dried 2-dram borosilicate vial (purchased from Fisher Scientific, catalogue # 03-339-22D), equip with a stir bar, was charged with 3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (0.01 eq., 0.01 mmol) and 2,5,6-triisopropylthiophenol (0.10 mmol, 0.20 eq.). For solid/non-volatile substrates, the substrate (0.50 mmol) was then added. 2,2,2-trifluoroethanol (5.0 mL) was added and vials were capped tightly with a Teflon lined phenolic resin septum cap (purchased through VWR international, Microliter Product # 15-0060K). The reaction mixture was the sparged by bubbling with nitrogen or argon for 5 minutes. Trimethylsilylazide (0.625 mmol, 1.25 eq.) was then added *via* microliter syringe. Prior to irradiation, vials were sealed with Teflon tape and electrical tape to ensure maximal oxygen exclusion. The reaction vial was then placed into the reactor and irradiated for 18 hours unless otherwise noted. Following irradiation, the reaction mixture was concentrated under reduced pressure and the desired products were isolated *via* flash column chromatography (see substrate/product details for solvent information). Unless otherwise noted, all reaction yields are reported as the average of two separate trials (including chromatography).

Catalyst and Substrate Synthesis:



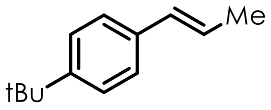
3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate was prepared according to published procedure. Spectral data matched that reported in the literature. [1]



2,4,6-triisopropylbenzenethiol was prepared according to the procedure of Knowles and coworkers. Spectral data matched that reported in the literature.[2]

General procedure for preparation of beta-methylstyrene derived substrates:

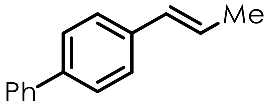
In a flame-dried round bottom flask under an atmosphere of nitrogen, ethyltriphenylphosphonium iodide (1.1 eq.) was stirred with THF (0.5 M) and cooled to 0 °C using an ice/water bath. Potassium *tert*-butoxide (1.1 eq.) was added portionwise across several minutes, resulting in the formation of a vibrant orange suspension. This suspension was stirred at 0 °C for one hour. Following this, the corresponding benzaldehyde derivative (1.0 eq.) was added, either by syringe for liquid aldehydes or portionwise for solid aldehydes. As the aldehyde was added, the bright orange color gradually faded, accompanied by the formation of a white precipitate. To simplify purification, the addition of aldehyde should be halted upon the complete disappearance of color. The reaction mixture was stirred and allowed to warm to RT overnight (12-18 hours). After ensuring that the reaction had reached completion by TLC, the reaction mixture was concentrated under reduced pressure to remove THF. Following this, the resulting crude mixture was loaded onto silica gel. The desired product was isolated *via* flash column chromatography (typically using hexane as the eluent). In some cases, distillation is also an effective purification method for more volatile substrates. Styrenes are typically isolated as a mixture of (E)- and (Z)- isomers. This isomeric mixture can be used in the hydroazidation reaction with no effect on yield or reaction efficiency.



1-(*tert*-butyl)-4-(prop-1-en-1-yl)benzene

The alkene was prepared according to the general procedure.

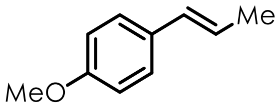
Spectral data matches those previously reported.[3]



4-(prop-1-en-1-yl)-1,1'-biphenyl

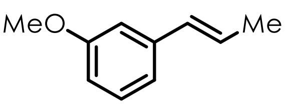
The alkene was prepared according to the general procedure.

Spectral data matched that reported in the literature.[4]



1-methoxy-4-(prop-1-en-1-yl)benzene

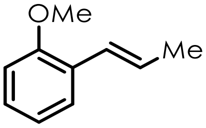
The alkene was purchased commercially and used with no additional purification.



1-methoxy-3-(prop-1-en-1-yl)benzene

The alkene was prepared according to the general procedure.

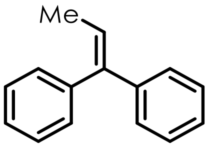
Spectral data matched that reported in the literature.[5]



1-methoxy-2-(prop-1-en-1-yl)benzene

The alkene was prepared according to the general procedure.

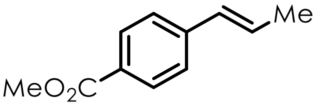
Spectral data matched that reported in the literature.[6]



prop-1-ene-1,1-diyldibenzene

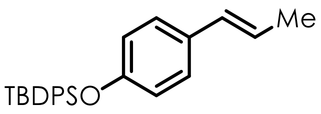
The alkene was prepared according to a modified general procedure. Instead of potassium *tert*-butoxide, *n*-butyllithium (1.6 M in hexanes) was used in the deprotonation step, per literature precedent.[7]

Spectral data matched that reported in the literature.[7]



methyl 4-(prop-1-en-1-yl)benzoate

The alkene was purchased commercially and used with no additional purification.



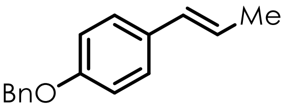
tert-butyldiphenyl(4-(prop-1-en-1-yl)phenoxy)silane

The alkene was prepared from the corresponding aldehyde according to the general procedure. The desired product was isolated as a pale yellow semi-solid following purification by flash column chromatography (60% yield, 1.24 g). NMR data is given for mixture of alkene isomers.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.79 – 7.67 (m, 5H), 7.57 – 7.49 (m, 1H), 7.48 – 7.33 (m, 9H), 7.26 – 7.17 (m, 2H), 7.13 – 6.99 (m, 2H), 6.71 (ddt, J = 27.1, 8.6, 2.3 Hz, 2H), 6.36 – 6.20 (m, 1H), 6.10 – 5.46 (m, 1H), 1.91 – 1.79 (m, 3H), 1.14 – 1.08 (m, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.68, 154.21, 135.82, 135.64, 134.93, 133.06, 130.00, 129.90, 129.44, 127.89, 127.39, 126.74, 125.13, 119.80, 119.45, 27.42, 26.64, 19.68, 19.60

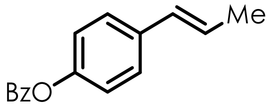
HRMS (APCI, positive mode): calculated: 373.1982, found: 373.1983 (M+H)



1-(benzyloxy)-4-(prop-1-en-1-yl)benzene

The alkene was prepared in two steps starting from 4-hydroxybenzaldehyde. 4-hydroxybenzaldehyde (2.00 g, 16.4 mmol), potassium carbonate (2.94 g, 21.3 mmol), benzyl bromide (3.08 g, 18.0 mmol) were stirred together in DMF (10 mL) and the mixture was heated at 60 °C for one hour. At this time, the mixture was cooled to RT and poured onto water. The resulting mixture was extracted with diethyl ether. The ethereal extracts were washed with brine, dried with magnesium sulfate, and concentrated under reduced pressure to yield the crude product as an oil (60% yield, 2.07 g). This material was used in the next step without further purification. The aldehyde was converted to the alkene product according to the general procedure. The desired product was isolated as a clear oil following purification by column chromatography (66% yield, 1.44 g).

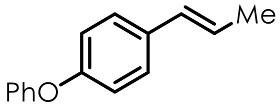
Spectral data matched that reported in the literature.[8]



4-(prop-1-en-1-yl)phenyl benzoate

The alkene was prepared in two steps starting from 4-hydroxybenzaldehyde. 4-hydroxybenzaldehyde (1.50 g, 12.0 mmol), triethylamine (2.5 mL, 18 mmol) and dichloromethane (35 mL) were stirred together in a flame-dried RBF and cooled to 0 °C using an ice/water bath. Benzoyl chloride (2.1 mL, 18 mmol) was added dropwise and the reaction mixture was stirred and warmed to RT overnight. The next day, the reaction mixture was quenched with sodium bicarbonate and extracted with dichloromethane (3 x 30 mL). The combined organic washings were washed with brine, dried with sodium sulfate, and concentrated under reduced pressure to yield the desired product as a yellow oil (quant.). The crude material was used in the next step according to the general procedure to prepare the alkene. The final product was isolated as a clear oil (62% yield, 1.31 g).

Spectral data matched that reported in the literature.[9]



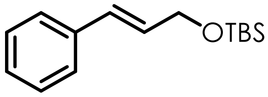
1-phenoxy-4-(prop-1-en-1-yl)benzene

The alkene was prepared according to the general procedure using the corresponding, known aldehyde. The desired product was isolated as a pale yellow oil following flash column chromatography as a 2.7:1 ratio of Z/E alkene isomers. NMR data is given for mixture of alkene isomers.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.40 – 7.27 (m, 4H), 7.11 (t, J = 7.7 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.98 – 6.93 (m, 2H), 6.40 (t, J = 14.6 Hz, 1H), 6.17 (dq, J = 19.4, 6.6 Hz, 1H), 5.77 (dq, J = 11.6, 7.2 Hz, 1H), 1.92 (d, J = 7.1 Hz, 1.5H), 1.89 (d, J = 6.8 Hz, 1.5H).

^{13}C NMR (151 MHz, Chloroform-d) δ 157.50, 157.35, 156.07, 155.75, 133.44, 132.91, 130.32, 130.26, 129.86, 129.83, 129.18, 127.19, 126.26, 124.99, 123.34, 123.22, 119.17, 118.97, 118.80, 118.65, 18.63, 14.78.

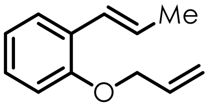
HRMS (APCI, positive mode): calculated: 211.1174, found: 211.1117 (M+H)



***tert*-butyl(cinnamyloxy)dimethylsilane**

The substrate was prepared with a previously reported method.[10]

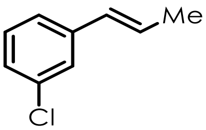
Spectral data matched that reported in the literature.[10]



1-(allyloxy)-2-(prop-1-en-1-yl)benzene

The corresponding aldehyde starting material was prepared from salicylaldehyde according to a previously reported procedure.[11] The alkene was prepared according to the general procedure. The desired product was isolated as a pale yellow oil following purification by flash column chromatography (100% hexane) (813 mg, 76% yield).

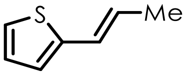
Spectral data matched those previously reported.[12]



1-chloro-3-(prop-1-en-1-yl)benzene

The alkene was prepared according to the general procedure.

Spectral data matched that reported in the literature.[13]

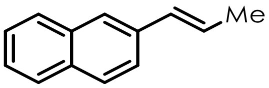


2-(prop-1-en-1-yl)thiophene

The alkene was prepared according to the general procedure.

Spectral data (^{1}H NMR) matched that reported in the literature.[14]

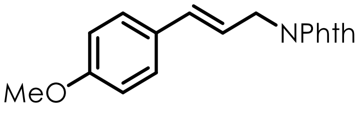
^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.70, 136.39, 131.02, 128.52, 128.05, 63.84, 28.13.



2-(prop-1-en-1-yl)naphthalene

The alkene was prepared according to the general procedure.

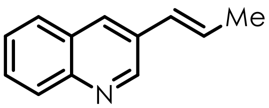
Spectral data matched that reported in the literature.[15]



(*E*)-2-(3-(4-methoxyphenyl)allyl)isoindoline-1,3-dione

Substrate was prepared according to a previously published procedure. Spectral data matched that reported in the literature.[12]

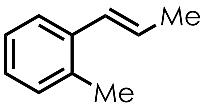
HRMS (APCI, positive mode): calculated: 294.1125, found: 294.1126 (M+H)



(*E*)-3-(prop-1-en-1-yl)quinoline

The alkene was prepared according to the general procedure.

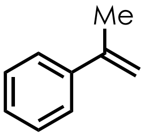
Spectral data matched that reported in the literature.[16]



(*E*)-1-methyl-2-(prop-1-en-1-yl)benzene

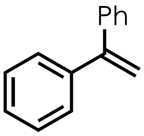
The alkene was prepared according to the general procedure.

Spectral data matched that reported in the literature.[6]



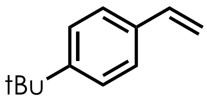
prop-1-en-2-ylbenzene

The alkene was purchased commercially and used without additional purification.



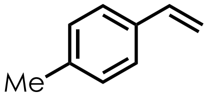
ethene-1,1-diyldibenzene

The alkene was purchased commercially and used without additional purification.



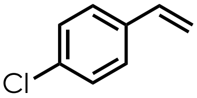
1-(*tert*-butyl)-4-vinylbenzene

The alkene was purchased commercially and used without additional purification.



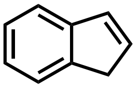
1-methyl-4-vinylbenzene

The alkene was purchased commercially and used without additional purification.



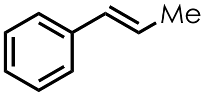
1-chloro-4-vinylbenzene

The alkene was purchased commercially and used without additional purification.



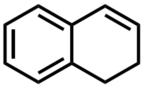
1*H*-indene

The alkene was purchased commercially and used without additional purification.



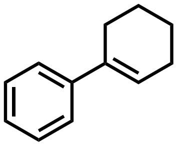
(*E*)-prop-1-en-1-ylbenzene

The alkene was purchased commercially and used without additional purification.



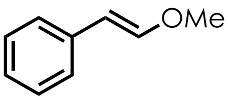
1,2-dihydronaphthalene

The alkene was purchased commercially and used without additional purification.



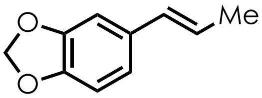
2,3,4,5-tetrahydro-1,1'-biphenyl

The alkene was purchased commercially and used without additional purification.



(*E*)-(2-methoxyvinyl)benzene

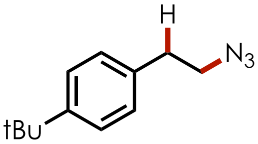
The alkene was purchased commercially and used without additional purification.



(*E*)-5-(prop-1-en-1-yl)benzo[*d*][1,3]dioxole

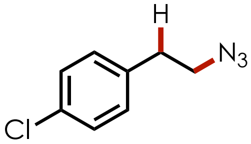
The alkene was purchased commercially and used without additional purification.

Hydroazidation Product Characterization:



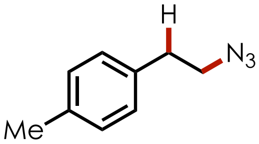
1-(2-azidoethyl)-4-(tert-butyl)benzene (1)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure. HMDSO was added as an internal standard and the resulting mixture was dissolved in deuterated chloroform and analyzed by NMR. Integration relative to the internal standard showed the product was formed in 43% yield (n=2).



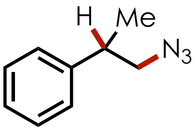
1-(2-azidoethyl)-4-chlorobenzene (2)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure. HMDSO was added as an internal standard and the resulting mixture was dissolved in deuterated chloroform and analyzed by NMR. Spectral data matched those previously reported. (22% yield, n =2).[17]



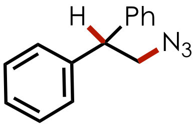
1-(2-azidoethyl)-4-methylbenzene (3)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure. HMDSO was added as an internal standard and the resulting mixture was dissolved in deuterated chloroform and analyzed by NMR. Spectral data matched those previously reported. (22% yield, n =2).[17]



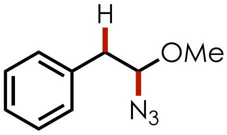
(1-azidopropan-2-yl)benzene (4)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure. HMDSO was added as an internal standard and the resulting mixture was dissolved in deuterated chloroform and analyzed by NMR. Spectral data matched those previously reported. (49% yield, n =2).[18]



(2-azidoethane-1,1-diyl)dibenzene (5)

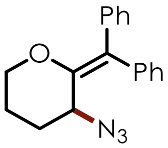
Following irradiation, the crude reaction mixture was concentrated under reduced pressure. HMDSO was added as an internal standard and the resulting mixture was dissolved in deuterated chloroform and analyzed by NMR. Spectral data matched those previously reported (ELI LILLY AND COMPANY - WO2005/821, 2005, A1), (24% yield, n =2).



(2-azido-2-methoxyethyl)benzene (6)

The desired product was isolated as a pale yellow oil following purification by flash column chromatography (100% hexane → 5% EtOAc/hexane gradient).

