Practical Regio- and Stereoselective Azidation and Amination of Terminal Alkenes

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General Information

All reactions were carried out under air in oven-dried glassware with magnetic stirring at room temperature. All commercially obtained reagents were used as received. Solvents were dried, degassed, and collected from a JC Meyer company solvent purification system. Heating was accomplished by silicone oil bath. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). TLC visualization was accompanied with UV light. Concentration in vacuo refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr).

^{1}H NMR spectra were recorded at 300 MHz, and 500 MHz are reported relative to $CDCl_3$ (δ 7.26), DMSO (δ 2.50), CD_3OD (δ 3.31). ^{1}H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), dt (double of triplets), and m (multiplet), respectively. Proton-decoupled ^{13}C NMR spectra were recorded at 75 MHz and 125 MHz and reported relative to $CDCl_3$ (δ 77), DMSO-d_6 (δ 39.5), or CD_3OD (δ 49). IR experiments were recorded with neat samples on a Bruker Alpha instruments fitted with diamond ATR sample plate. High-resolution (HR) mass spectra were recorded at the Shimadzu Center Laboratory for Biological Mass Spectrometry at UTA.

References to Known Terminal Alkenes

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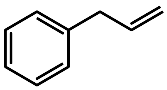
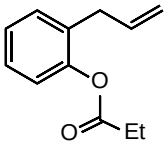
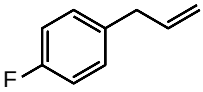
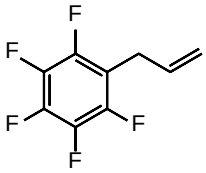
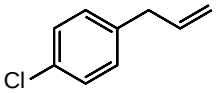
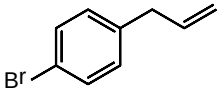
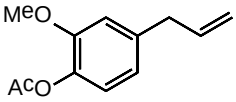
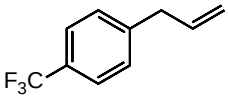
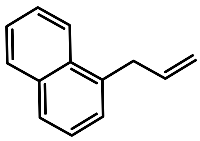
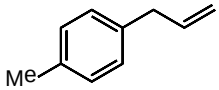
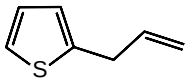
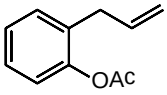
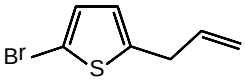
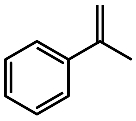
1a		S1	**1h**		S5
1b		S1	**1i**		S1
1c		S2			
1d		S2	**1j**		S6
1e		S1	**1k**		S3
1f		S1	**1l**		S7
1g		S4	**1m**		S8
			1n		S1

Preparation of Terminal Alkenes. Olefins were either obtained from commercial sources or prepared in accordance with previously reported procedures. The spectra data matched the following cited literature.

References:

S1) Commercial available (Sigma-Aldrich).
S2) D. F. Taber, C. M. Paquette, P. M. Gu, W. W. Tian, *J. Org. Chem.*, 2013, **78**, 9772-9780.
S3) S. Lin, C. X. Song, G. X. Cai, W. H. Wang, Z. J. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 12901-12903.
S4) G. D. Liu, J. M. Wurst, D. S. Tan, *Org. Lett.*, 2009, **11**, 3670-3673.
S5) A. E. Díaz-Alvarez, P. Crochet, V. Cadierno, *Tetrahedron*, 2012, **68**, 2611-2620.
S6) J. M. Álvarez-Calero, Z. D. Jorge, G. M. Massanet, *Org. Lett.*, 2016, **18**, 6344-6347.
S7) N. J. Race, J. F. Bower, *Org. Lett.*, 2013, **15**, 4616-4619.
S8) N. Marshall, S. K. Sontag, J. Locklin, *Macromolecules*, 2010, **43**, 2137-2144.

List of Known and New Allylic Azides

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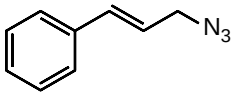
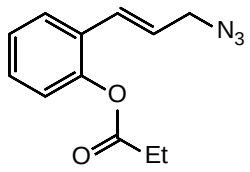
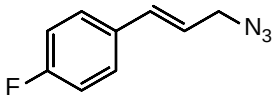
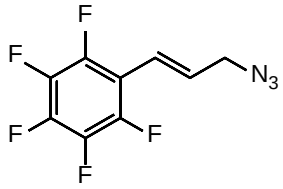
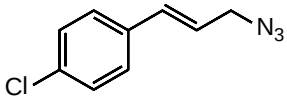
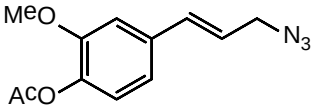
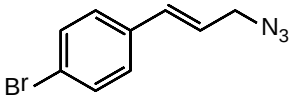
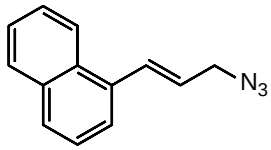
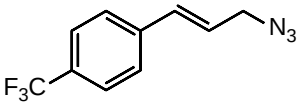
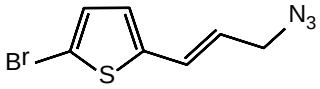
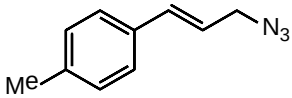
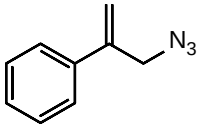
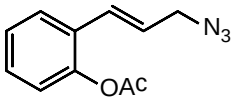
3a		S9	**3h**		-
3b		S9	**3i**		-
3c		S10	**3j**		-
3d		-	**3k**		-
3e		S10	**3l**		-
3f		S9	**3n**		S11
3g		-			

References:

S9) M. Rueping, C. Vila, U. Uria, *Org. Lett.*, 2012, **14**, 768-771.
S10) B. V. Rokade, G. K. Karthik, K. R. Prabhu, *Eur. J. Org. Chem*., 2015, 2706-2717.
S11) M. Gardiner, R. Grigg, M. Kordes, V. Sridharan, N. Vicker, *Tetrahedron*, 2001, **57**, 7729-7735.

Azide Precautions

Organic and inorganic azides are known to be high-energy materials and explosions have been reported with their use. All the azides reported herein were synthesized without incident; however, several precautions were taken. First, all azides synthesized herein have a C/N ratio of ≥ 3:1. Second, reactions with more than 1 mmol of azide were placed behind safety shields both in the fume hood and during rotary evaporation.[S12]

[S12] S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem. Int. Ed.*, 2005, **44**, 5188-5240.

List of Known and New Allylic Amines

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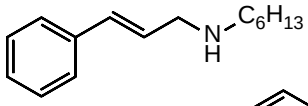
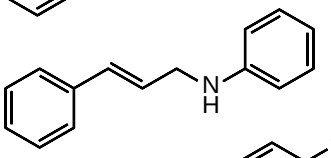
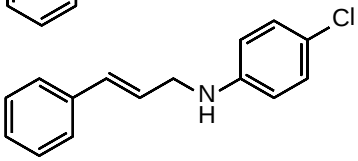
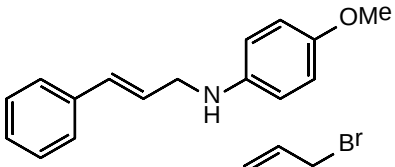
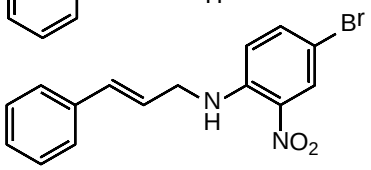
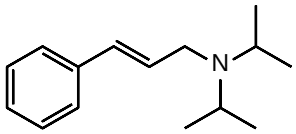
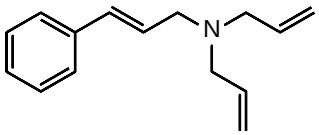
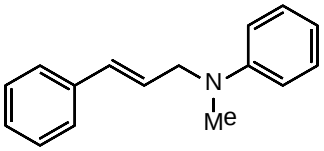
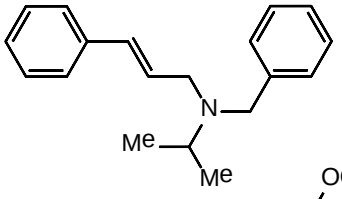
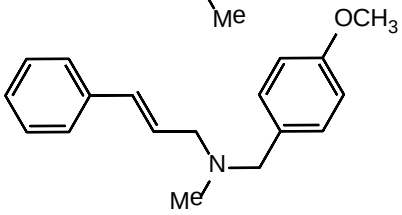
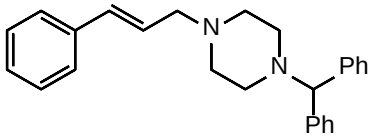
4a		S13
4b		S14
4c		S14
4d		S14
4e		-
4f		S15
4g		S16
4h		S15
4i		-
4j		-
4k		S14

References:

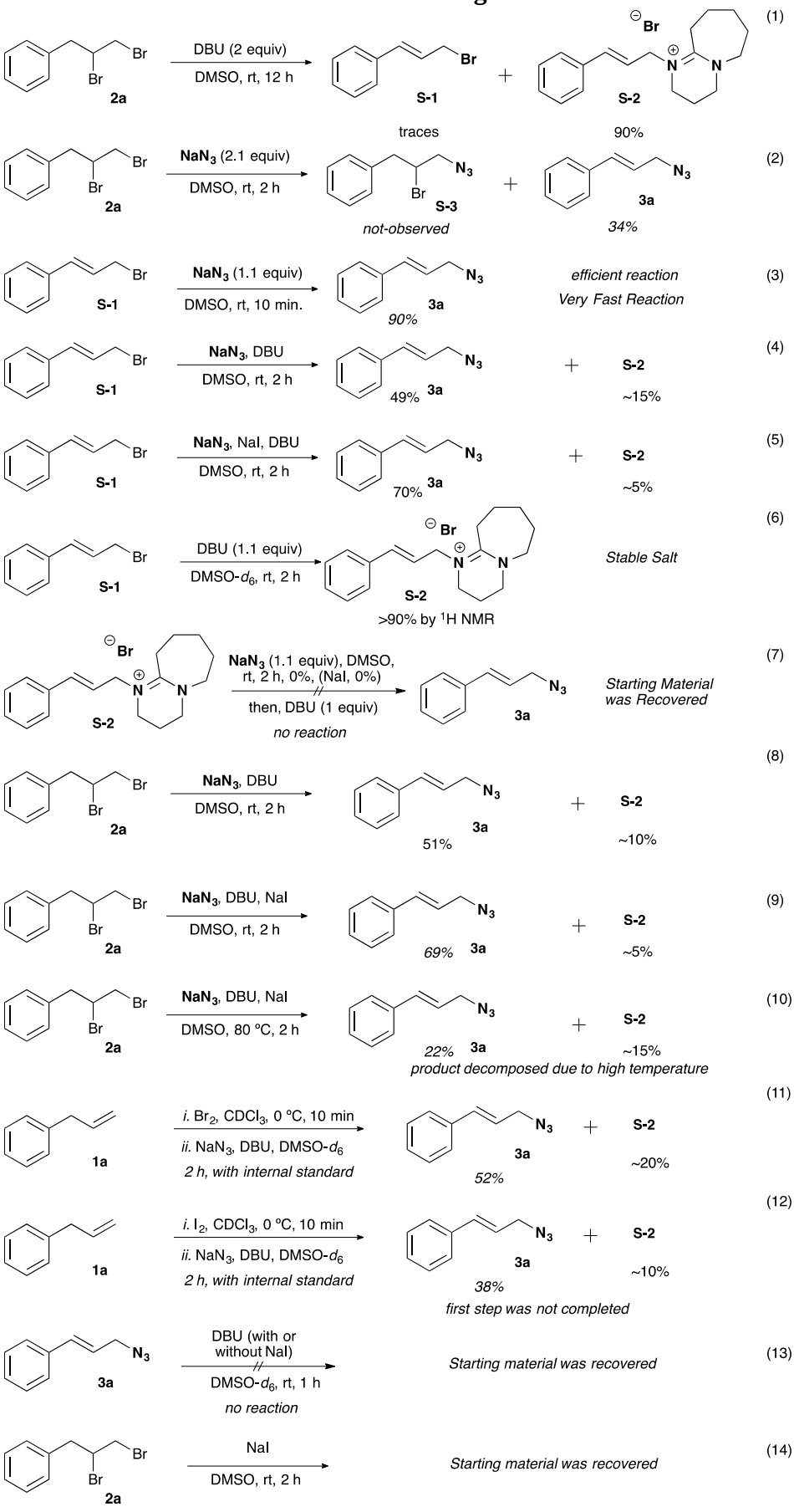
S13) M. Utsunomiya, Y. Miyamoto, J. Ipposhi, T. Ohshima, K. Mashima, *Org. Lett*., 2007, **9**, 3371-3374.

S14) R. Blieck, J. Bahri, M. Taillefer, F. Monnier, *Org. Lett*., 2016, **18**, 1482-1485.

S15) G. Hirata, H. Satomura, H. Kumagae, A. Shimizu, G. Onodera, M. Kimura, *Org. Lett*., 2017, **19**, 6148-6151.

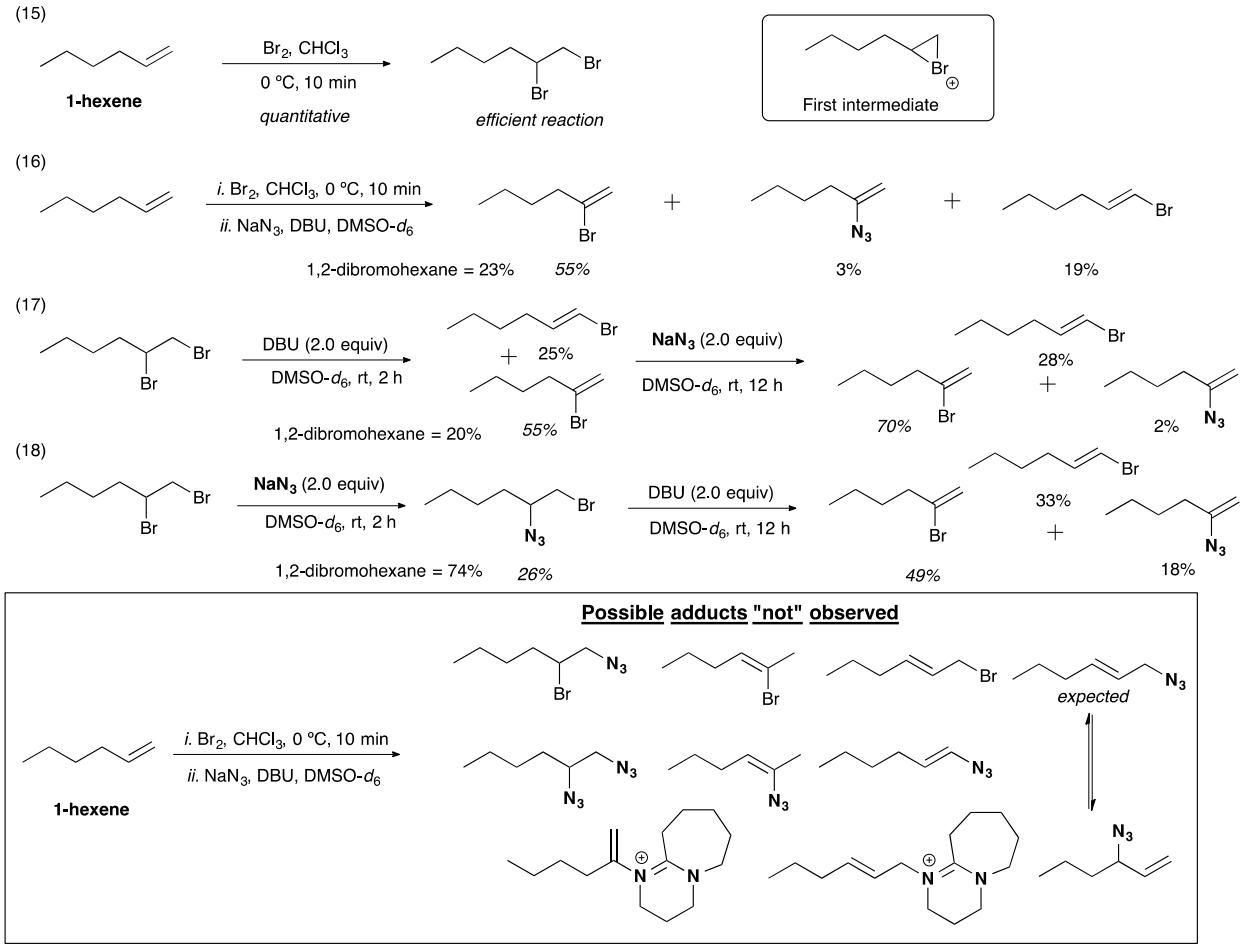
S16) T. H. West, S. S. M. Spoehrle, A. D. Smith, *Tetrahedron*, 2017, **73**, 4138-4149.

Mechanistic Investigation



1-Hexene

To obtain additional insight into the reaction mechanism, *1-hexene and sodium azide were used as the starting materials for our one-pot transformation.* It was observed a mixture of brominated adducts; including vinyl bromides, but none of the adducts could be identified as the expected allylic azide. This due to the lack of benzylic (acidic) protons.



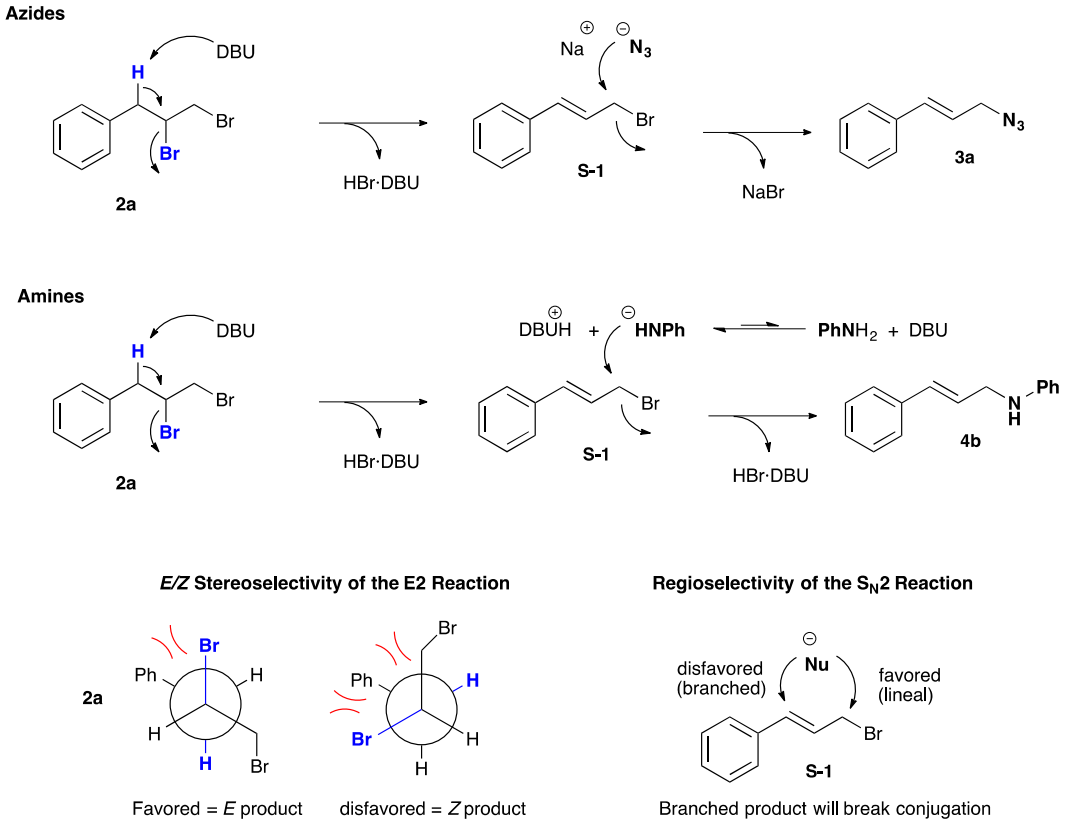
Equation 15 shows the quantitative bromination of 1-hexene. However, when the base (DBU) and the nucleophile (NaN_3) were added to the reaction, a mixture of products was observed (Eq. 16). The three major products were 1-bromohexane, 2-bromohexene, and 2-azidohexene. We also subjected 1,2-dibromohexane to DBU and 55% of 2-bromohexene together with 25% of 1-bromohexane were observed as the major products (Eq. 17). Then, to this reaction mixture was added sodium azide and stirred for 12 h. After which time, we were able to observed only 2% of the vinyl azide (Eq. 17, right). We also performed the previous reactions inversing the order (Eq. 18). First, we subjected 1,2-dibromohexane to NaN_3 and only a little conversion to 2-azido-1-bromohexane was observed (26%). After 2 hours, DBU was added to the reaction mixture. The reaction mixture was stirred for 12 additional hours, after which time a similar mixture of products were observed. The only difference that this time (Eq. 18, right), more of the 2-azidohexene (18%) was observed compared with the previous reaction (Eq. 17, right). This data indicates that the bromonium ion is formed (also observed by GC-MS) during the reaction so that the secondary alkyl bromide is more prompt to substitution. Finally, the box depicted above shows several potentials adducts that were not observed during our NMR studies.

Mechanistic Details

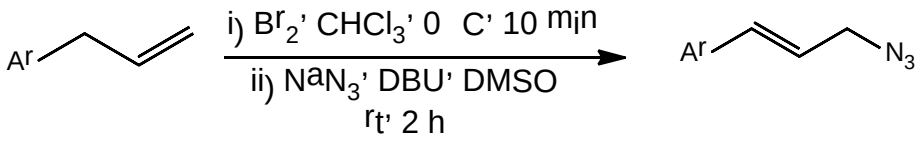
Based on our observations and the previous set of experiments (Page S-5), it is clear that the dihalogenation reaction occurs in almost quantitative yields when bromine is used for all the substrates. However, iodination is slow and less efficient (eq. 12). Therefore, bromination was selected as the optimal condition. For the second step, two reactions have to occur, a stereoselective E2 elimination follow by a regioselective S_N2 reaction. Our experiments suggest that the rate determining step is the E2 reaction, since the S_N2 reaction is very fast (see equations 3 and 6) and the cinnamyl bromide (**S-1**) is quickly consumed and it is never in a large amount in the reaction mixture. Consequently, and in order to increase the reaction yields, the key component in the conversion of terminal olefins to allylic azides or amines is the base. We performed a comprehensive screening for the best base for the title transformation, from organic to inorganic, and from non-nucleophilic bases to somehow nucleophilic bases. This extensive screening led us to discover that DBU is the best base to employ in our reported one-pot reactions. Albeit, DBU also produces an average of around ~10% of the ammonium salt (eq. 8). Nonetheless, this salt is very easy to isolate and the reaction yields for the expected products are superiors to any of those from other bases. Important to note that other bases, for example Cs_2CO_3 (inorganic, non-nucleophilic), were screening with longer reactions times, or at higher temperatures. However, all gave lower yields, due to product decomposition and even azide transpositions. Finally, addition of NaI helped to increase the reactions yields in all reactions, perhaps due to the increased hindrance during the S_N2 reaction, making the big DBU molecule harder to approach. Note: addition of NaI to alkyl dibromide (**2a**) without base, did not reacted at all. Indicating, that a bromonium/iodonium intermediate doesn't participate in this transformation.

To obtain additional insight into the reaction mechanism, *1-hexene and sodium azide were used as the starting materials for our one-pot transformation.* It was observed a mixture of brominated adducts; including vinyl bromides, but none of the adducts could be identified as the expected allylic azide. This due to the lack of benzylic (acidic) protons.

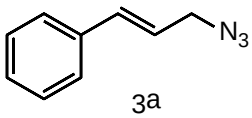
Proposed Mechanism



General Procedure and Characterization Data for Allylic Azides

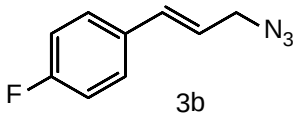


To a 10 mL round bottom flask, open to the atmosphere, was added the respective olefin (0.4 mmol, 1 equiv) and $CHCl_3$ (1 mL), at room temperature. The mixture was cooled to 0 ˚C, followed by dropwise addition of Br_2 (0.44 mmol, 1.1 equiv). After stirring for 10 minutes, the mixture was concentrated *in vacuo* to afford the respective crude dibromide adduct. To this crude dibromo adduct, DMSO (1 mL), NaN_3 (0.48 mmol, 1.2 equiv), DBU (0.44 mmol, 1.1 equiv) were added sequentially. The reaction flask was capped and stirred at rt for 2 h. Purification by flash chromatography (SiO_2, EtOAc/hexanes mixtures) provided pure product. For reactions using sodium iodide as the additive, NaI (0.4 mmol, 1.0 equiv) was added just before adding DBU. The rest of the reaction protocol was follow as described above.



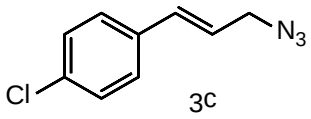
3a

1-((E)-3-azidoprop-1-enyl)benzene (**3a**). Colorless oil (33 mg, 51%, with NaI = 44 mg, 69%). 1-gram scale, 848 mg, 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.44 (m, 5H), 6.66 (d, *J* = 15.0 Hz, 1H), 6.26 (dt, *J* = 15.6, 6.6 Hz, 1H), 3.96 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.9, 134.4, 128.6, 128.1, 126.5, 122.3, 52.9 ppm.



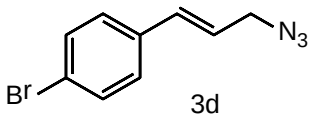
3b

1-((E)-3-azidoprop-1-enyl)-4-fluorobenzene (**3b**). Colorless oil (37 mg, 53%, with NaI = 44 mg, 62%). 1-gram scale, 702 mg, 54%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.39 (m, 2H), 7.00-7.05 (m, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.6, 6.6 Hz, 1H), 3.94 (d, *J* = 6.30 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 162.6 (d, $^1J_{CF}$ = 245.2 Hz), 133.3, 132.0, 128.1 (d, $^3J_{CF}$ = 7.8 Hz), 122.1, 115.6 (d, $^2J_{CF}$ = 21.5), 52.9 ppm.