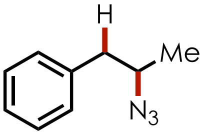
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 6.98 (m, 5H), 4.49 (t, *J* = 6.0 Hz, 1H), 3.47 (s, 3H), 3.07 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.99 (dd, *J* = 14.0, 5.8 Hz, 1H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.79, 129.65, 128.65, 127.11, 94.67, 56.96, 41.25.
MS (EI): calculated: 177.090, found: 177.00 (M^+)



3-azido-2-(diphenylmethylene)tetrahydro-2H-pyran (7)

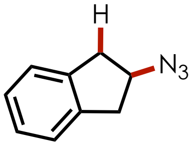
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.32 – 7.25 (m, 5H), 7.25 – 7.17 (m, 3H), 4.31 (t, *J* = 3.2 Hz, 1H), 4.27 (ddt, *J* = 11.0, 4.5, 1.9 Hz, 1H), 3.80 (ddd, *J* = 12.4, 11.0, 2.8 Hz, 1H), 2.29 – 2.17 (m, 1H), 1.97 – 1.90 (m, 1H), 1.88 – 1.80 (m, 1H), 1.63 – 1.51 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.89, 139.35, 138.66, 130.67, 129.86, 128.61, 127.91, 127.49, 127.37, 126.99, 70.09, 56.02, 28.66, 20.37.
HRMS (APCI, positive mode): calculated: 264.1310, found: 264.1382 (M+H, -N$_2$)



(2-azidopropyl)benzene (9)

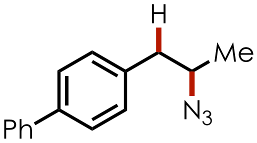
Following irradiation, the crude reaction mixture was concentrated under reduced pressure to yield a yellow oil. HMDSO was added as an internal standard and the resulting mixture was dissolved in CDCl$_3$ and analyzed by ^{1}H NMR to determine yield (98% yield, n=2). Spectral data matched those previously reported.[19]



2-azido-2,3-dihydro-1H-indene (10)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a pale yellow oil following column chromatography (100% hexane -> 1% EtOAc/hex, 52% yield, n=3). Spectral data matched those previously reported.[20]

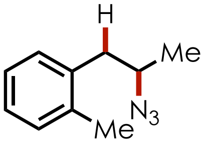
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 5.3, 3.5 Hz, 2H), 7.26 – 7.17 (m, 2H), 4.40 (dt, *J* = 11.1, 6.7, 4.4 Hz, 1H), 3.28 (dd, *J* = 16.2, 6.7 Hz, 2H), 3.06 (dd, *J* = 16.2, 4.4 Hz, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.23, 127.10, 124.77, 61.86, 39.09.
MS (EI): calculated: 159.08, found: 159.10



4-(2-azidopropyl)-1,1'-biphenyl (11)

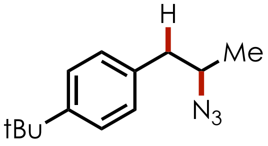
Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a pale yellow oil following column chromatography (100% hexane -> 1% EtOAc/hex, 97% yield, n=2). Spectral data matches those previously reported.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (dd, *J* = 26.1, 7.7 Hz, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 3.77 (h, *J* = 6.6 Hz, 1H), 2.92 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.82 (dd, *J* **= 13.7, 6.4 Hz, 1H), 1.35 (d, *J* = 6.5 Hz, 3H).**
^{13}C NMR (151 MHz, Chloroform-*d*) δ 140.90, 139.73, 136.91, 129.79, 128.84, 127.29, 127.10, 59.04, 42.24, 19.22.
HRMS (APCI, positive mode): calculated 210.1277, found: 210.1278 (M+H, -N_2)



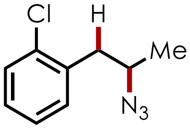
1-(2-azidopropyl)-2-methylbenzene (12)

The desired product was isolated as a clear oil following purification by flash chromatography (100% hexane, 76% yield, n=2).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 – 7.12 (app s., 4H), 3.72 (m, 1H), 2.92 (dd, *J* = 13.7, 7.4 Hz, 1H), 2.77 (dd, *J* = 13.7, 6.6 Hz, 1H), 2.38 (s, 3Hu), 1.33 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.40, 136.19, 130.53, 130.20, 126.95, 126.11, 58.36, 39.87, 19.65, 19.42.
HRMS (APCI, positive mode): calculated: 193.1447, found: 193.1423 (M+NH_4)



1-(2-azidopropyl)-4-(tert-butyl)benzene (13)

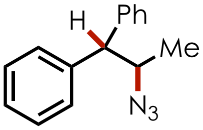
Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a pale yellow oil following column chromatography (100% hexane -> 1% EtOAc/hex, 51% yield, n=2). Spectral data matched those previously reported.[19]



1-(2-azidopropyl)-2-chlorobenzene (14)

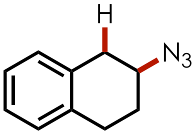
Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a pale yellow oil following column chromatography (100% hexane -> 3% EtOAc/hex, 64% yield, n=2).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.28 (dd, *J* = 7.1, 2.3 Hz, 1H), 7.25 – 7.19 (m, 2H), 3.85 (h, *J* = 6.7 Hz, 1H), 3.00 – 2.84 (m, 2H), 1.33 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 135.70, 134.32, 131.85, 129.74, 128.42, 126.95, 57.57, 40.40, 19.43.
MS (EI): calculated: 195.056, found: 195.05 (M^+)



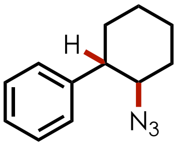
(2-azidopropane-1,1-diyl)dibenzene (15)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a clear oil following column chromatography (100% hexane -> 1% EtOAc/hex, 66% yield, n=2). Spectral data matched those previously reported.[21]



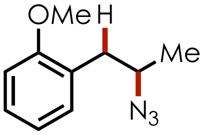
2-azido-1,2,3,4-tetrahydronaphthalene (16)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a clear oil following column chromatography (100% hexane -> 1% EtOAc/hex, 81% yield, n=2). Spectral data matched those previously reported.[22]



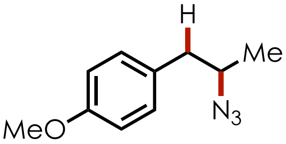
(2-azidocyclohexyl)benzene (17)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a clear oil following column chromatography (100% hexane -> 1% EtOAc/hex, 81% yield, n=2) as a single diastereomer. Spectral data matched those previously reported.[23]



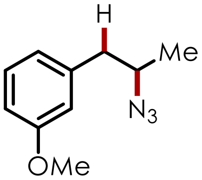
1-(2-azidopropyl)-2-methoxybenzene (18)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.24 (td, *J* = 7.8, 1.7 Hz, 1H), 7.14 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.91 (td, *J* = 7.4, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.0 Hz, 1H), 3.83 (s, 3H), 3.81 – 3.72 (m, 1H), 2.85 (dd, *J* = 13.3, 7.3 Hz, 1H), 2.76 (dd, *J* = 13.4, 6.6 Hz, 1H), 1.24 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.66, 131.32, 128.23, 126.35, 120.55, 110.38, 57.73, 55.35, 37.51, 19.48
MS (EI): calculated: 191.106, found: 191.10 (M^{+})



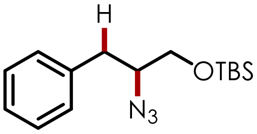
1-(2-azidopropyl)-4-methoxybenzene (19)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.64 (h, *J* = 6.6 Hz, 1H), 2.77 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.67 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.25 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.52, 130.39, 129.92, 114.01, 59.36, 55.39, 41.80, 19.18
MS (EI): calculated: 191.106, found: 191.10 (M$^+$)



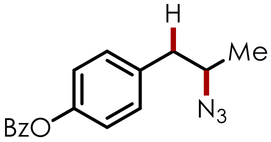
1-(2-azidopropyl)-3-methoxybenzene (20)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 (t, *J* = 7.9 Hz, 1H), 6.89 – 6.68 (m, 3H), 3.81 (s, 3H), 3.68 (p, *J* = 6.6 Hz, 1H), 2.82 (dd, *J* = 13.6, 7.3 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.5 Hz, 1H), 1.27 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.77, 139.47, 129.62, 121.76, 115.22, 112.04, 59.07, 55.32, 42.72, 19.31
MS (EI): calculated: 191.106, found: 191.05 (M$^+$)



(2-azido-3-phenylpropoxy)(tert-butyl)dimethylsilane (21)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure. HMDSO was added as an internal standard and the sample was dissolved in deuterated chloroform and analyzed by NMR. Integration relative to the internal standard showed that the product was formed in 39% yield (n = 2).



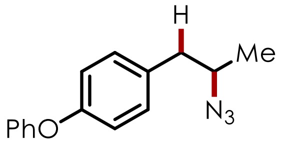
4-(2-azidopropyl)phenyl benzoate (22)

Following irradiation, the crude reaction mixture was concentrated under reduced pressure and dry loaded onto silica gel. The desired product was isolated as a clear oil following purification by column chromatography (5 % EtOAc/hexane to 30 % EtOAc/hex, 62% yield, n =2).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.68 – 7.60 (m, 1H), 7.58 – 7.44 (m, 2H), 7.32 – 7.24 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.71 (h, *J* = 6.6 Hz, 1H), 2.86 (dd, *J* = 13.7, 7.3 Hz, 1H), 2.75 (dd, *J* = 13.7, 6.4 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.19, 149.76, 135.39, 133.60, 130.33, 130.17, 129.56, 128.58, 121.72, 58.96, 41.97, 19.12.

HRMS (APCI, positive mode): calculated: 254.1175, found: 254.1175 (M+H, -N_2)



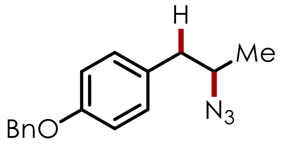
1-(2-azidopropyl)-4-phenoxybenzene (23)

The desired product was isolated as a clear oil following purification by column chromatography (100% hexane -> 1 % EtOAc/Hexane, 91% yield, n=2)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.06 (m, 1H), 7.01 (dd, *J* = 8.7, 1.1 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.77 – 3.47 (m, 1H), 2.80 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.72 (dd, *J* = 13.8, 6.3 Hz, 1H), 1.28 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.31, 156.03, 132.62, 130.57, 129.72, 123.18, 118.96, 118.78, 59.14, 41.87, 19.16.

HRMS (APCI, positive mode): calculated: 226.1226, found: 226.1227 (M+H, -N_2)



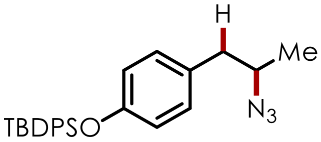
1-(2-azidopropyl)-4-(benzyloxy)benzene (24)

The desired product was isolated as clear oil and purified using column chromatography (1 % EtOAc/hexane, Yield: 91 %, n =2).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 6.9 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.05 (s, 2H), 3.64 (h, *J* = 6.7 Hz, 1H), 2.77 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.67 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.25 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-d) δ 157.69, 137.07, 130.29, 130.12, 128.59, 127.95, 127.49, 114.87, 70.06, 59.20, 41.71, 19.05.

HRMS (APCI, positive mode): calculated: 240.1383, found: 240.1383 (M+H, -N_2)



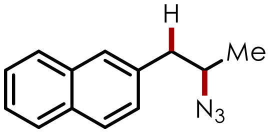
(4-(2-azidopropyl)phenoxy)(tert-butyl)diphenylsilane (25)

The desired product was isolated as clear oil following purification by column chromatography (100 % pentane to 100 % hexane, 76% yield, n=2)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 6.8, 1.3 Hz, 4H), 7.47 – 7.38 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 3.57 (h, *J* = 6.6 Hz, 1H), 2.69 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.58 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.09 (s, 9H).

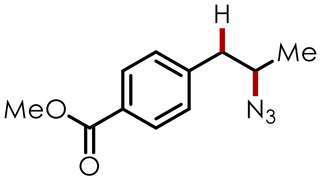
^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.40, 135.53, 132.99, 130.17, 130.01, 129.84, 127.73, 119.69, 59.21, 41.80, 26.53, 19.47, 19.04

HRMS (APCI, positive mode): calculated: 388.2018, found: 388.2090 (M+H, -N_2)



2-(2-azidopropyl)naphthalene (26)

The desired product was isolated as a clear oil following purification by column chromatography (100% hexane -> 2% EtOAc/hexane, 67% yield, n=2). Spectral data matched those previously reported.[24]



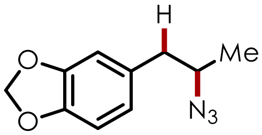
methyl 4-(2-azidopropyl)benzoate (27)

The desired product was isolated as clear oil and purified using column chromatography (100 % hexane, 70% yield, n=2)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.91 (s, 3H), 3.72 (h, *J* = 6.5 Hz, 1H), 2.87 (dd, *J* = 13.7, 7.5 Hz, 1H), 2.79 (dd, *J* = 13.7, 6.2 Hz, 1H), 1.28 (d, *J* = 6.5 Hz, 3H).

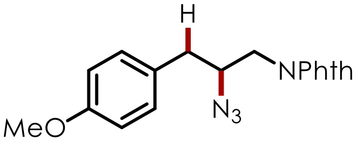
^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.94, 143.11, 129.82, 129.35, 128.74, 58.65, 52.08, 42.54, 19.21.

HRMS (APCI, positive mode): calculated: 192.1019, found: 192.1019(M+H, -N_2)



5-(2-azidopropyl)benzo[d][1,3]dioxole (28)

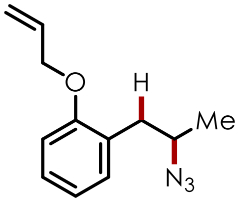
The desired product was isolated as a pale yellow oil following purification by column chromatography (100% hexane -> 3%EtOAc/hex, 92% yield, n =2). Spectral data matched those previously reported.[25]



2-(2-azido-3-(4-methoxyphenyl)propyl)isoindoline-1,3-dione (29)

The desired product was isolated as a clear oil following purification by flash chromatography (100% hexane → 1% EtOAc/hexane gradient).

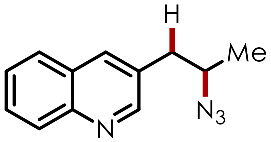
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 3.99 (tt, *J* = 8.6, 5.1 Hz, 1H), 3.82 (dd, *J* = 14.0, 8.9 Hz, 1H), 3.75 (s, 2H), 3.70 (dd, *J* = 14.0, 4.6 Hz, 1H), 2.88 (dd, *J* = 14.2, 5.5 Hz, 1H), 2.81 (dd, *J* = 14.2, 8.4 Hz, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.08, 158.60, 134.17, 131.78, 130.16, 128.44, 123.44, 114.08, 61.52, 55.19, 41.20, 38.01.
HRMS (APCI, positive mode): calculated: 337.1295, found: 337.1295 (M+H)



1-(allyloxy)-2-(2-azidopropyl)benzene (30)

The desired product was isolated as a clear oil following purification by flash chromatography (100% hexane → 1% EtOAc/hexane gradient).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 1H), 7.21 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.96 (td, *J* = 7.4, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.11 (ddd, *J* = 17.3, 10.3, 5.0 Hz, 1H), 5.46 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.33 (dd, *J* = 10.3, 1.5 Hz, 1H), 4.68 – 4.46 (m, 2H), 3.85 (h, *J* = 6.7 Hz, 1H), 2.95 (dd, *J* = 13.3, 7.3 Hz, 1H), 2.85 (dd, *J* = 13.3, 6.7 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.62, 133.42, 131.39, 128.12, 126.59, 120.73, 117.08, 111.63, 68.67, 57.75, 37.57, 19.42.
HRMS (APCI, positive mode): calculated: 190.1226, found: 190.1226 (M+H, -N_2)

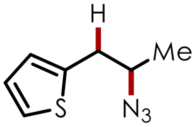


3-(2-azidopropyl)quinoline (31)

The desired product was isolated as a clear oil following purification by column chromatography (3% EtOAc/hexane to 30% EtOAc/hexane)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.79 (d, *J* = 2.2 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.04 – 7.95 (m, 1H), 7.82 – 7.76 (m, 1H), 7.70 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 3.85 – 3.78 (m, 1H), 2.98 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.94 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.35 (d, *J* = 6.5 Hz, 3H).**^{13}C NMR (151 MHz, Chloroform-*d*)** δ 151.91, 147.16, 135.82, 130.48, 129.18, 127.93, 126.83, 58.57, 39.79, 19.15.

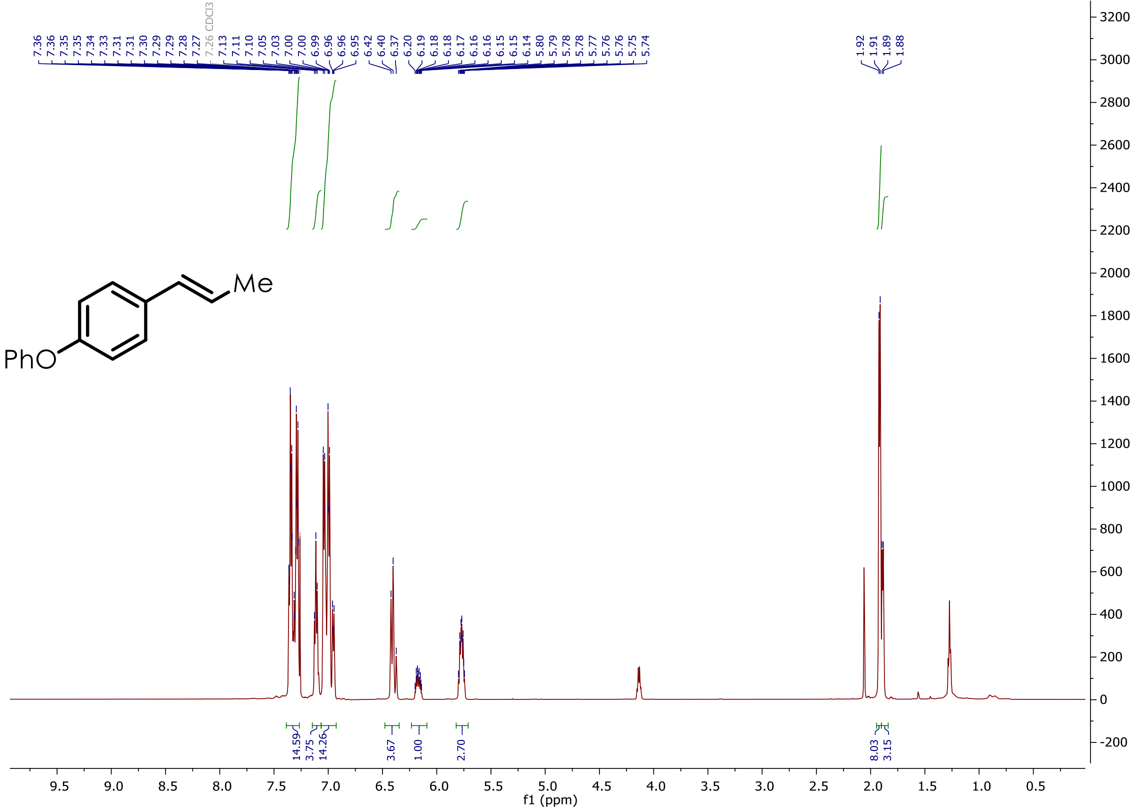
HRMS (APCI, positive mode): calculated: 185.1073, found: 185.1074 (M+H, -N_2)

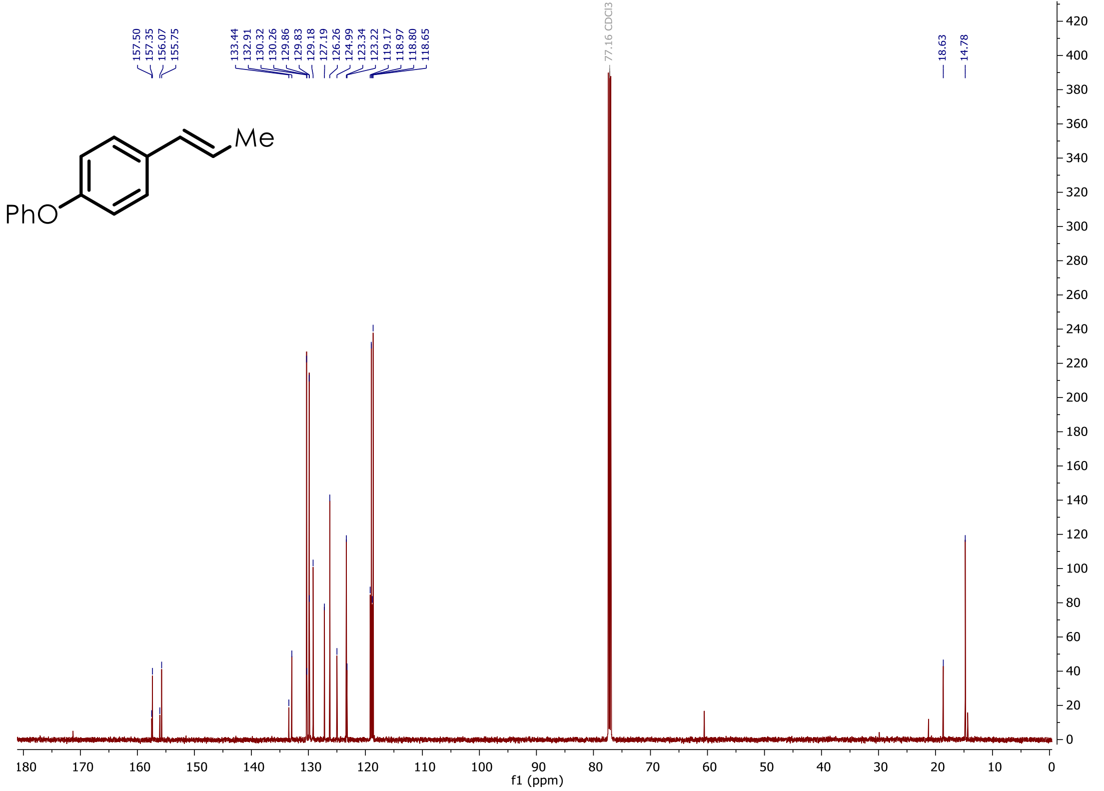


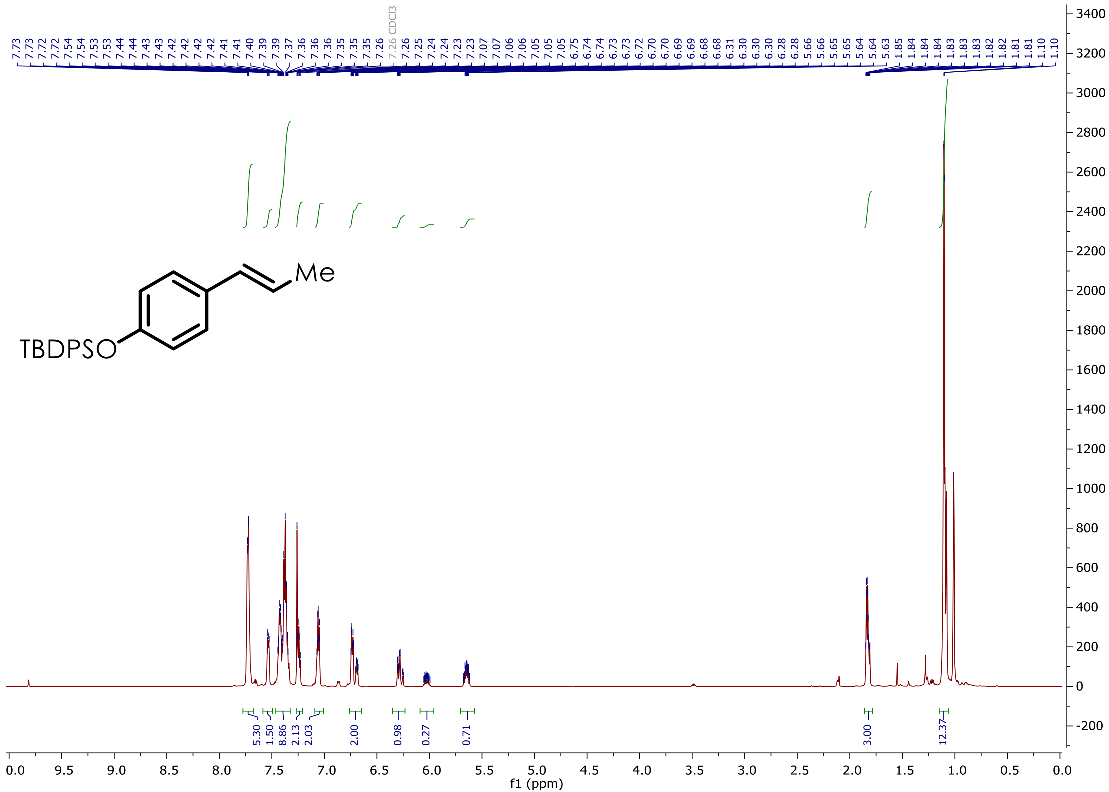
2-(2-azidopropyl)thiophene (32)

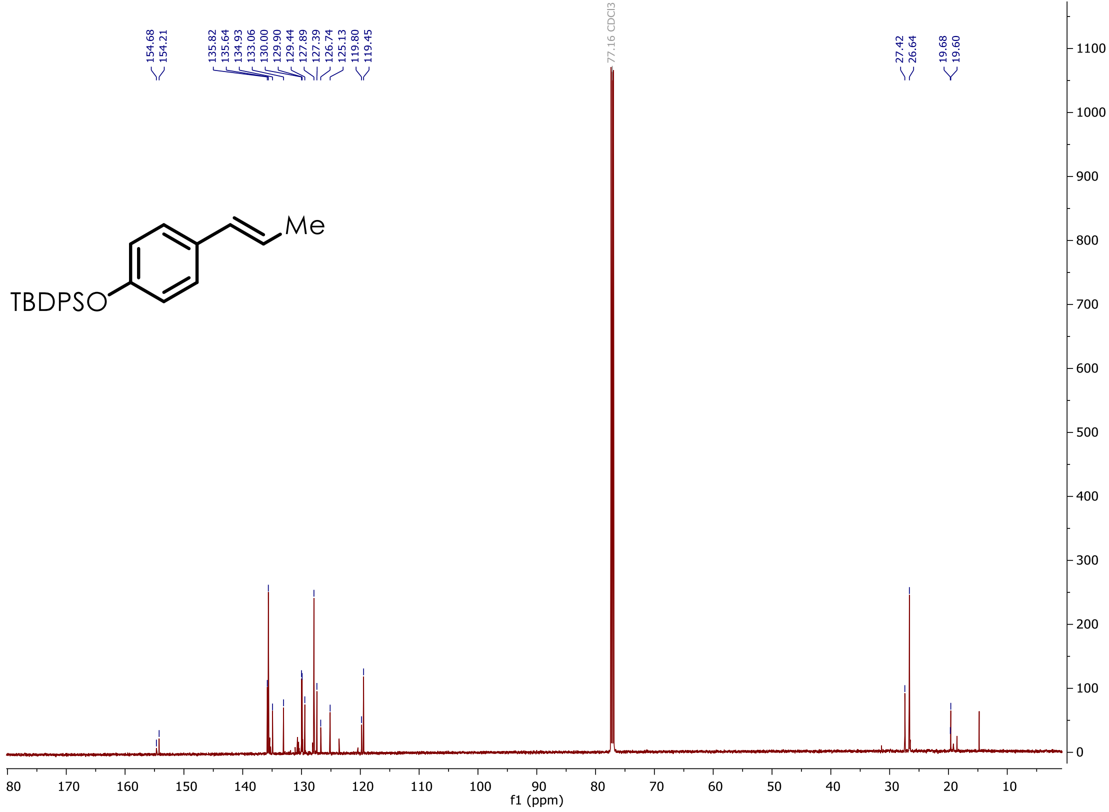
Following irradiation, the reaction mixture was concentrated under reduced pressure to yield a red oil. This oil was dissolved in deuterated chloroform and HMDSO was added as an internal standard. Yield was then determined *via* NMR spectroscopy (average (n=2) = 65% yield).
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.91 – 6.88 (m, 1H), 3.74 (h, *J* = 6.6 Hz, 1H), 3.03 (dd, *J* = 14.7, 7.1 Hz, 1H), 2.98 (dd, *J* = 14.7, 6.1 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.72, 126.99, 126.33, 124.48, 59.03, 36.67, 19.09.
MS (EI): calculated: 167.051, found: 167.05 (M^+)

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

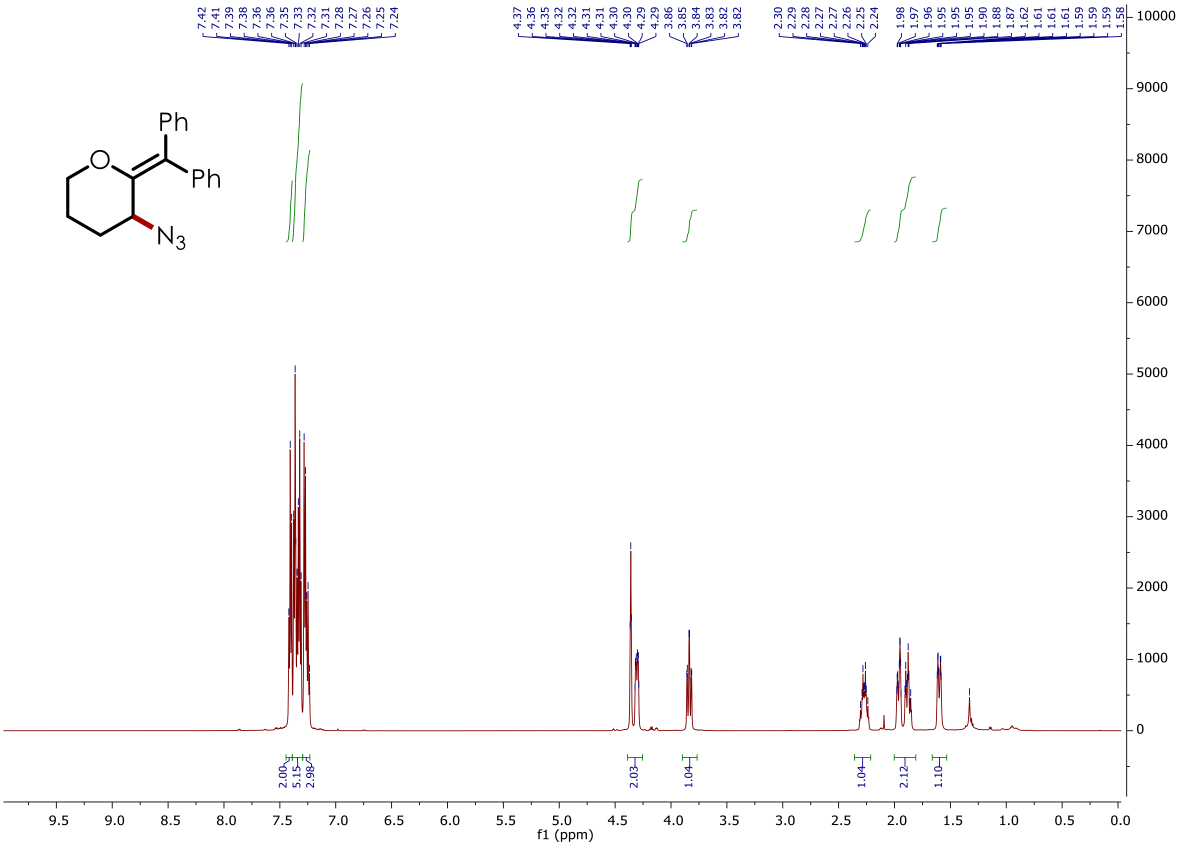


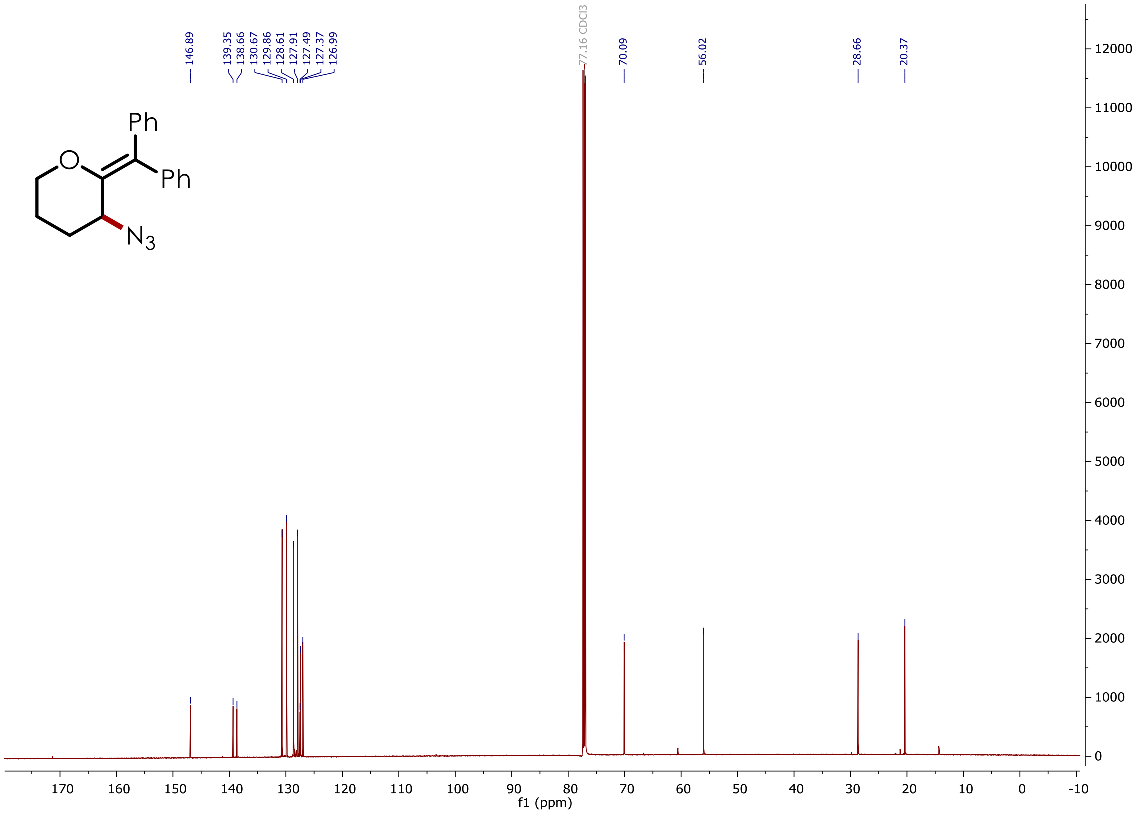



7.73 7.73 7.72 7.72 7.54 7.54 7.53 7.53 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.40 7.39 7.39 7.37 7.36 7.36 7.35 7.35 7.35 7.26 CDCl3 7.26 7.25 7.24 7.24 7.23 7.23 7.07 7.07 7.06 7.05 7.05 7.05 6.75 6.74 6.73 6.73 6.72 6.70 6.70 6.69 6.69 6.68 6.68 6.31 6.30 6.30 6.30 6.28 5.66 5.66 5.65 5.65 5.64 5.64 5.63 1.85 1.84 1.84 1.84 1.83 1.83 1.83 1.83 1.82 1.82 1.81 1.81 1.10 1.10
Me
TBDPSO
5.30
1.50
8.86
2.13
2.03
2.00
0.98
0.27
0.71
3.00
12.37
f1 (ppm)

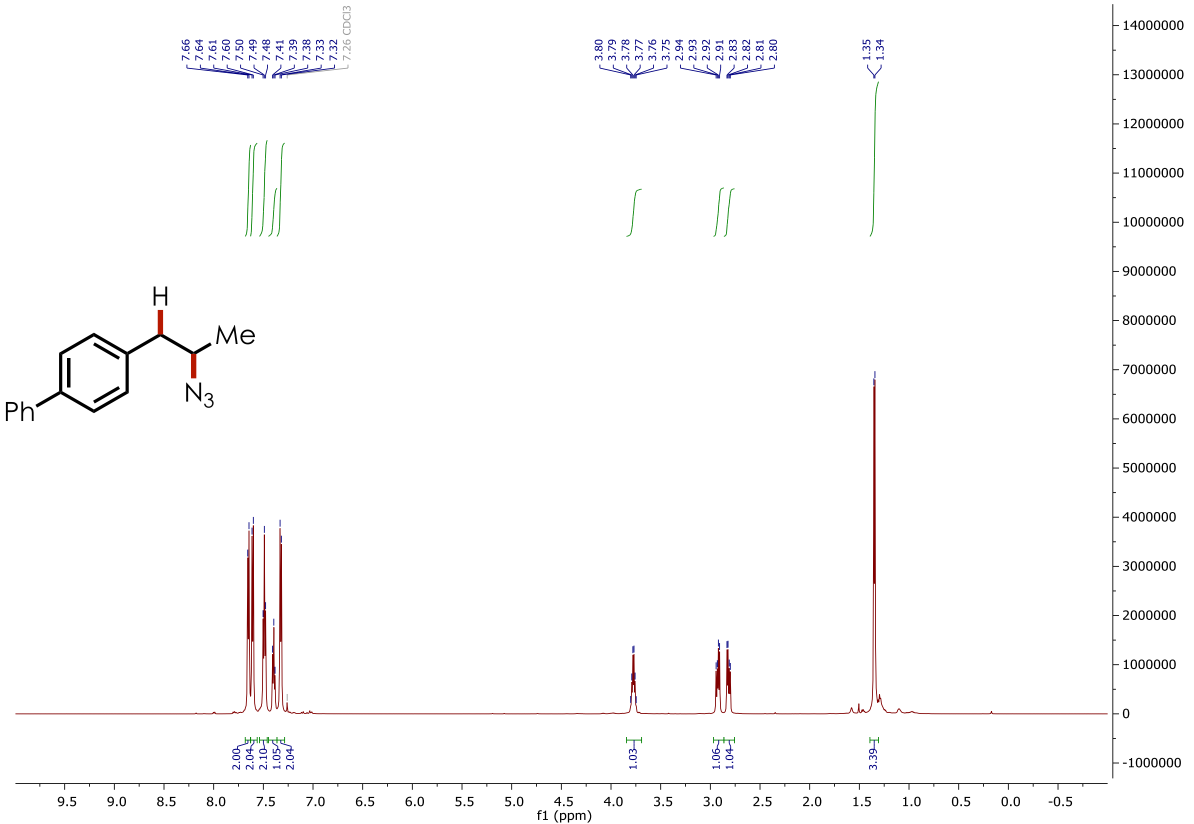

154.68 154.21
135.82 135.64 134.93 133.06 130.00 129.90 129.44 127.89 127.39 126.74 125.13 119.80 119.45
77.16 CDCl3
27.42 26.64
19.68 19.60
Me
TBDPSO
f1 (ppm)