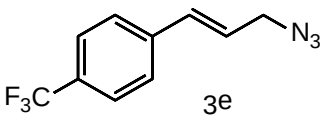
3c

1-((E)-3-azidoprop-1-enyl)-4-chlorobenzene (**3c**). Colorless oil (36 mg, 47%, with NaI = 45 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.31 (m, 4H), 6.59 (d, *J* = 15.0 Hz, 1H), 6.21 (dt, *J* = 15.3, 6.6 Hz, 1H), 3.94 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.5, 133.9, 133.2, 128.9, 127.9, 123.2, 52.8 ppm.

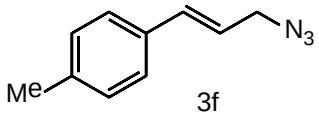


3d

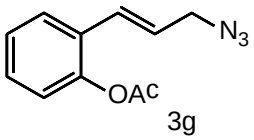
1-((E)-3-azidoprop-1-enyl)-4-bromobenzene (**3d**). Colorless oil (38 mg, 40%, with NaI = 48 mg, 50%). IR (neat, cm^{-1}): 2924, 2854, 2095, 1587, 1070, 966, 795. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.47 (m, 2H), 7.24-7.27 (m, 2H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.23 (dt, *J* = 15.6, 6.6 Hz, 1H), 3.94 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.8, 133.1, 131.7, 128.1, 123.2, 121.9, 52.8 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M+H-N_2]^+$ Calcd for C_9H_9BrN = 209.9913; Found 209.9944



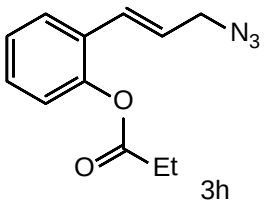
1-((E)-3-azidoprop-1-enyl)-4-(trifluoromethyl)benzene (**3e**). Colorless oil (48 mg, 53%, with NaI = 61 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.47-7.53 (m, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.6, 6.3 Hz, 1H), 3.99 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 132.6, 129.8 (q, $^{2}J_{CF}$ = 32.1 Hz),126.7, 125.5 (q, $^{3}J_{CF}$ = 3.6 Hz), 125.2, 124.0 (q, $^{1}J_{CF}$ = 270.3 Hz), 52.6 ppm.



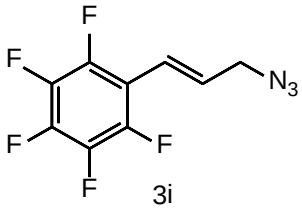
1-((E)-3-azidoprop-1-enyl)-4-methylbenzene (**3f**). Colorless oil (31 mg, 44%, with NaI = 40 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.93 (d, *J* = 6.6 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.1, 134.5, 133.1, 129.3, 126.5, 121.2, 53.1, 21.2 ppm.



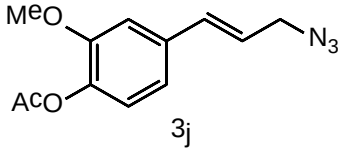
2-((E)-3-azidoprop-1-enyl)phenyl acetate (**3g**). Colorless oil (46.2 mg, 53%, with NaI = 54 mg, 62%). IR (neat, cm^{-1}): 2930, 2097, 1763, 1738, 1483, 1199, 1174, 966, 750. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 6.0, 1.6 Hz, 1H), 7.21-7.34 (m, 2H), 7.07 (dd, *J* = 6.0, 0.9 Hz, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.95 (d, *J* = 6.6 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 147.9, 128.9, 128.6, 127.6, 126.9, 126.1, 125.0, 122.6, 52.8, 20.8 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{11}N_3O_2Na$ 240.0743; Found 240.0726.



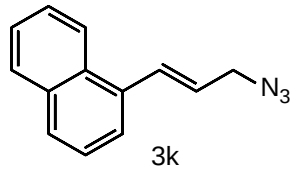
2-((E)-3-azidoprop-1-enyl)phenyl propionate (**3h**). Colorless oil (45 mg, 49%, with NaI = 54 mg, 58%). IR (neat, cm^{-1}): 2982, 2942, 2097, 1758, 1640 1130, 751. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 6.0, 1.5 Hz, 1H), 7.19-7.33 (m, 2H), 7.05-7.07 (m, 1H), 6.67 (d, *J* = 16 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.3 Hz, 1H), 3.94 (d, *J* = 6 Hz, 2H), 2.65 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 148.0, 128.9, 128.6, 127.6, 126.8, 126.0, 124.8, 122.6, 52.8, 27.5, 9.0 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{13}N_3O_2Na$ 254.0900; Found 254.0880.



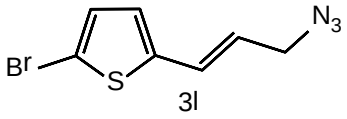
1-((E)-3-azidoprop-1-enyl)-2,3,4,5,6-pentafluorobenzene (**3i**). Colorless oil (45 mg, 45%, with NaI = 55 mg, 55%). IR (neat, cm^{-1}): 2104, 1643, 1518, 1499, 986, 969. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (d, *J* = 7.5 Hz, 1H), 4.88 (q, *J* = 7 Hz, 1H), 3.46 (dd, *J* = 7.5 Hz, 1.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ δ 144.8 (dm, *J* = 249.1 Hz), 140.3 (dm, *J* = 252.7 Hz), 137.6 (dm, *J* = 250.3 Hz), 132.0 (m), 117.7, 110.9 (m), 53.1 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M]^+$ Calcd for $C_9H_4F_5N_3$ 249.0320; Found 249.0381.



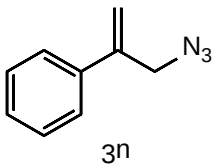
4-((E)-3-azidoprop-1-enyl)-2-methoxyphenyl acetate (**3j**). Colorless oil (34 mg, 35%, with NaI = 51 mg, 52%). IR (neat, cm^{-1}): 2971, 2935, 1759, 1745, 1622, 1121, 1045, 691. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96-7.02 (m, 3H), 6.62 (d, *J* = 16 Hz, 1H), 6.19 (dt, *J* = 15.5, 6.6 Hz, 1H), 3.94 (d, *J* = 6.6 Hz, 2H), 3.85 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 151.0, 139.5, 134.9, 133.4, 122.7, 122.6, 119.2 110.1, 55.7, 52.8, 20.5 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{13}N_3O_3Na$ 270.0849; Found 270.0838.



1-((E)-3-azidoprop-1-enyl)naphthalene (**3k**). Brown oil (35 mg, 42%, with NaI = 44 mg, 53%). IR (neat, cm^{-1}): 2925, 2854, 2093, 1590, 1437, 965. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.55 Hz, 1H), 7.81-7.89 (m, 2H), 7.39-7.63 (m, 5H), 6.28 (dt, *J* = 15.6, 6.0 Hz, 1H), 4.06 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.7, 133.5, 131.8, 131.0, 128.5, 128.4, 126.2, 125.8, 125.5, 125.5, 124.1, 123.6, 53.0 ppm. HRMS (ESI/IT-TOF) *m/z*: $[M - N_3]^+$ Calcd for $C_{13}H_{11}$ 167.0855; Found 167.0840.

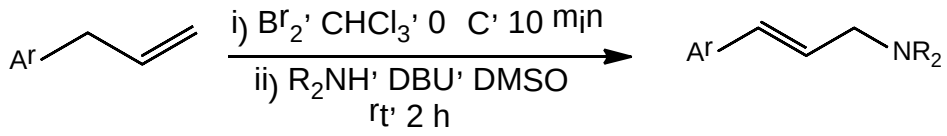


2-((E)-3-azidoprop-1-enyl)-5-bromothiophene (**3l**). Yellow oil (50 mg, 52%, with NaI = 60 mg, 61%). IR (neat, cm^{-1}): 2920, 2102, 1592, 1406, 965, 790. ^1H NMR (300 MHz, $CDCl_3$) δ 6.93 (d, *J* = 3.9 Hz, 1H), 6.74 (d, *J* = 3.9 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 5.96 (dt, *J* = 15.3, 6.6 Hz, 1H), 3.89 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 130.2, 126.8, 126.7, 122.4, 111.8, 52.5 ppm. HRMS (ESI/IT-TOF) m/z: $[M + H - N_2]^+$ Calcd for C_7H_7BrNS 215.9477; Found 215.9413.

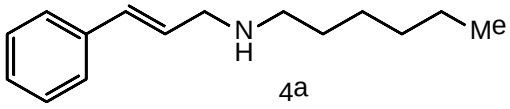


1-(1-azidoprop-2-en-2-yl)benzene (**3n**). Colorless oil (25 mg, 39%, with NaI = 30 mg, 47%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.47 (m, 2H), 7.33-7.37 (m, 3H), 5.62 (s, 1H), 5.35 (d, *J* = 0.5 Hz, 1H), 4.18 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 137.9, 128.5, 128.2, 125.9, 116.1, 54.9 ppm.

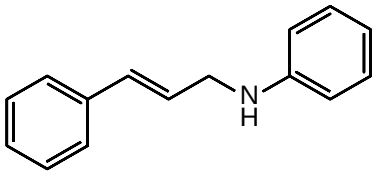
General Procedure and Characterization Data for Allylic Amines



To a 10 mL round bottom flask was added olefin (0.40 mmol, 1.0 equiv), $CHCl_3$ (1 mL), at room temperature open to air. The mixture was cooled to 0 ˚C, followed by adding Br_2 (0.44 mmol, 1.1 equiv) dropwise. After 10 minutes, the mixture was concentrated *in vacuo* to afford crude dibromide adduct. To the crude dibromo adduct, DMSO (1 mL), amine nucleophiles (0.48 mmol, 1.2 equiv), [NaI (0.4 mmol, 1.0 equiv)], DBU (0.44 mmol, 1.1 equiv) were added sequentially. The reaction flask was capped and stirred at rt for 2 h. Purification by flash chromatography (SiO_2, EtOAc/hexanes mixtures) provided the pure product.

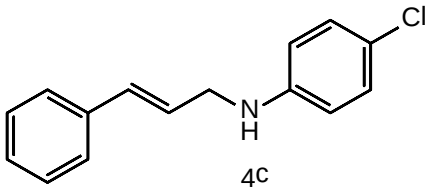


N-cinnamylhexan-1-amine (**4a**). Light-yellow oil (37 mg, 43%, with NaI = 44 mg, 51%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 2H), 7.32 (t, *J* = 15 Hz, 2H), 7.24 (t, *J* = 15 Hz, 1H), 6.54 (d, *J* = 16 Hz, 1H), 6.32 (dt, *J* = 16, 6.5 Hz, 1H), 3.32 (d, *J* = 6.5 Hz, 2H), 2.53-2.56 (m, 1H), 1.53-1.56 (m, 1H), 1.27-1.34 (m, 4H), 0.87-0.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.0, 132.5, 128.5, 127.3, 126.2, 56.2, 53.6, 31.7, 27.1, 26.9, 22.6, 14.0 ppm.



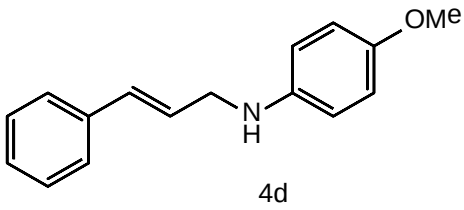
4b

N-cinnamylbenzenamine (**4b**). Light-yellow oil (46 mg, 55%, with NaI = 54 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.39 (m, 2H), 7.30-7.33 (m, 3H), 7.21-7.26 (m, 3H), 6.78-6.83 (m, 3H), 6.63 (d, *J* = 16 Hz, 1H), 6.35 (dt, *J* = 15.5, 6.5 Hz, 1H), 3.96 (dd, *J* = 6, 1.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 136.6, 132.3, 129.4, 128.5, 127.6, 126.3, 125.9, 118.8, 114.1, 47.0 ppm.



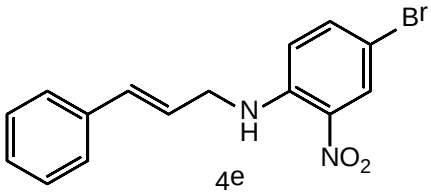
4c

4-chloro-N-cinnamylbenzenamine (**4c**). Yellow solid (44 mg, 45%, with NaI = 55 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.36 (m, 2H), 7.29-7.32 (m, 2H), 7.24-7.26 (m, 1H), 7.16 (dd, *J* = 6.5, 2 Hz, 2H), 6.71 (dd, *J* = 7.0, 2 Hz, 2H), 6.60 (d, *J* =15.5 Hz, 1H), 6.30 (dt, *J* = 15.5, 6.0 Hz, 1H), 3.92 (d, *J* = 6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 136.4, 132.8, 129.2, 128.6, 127.7, 126.3, 125.0, 124.0, 115.6, 47.4 ppm.



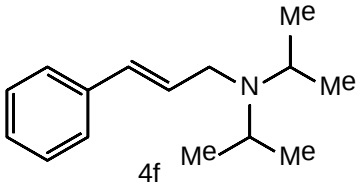
4d

N-cinnamyl-4-methoxybenzenamine (**4d**). Light-yellow solid (47 mg, 49%, with NaI = 58 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.0 Hz, 2H), 7.29 (t, *J* = 15 Hz, 2H), 7.23-7.25 (m, 1H), 6.80 (dd, *J* = 13, 2.5 Hz, 2H), 6.72 (dd, *J* = 13, 2.0 Hz, 2H), 6.62 (d, *J* = 15.5 Hz, 1H), 6.35 (dt, *J* = 16.0, 6.0 Hz, 1H), 3.90 (dd, *J* = 6.0, 1.0 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 141.0, 136.7, 132.0, 128.5, 127.5, 126.5, 126.3, 115.2, 114.8, 55.7, 47.7 ppm.



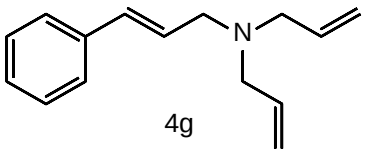
4e

4-bromo-N-cinnamyl-2-nitrobenzenamine (**4e**). Orange solid (48 mg, 36%, with NaI = 64 mg, 48%). Melting point: 77-78 °C. IR (neat, cm^{-1}): 3371, 2935, 1609, 1500, 966, 804. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2 Hz, 1H), 8.24 (b, 1H), 7.47-7.50 (m, 1H), 7.24-7.39 (m, 5H), 6.81 (d, *J* = 9 Hz, 1H), 6.61 (d, *J* = 16 Hz, 1H), 6.26 (dt, *J* = 16, 5.5 Hz, 1H), 4.14 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 138.9, 136.0, 132.5, 128.9, 128.6, 128.0, 126.4, 124.0, 115.8, 106.7, 45.0 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}BrN_2O_2$ 333.0233; Found 333.0020.



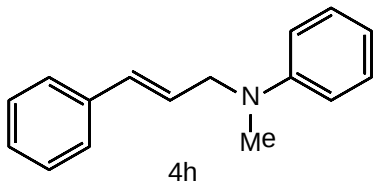
4f

(E)-N,N-diisopropyl-3-phenylprop-2-en-1-amine (**4f**). Light-yellow oil (41 mg, 47%, with NaI = 49 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 15.5 Hz, 2H), 7.22 (t, *J* = 14.5 Hz, 1H), 6.54 (d, *J* = 16 Hz, 1H), 6.28 (dt, *J* = 16, 6 Hz, 1H), 3.32 (d, *J* = 5.5 Hz, 2H), 3.14 (sept, *J* = 6.5 Hz, 2H), 1.08 (d, *J* = 6 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 131.6, 129.9, 128.4, 126.8, 126.0, 48.2, 47.5, 20.6 ppm.



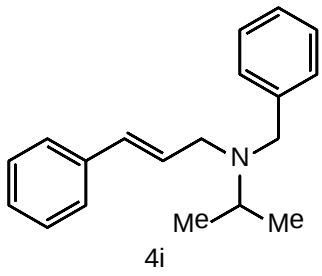
4g

N-allyl-N-cinnamylprop-2-en-1-amine (**4g**). Colorless oil (43 mg, 50%, with NaI = 52 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 13 Hz, 2H), 7.24 (t, *J* = 13 Hz, 1H), 6.52 (d, *J* = 16 Hz, 1H), 6.28 (dt, *J* = 15.5, 6.5 Hz , 1H), 5.88-5.92 (m, 2H), 5.19-5.24 (m, 4H), 3.29 (d, *J* = 7 Hz, 2H), 3.18 (d, *J* = 6.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.8, 134.7, 133.2, 128.5, 127.4, 126.2, 118.3, 56.2, 55.5 ppm.



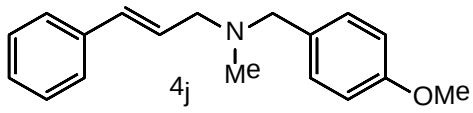
4h

N-cinnamyl-N-methylbenzenamine (**4h**). Colorless oil (41 mg, 46%, with NaI = 53 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7 Hz, 2H), 7.29-7.40 (m, 5H), 6.91 (d, *J* = 8 Hz, 2H), 6.85 (t, *J* = 14 Hz, 1H), 6.61 (d, *J* = 16 Hz, 1H), 6.34 (dt, *J* = 16, 6 Hz, 1H), 4.16 (dd, *J* = 6, 1 Hz, 2H), 3.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 136.7, 131.3, 129.1, 128.4, 127.3, 126.2, 125.4, 116.7, 112.7, 54.9, 38.0 ppm.



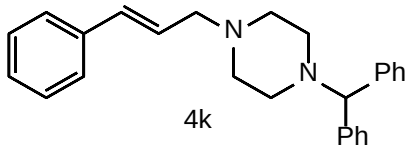
4i

(E)-N-benzyl-N-isopropyl-3-phenylprop-2-en-1-amine (**4i**). Colorless oil (43 mg, 40%, with NaI = 53 mg, 50%). IR (neat, cm^{-1}): 3060, 2961, 1599, 1493, 1027, 725. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.31-7.38 (m, 6H), 7.22-7.25 (m, 2H), 6.55 (d, *J* = 16 Hz, 1H), 6.26 (dt, *J* = 16, 6.5 Hz, 1H), 3.64 (s, 2H), 3.27 (d, *J* = 6 Hz, 2H), 3.09-3.12 (m, 1H), 1.11 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 131.2, 129.5, 128.5, 128.4, 128.1, 127.0, 126.5, 126.1, 53.1, 52.0, 49.3, 17.9 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{24}N$ 266.1903; Found 266.1869.



4j

(E)-N-(4-methoxybenzyl)-N-methyl-3-phenylprop-2-en-1-amine (**4j**). Light-yellow oil (46 mg, 43%, with NaI = 60 mg, 56%). IR (neat, cm^{-1}): 2935, 1610, 1509, 1104, 805. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8 Hz, 2H), 7.33 (t, 15.5 Hz, 2H), 7.23-7.29 (m, 3H), 6.89 (dd, *J* = 10, 2.5 Hz, 2H), 6.55 (d, *J* = 15.5 Hz, 1H), 6.34 (dt, *J* = 16, 6.5 Hz, 1H), 3.81 (s, 3H), 3.53 (s, 2H), 3.21 (d, *J* = 6.5 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 136.9, 132.6, 130.4, 130.2, 128.4, 127.3, 127.2, 126.2, 113.5, 61.0, 59.5, 55.1, 41.8 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{22}NO$ 268.1696; Found 268.1666.

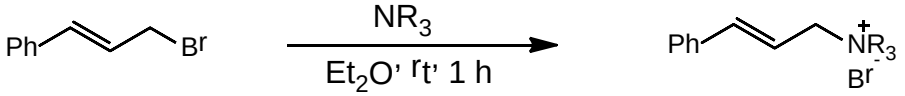


4k

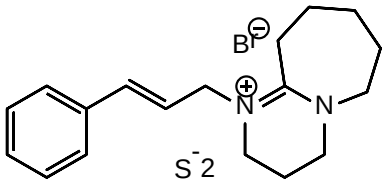
1-benzhydryl-4-cinnamylpiperazine (**4k**). White solid (58 mg, 39%, with NaI = 74 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 4H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.22-7.33 (m, 7H), 7.19 (t, *J* = 14.5 Hz, 2H), 6.54 (d, *J* = 15.5 Hz, 1H), 6.31 (dt, *J* = 15.5, 7 Hz, 1 H), 4.28 (s, 1H), 3.23 (d, *J* = 6 Hz, 2H), 2.50-2.60 (b, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 136.7, 133.4, 128.4, 128.4, 127.7, 127.4, 126.8, 126.2, 125.8, 76.0, 60.8, 53.2, 51.5 ppm.

General Procedure and Characterization Data for the Synthesis of Ammonium Salts

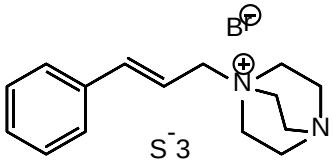
Note: To check the reactivity of tertiary amines with cinnamyl bromide and perhaps to prove the formation of ammonium salts, we run the following experiments:



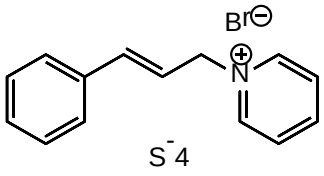
To a 10 mL round bottom flask containing trans-cinnamyl bromide (0.50 mmol), 2 mL diethyl ether were added. The reaction was stirred to produce a homogenous mixture, then (0.55 mmol, 1.10 equiv) of a tertiary amine was added. The reaction mixture was stirred during 1 h, filtered and dried under reduced pressure to afford pure solid.



N-Cinnamyl-2,3,4,6,7,8,9,10-octahydropyrimidonium[1,2-a]azepine bromide (**S-2**).[S17] White solid (157 mg, 90%). ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 15.5 Hz, 2H), 7.28 (t, *J* = 15 Hz, 1H), 6.62 (d, *J* = 16 Hz, 1H), 6.31 (dt, *J* = 16, 5.5 Hz, 1H), 4.35 (d, *J* = 4 Hz, 2H), 3.65-3.67 (m, 2H), 3.48-3.53 (m, 4H), 2.87-2.90 (m, 2H), 2.03 (pent, *J* = 5.5 Hz 2H), 1.62-1.69 (m, 6H); ^{13}C NMR (125 Hz, d_6-DMSO) δ 166.8, 136.4, 132.2, 129.0, 128.4, 126.9, 123.9, 55.0, 54.5, 48.9, 47.1, 28.2, 27.9, 25.9, 22.9, 19.9 ppm.

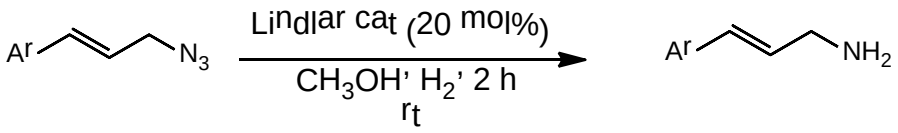


N-Cinnamyl triethylenediaminium bromide (**S-3**). Vivid white solid (152 mg, 98%). IR (neat, cm^{-1}): 3026, 2951, 1596, 696. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.38-7.41 (m, 2H), 7.34-7.36 (m, 2H), 6.88 (d, *J* = 16 Hz, 1H), 6.46 (dt, *J* = 16, 7.5 Hz, 1H), 4.08 (d, *J* = 7.5 Hz, 2H), 3.35 (t, *J* = 13.5 Hz, 8H), 3.04 (t, *J* = 15 Hz, 4H); ^{13}C NMR (125 Hz, d_6-DMSO) δ 140.5, 135.4, 129.0, 128.8, 127.3, 116.4, 65.1, 51.7, 44.9 ppm. HRMS (APCI/IT-TOF) *m/z*: [M – Br]$^+$ Calcd for $C_{15}H_{21}N_2$ 229.1699; Found 229.1661.

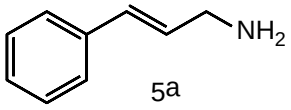


N-Cinnamylpyridinium bromide (**S-4**). White solid (108 mg, 78%). IR (neat, cm^{-1}): 3474, 3051, 2962, 1601, 1588, 1014, 726. ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.27 (d, *J* = 6 Hz, 2H), 8.66 (t, *J* = 15 Hz, 1H), 8.21 (t, *J* = 14.5 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 15 Hz, 2H), 7.27-7.29 (m, 1H), 6.96 (d, *J* = 16 Hz, 1H), 6.66 (dt, *J* = 16, 7 Hz, 1H), 5.55 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 Hz, d_6-DMSO) δ 145.9, 144.8, 136.6, 135.3, 128.8, 128.7, 128.3, 126.9, 122.6, 62.0 ppm. HRMS (APCI/IT-TOF) *m/z*: [M – Br]$^+$ Calcd for $C_{14}H_{14}N$ 196.1121; Found 196.1093.

Synthesis of *(E)*-3-Phenylprop-2-en-1-amine Derivatives:

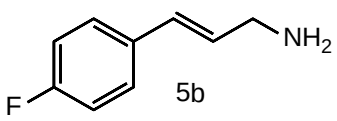


To a flame dried 10 mL round bottom flask; 0.40 mmol, 1.0 equivalent of allylic azide, 2 mL of dry methanol, and 20 mol% of Lindlar catalyst were added. Then, H_2 gas was bubbled into the reaction and stirred for 2 h. After the reaction has deemed completed (by TLC), the reaction mixture was filter over a Celite pad. Finally, the filtrate was evaporated under reduced pressure.