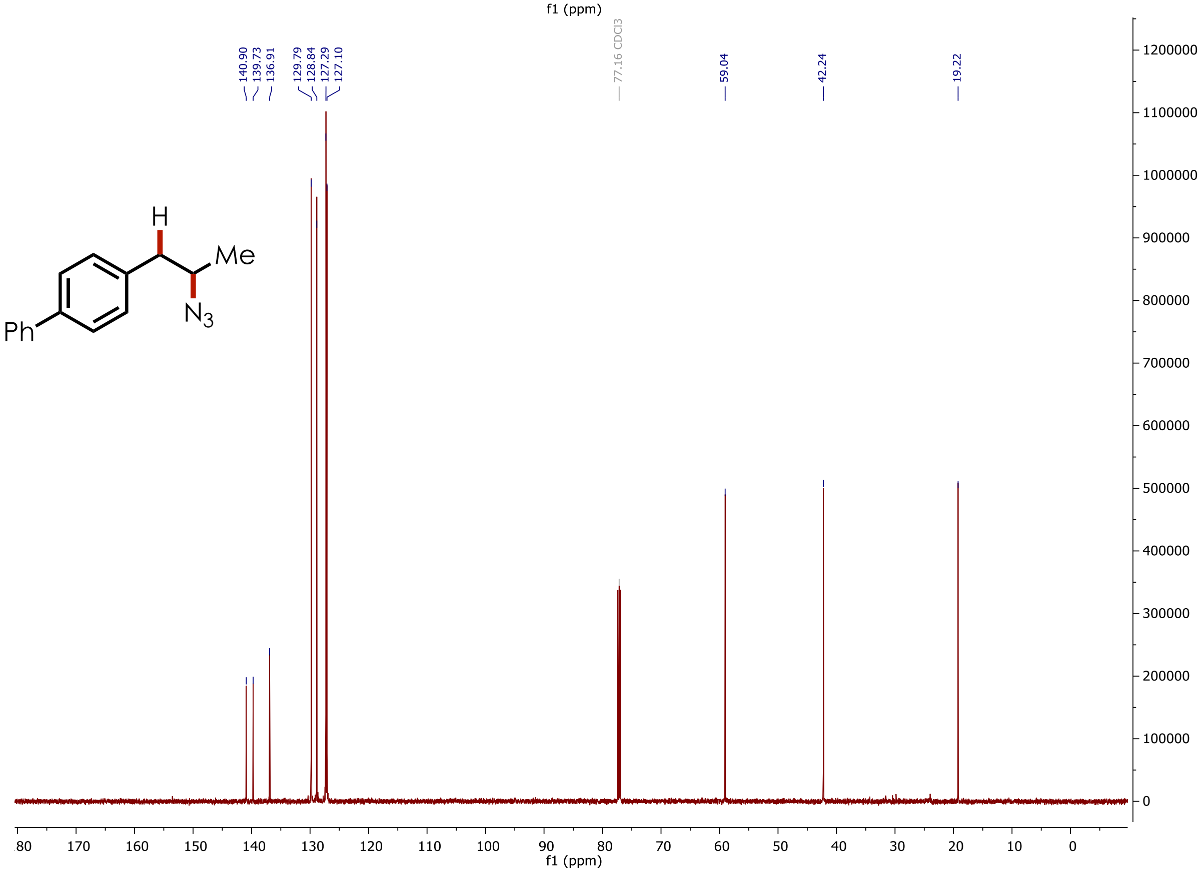
3-azido-2-(diphenylmethylene)tetrahydro-2H-pyran (7)



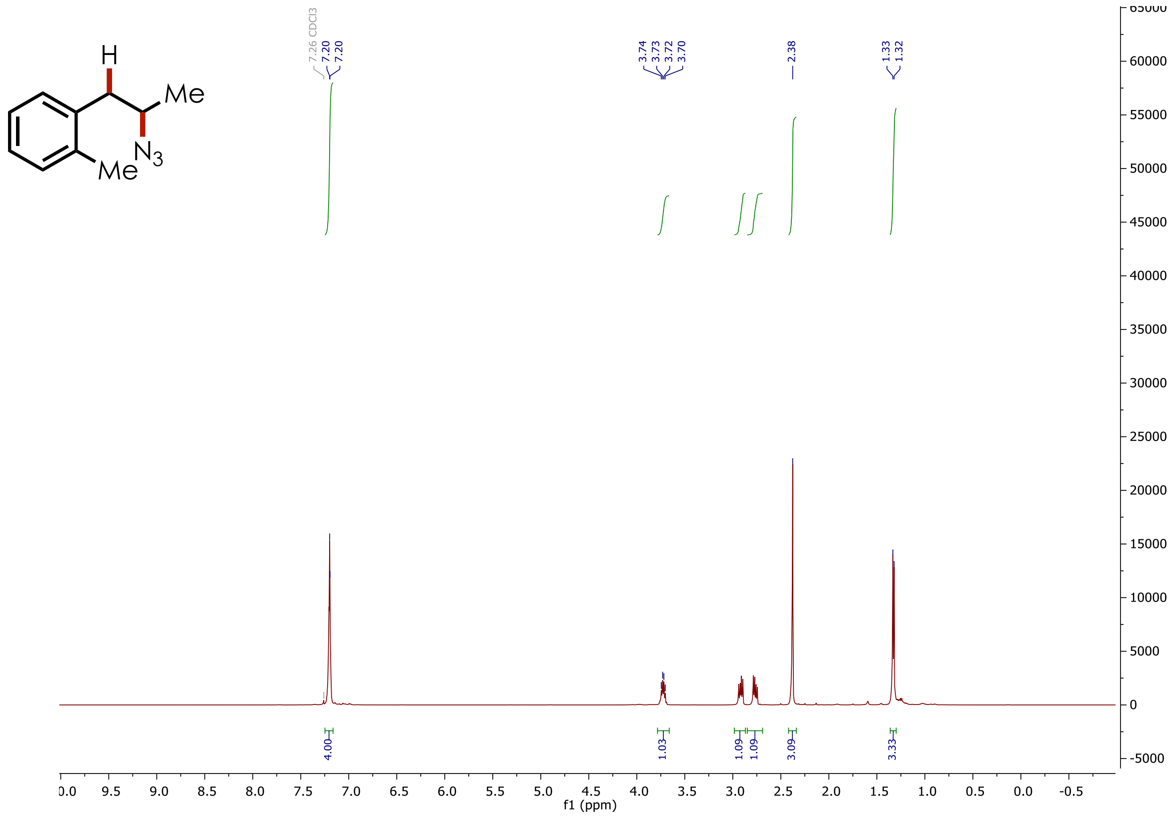


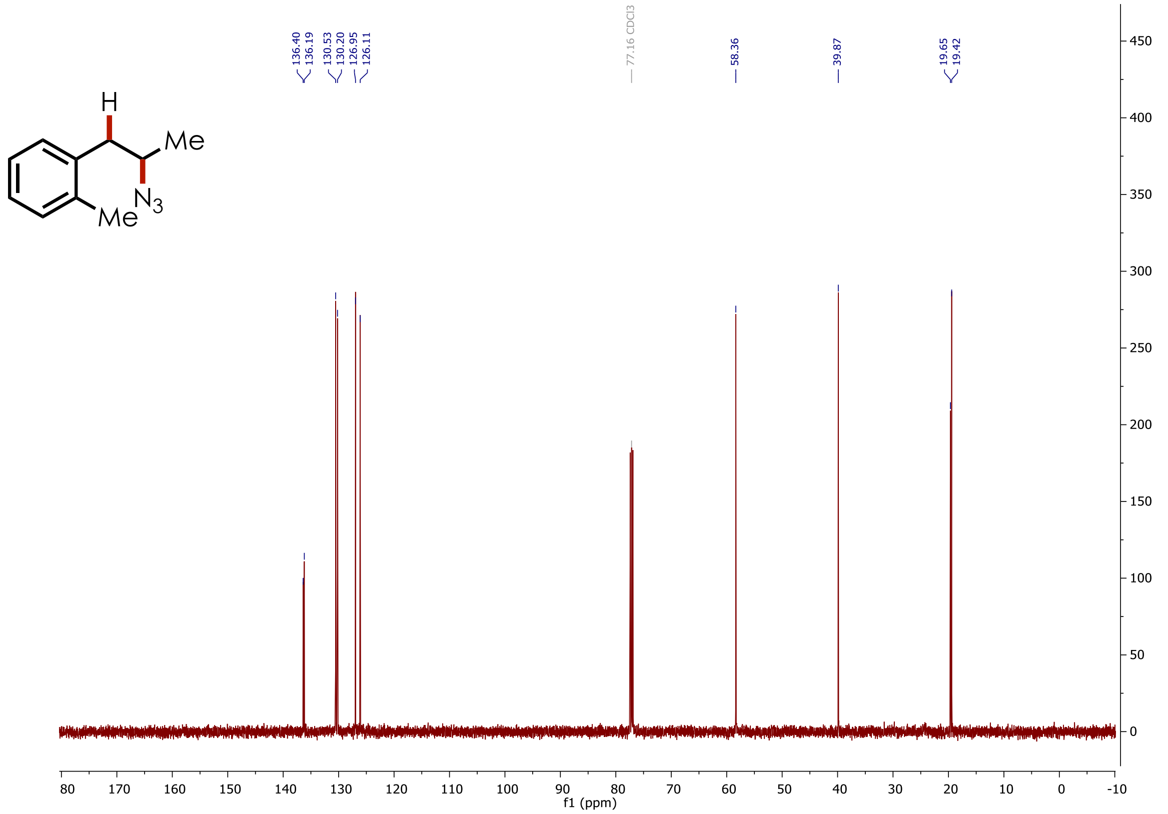
4-(2-azidopropyl)-1,1'-biphenyl (11)



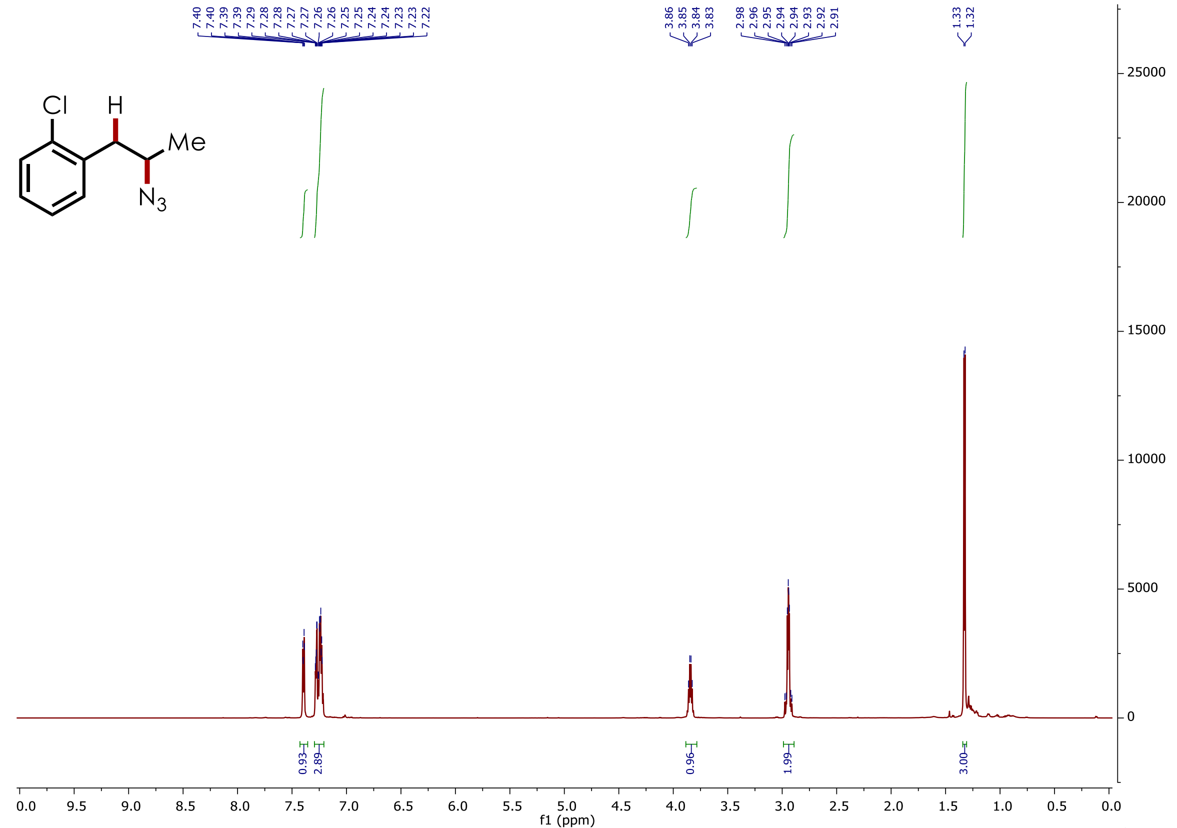


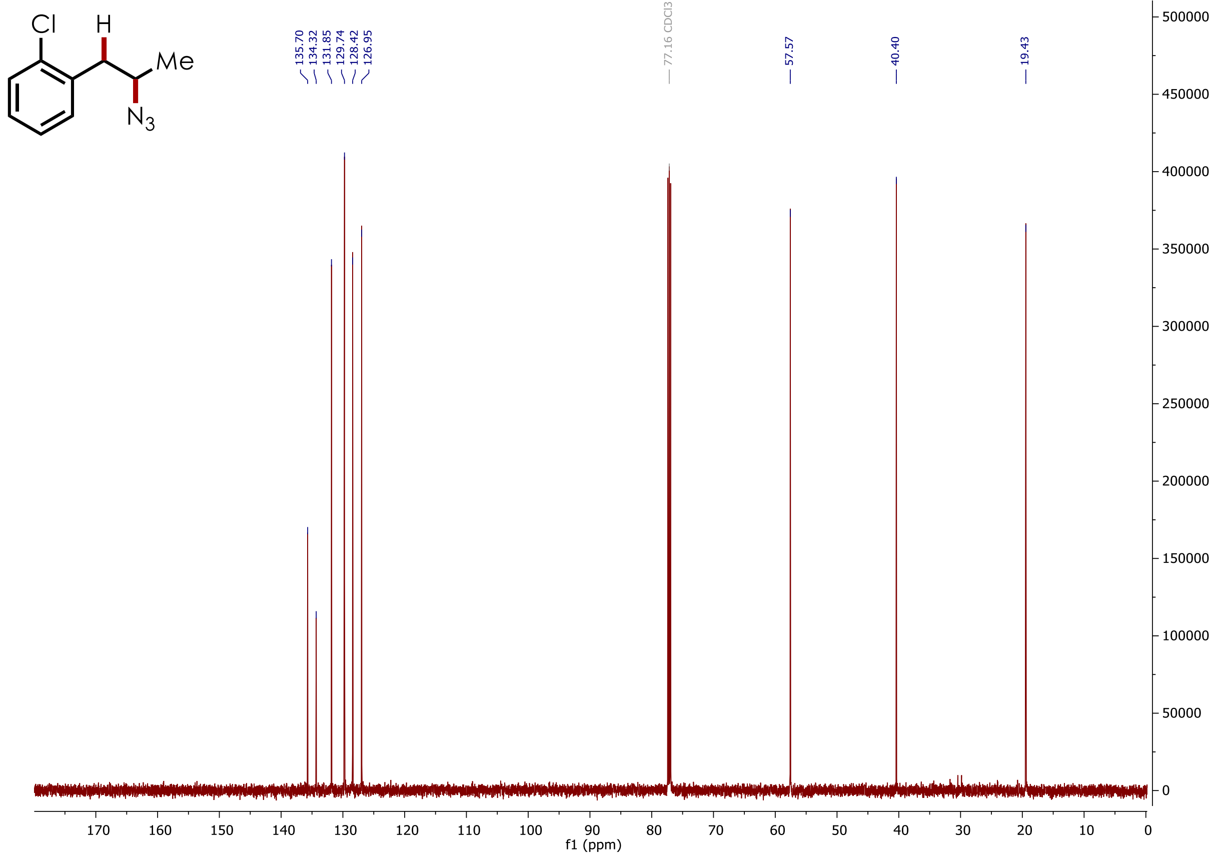
1-(2-azidopropyl)-2-methylbenzene (12)



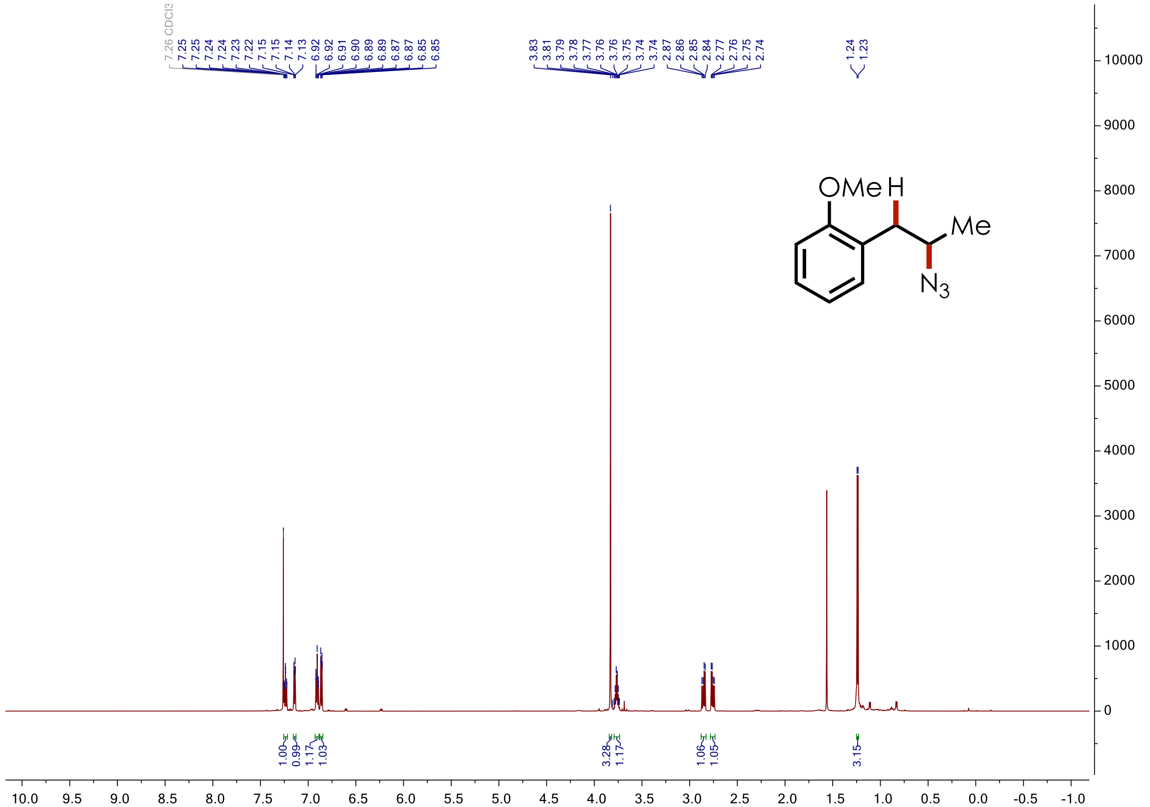


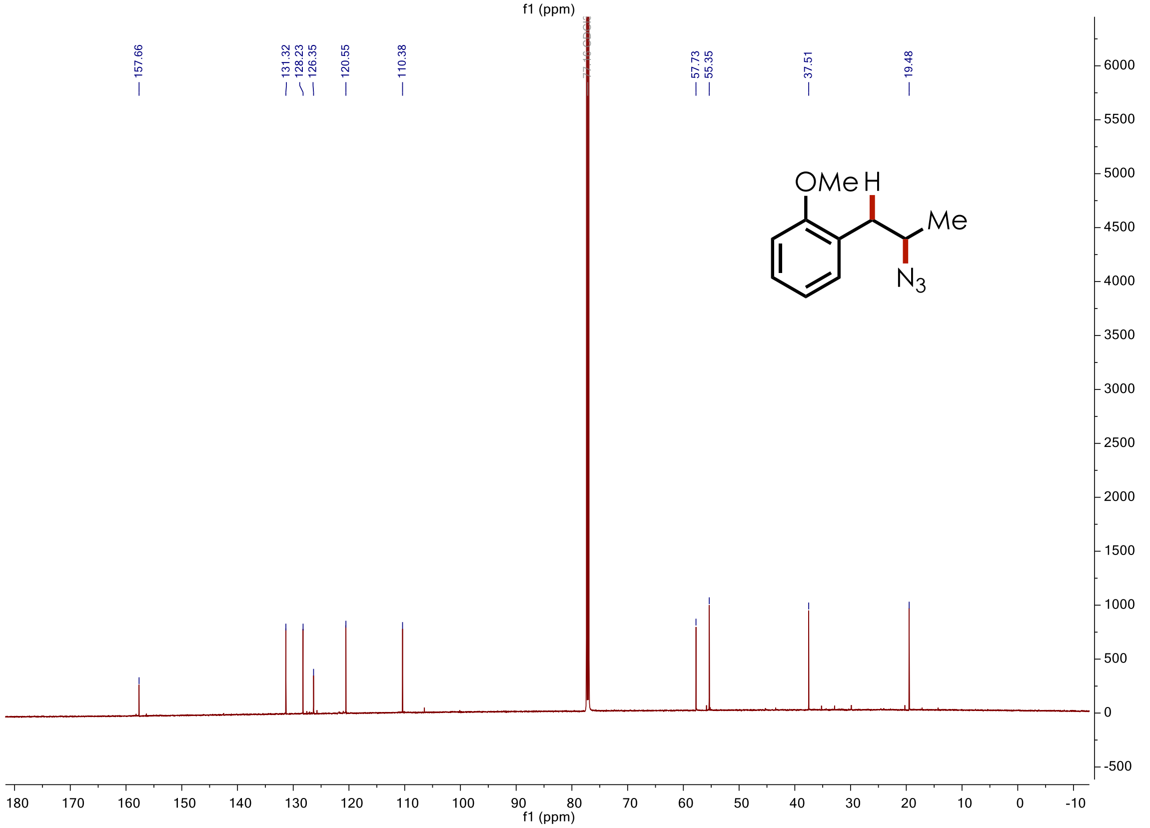
1-(2-azidopropyl)-2-chlorobenzene (14)



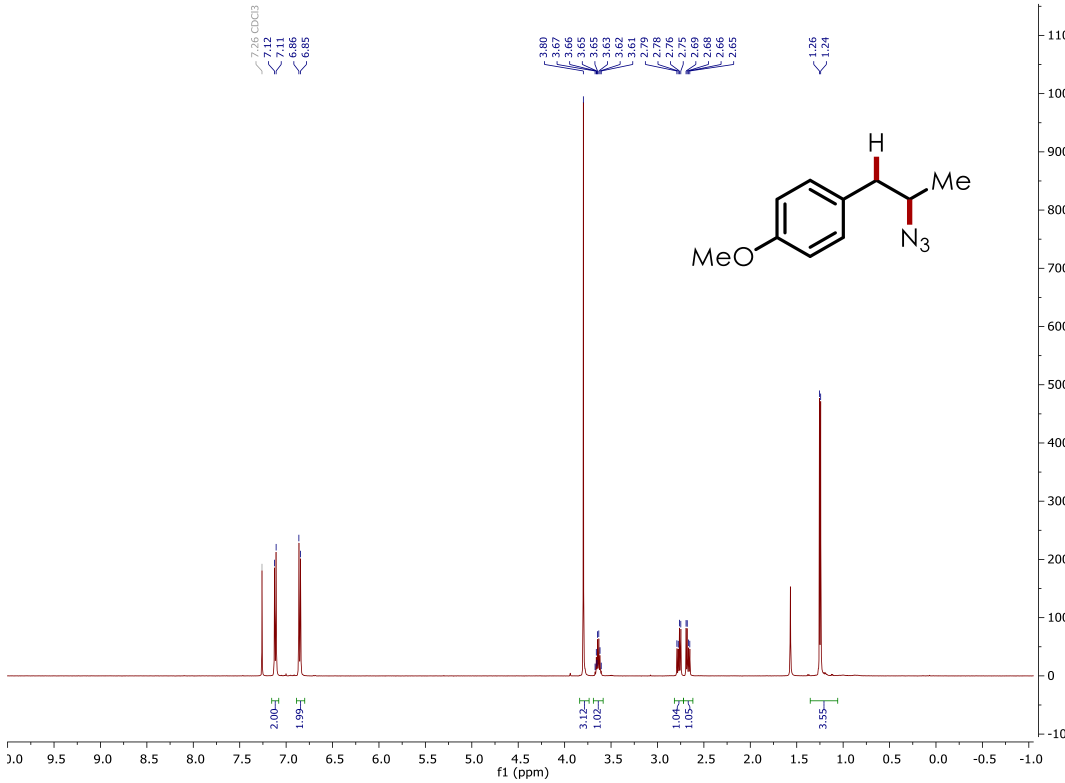


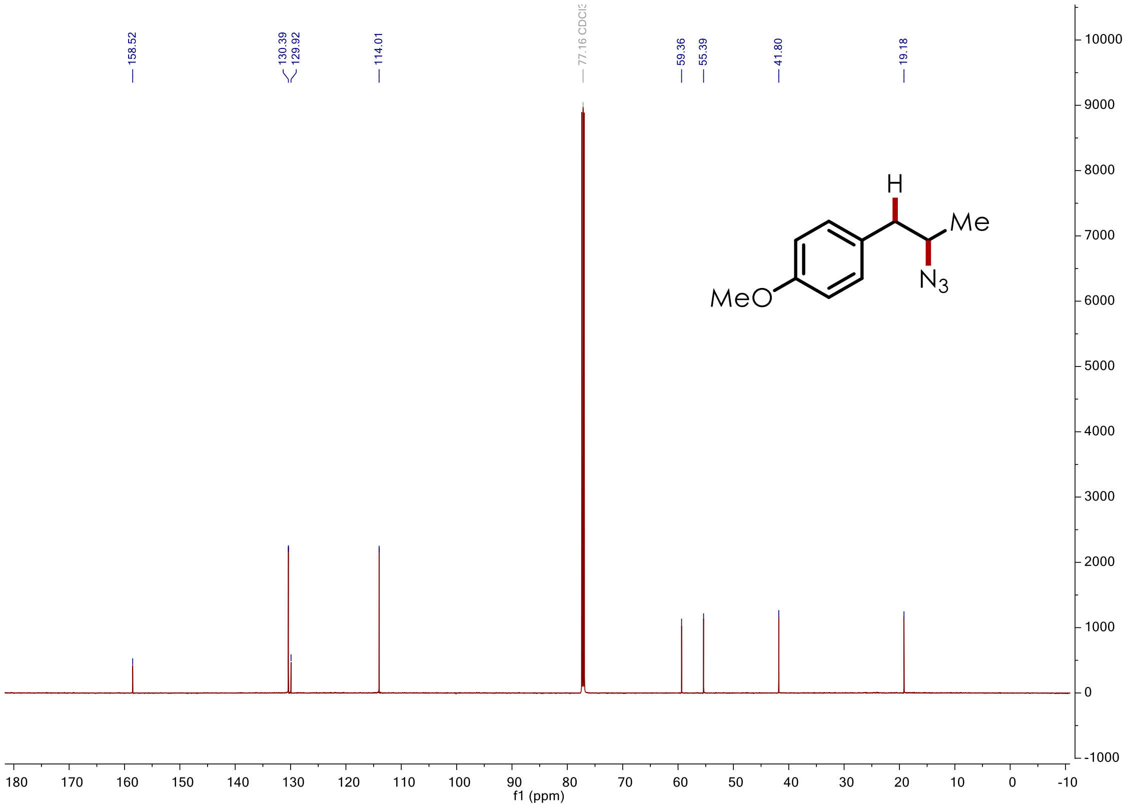
1-(2-azidopropyl)-2-methoxybenzene (18)



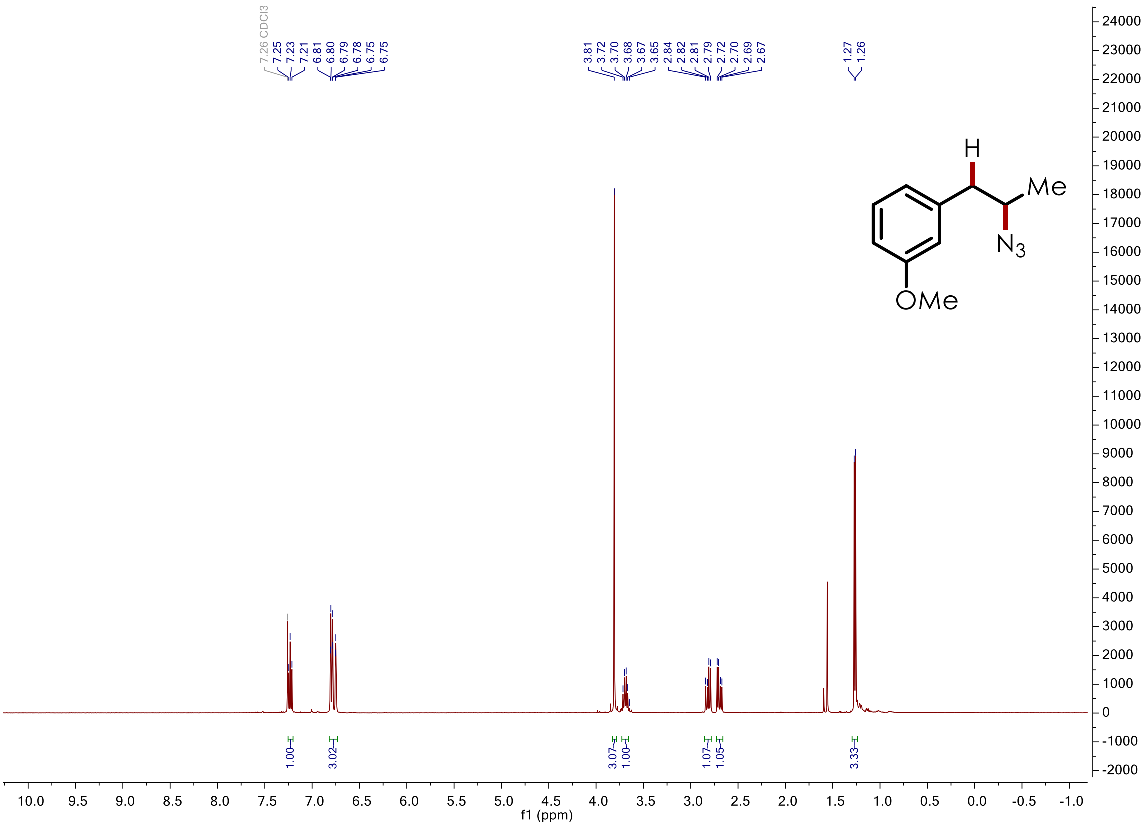


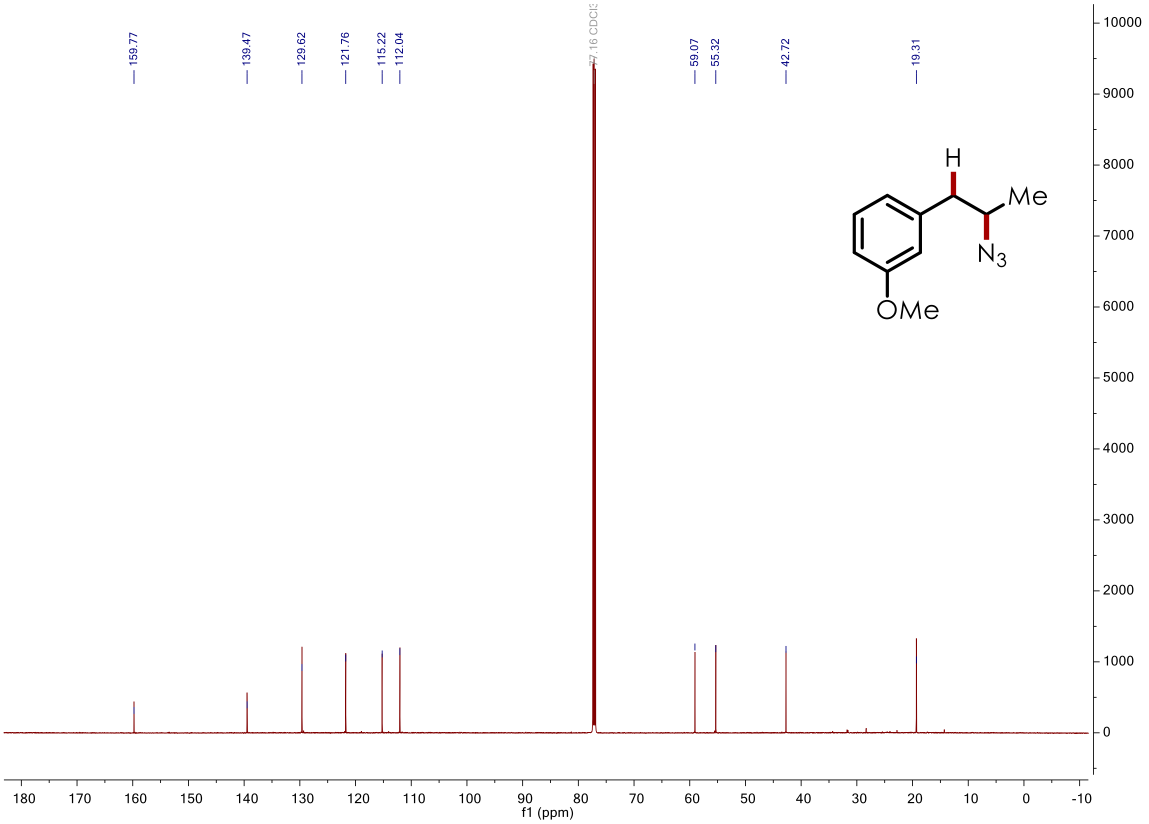
1-(2-azidopropyl)-4-methoxybenzene (19)