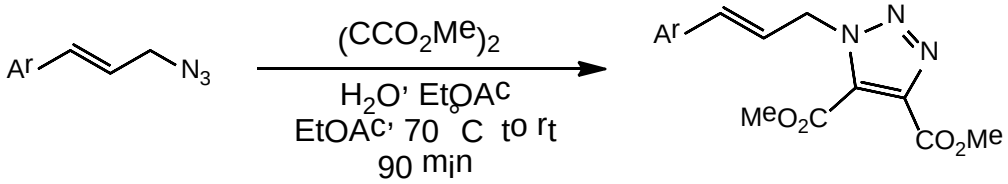
(E)-3-phenylprop-2-en-1-amine (**5a**).[S18] Prepared from **3a** following the representative procedure. Yellow solid (48 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 15.5 Hz, 2H), 7.20 (t, *J* = 14.5Hz, 1H), 6.55 (d, *J* = 16 Hz, 1H), 6.22 (dt, *J* = 15.5, 5.5 Hz, 1H), 3.42 (d, *J* = 6 Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 138.2, 132.4, 129.5, 129.1, 128.5, 127.3, 44.1 ppm.

[S17] X. Huang, B. Fulton, K. White, A. Bugarin, *Org. Lett.*, 2015, **17**, 2594-2597.
[S18] X. Huang, N. Jiao, *Org. Biomol. Chem.*, 2014, **12**, 4324-4328.

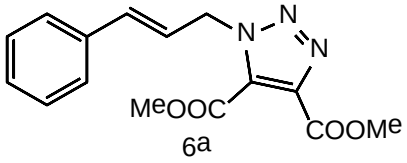


(E)-3-(4-fluorophenyl)prop-2-en-1-amine (**5b**). Prepared from **3b** following the representative procedure. Pale white semi-solid (51 mg, 84%). IR (neat, cm^{-1}): 3340, 3249, 2962, 2403, 1656, 1506, 1223, 848, 818. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.32 (m, 2H), 6.93-7.01 (m, 2H), 6.45 (d, *J* = 16 Hz, 1H), 6.22 (dt, *J* = 15.5, 5.5 Hz, 1H), 3.45 (t, *J* = 15.5 Hz, 2H), 2.04 (b, s, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 163.8 (d, $^1J_{CF}$ = 244.5 Hz) 134.3, 133.1, 129.3 (d, $^3J_{CF}$ = 7.1 Hz), 126.2, 116.3 (d, $^2J_{CF}$ = 21.5), 43.4 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{11}FN$ 152.0870; Found 152.0882.

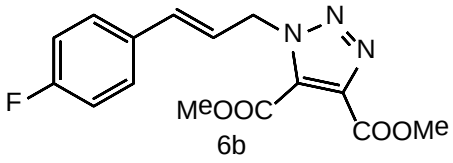
Synthesis of 1,2,3-Triazole-4,5-dicarboxylate Derivatives



To a round-bottom flask (rbf) containing allylic azide (0.63 mmol), 2 mL of water were added and (0.69 mmol) of dimethyl acetylene dicarboxylate were added as well. The mixture was stirred in a pre-heated oil bath at 70 °C for 1 h. Then, reaction mixture was cooled down to room temperature followed by the addition of 3 mL of EtOAc, and the stirring was continued for 30 minutes. The mixture was extracted, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the resulting oil was isolated using silica gel flash chromatography to afford pure products.



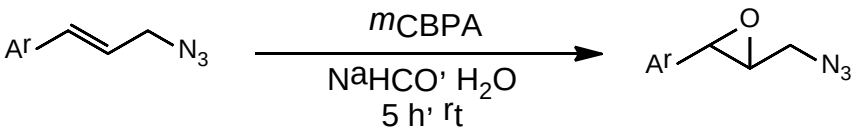
Dimethyl 1-cinnamyl-1H-1,2,3-triazole-4,5-dicarboxylate (**6a**).[S19] Prepared from **3a** following the representative procedure. Colorless oil (162 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.32 (m, 5H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.26 (dt, *J* = 15.5, 6 Hz, 1H), 5.33 (dd, *J* = 6.0, 1.0 Hz, 2H), 3.92 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 158.7, 139.8, 135.7, 135.1, 129.7, 128.5, 128.4, 126.5, 120.9, 53.2, 52.5, 52.3 ppm.



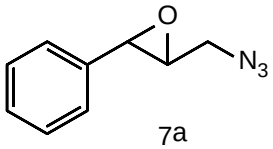
Dimethyl 1-(4-fluorocinnamyl)-1H-1,2,3-triazole-4,5-dicarboxylate (**6b**). Prepared from **3b** following the representative procedure. Colorless oil (164 mg, 82%). IR (neat, cm^{-1}): 2954, 1729, 1508, 1220, 751. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.31 (m, 2H), 6.96-7.00 (m, 2H), 6.59 (d, *J* = 16 Hz, 1H), 6.20 (dt, *J* = 16, 6.5 Hz, 1H), 5.35 (d, *J* = 6.5 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7 (d, $^1J_{CF}$ = 246.8 Hz), 160.3, 158.8, 140.0, 134.6, 131.4 (d, $^4J_{CF}$ = 2.3 Hz), 129.7, 128.3 (d, $^3J_{CF}$ = 8.3 Hz), 120.7, 115.6 (d, $^2J_{CF}$ = 21.5), 53.3, 52.6, 52.3 ppm. HRMS (APCI/IT-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}FN_3O_4$ 320.1041; Found 320.1015.

[S19] Y. Uozumi, T. Suzuka, R. Kawade, H. Takenaka, *Synlett*, 2006, **13**, 2109-2113.

Synthesis of Azidophenyl Oxirane Derivatives

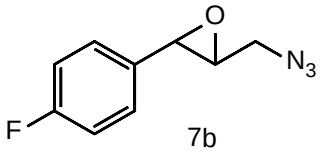


0.40 mmol of allylic azide and 3 mL of 0.30 M aqueous solution of $NaHCO_3$ were added into an oven dried 10 mL rbf. To this mixture, (0.48 mmol, 1.2 equiv) *m*-CPBA was added over 5 minutes. The reaction mixture was vigorously stirred, at room temperature for 5 h. Upon completion of the reaction, the reaction mixture was extracted three times using diethyl ether and washed twice with 10% aqueous NaOH. Dried over $MgSO_4$ and the extract was filtered and concentrated under reduced pressure. The resulting oil was purified using silica gel flash chromatography.[S20]



7a

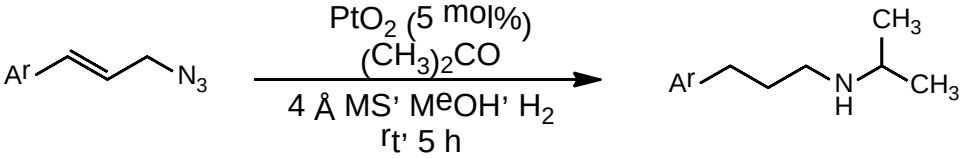
2-(azidomethyl)-3-phenyloxirane (**7a**).[S21] Prepared from **3a** following the representative procedure. Colorless oil (40 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.38 (m, 3H), 7.27-7.29 (m, 2H), 3.86 (d, *J* = 2 Hz, 1H), 3.66 (dd, *J* = 13.5, 3.0 Hz, 1H), 3.45 (dd, *J* = 13.5, 5 Hz, 1H), 3.24 (sep, *J* = 2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.0, 128.5, 128.5, 125.6, 60.2, 56.3, 51.6 ppm.



7b

2-(azidomethyl)-3-(4-fluorophenyl)oxirane (**7b**). Prepared from **3b** following the representative procedure. Colorless oil (39 mg, 51%). IR (neat, cm^{-1}): 2925, 2097, 1607, 1511, 1220, 831. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.26 (m, 2H), 7.03-7.07 (m, 2H), 3.85 (d, *J* = 1.5 Hz, 1H), 3.65 (dd, 13, 3 Hz, 1H), 3.45 (dd, 13.5, 4.5 Hz, 1H), 3.19 (seq, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 162.8 (d, $^1J_{CF}$ = 245.6 Hz), 131.8, 127.3 (d, $^3J_{CF}$ = 8.3 Hz), 115.6 (d, $^2J_{CF}$ = 22.6 Hz), 60.2, 55.7, 51.5 ppm. HRMS (APCI/IT-TOF) *m/z*: [M + H - N_2]$^+$ Calcd for C_9H_9FNO 166.0663; Found 166.0636.

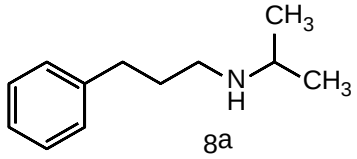
Synthesis of *N*-Isopropylpropan-1-amine Derivatives



To a 10 mL rbf, equipped with a magnetic stir bar, were added 0.60 mmol of allylic azide, 2 mL of methanol, 5 mol% of platinum oxide, (51 µL, 0.66 mmol) acetone, and 90 mg of (4 Å) molecular sieves. The reaction mixture was flushed and maintained with hydrogen gas (1 atm, balloon) and stirred during 5 h, at room temperature. Finally, the reaction mixture was filtered over a Celite pad. The crude filtrate was purified using flash column chromatography (SiO_2, methanol/DCM mixtures) to provide the respective pure products.

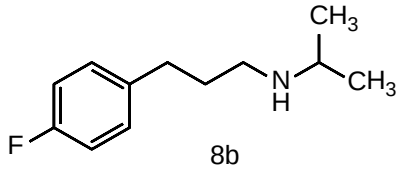
[S20] A. K. Feldman, B. Colasson, K. B. Sharpless, V. V. Fokin, *J. Am. Chem. Soc*., 2005, **127**, 13444-13445.

[S21] N. Viswanadh, P. Mujumdar, M. Sasikumar, S. S. Kunte, M. Muthukrishnan, *Tetrahedron Lett.*, 2016, **57**, 861-863.



8a

N-isopropyl-3-phenylpropan-1-amine (**8a**).[S22] Prepared from **3a** following the representative procedure. Colorless oil (87 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.24 (m, 2H), 7.12-7.15 (m, 3H), 3.07 (t, *J* = 6.5 Hz, 1H), 2.76 (t, *J* = 8 Hz, 2H), 2.62 (t, *J* = 8 Hz, 2H), 2.08 (q, *J* = 8 Hz, 2H), 1.25 (d, *J* = 6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 128.2, 128.1, 125.9, 49.6, 44.8, 32.9, 28.5, 20.0 ppm.



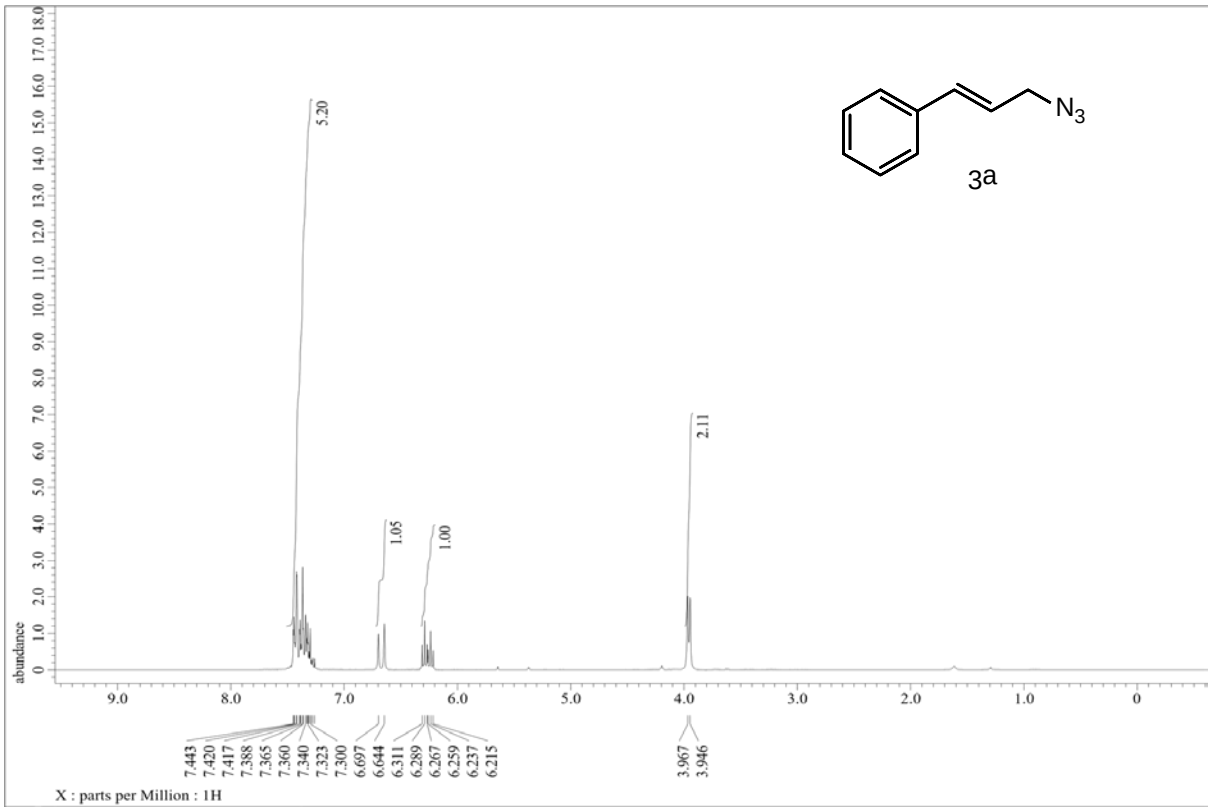
8b

3-(4-fluorophenyl)-N-isopropylpropan-1-amine (**8b**).[S23] Prepared from **3b** following the representative procedure. Colorless oil (94 mg, 80%). IR (neat, cm^{-1}): 3330, 3040, 2963, 1508, 1220. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.0, 5.5 Hz, 2H), 6.94 (t, *J* = 8.5 Hz, 2H), 2.85 (q, *J* = 6.5 Hz, 1H), 2.63 (q, *J* = 8 Hz, 4H), 1.85 (q, *J* = 7.5 Hz, 2H), 1.10 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2 (d, $^{1}J_{CF}$ = 242.1 Hz), 137.2, 129.6 (d, $^{3}J_{CF}$ = 7.1 Hz), 114.5 (d, $^{2}J_{CF}$ = 20.2), 48.9, 46.2, 32.7, 31.1, 22.1 ppm.

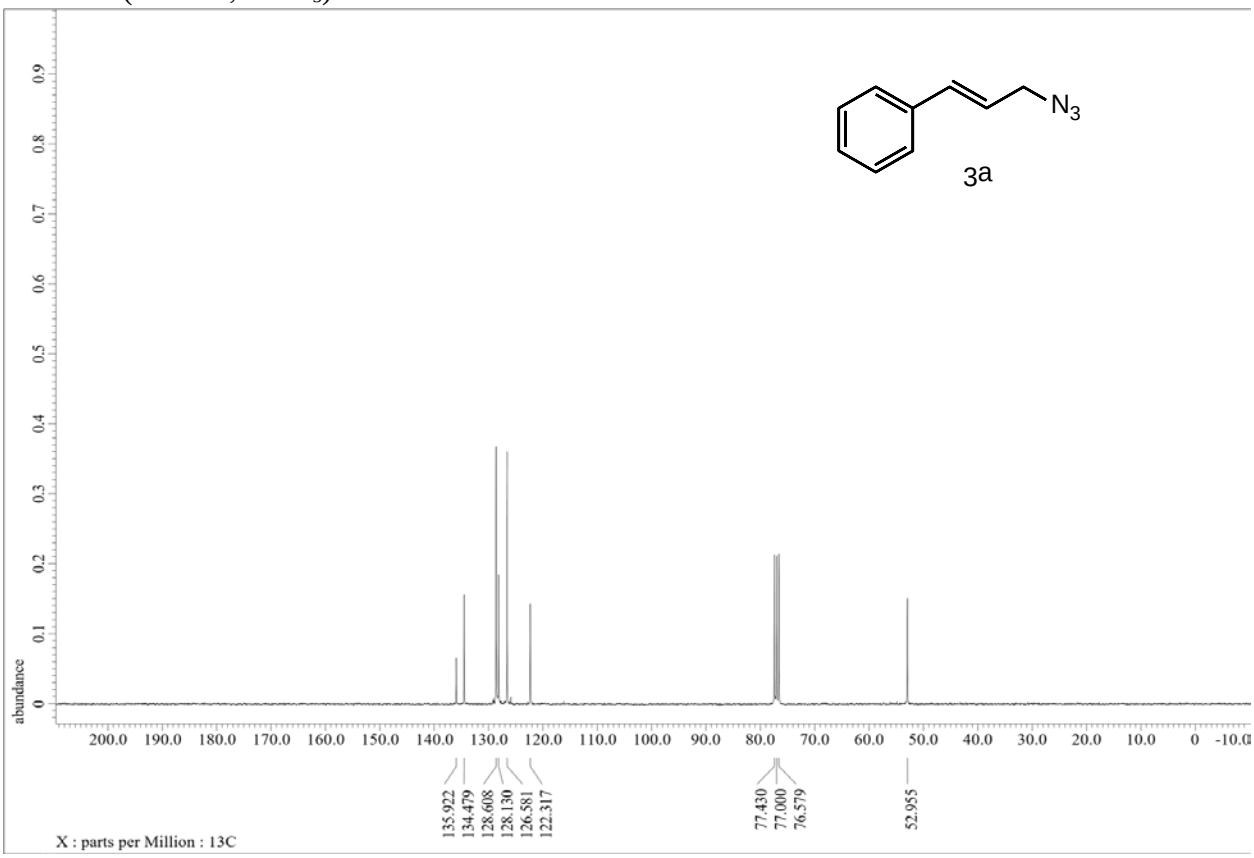
[S22] P. Huang, H. Geng, *Org. Chem. Front.*, 2015, **2**, 150-158.
[S23] Y. Lin, E. B. Ali, H. Alper, *Tetrahedron Lett.*, 2001, **42**, 2423-2425.

^{1}H NMR & ^{13}C NMR SPECTRA

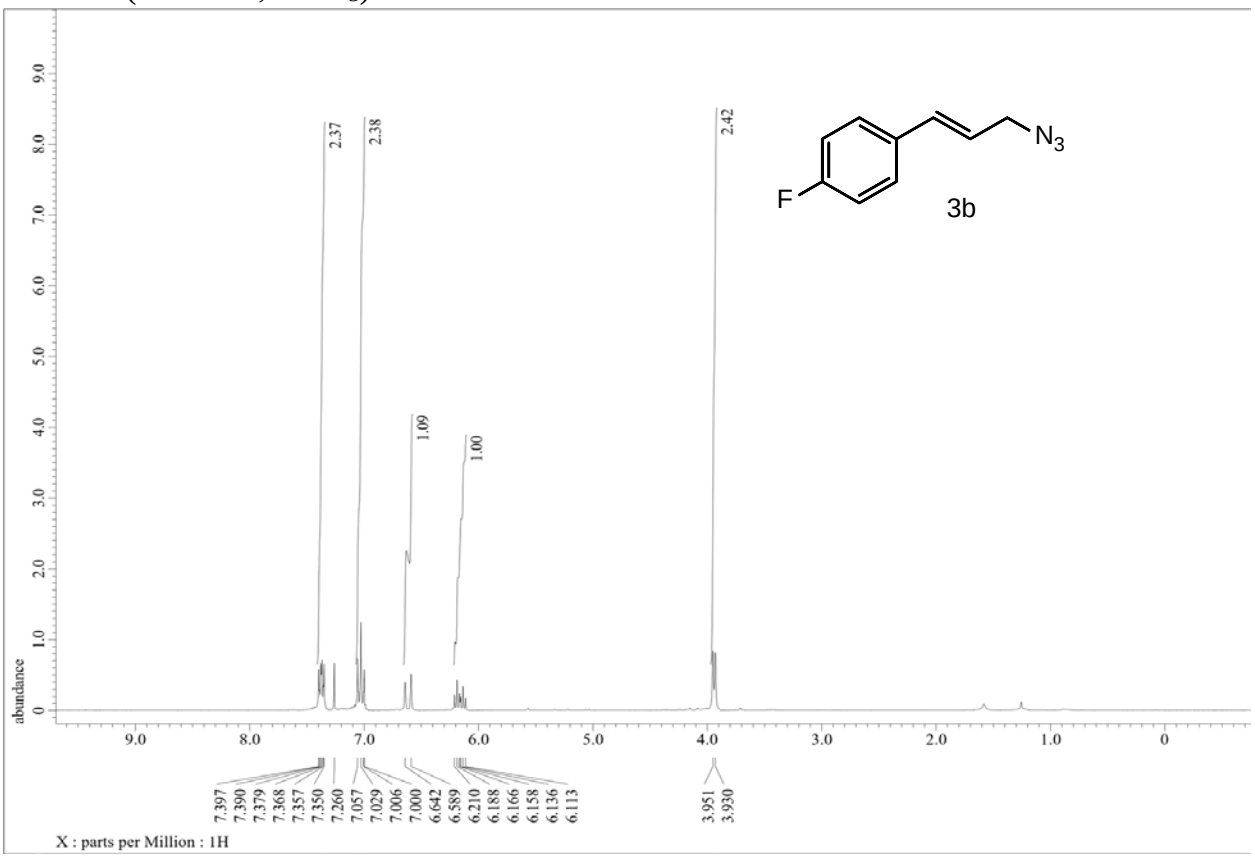
^{1}H NMR (300 MHz, $CDCl_3$)



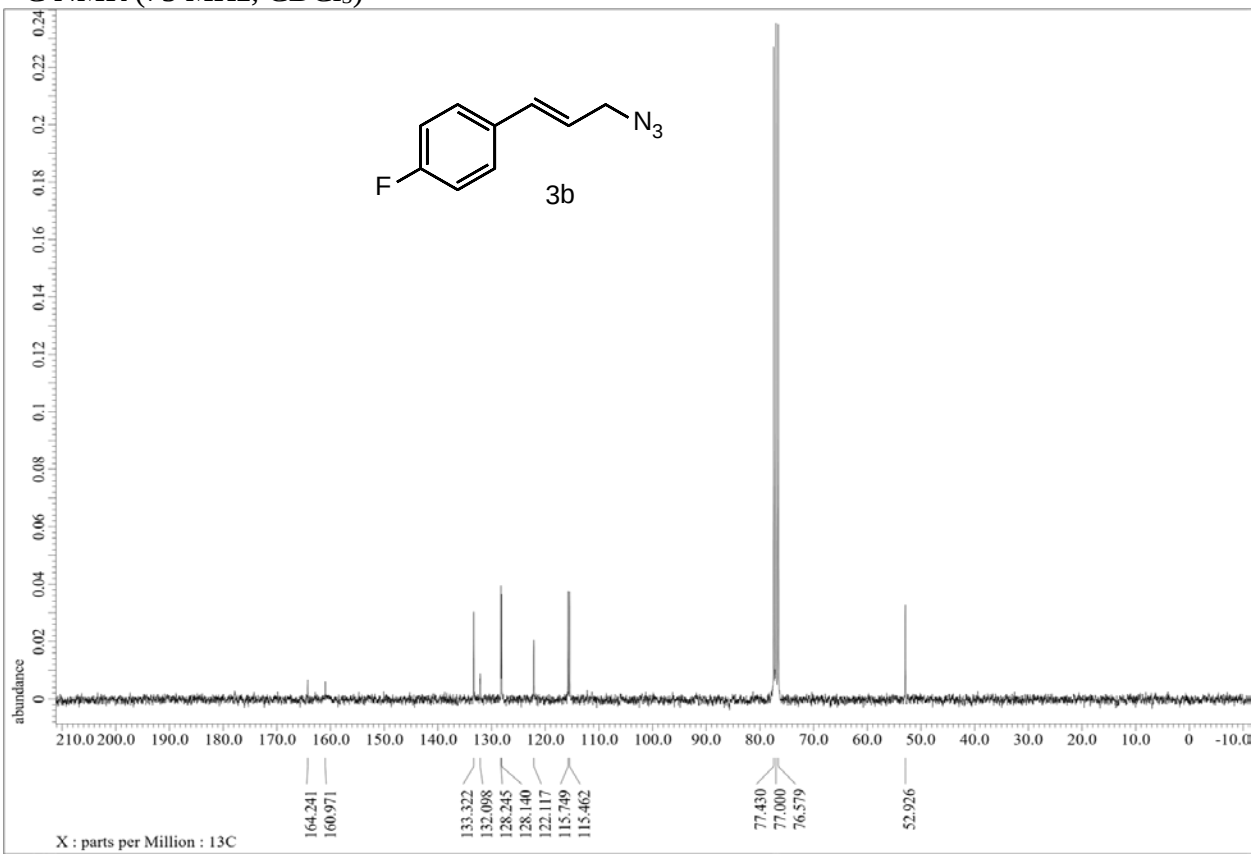
^{13}C NMR (75 MHz, $CDCl_3$)



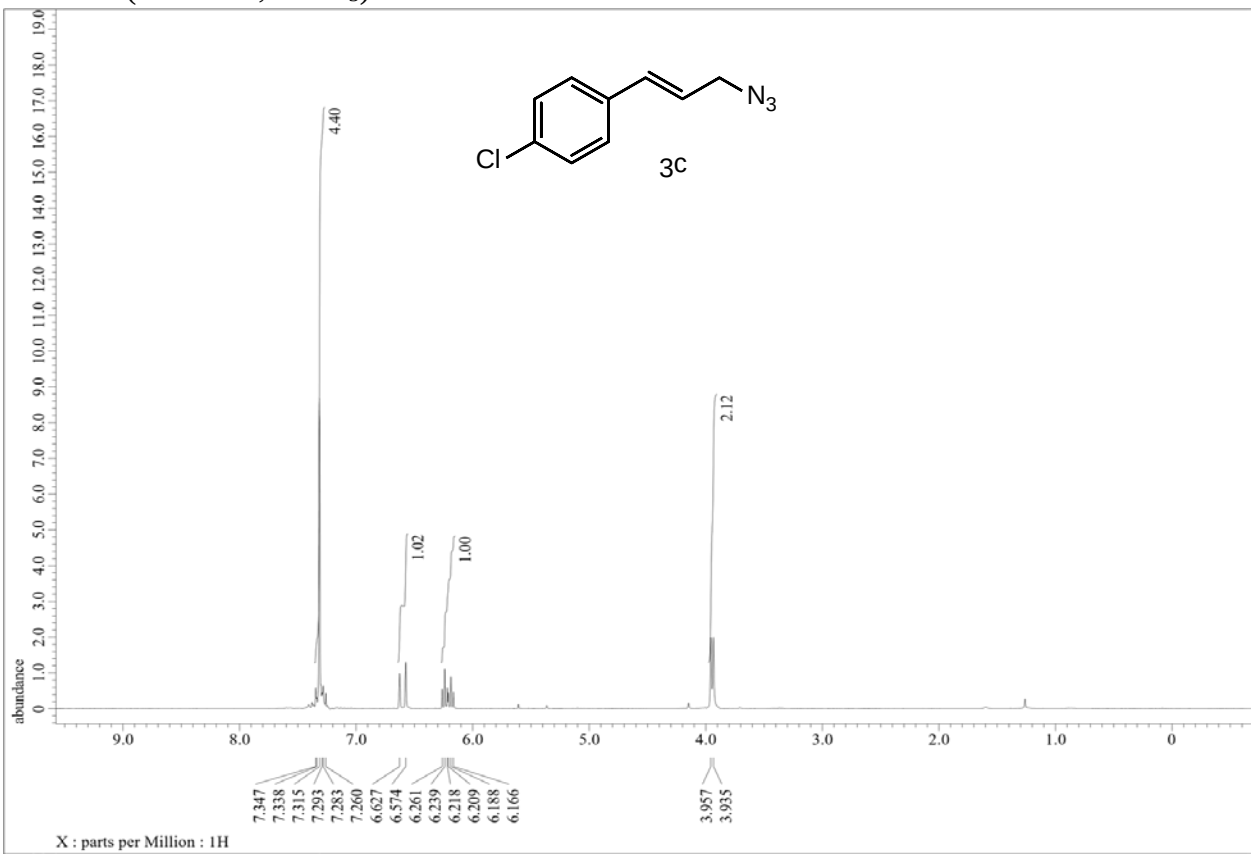
^{1}H NMR (300 MHz, $CDCl_3$)



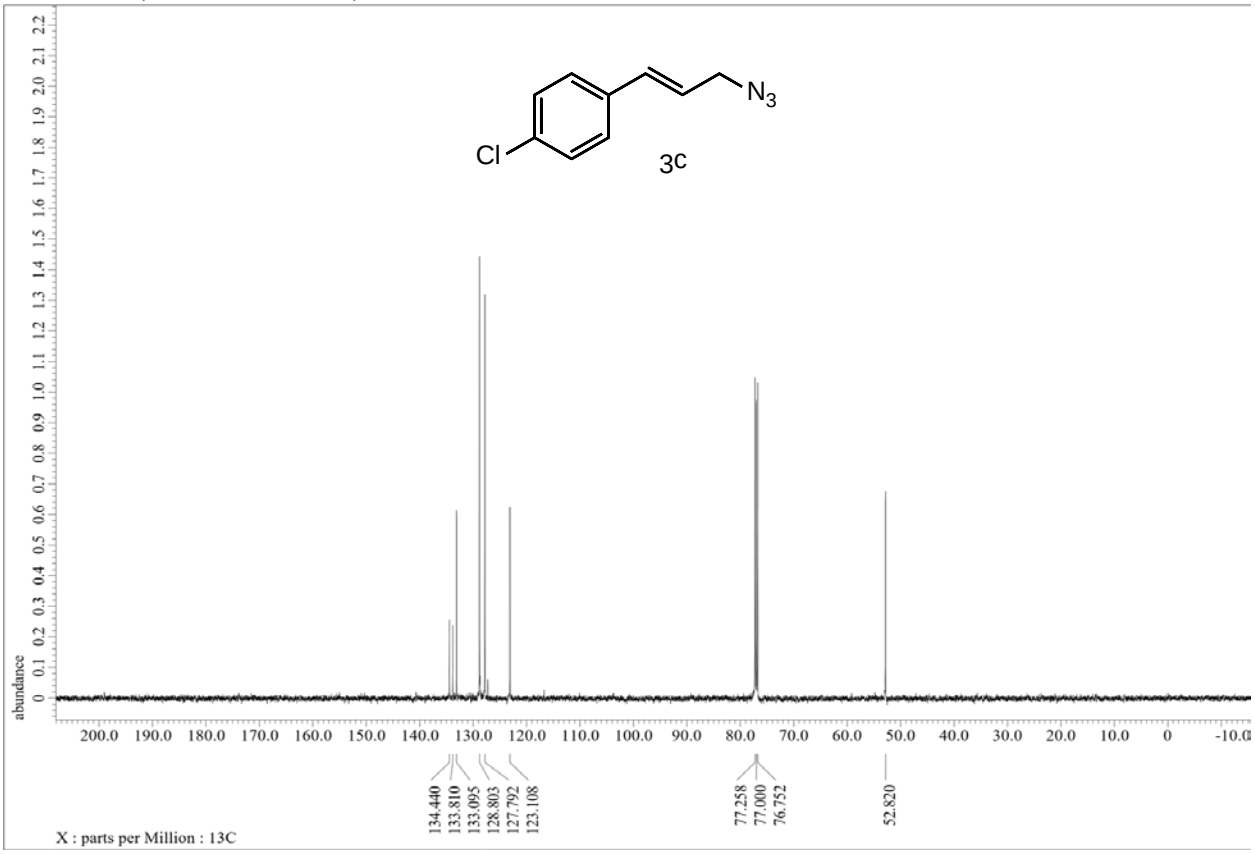
^{13}C NMR (75 MHz, $CDCl_3$)



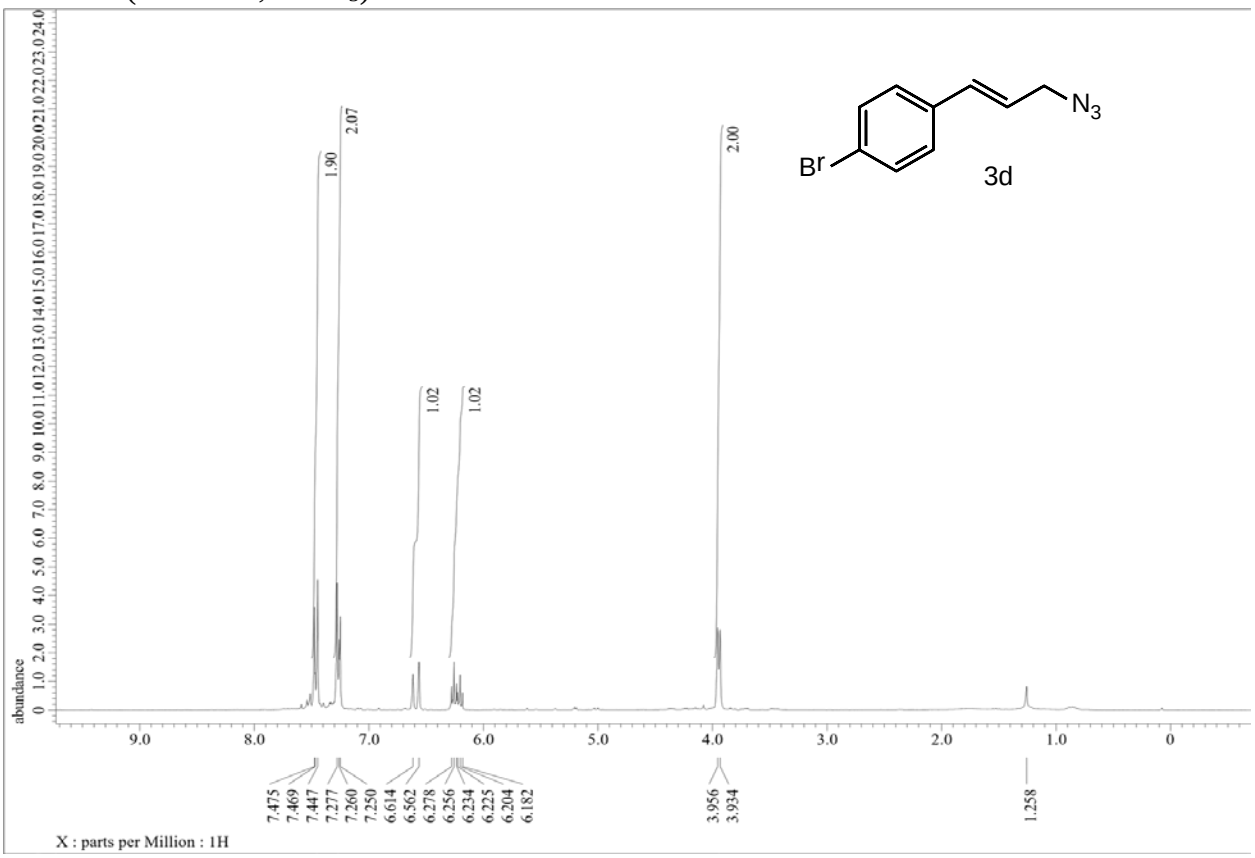
^{1}H NMR (300 MHz, $CDCl_3$)



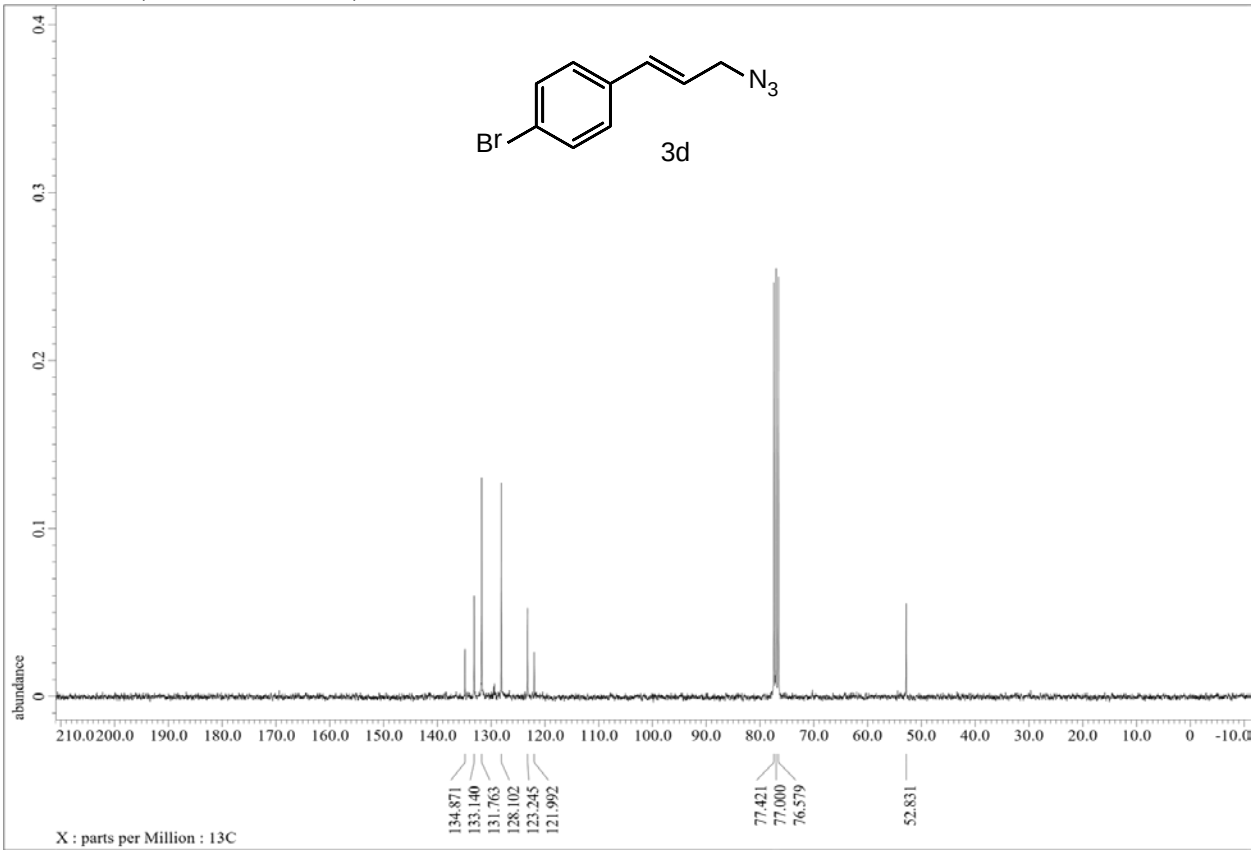
^{13}C NMR (75 MHz, $CDCl_3$)



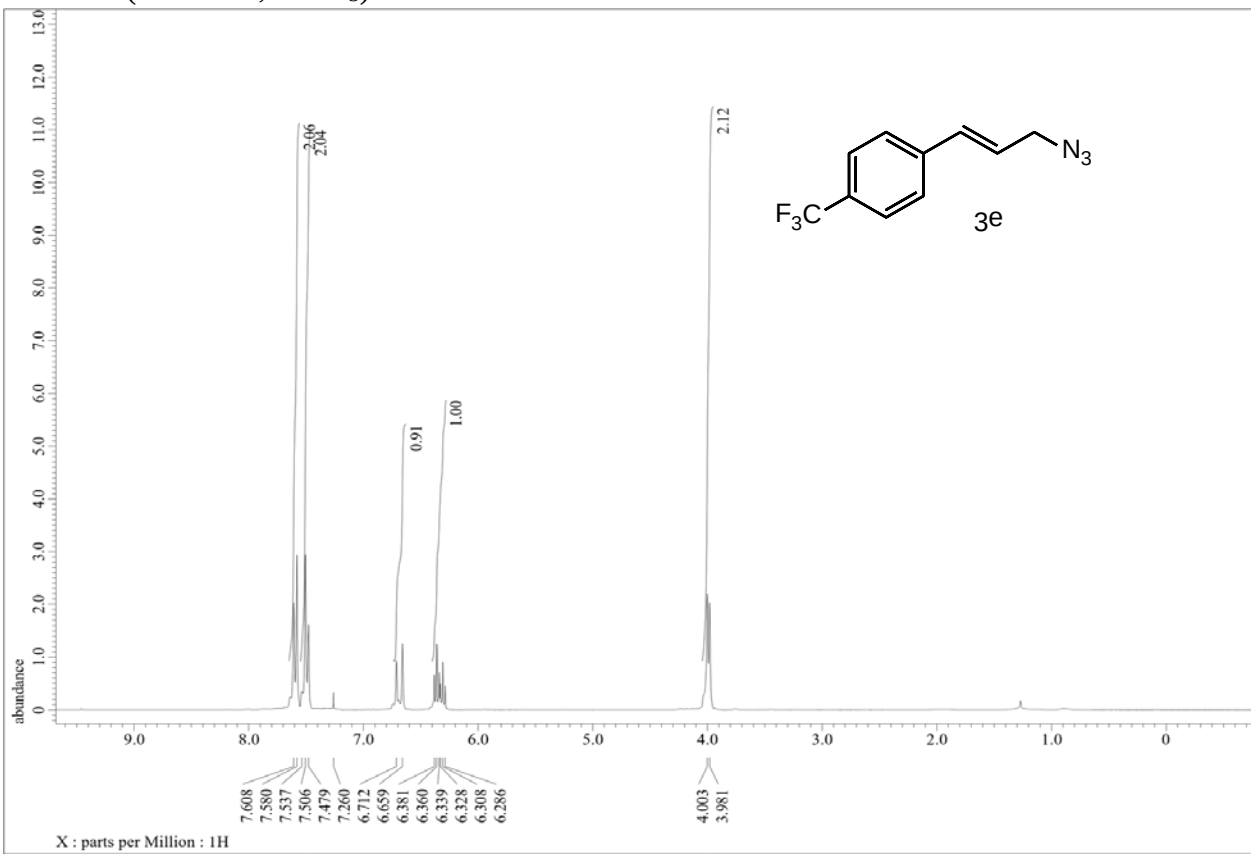
^{1}H NMR (300 MHz, $CDCl_3$)



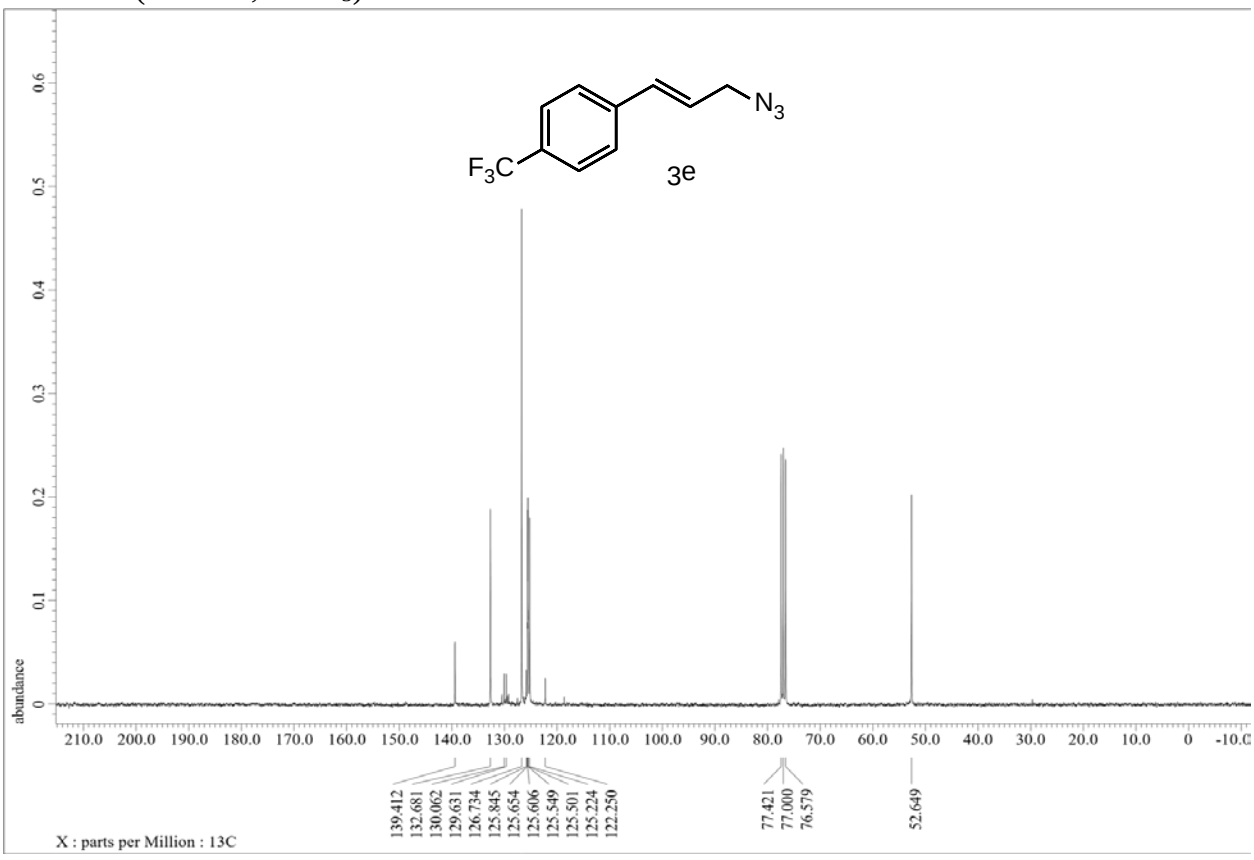
^{13}C NMR (75 MHz, $CDCl_3$)



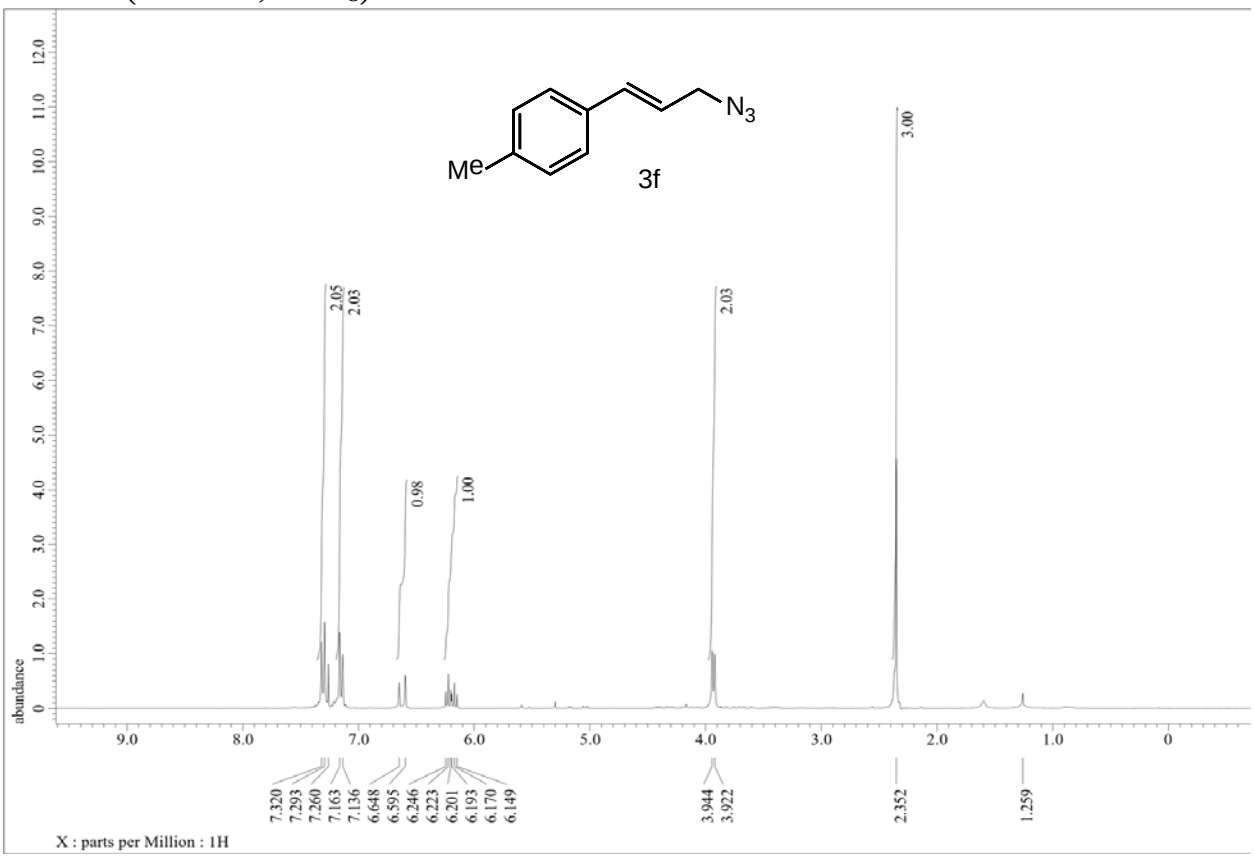
^{1}H NMR (300 MHz, $CDCl_3$)



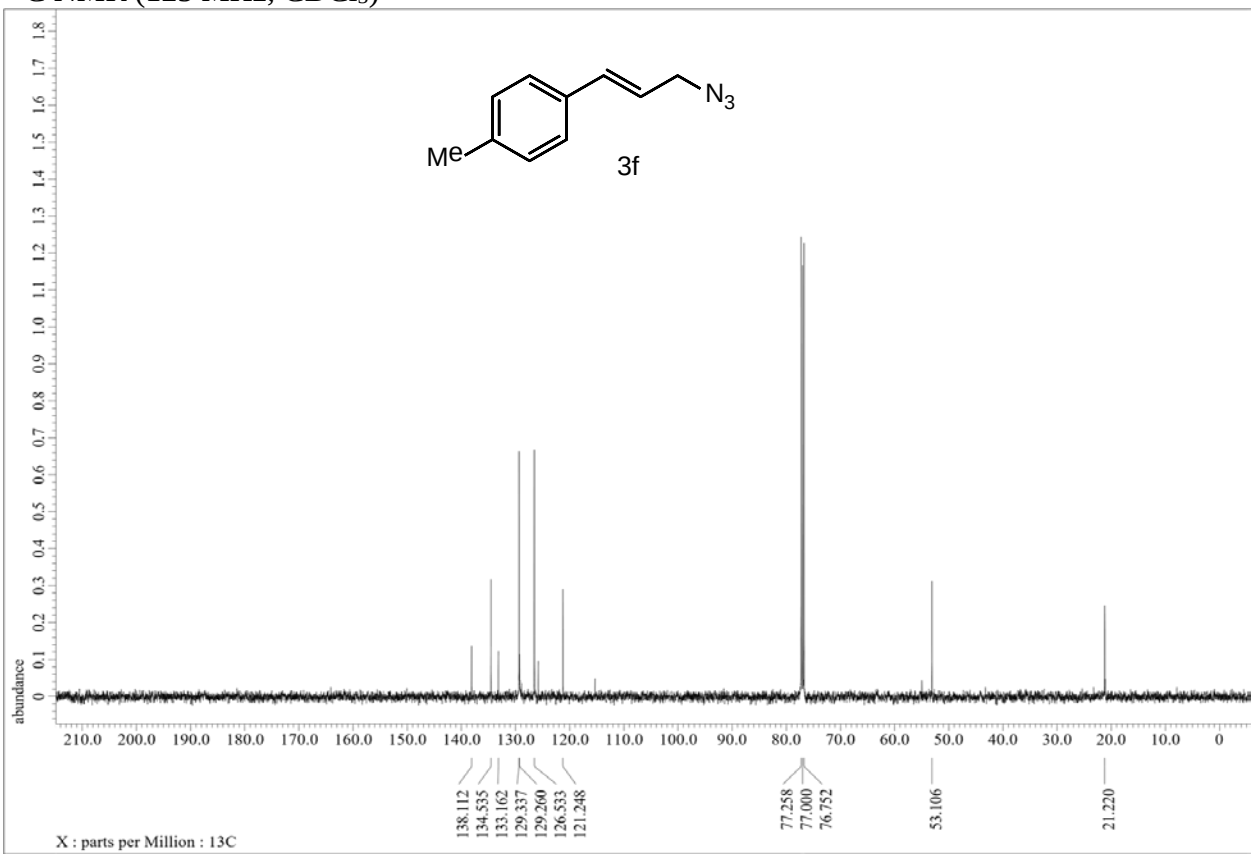
^{13}C NMR (75 MHz, $CDCl_3$)