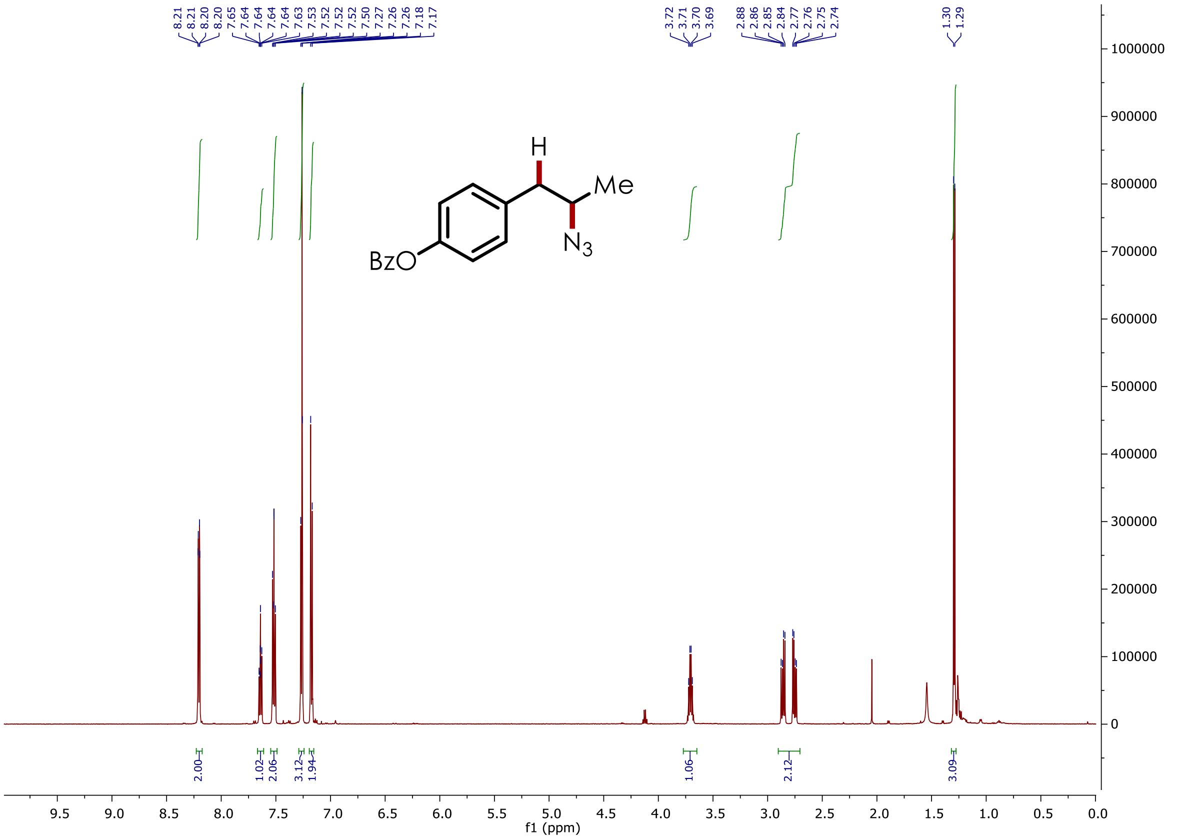


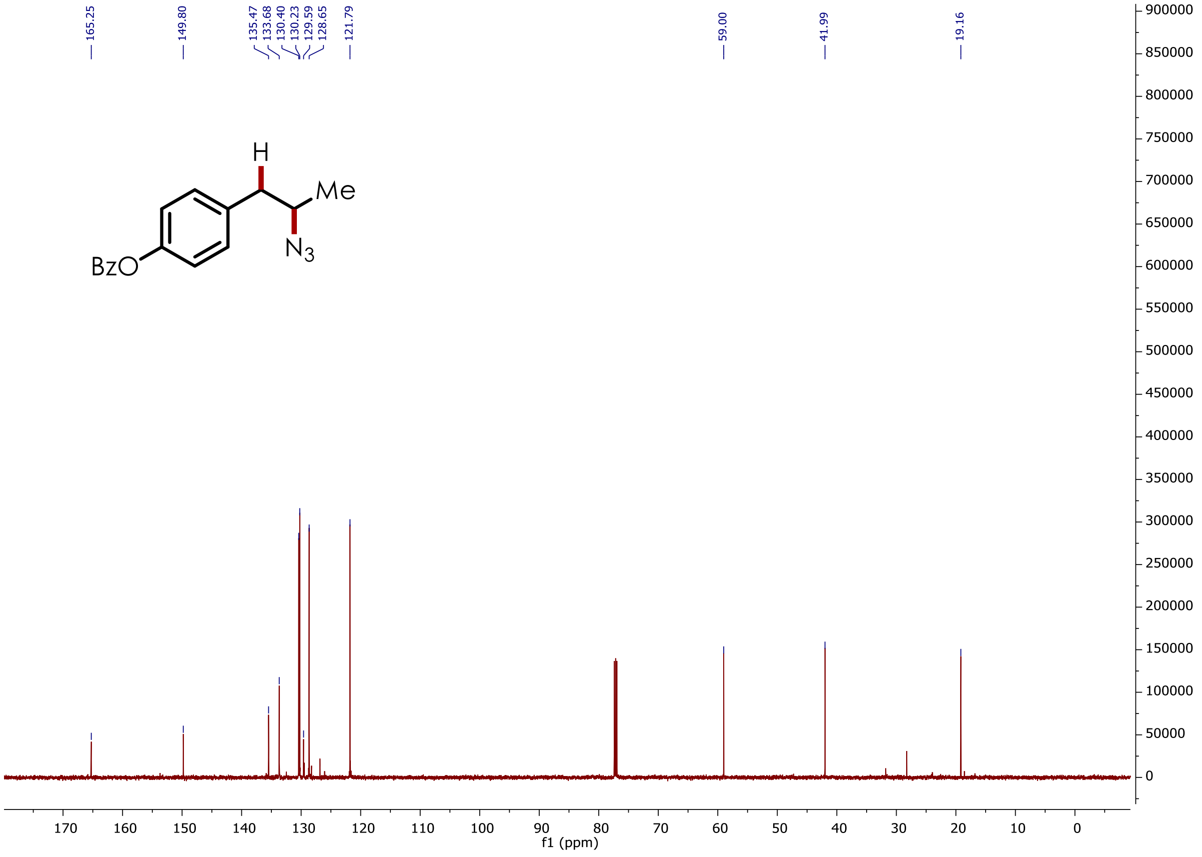
1-(2-azidopropyl)-3-methoxybenzene (20)



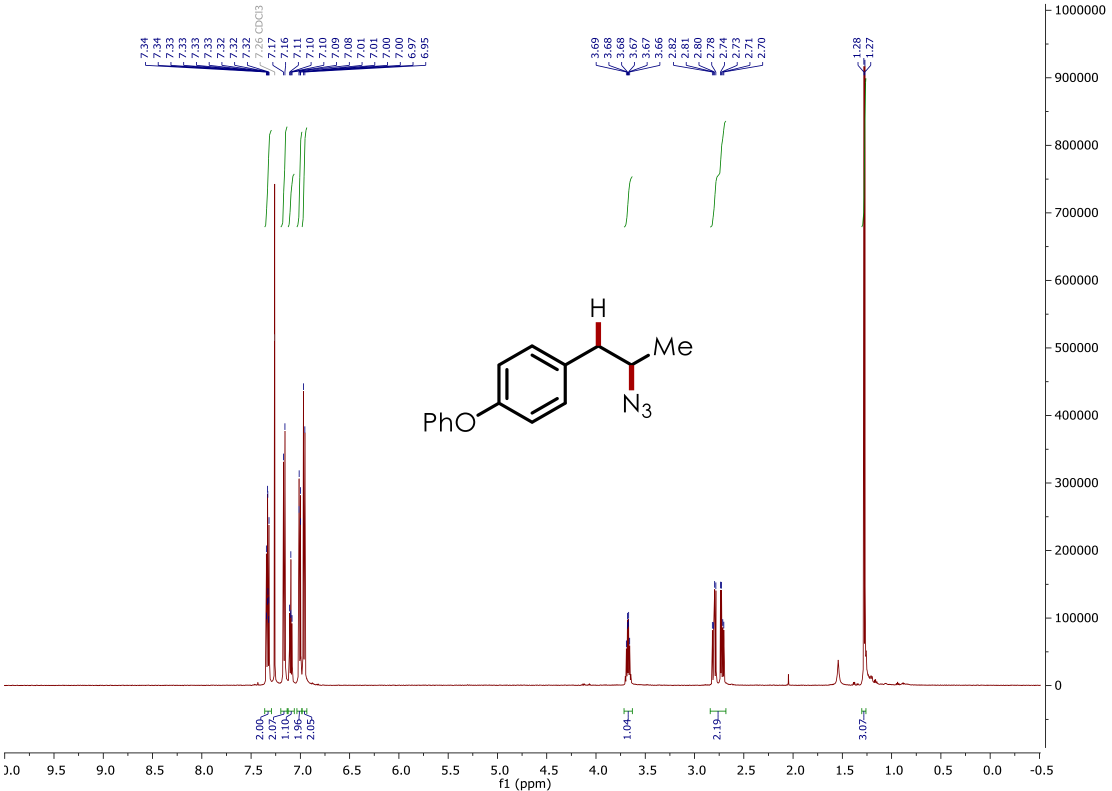


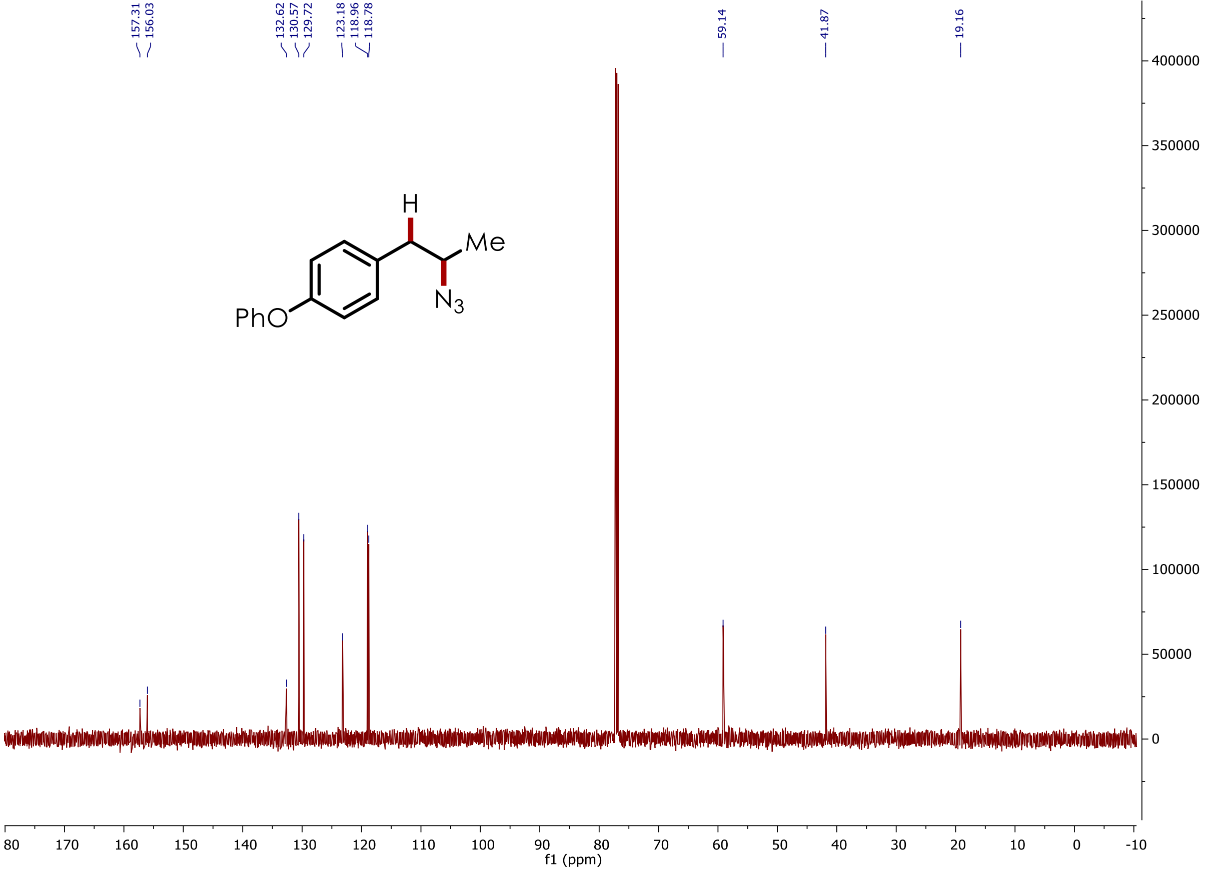
4-(2-azidopropyl)phenyl benzoate (22)



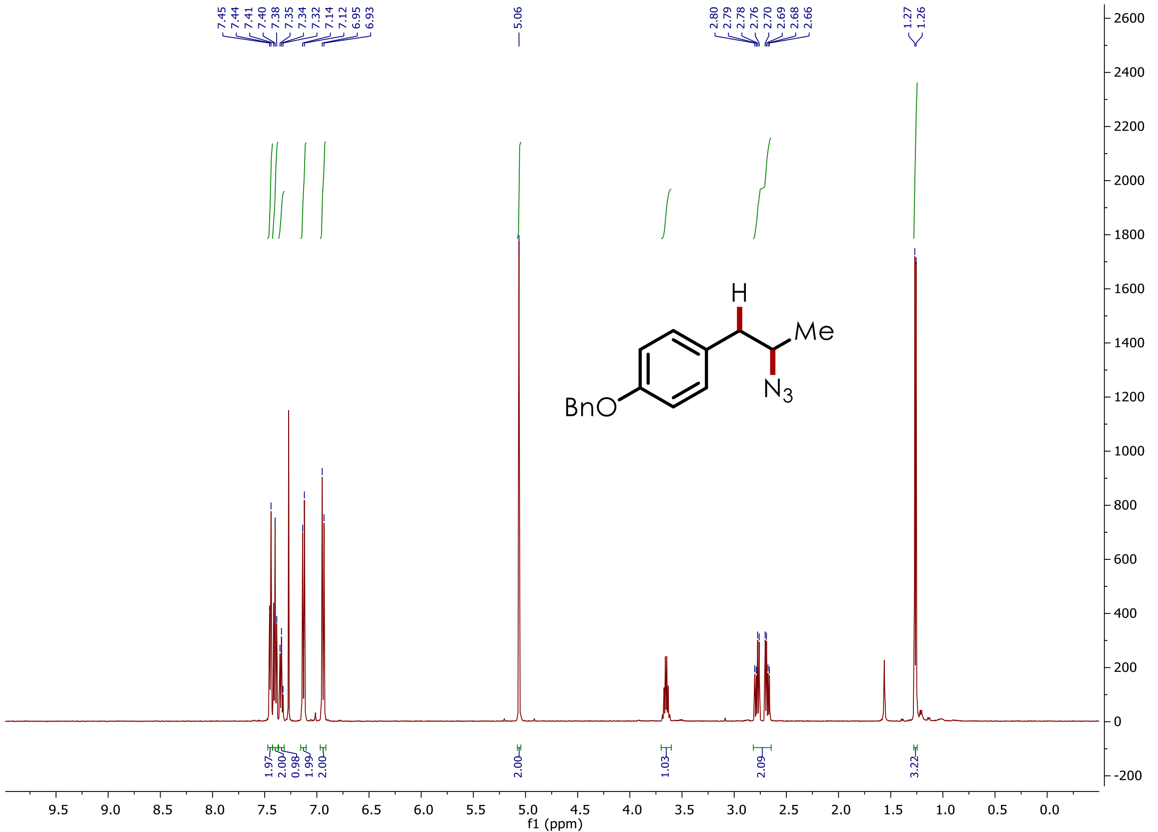


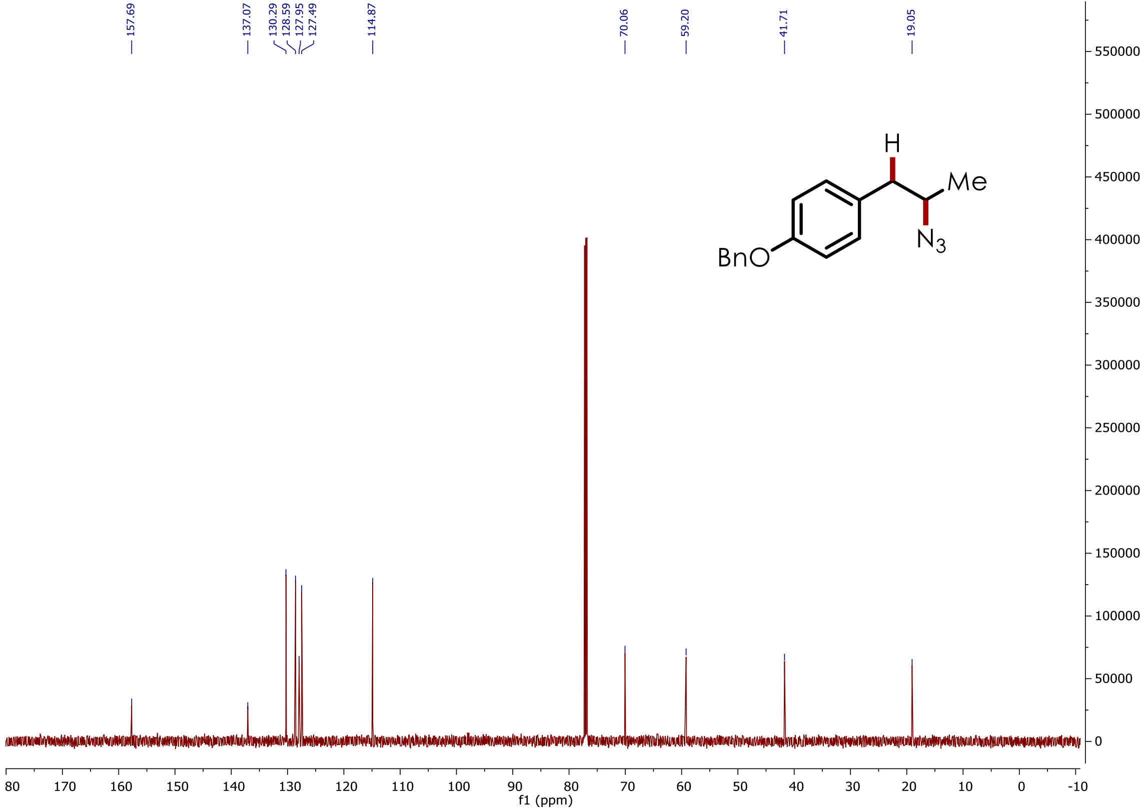
1-(2-azidopropyl)-4-phenoxybenzene (23)