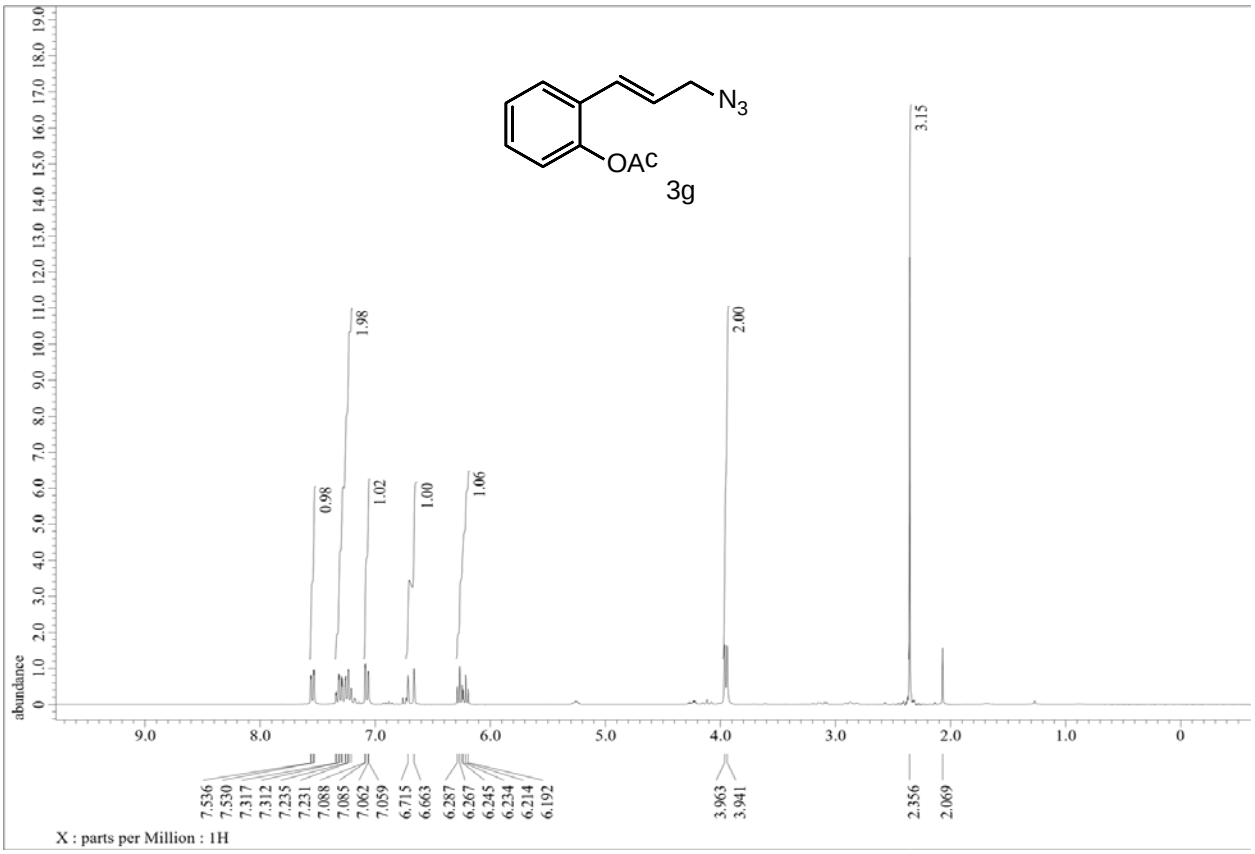
^{1}H NMR (300 MHz, $CDCl_3$)



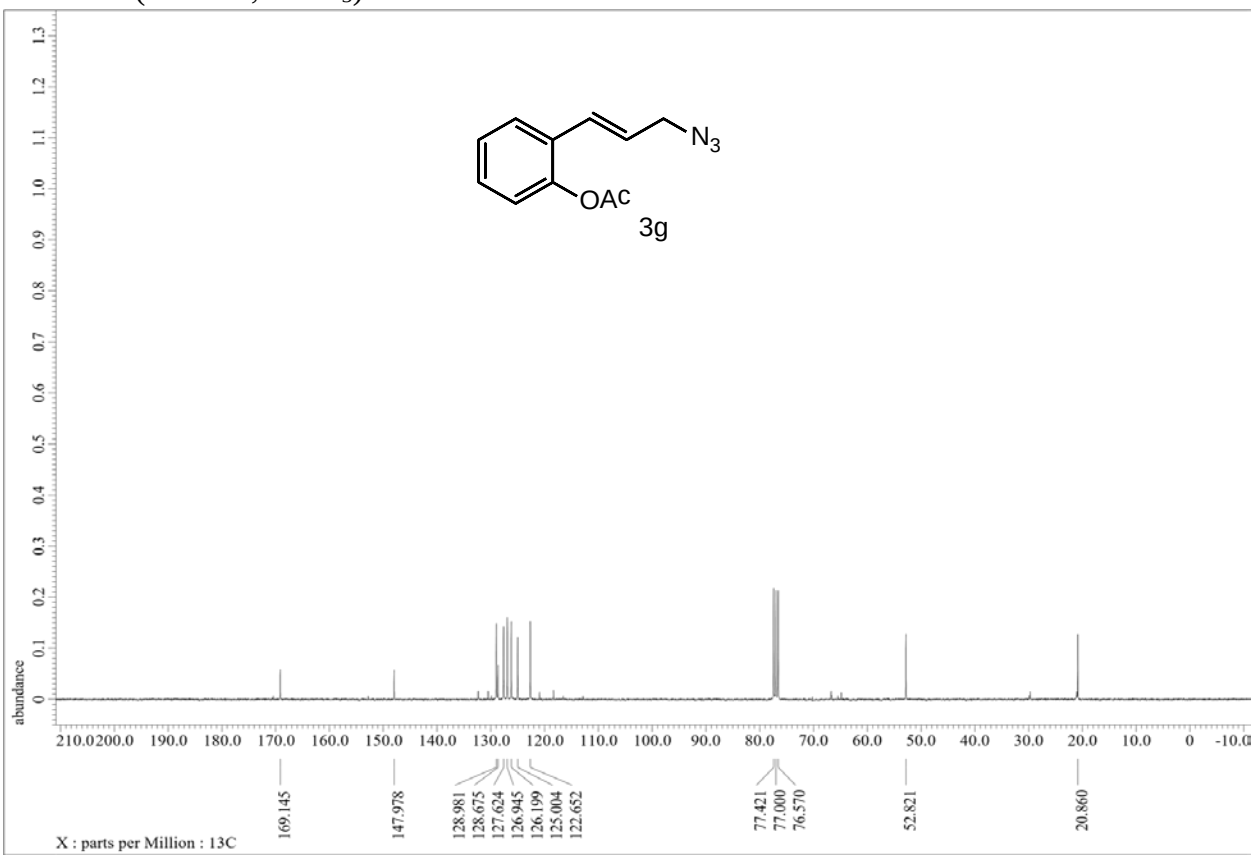
^{13}C NMR (125 MHz, $CDCl_3$)



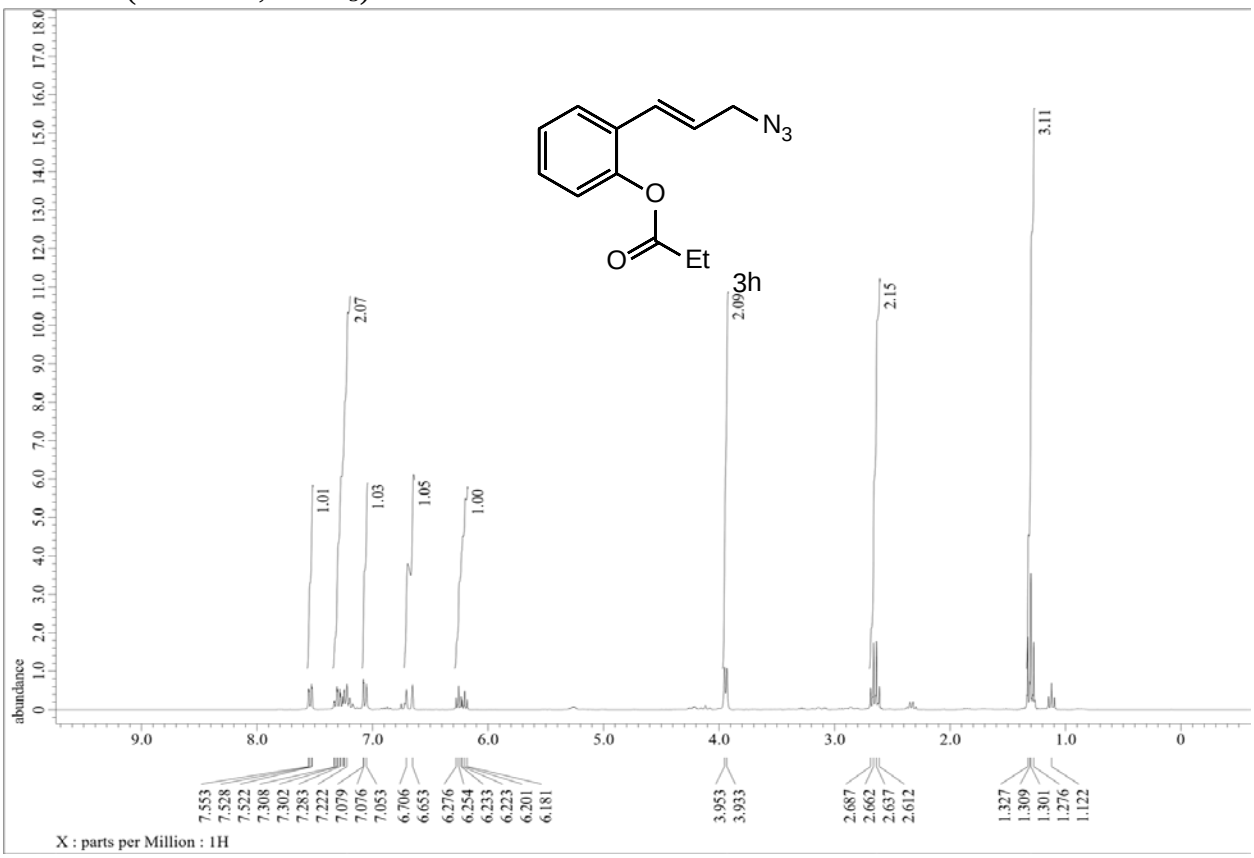
^{1}H NMR (300 MHz, $CDCl_3$)



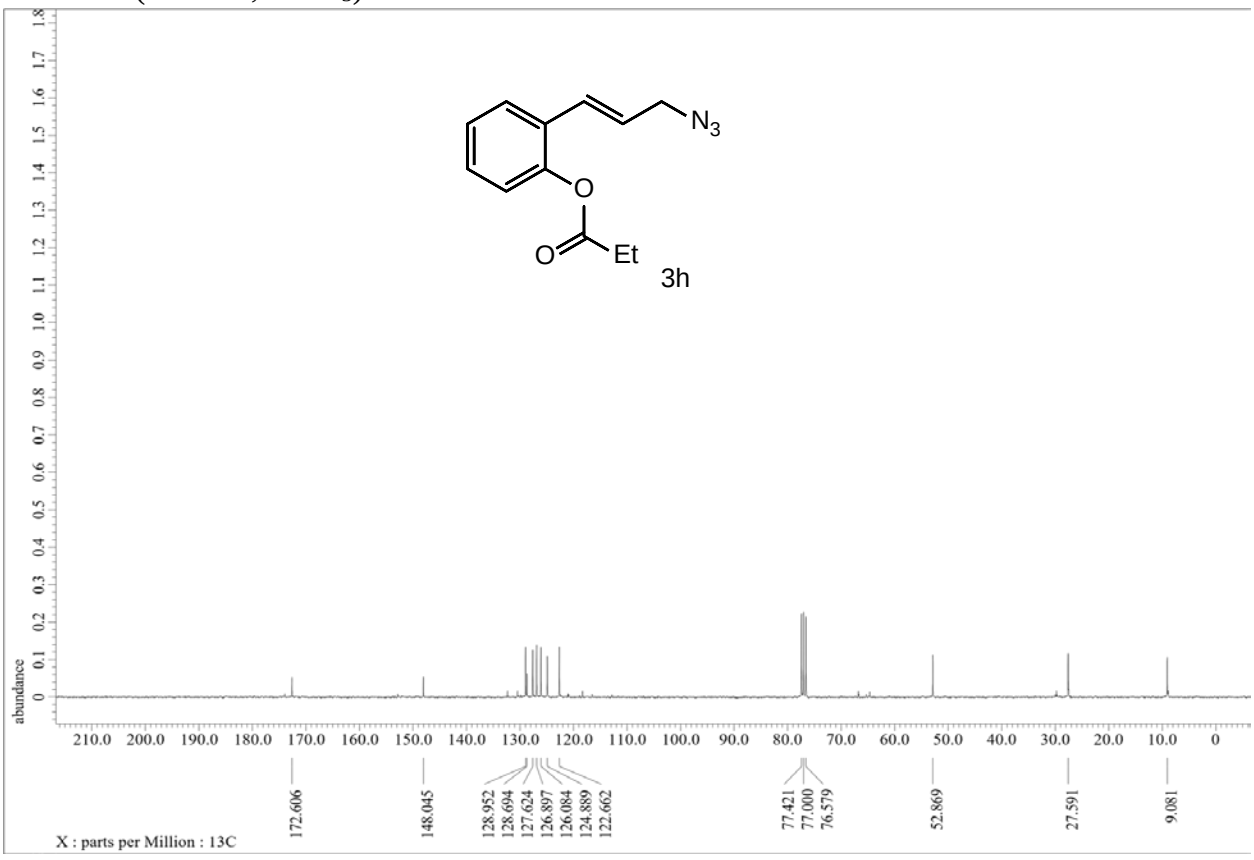
^{13}C NMR (75 MHz, $CDCl_3$)



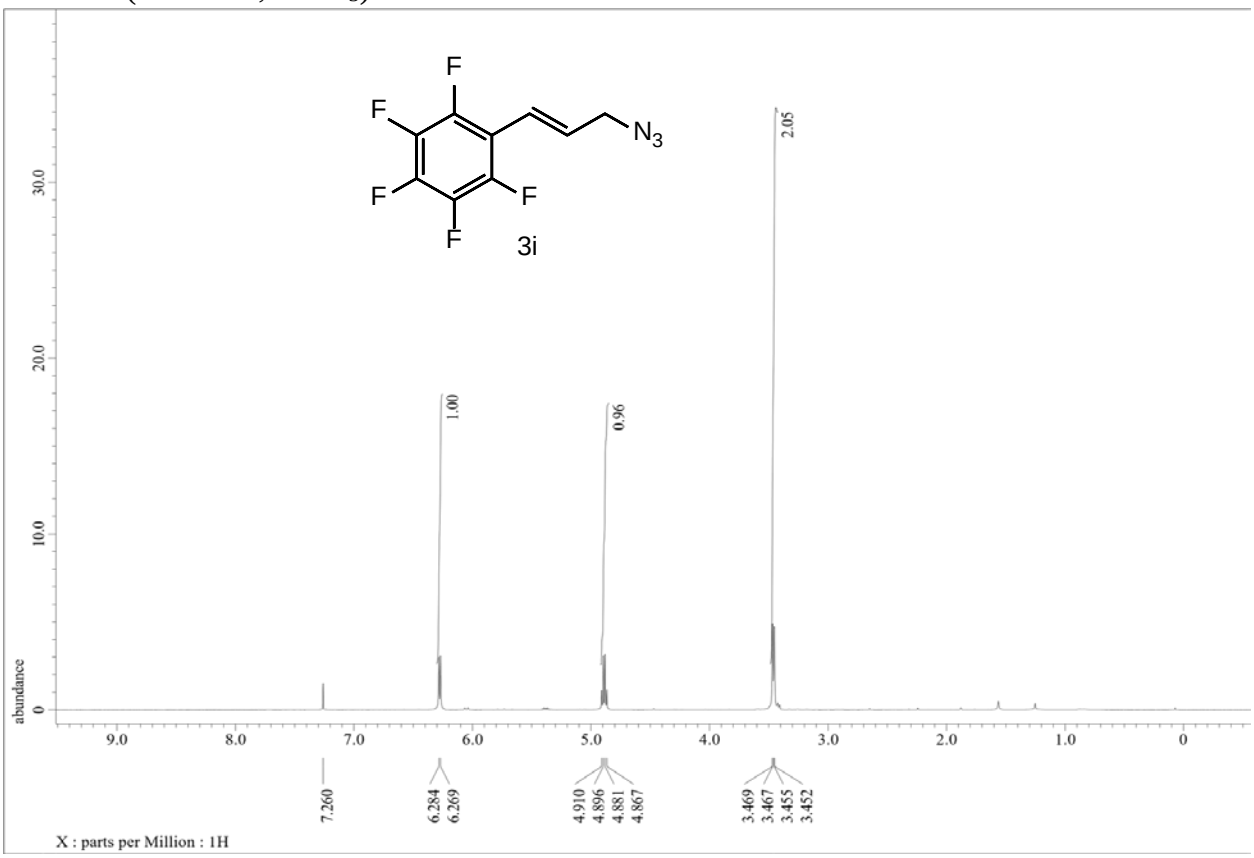
^{1}H NMR (300 MHz, $CDCl_3$)



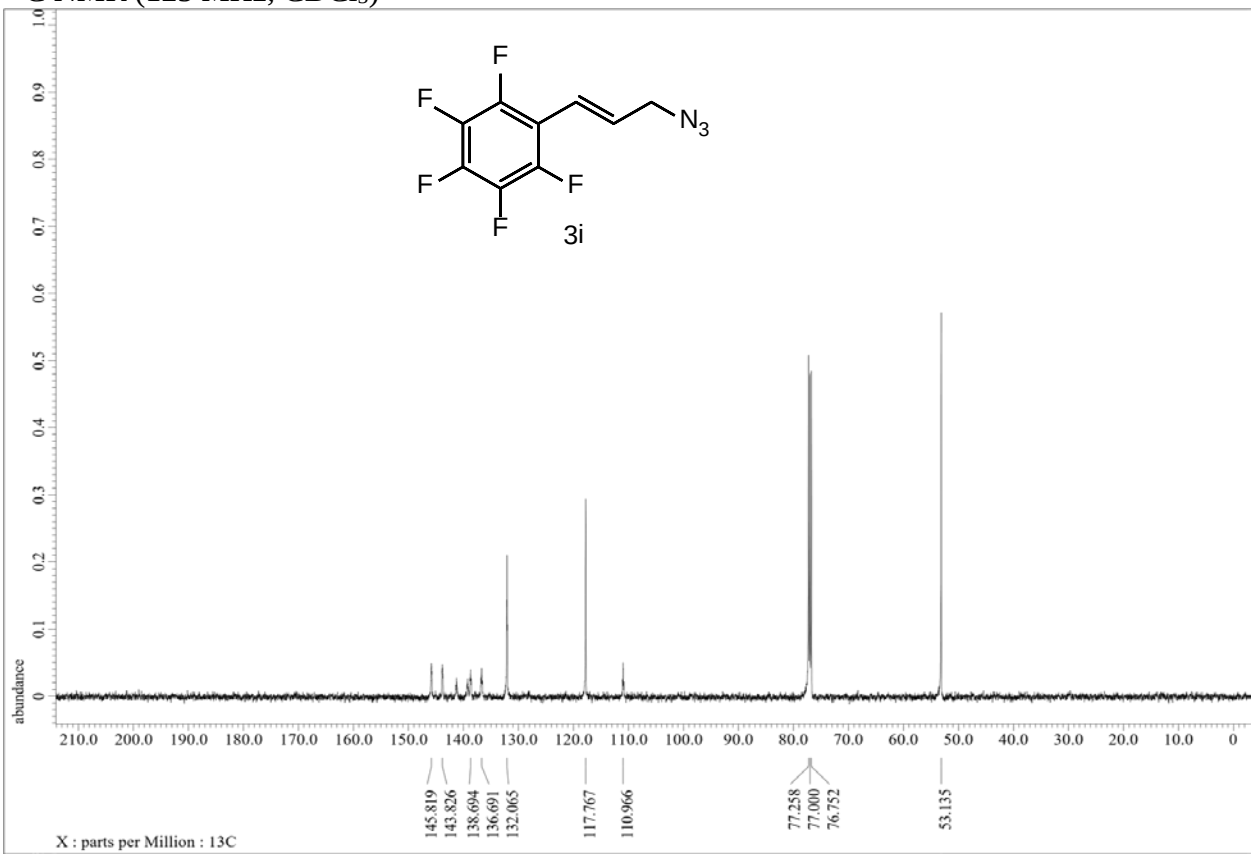
^{13}C NMR (75 MHz, $CDCl_3$)



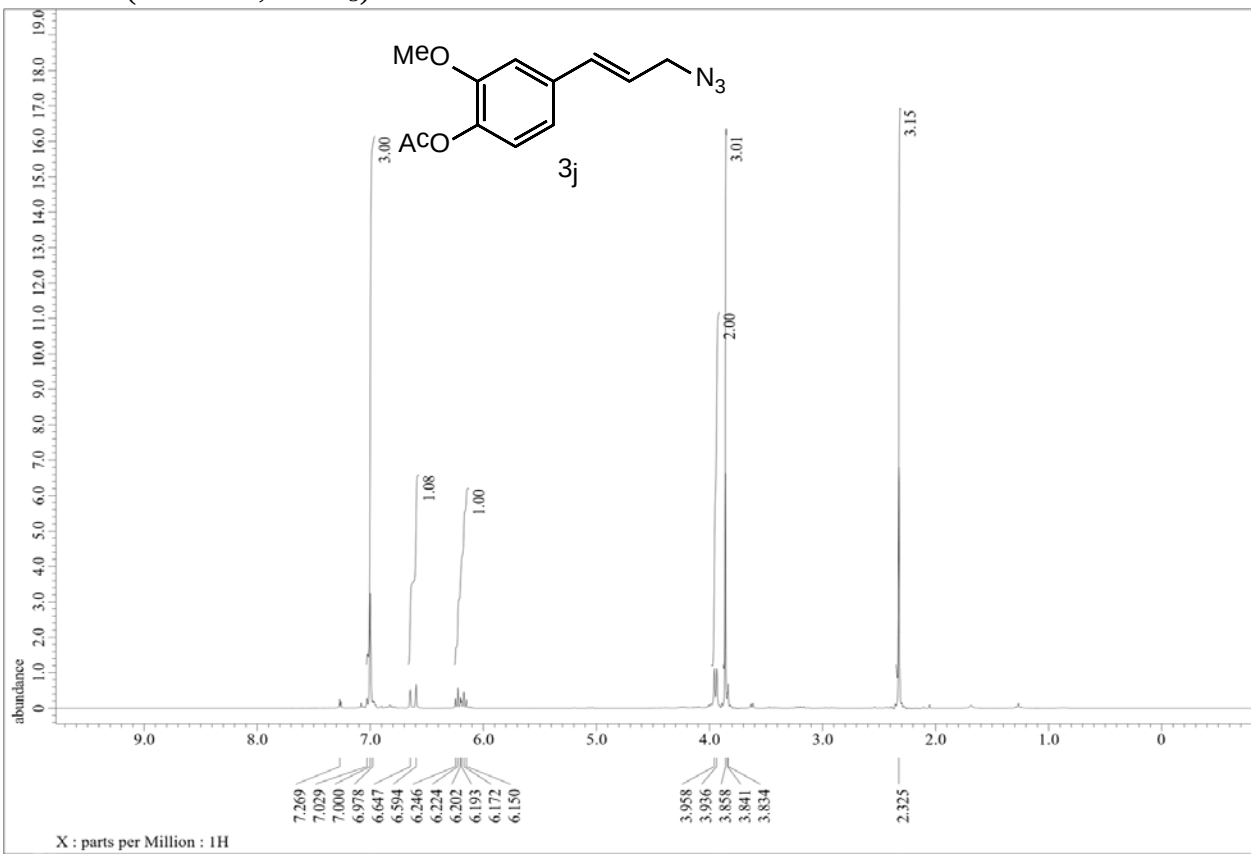
^{1}H NMR (500 MHz, $CDCl_3$)



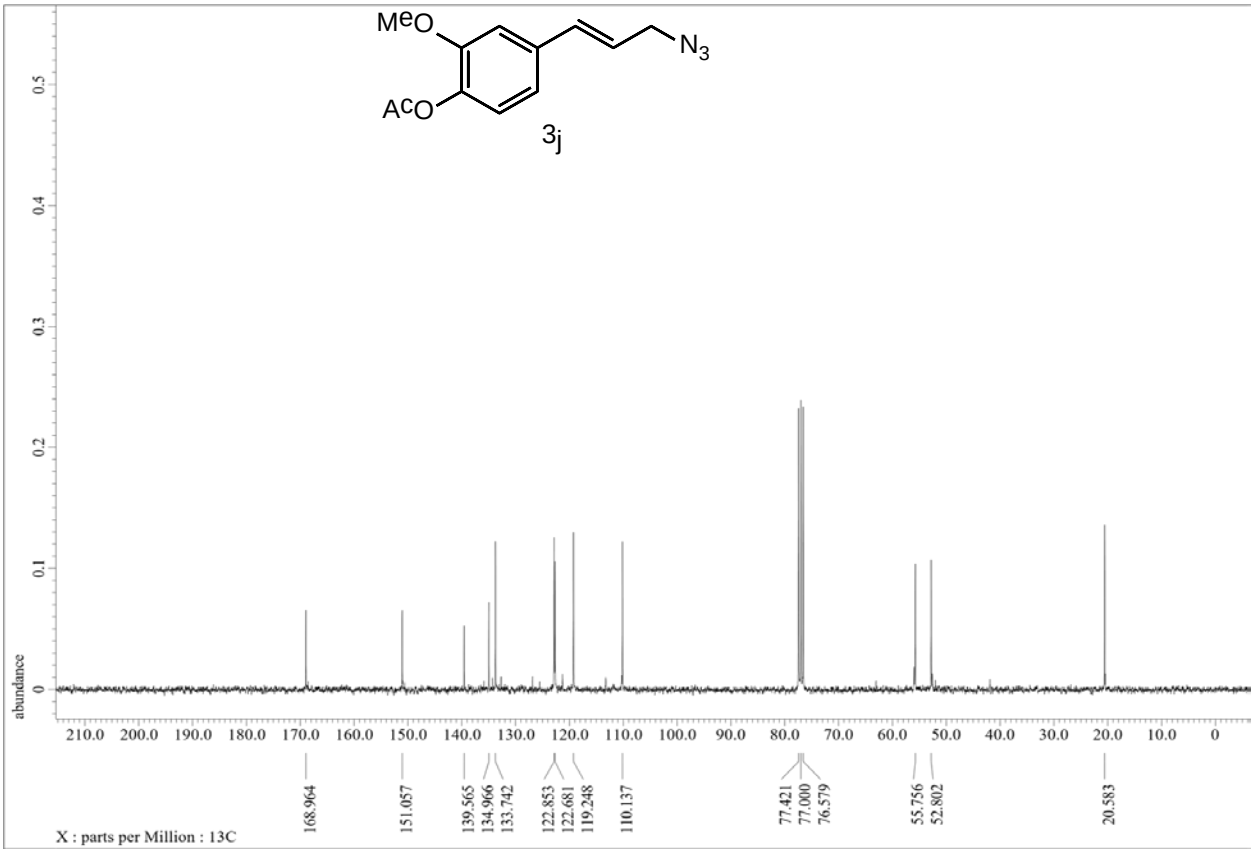
^{13}C NMR (125 MHz, $CDCl_3$)



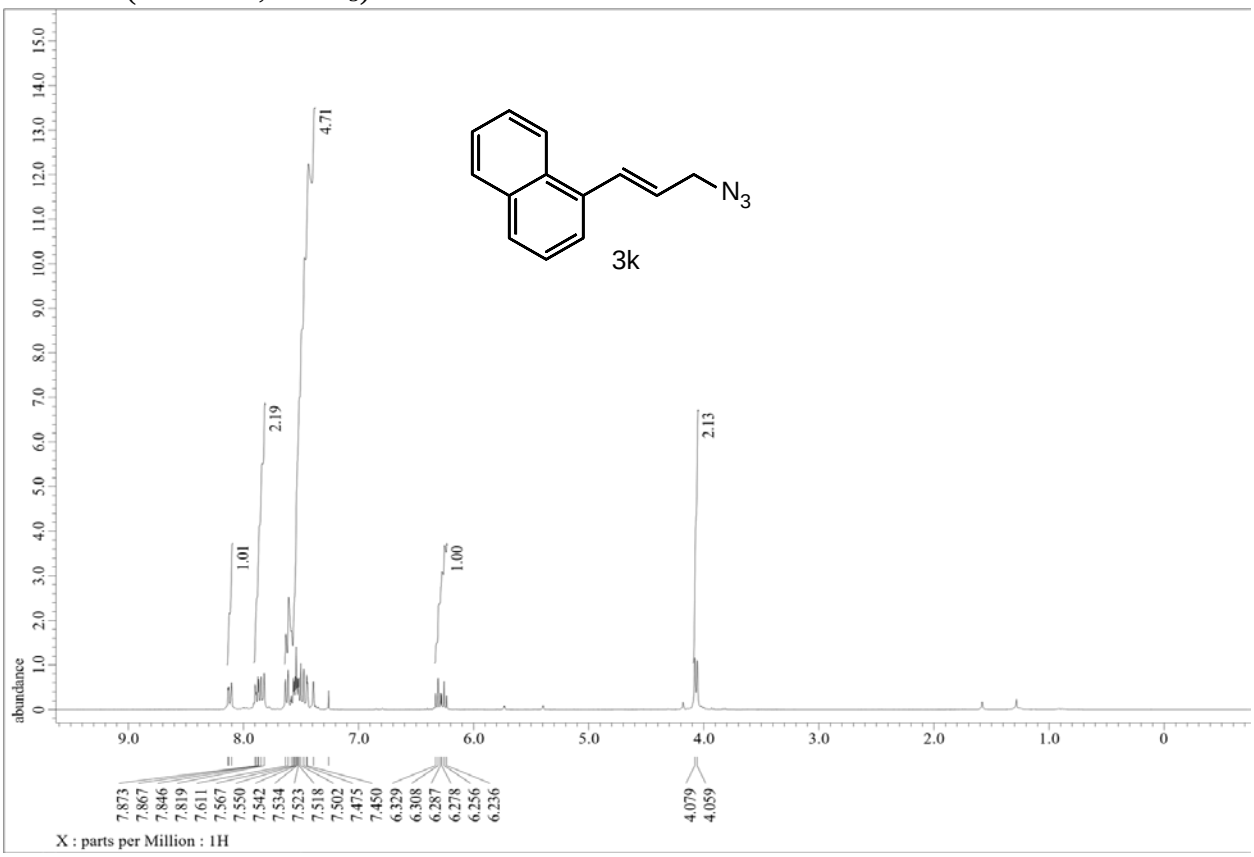
^{1}H NMR (300 MHz, $CDCl_3$)



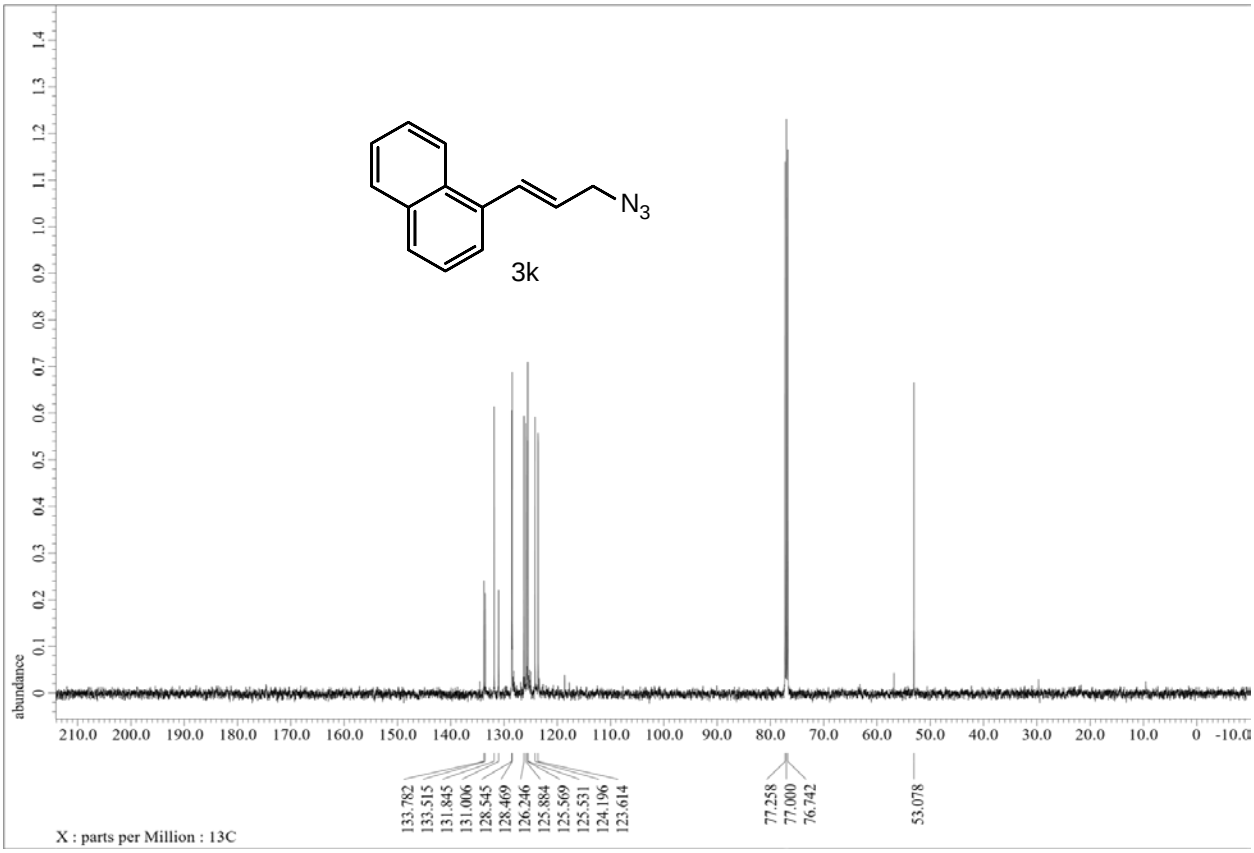
^{13}C NMR (75 MHz, $CDCl_3$)



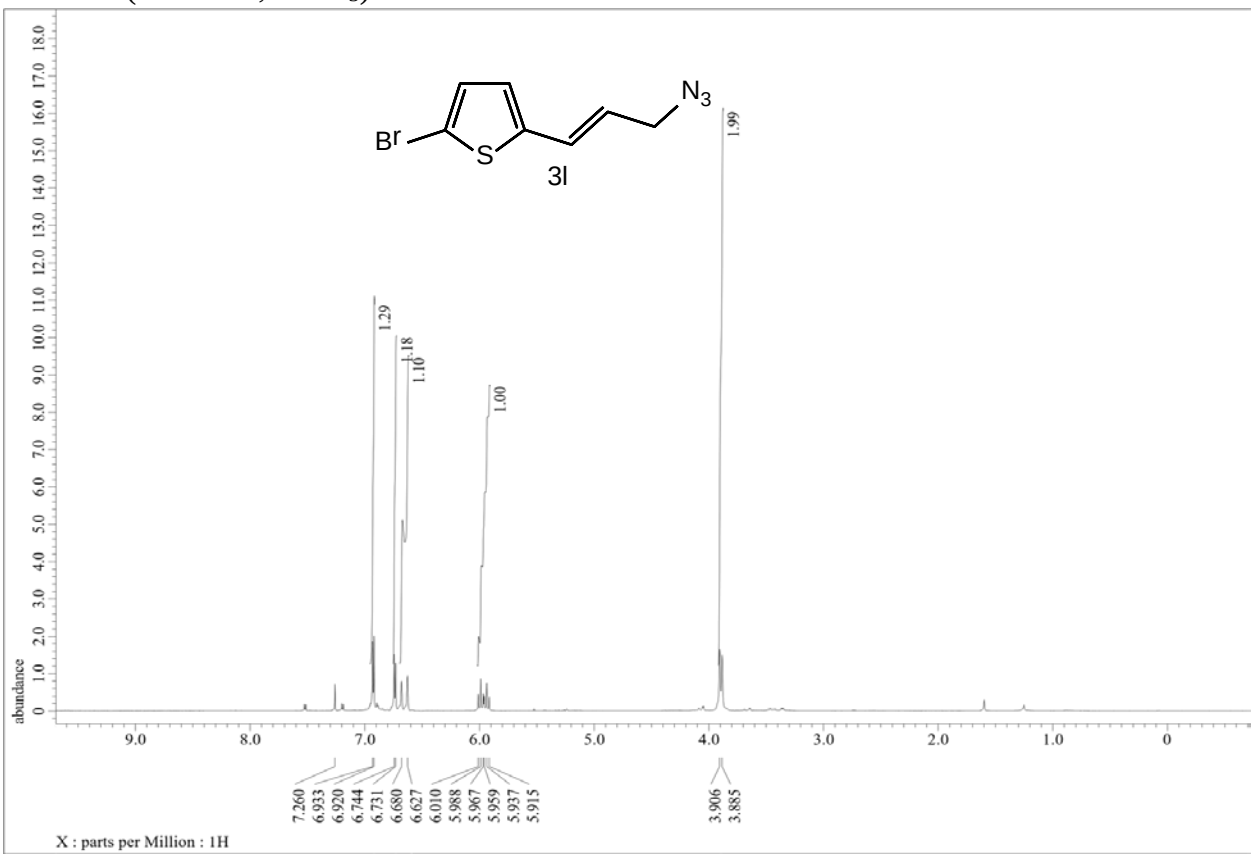
^{1}H NMR (300 MHz, $CDCl_3$)



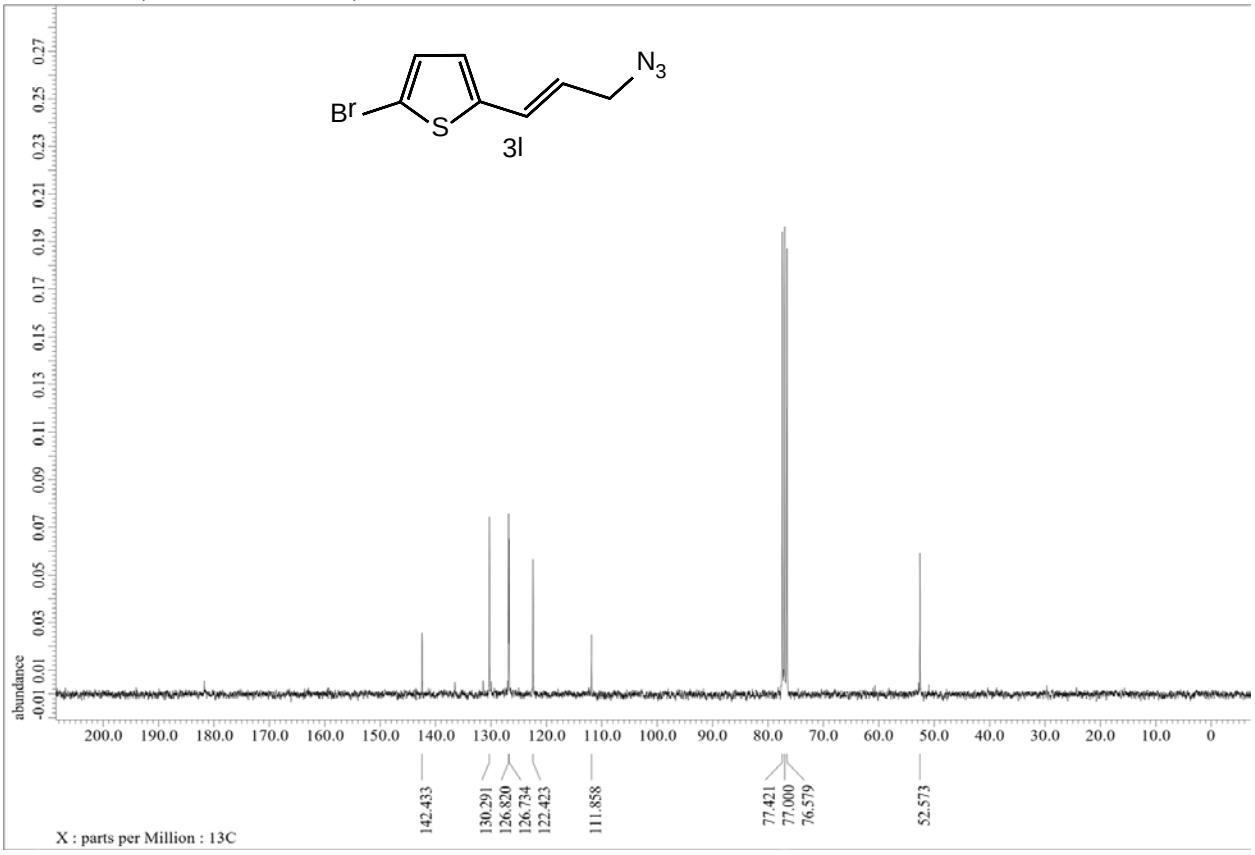
^{13}C NMR (75 MHz, $CDCl_3$)



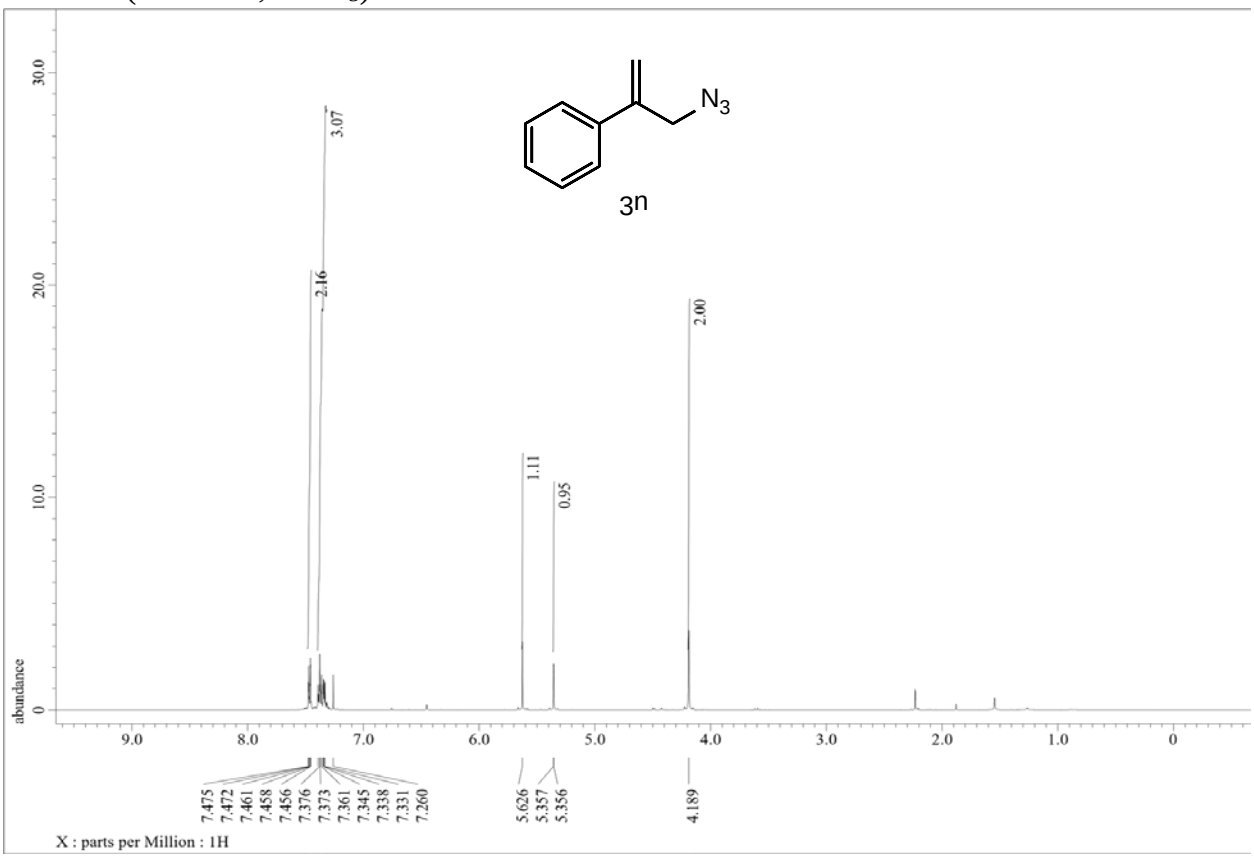
^{1}H NMR (300 MHz, $CDCl_3$)



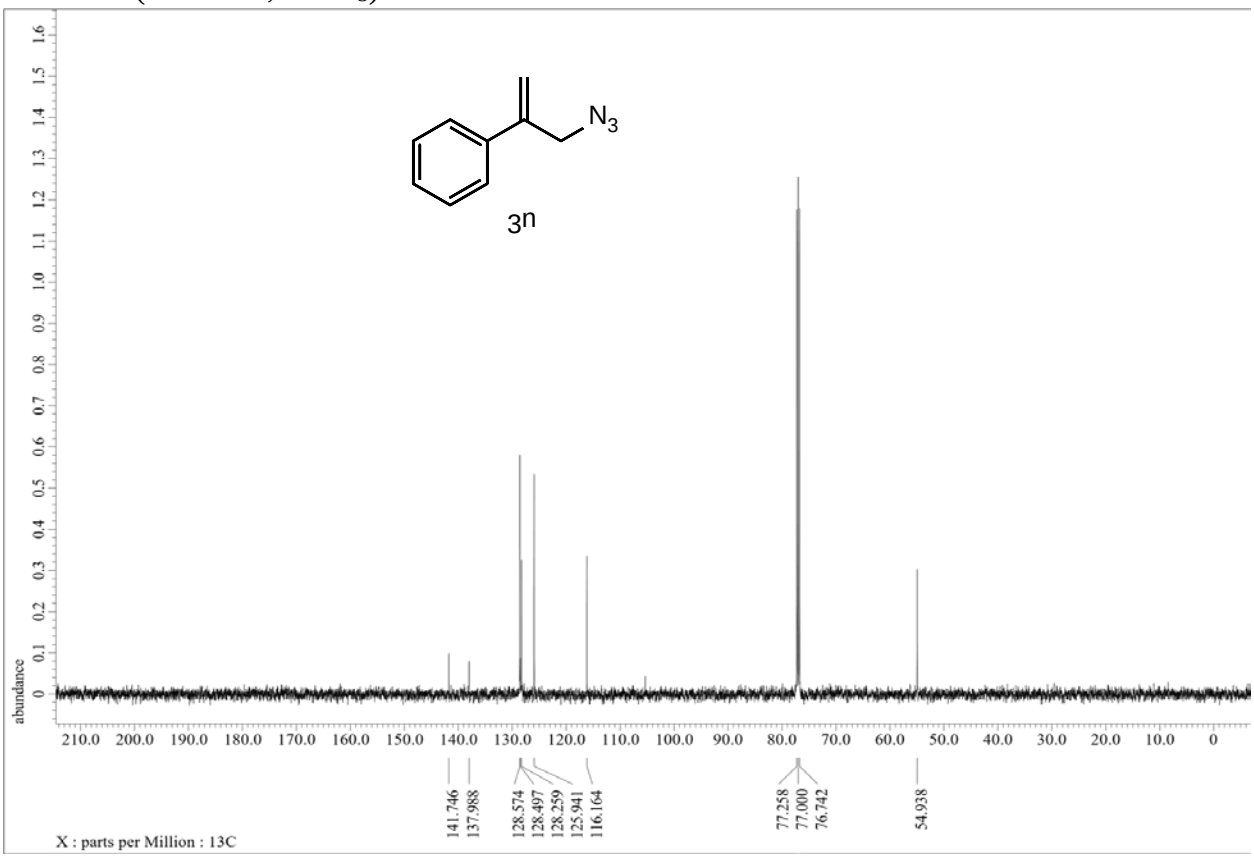
^{13}C NMR (75 MHz, $CDCl_3$)



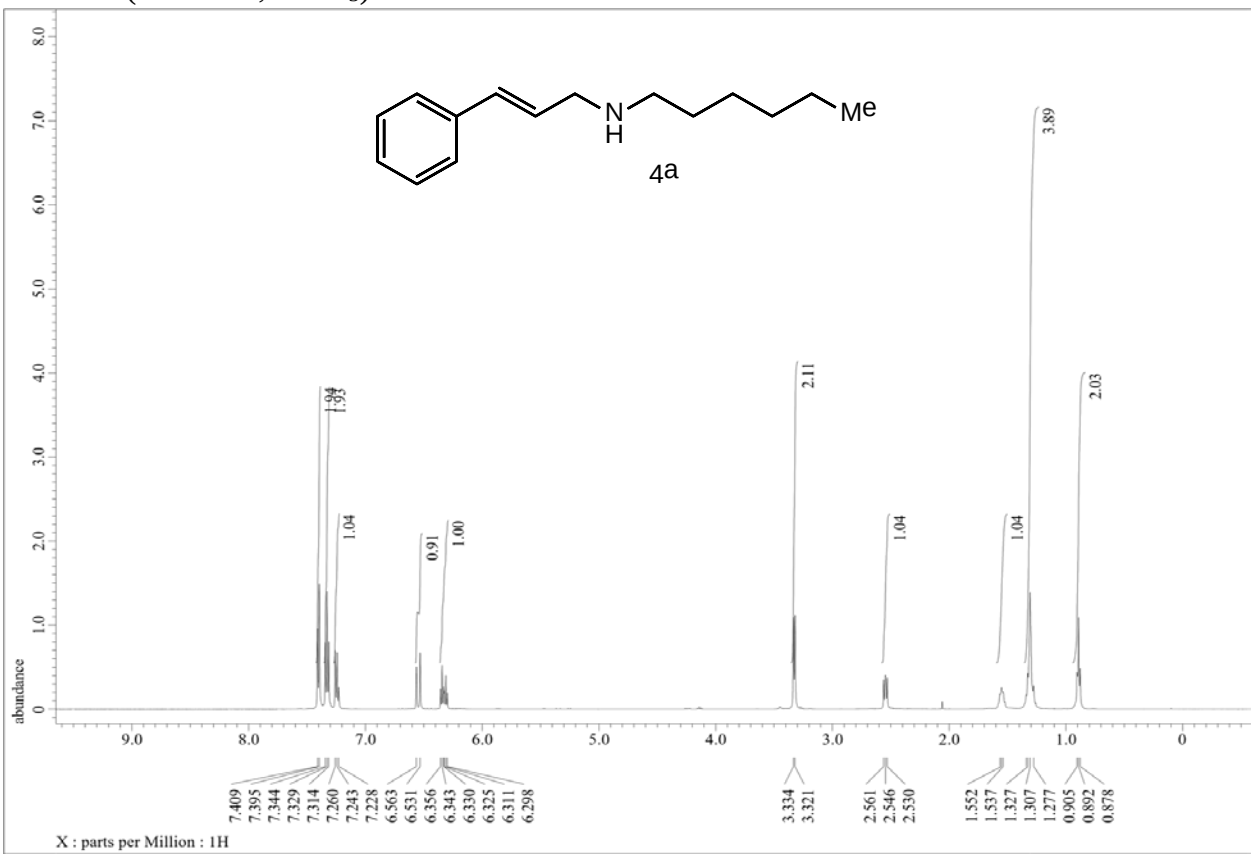
^{1}H NMR (500 MHz, $CDCl_3$)