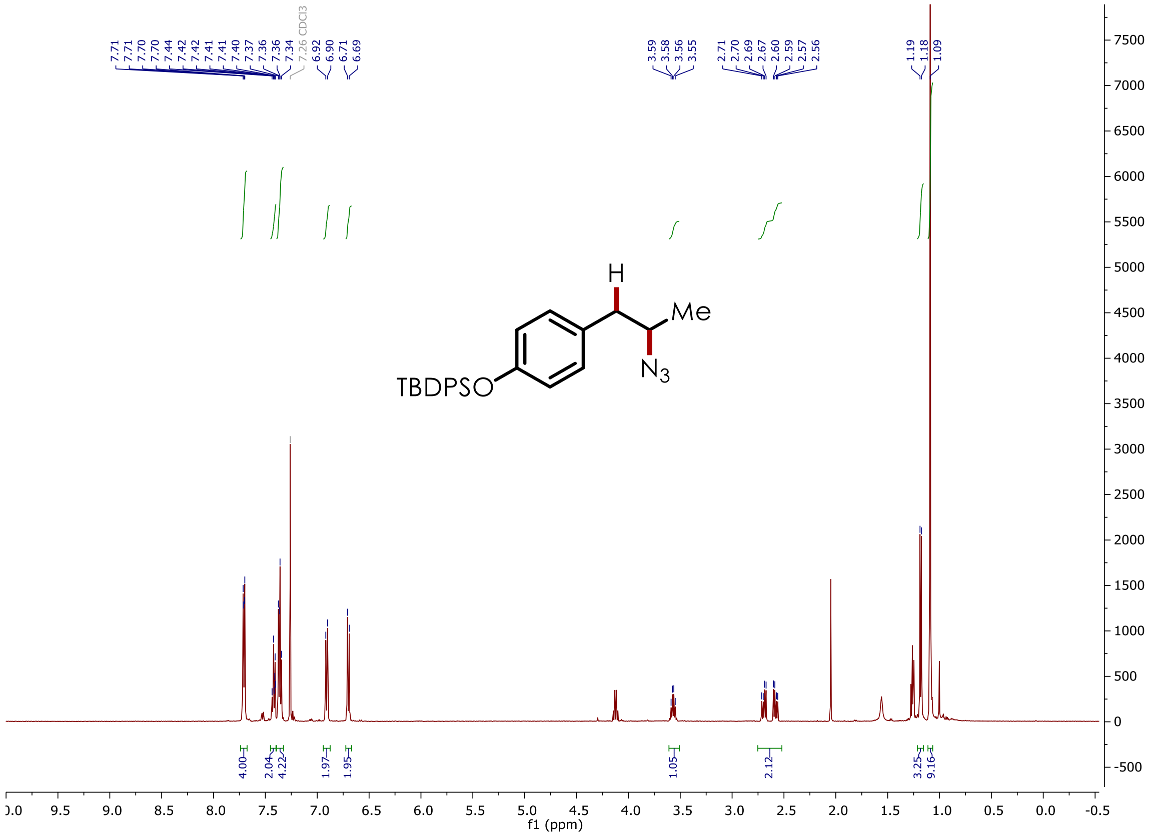


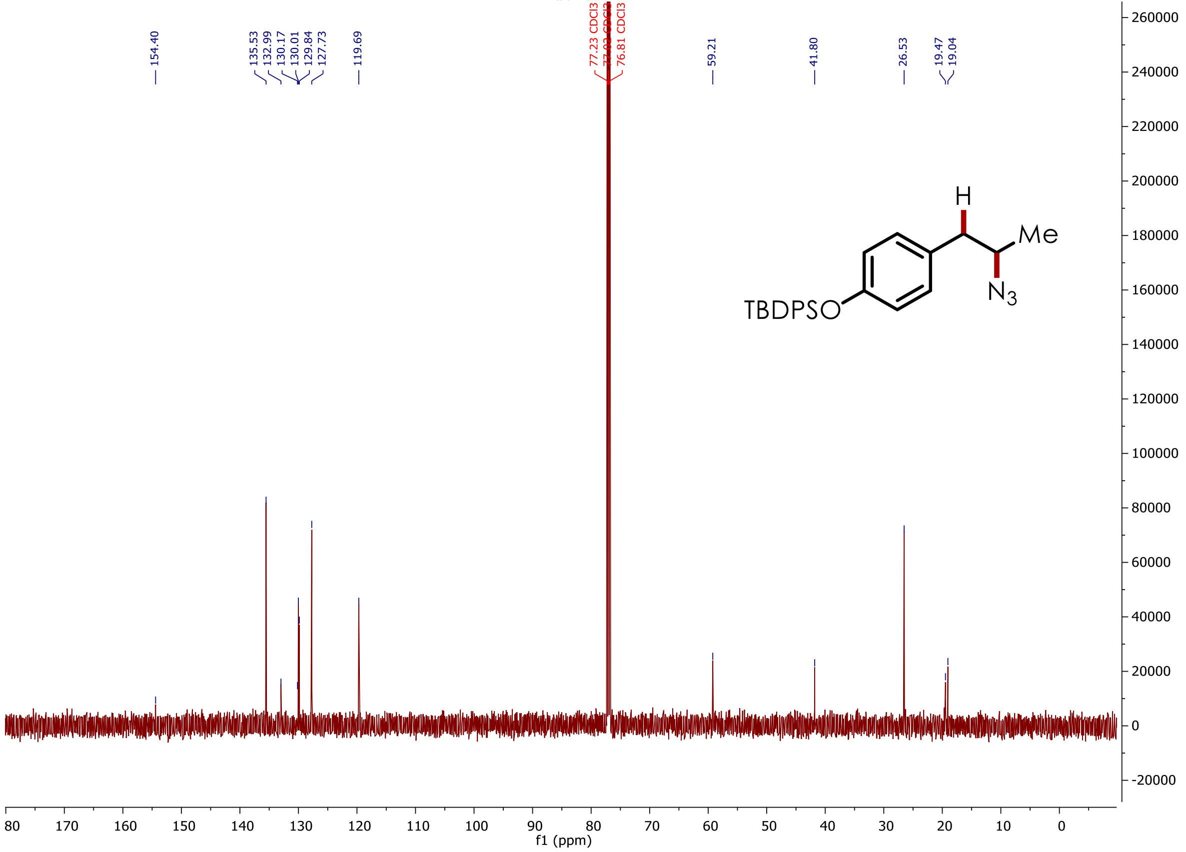
1-(2-azidopropyl)-4-(benzyloxy)benzene (24)



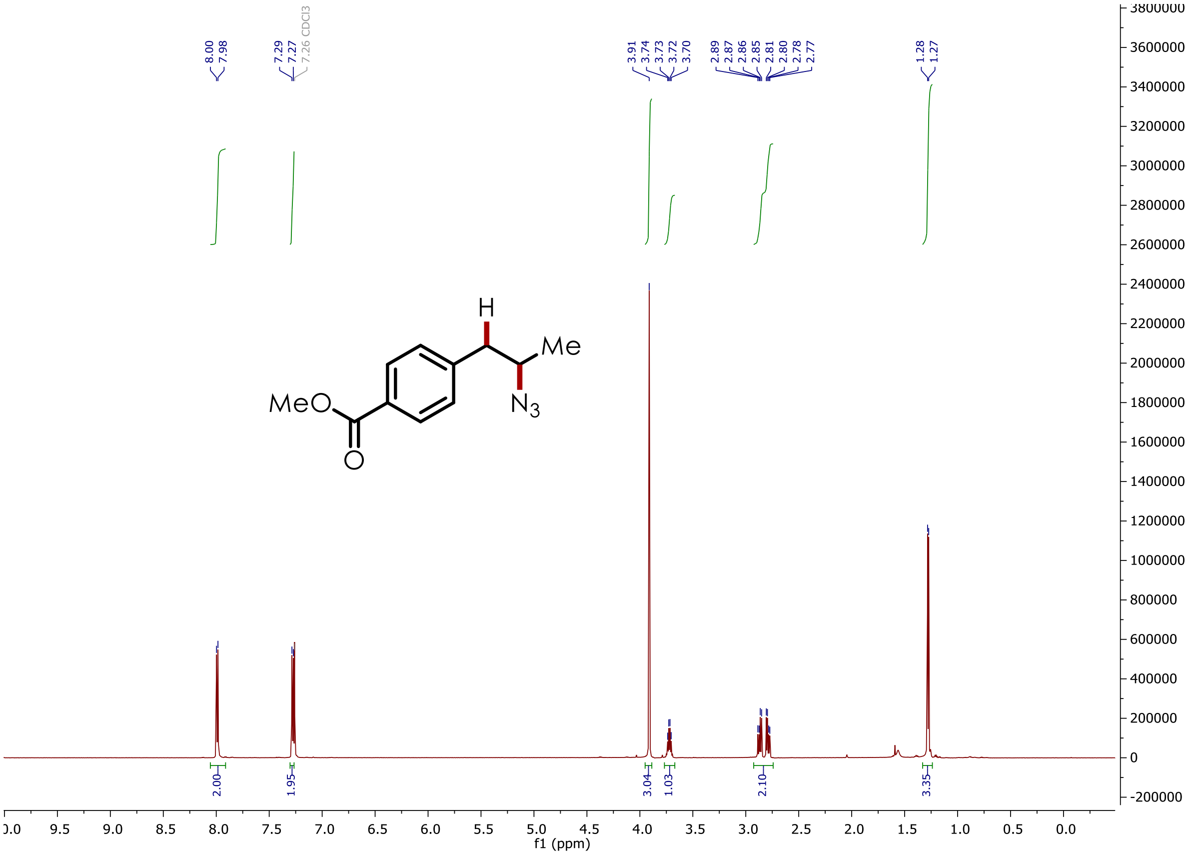


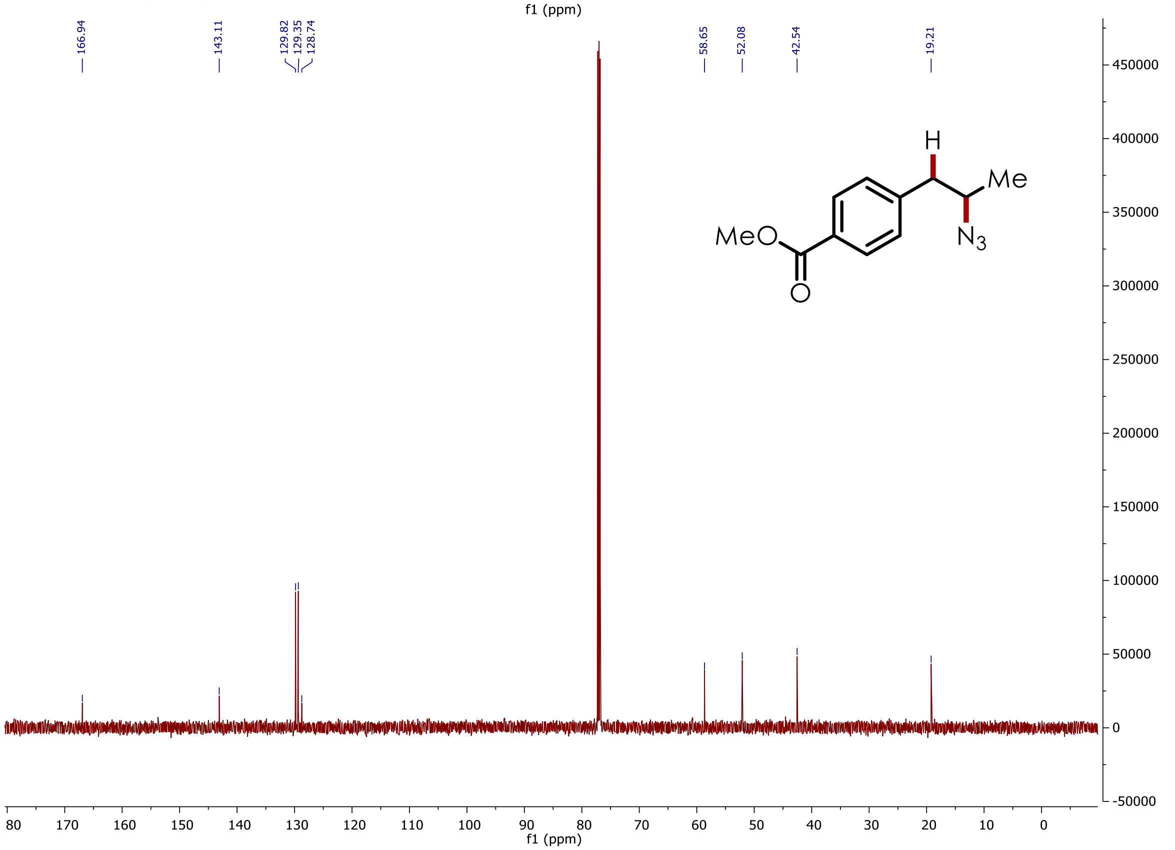
(4-(2-azidopropyl)phenoxy)(tert-butyl)diphenylsilane (25)



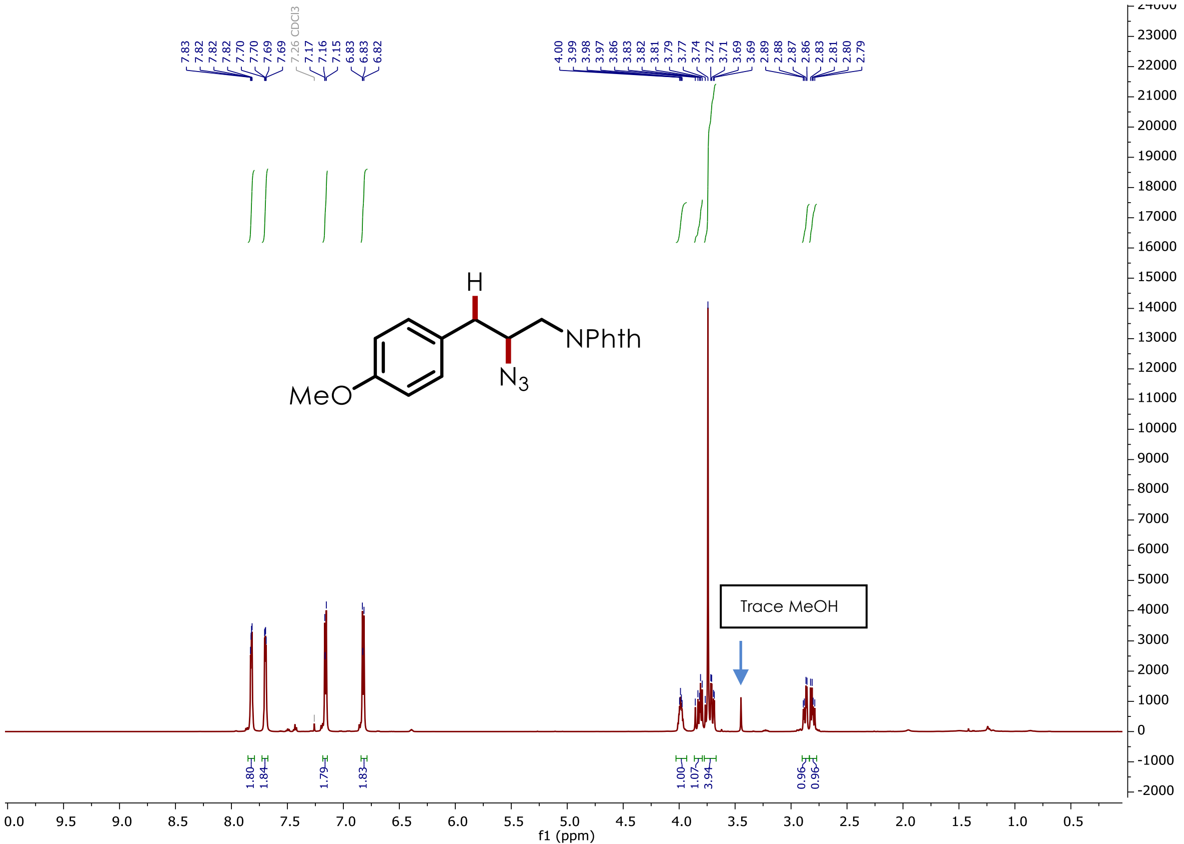


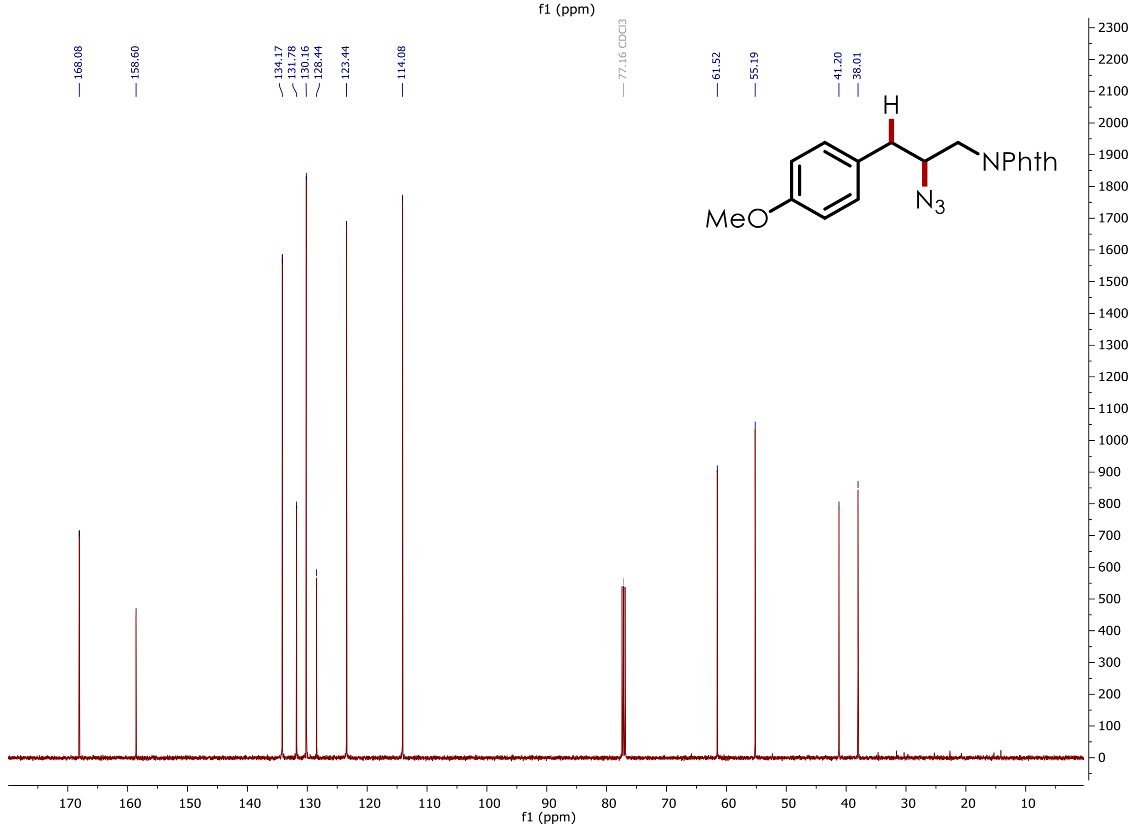
methyl 4-(2-azidopropyl)benzoate (27)