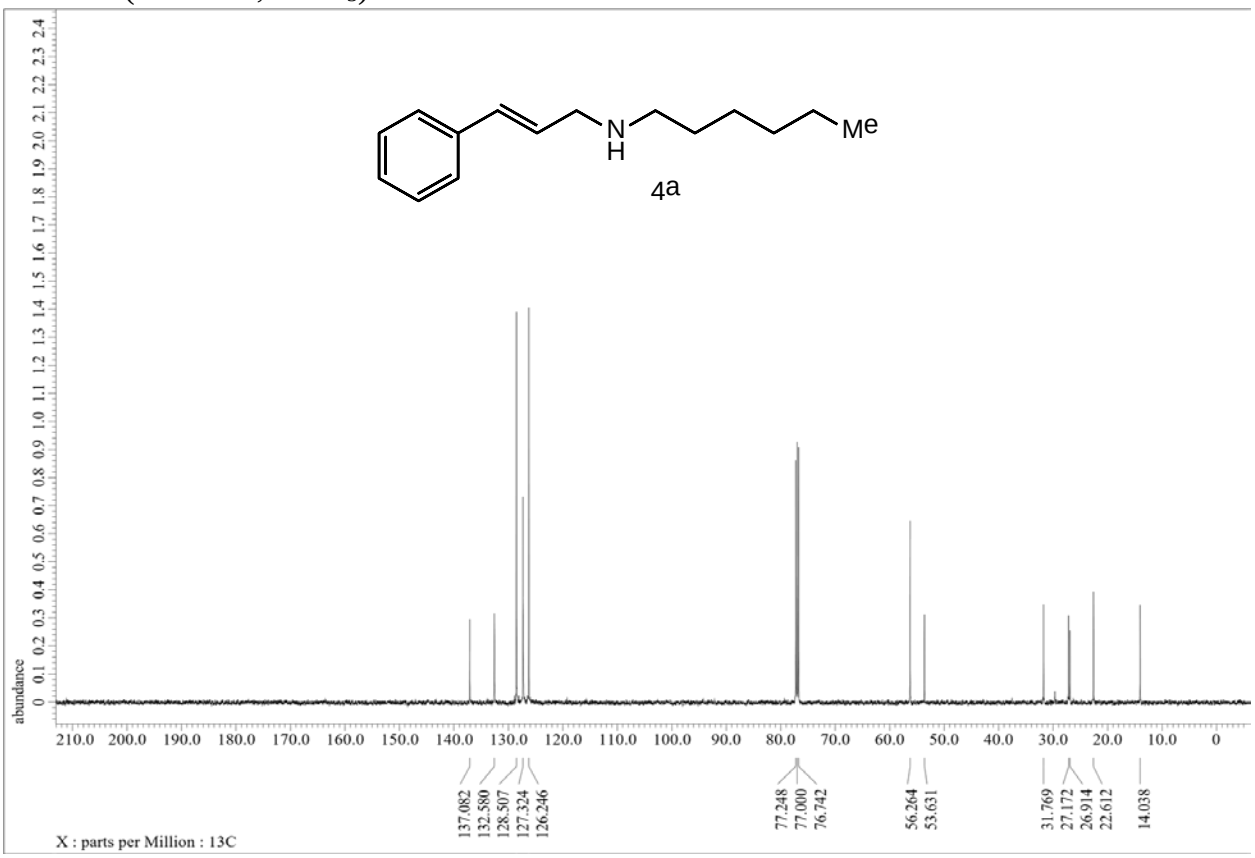
^{13}C NMR (125 MHz, $CDCl_3$)



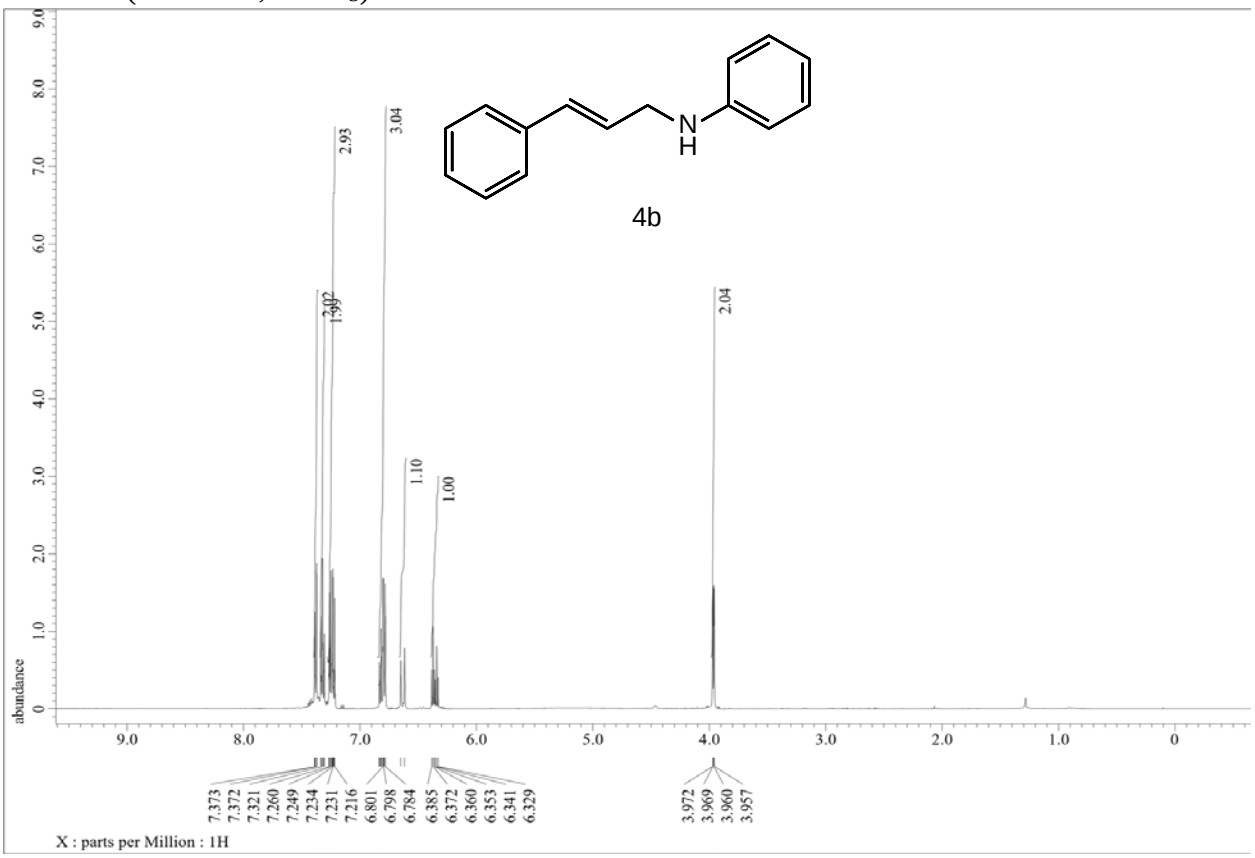
^{1}H NMR (500 MHz, $CDCl_3$)



^{3}C NMR (125M Hz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



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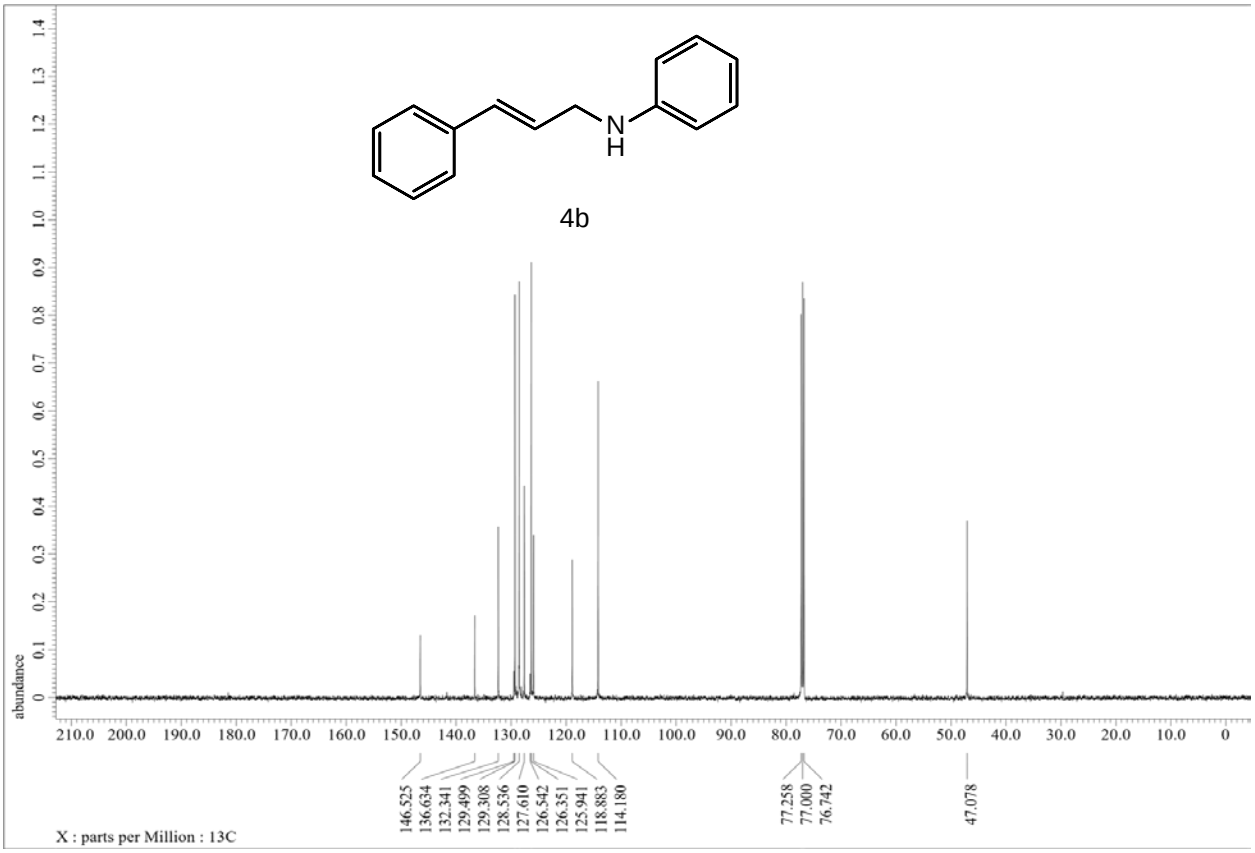

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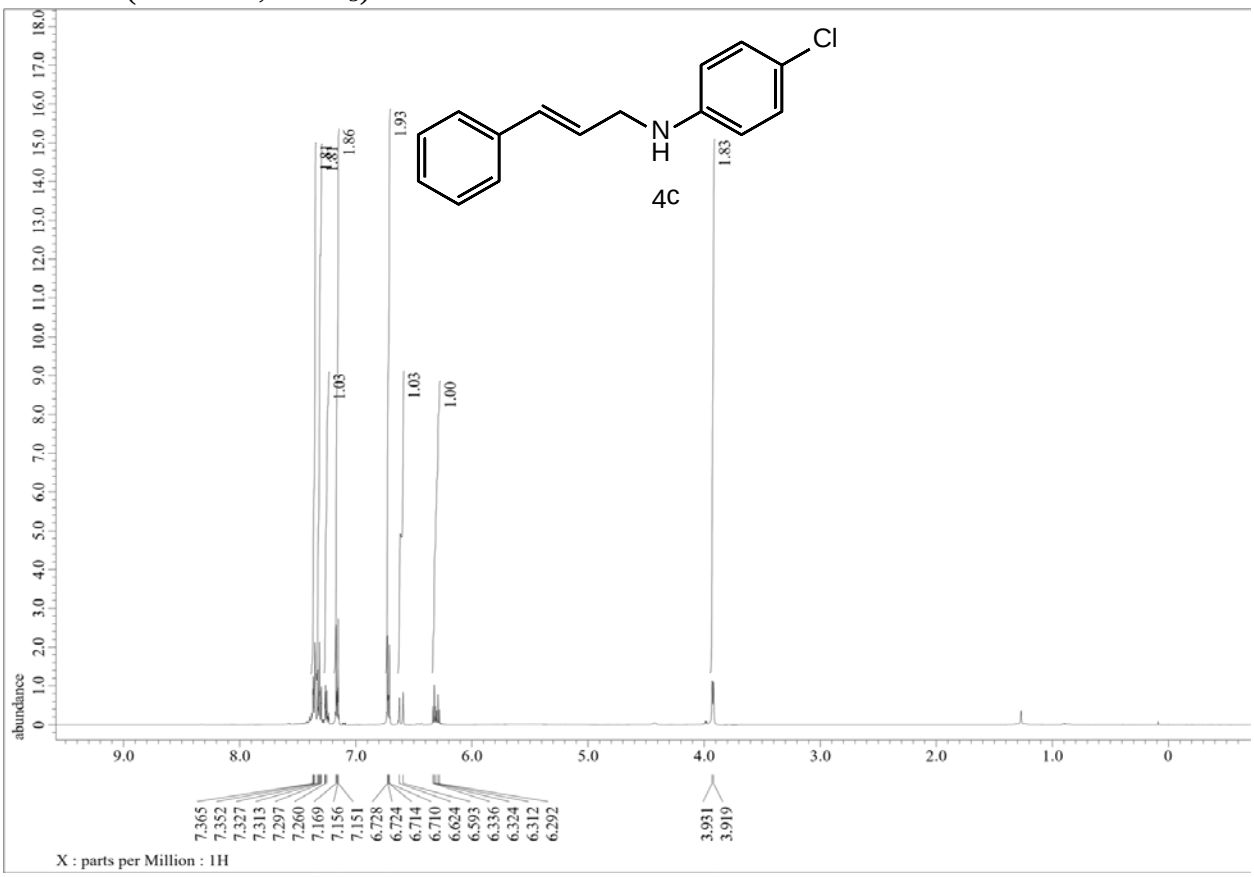

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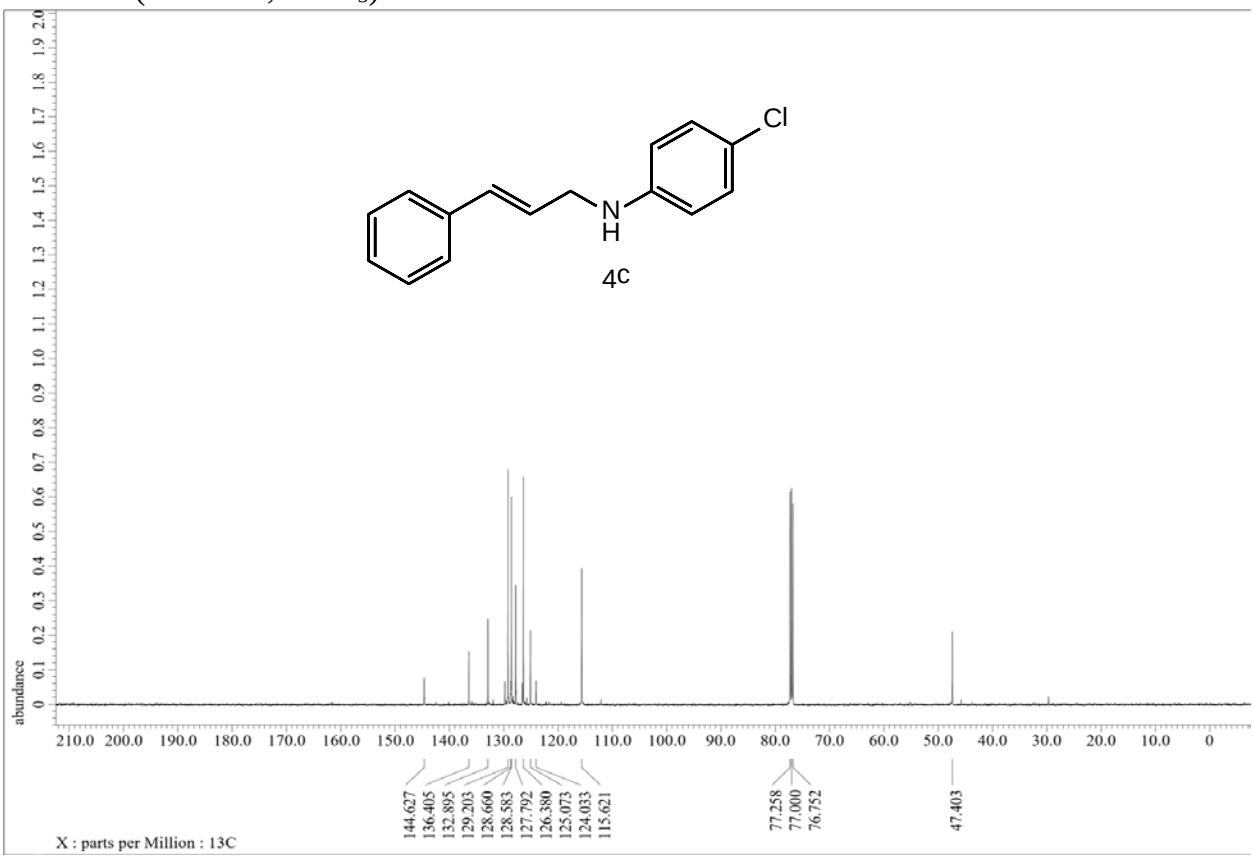
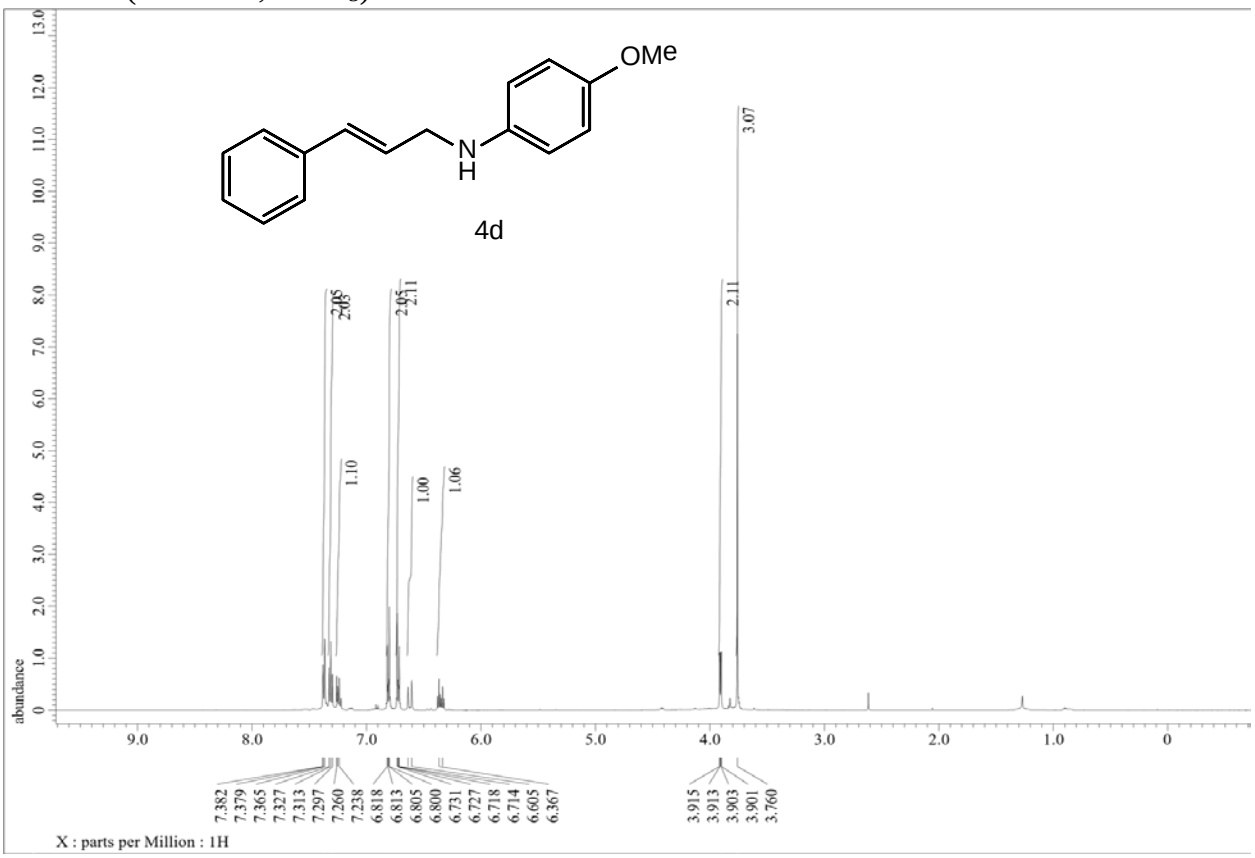
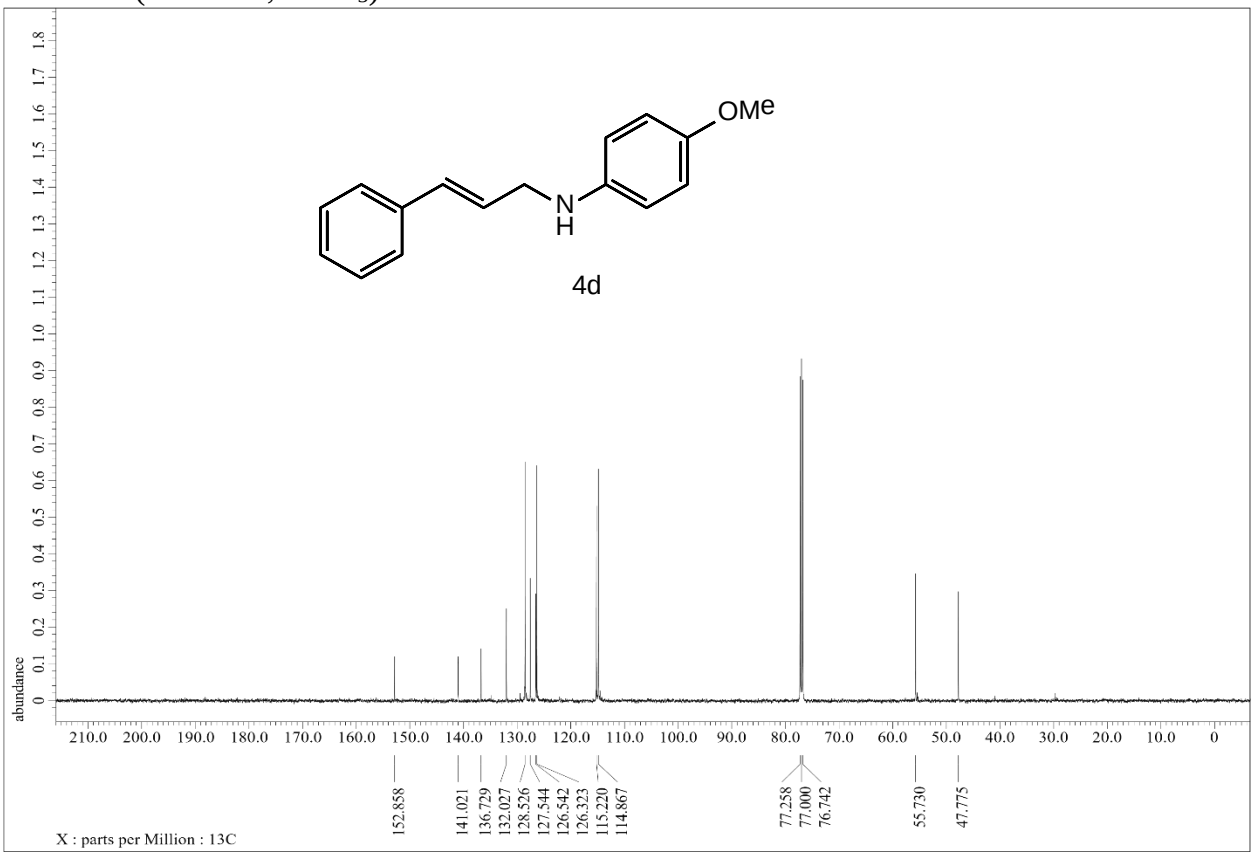


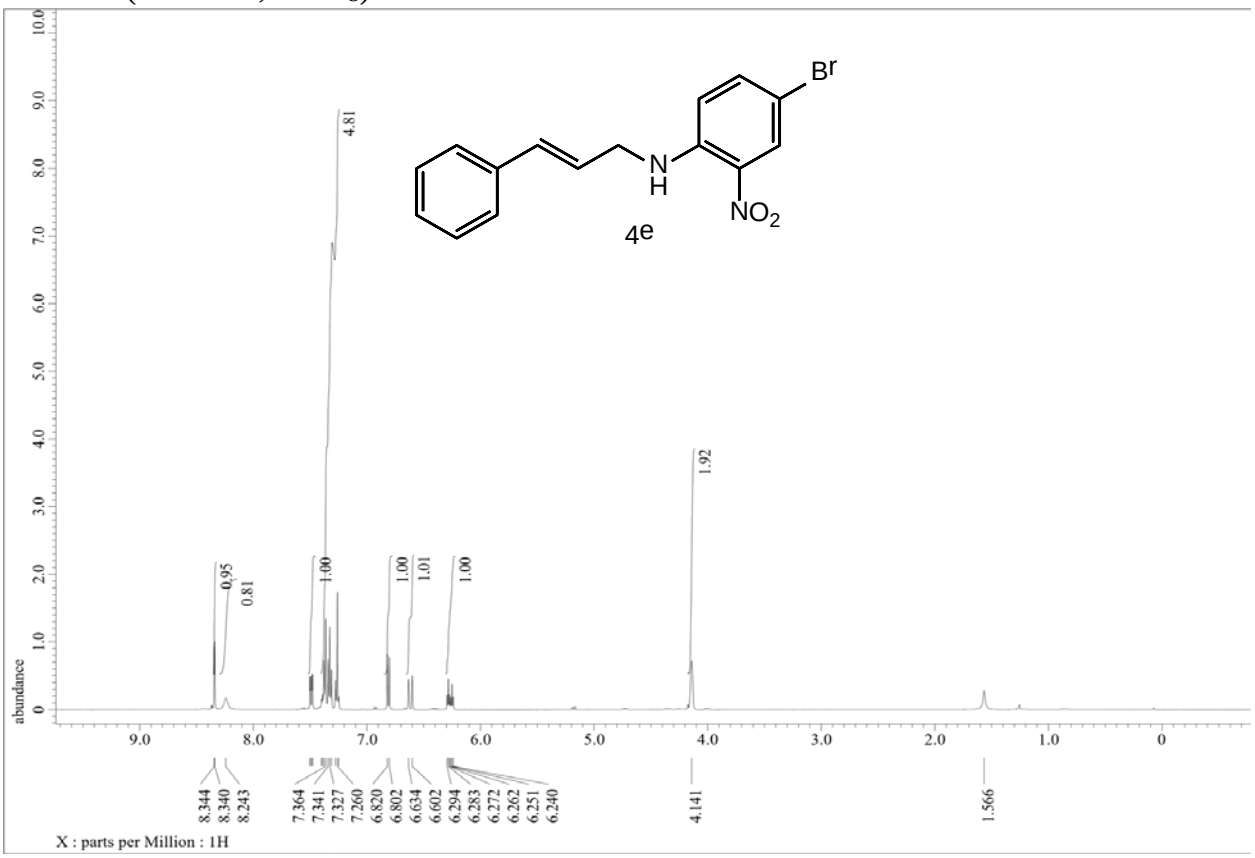
^{1}H NMR (500 MHz, $CDCl_3$)