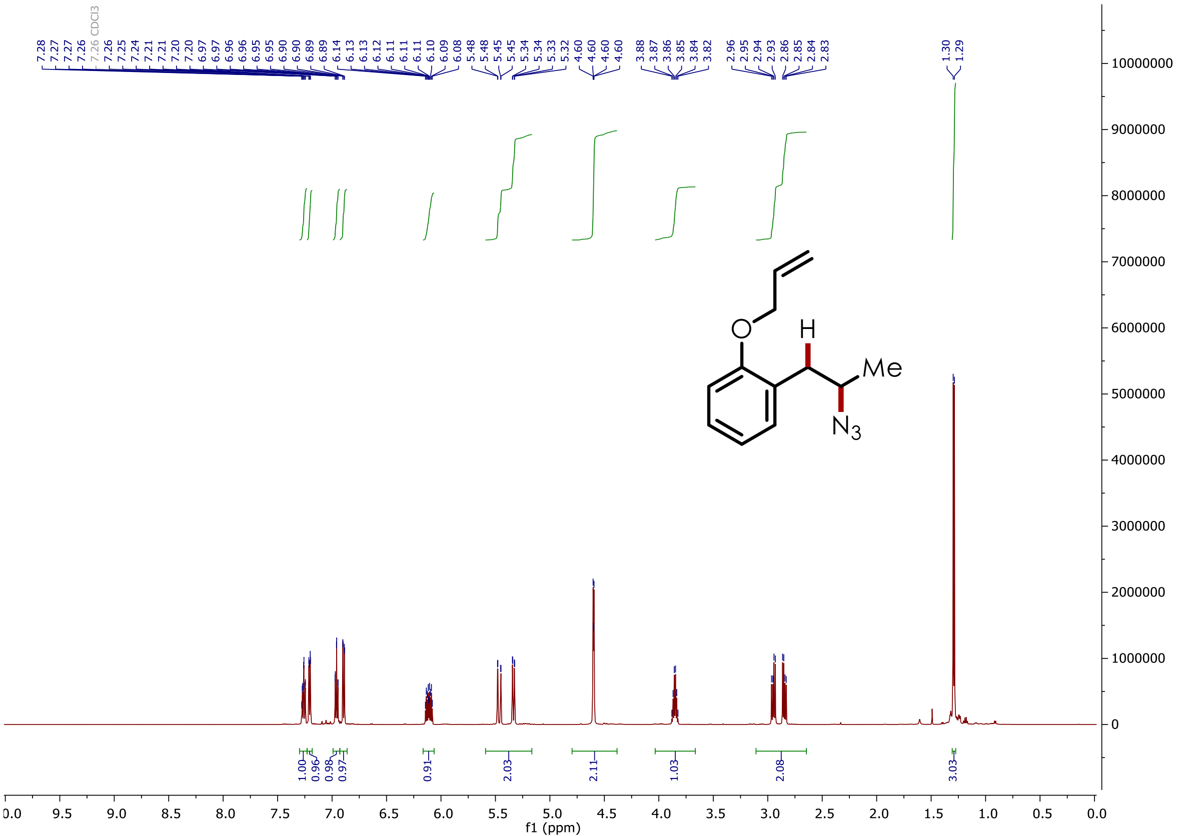
-(2-azido-3-(4-methoxyphenyl)propyl)isoindoline-1,3-dione (29)

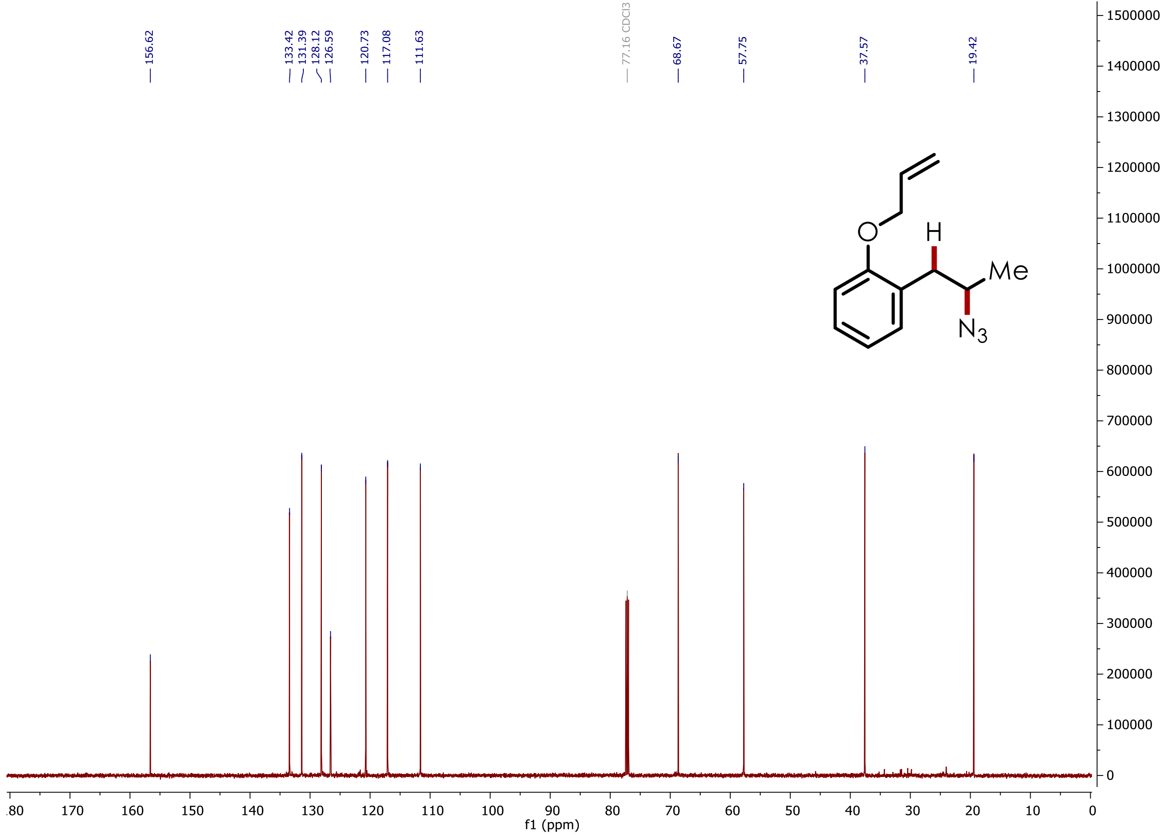




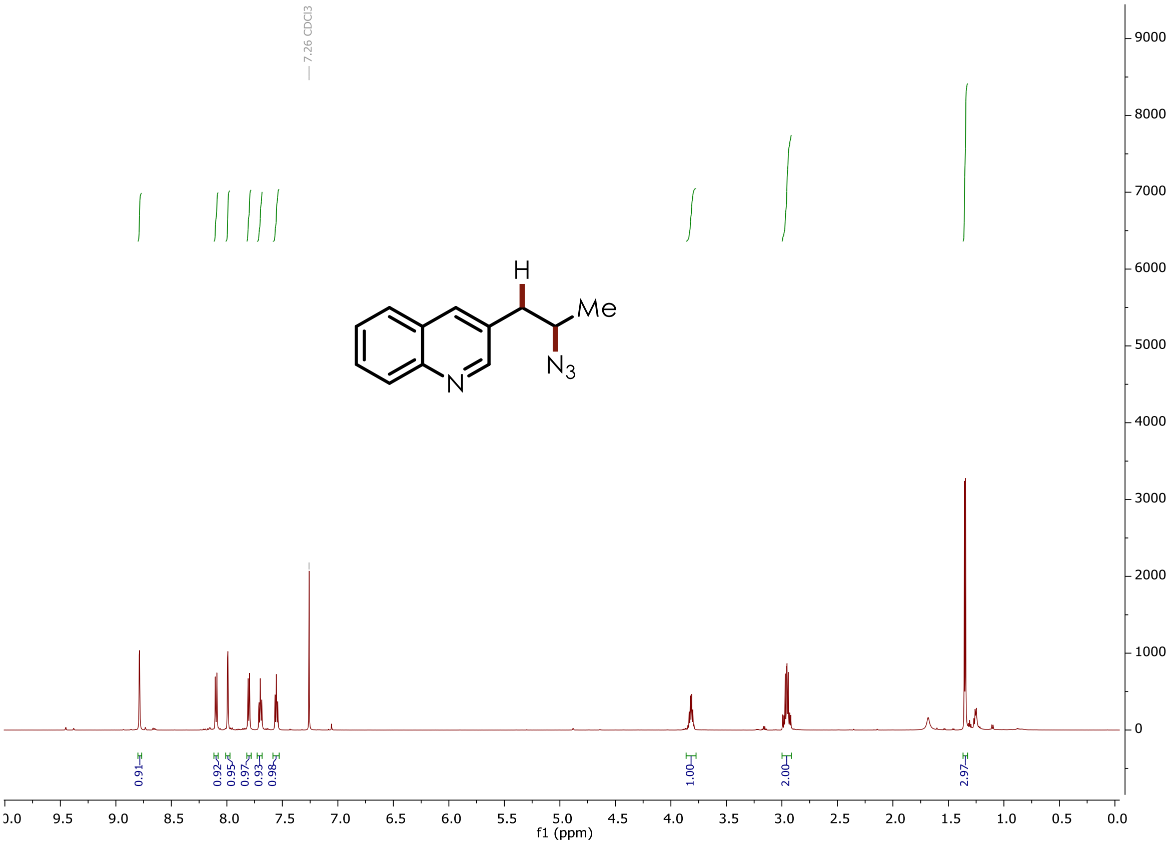
1-z

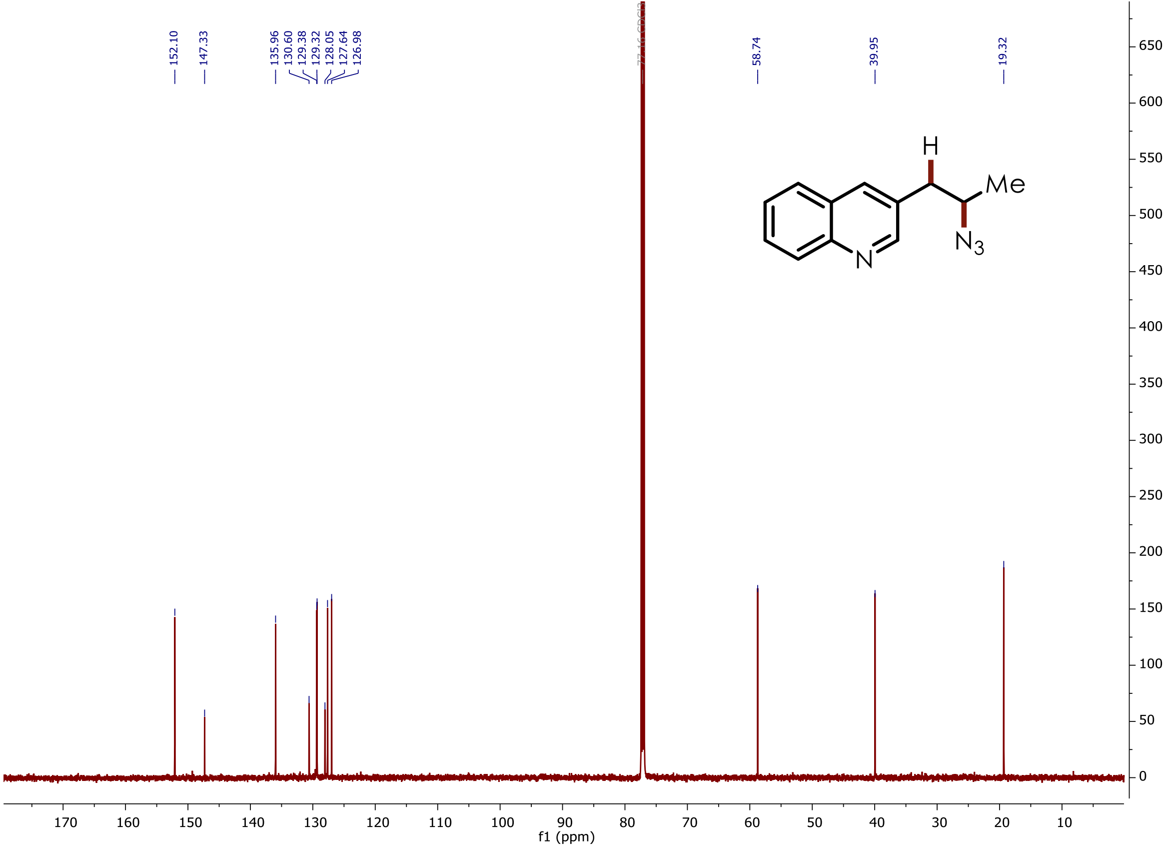
(allyloxy)-2-(2-azidopropyl)benzene (30)



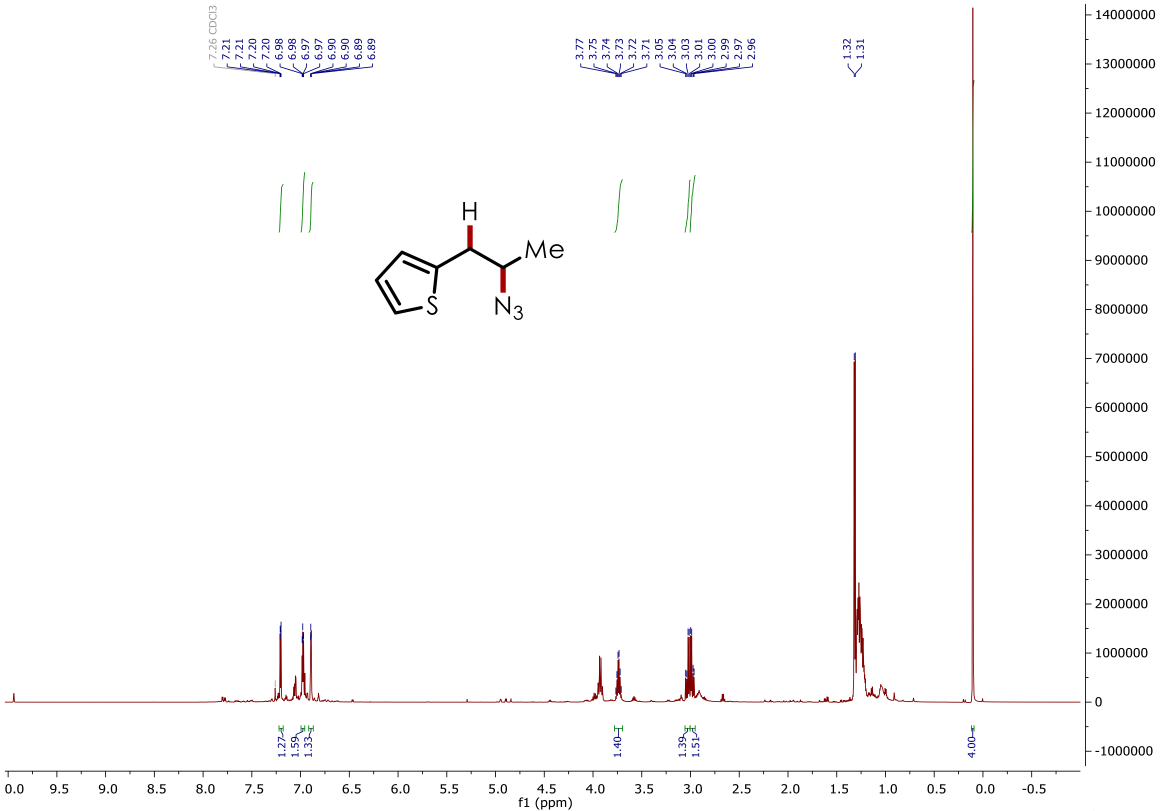


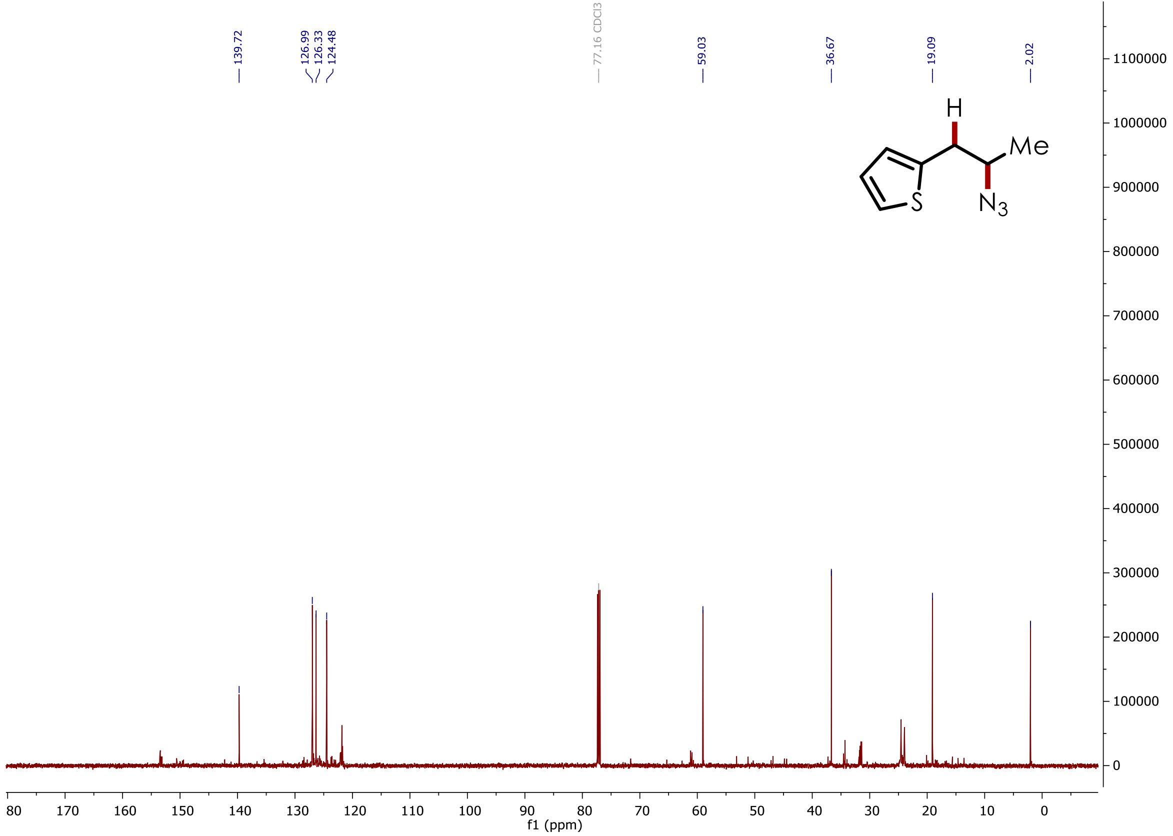
3-(2-azidopropyl)quinoline (31)





2-(2-azidopropyl)thiophene (32) – Crude NMRs (Not purified, yield taken via proton NMR with HMDSO as an internal standard)





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