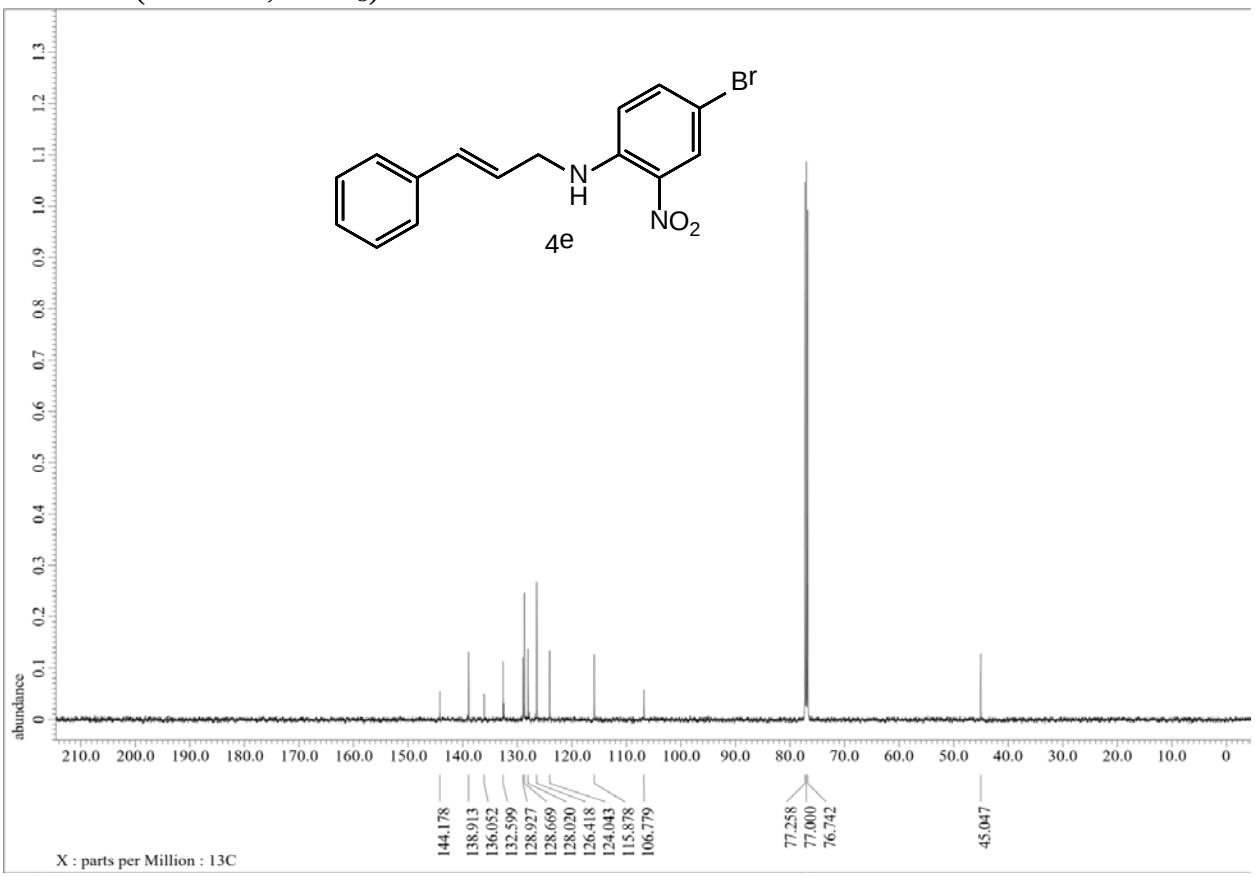
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

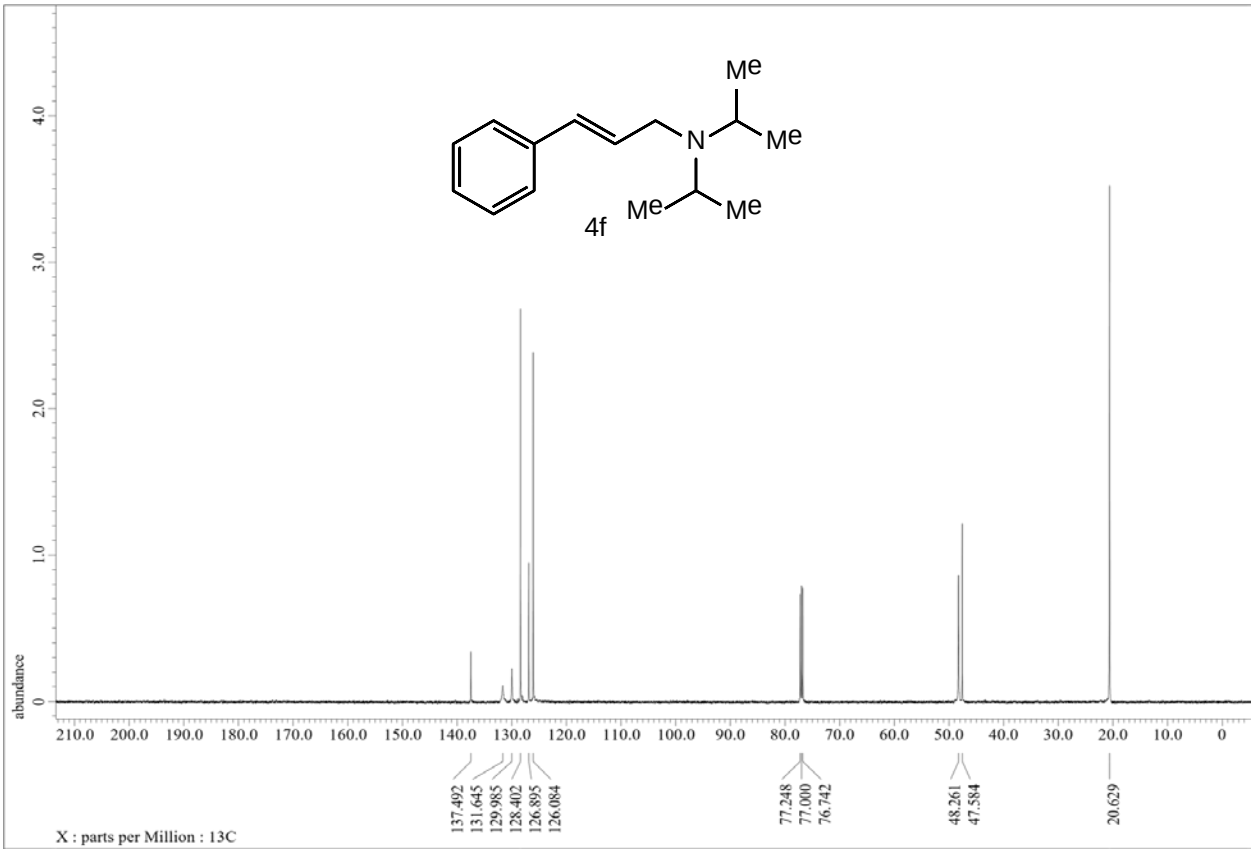


^{13}C NMR (125 MHz, $CDCl_3$)

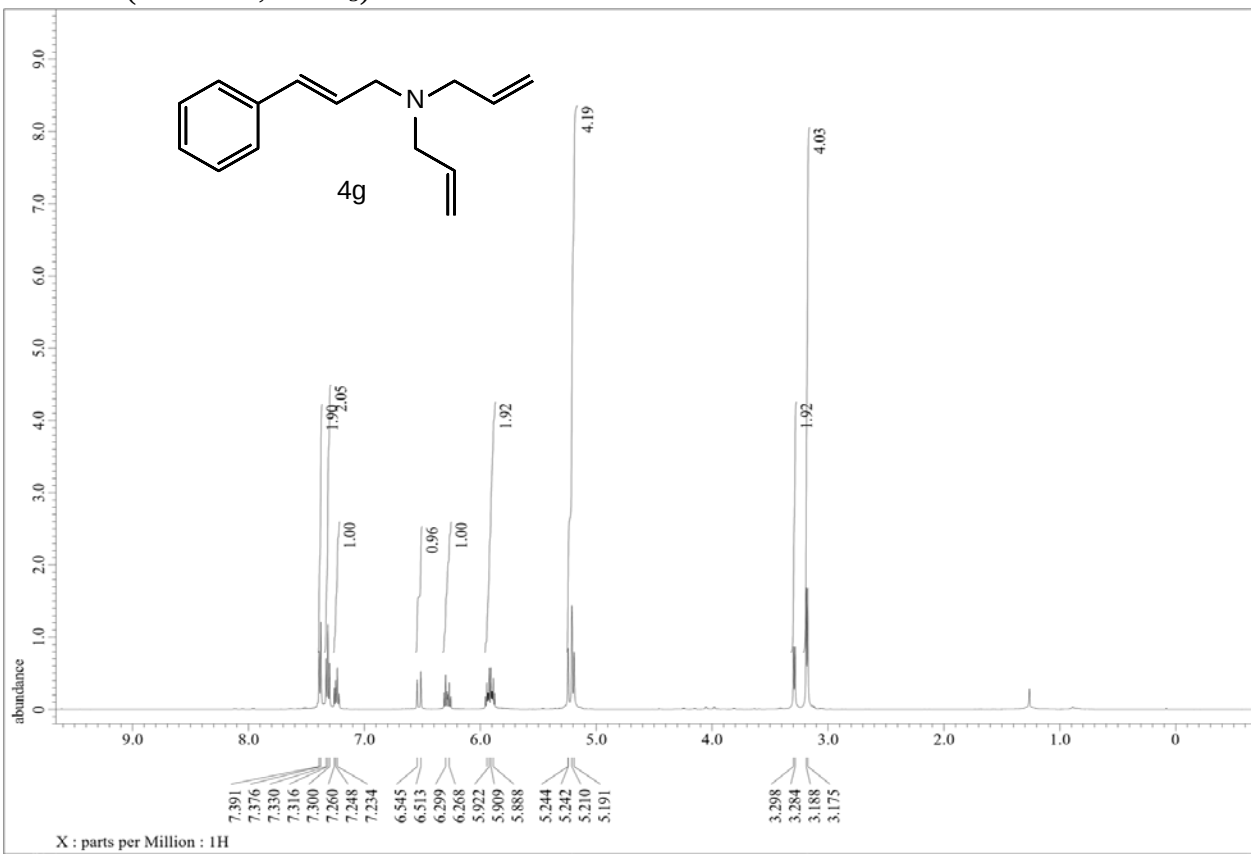


^{1}H NMR (500 MHz, $CDCl_3$)

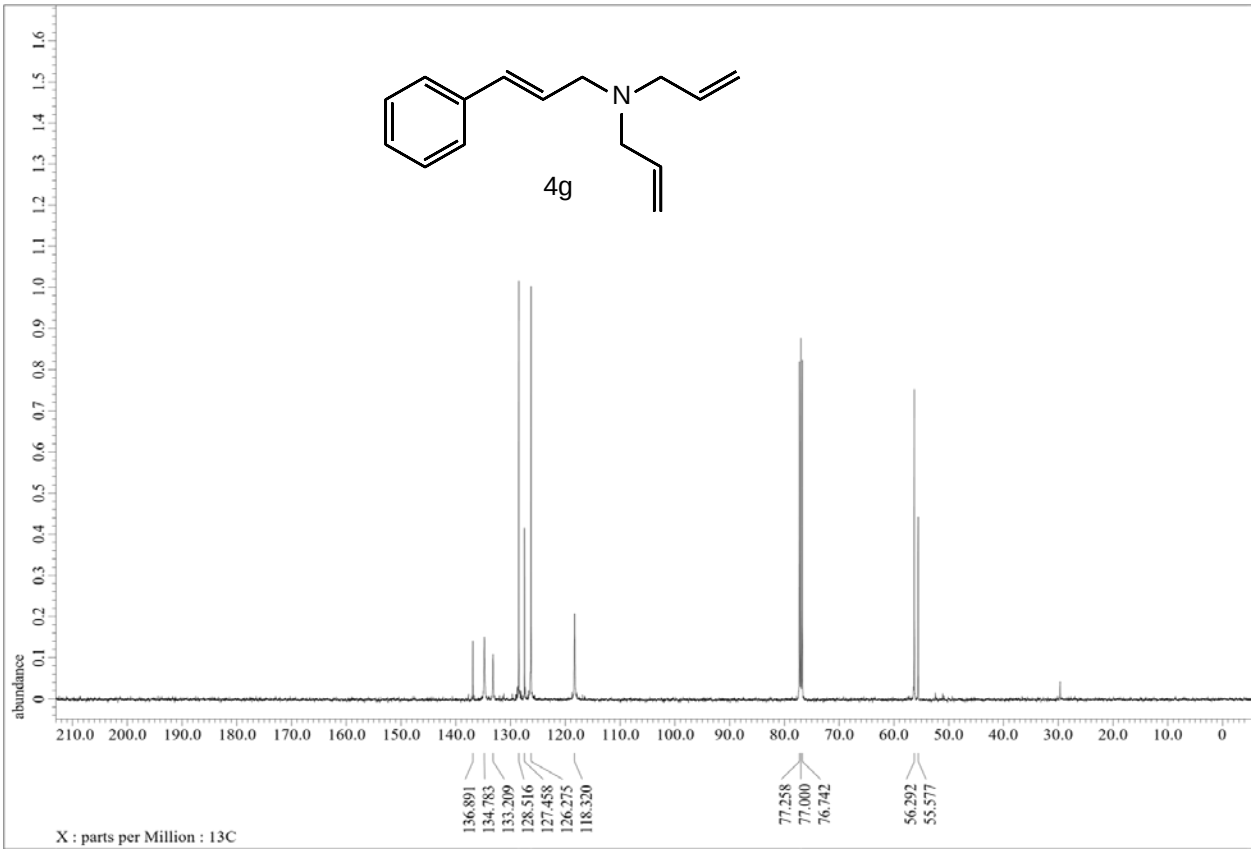
^{13}C NMR (125 MHz, $CDCl_3$)



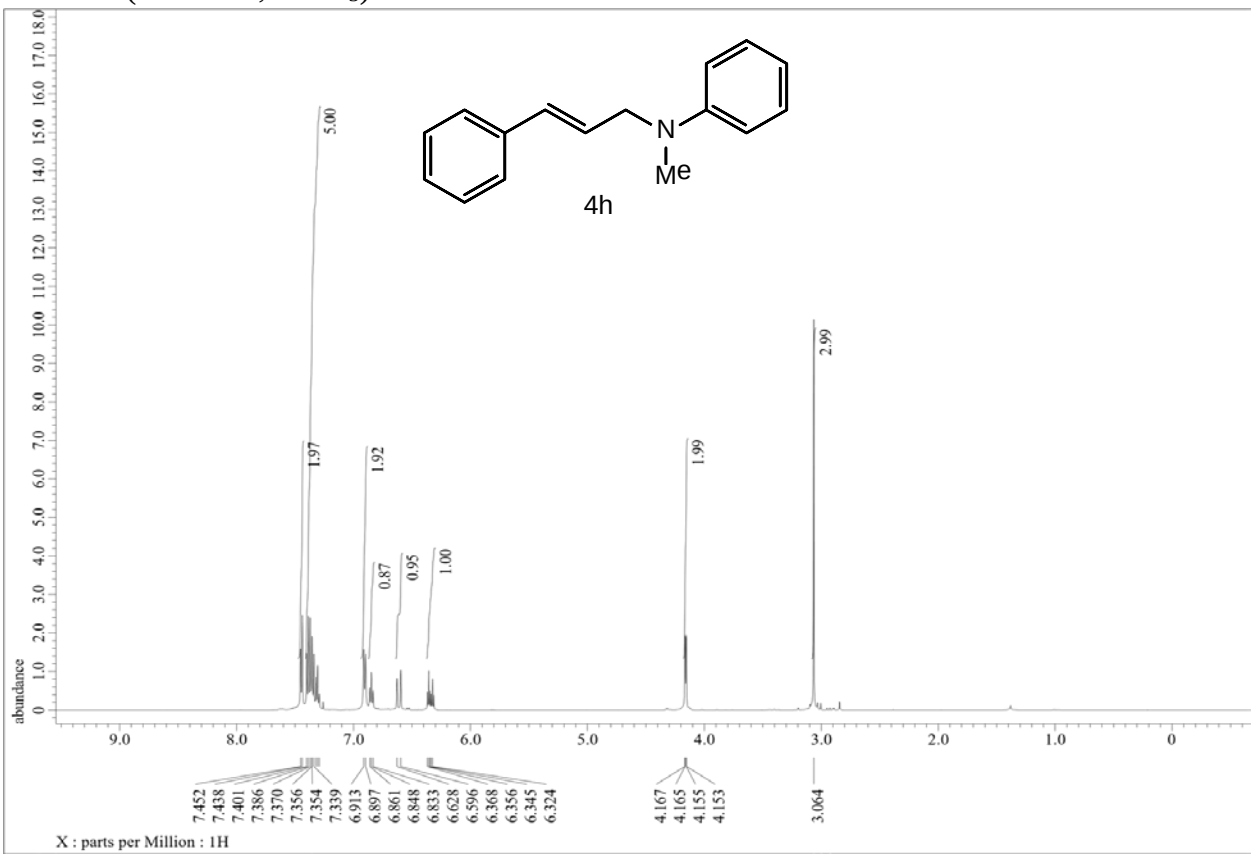
^{1}H NMR (500 MHz, $CDCl_3$)



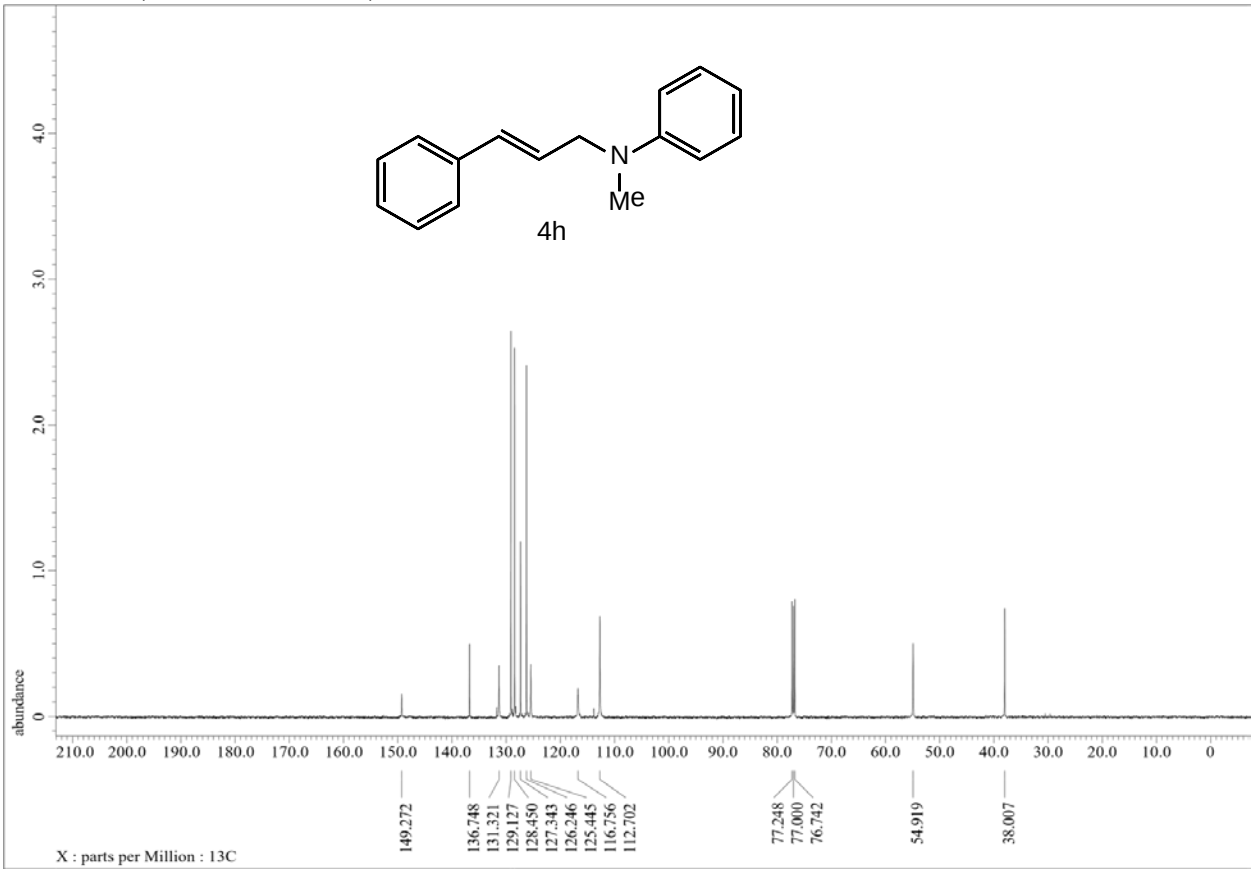
^{13}C NMR (125 MHz, $CDCl_3$)



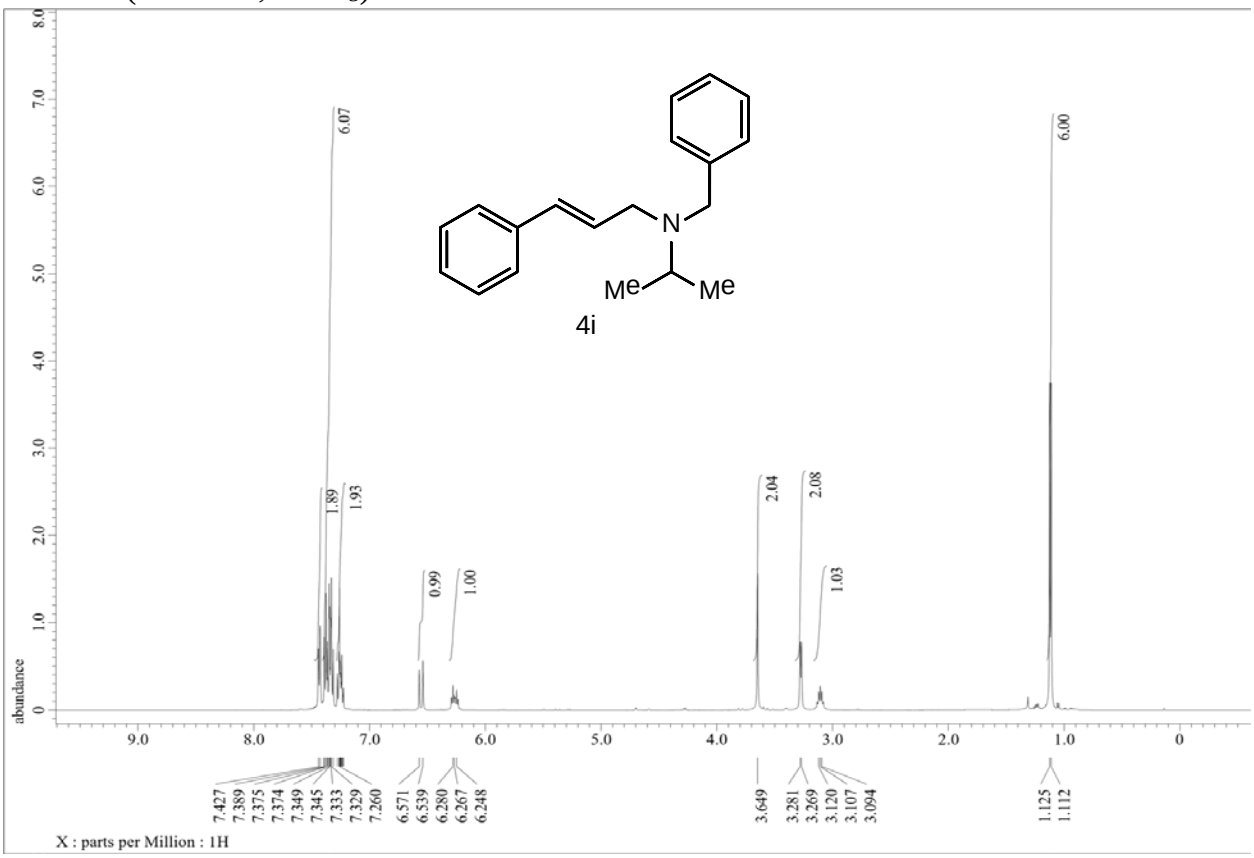
^{1}H NMR (500 MHz, $CDCl_3$)



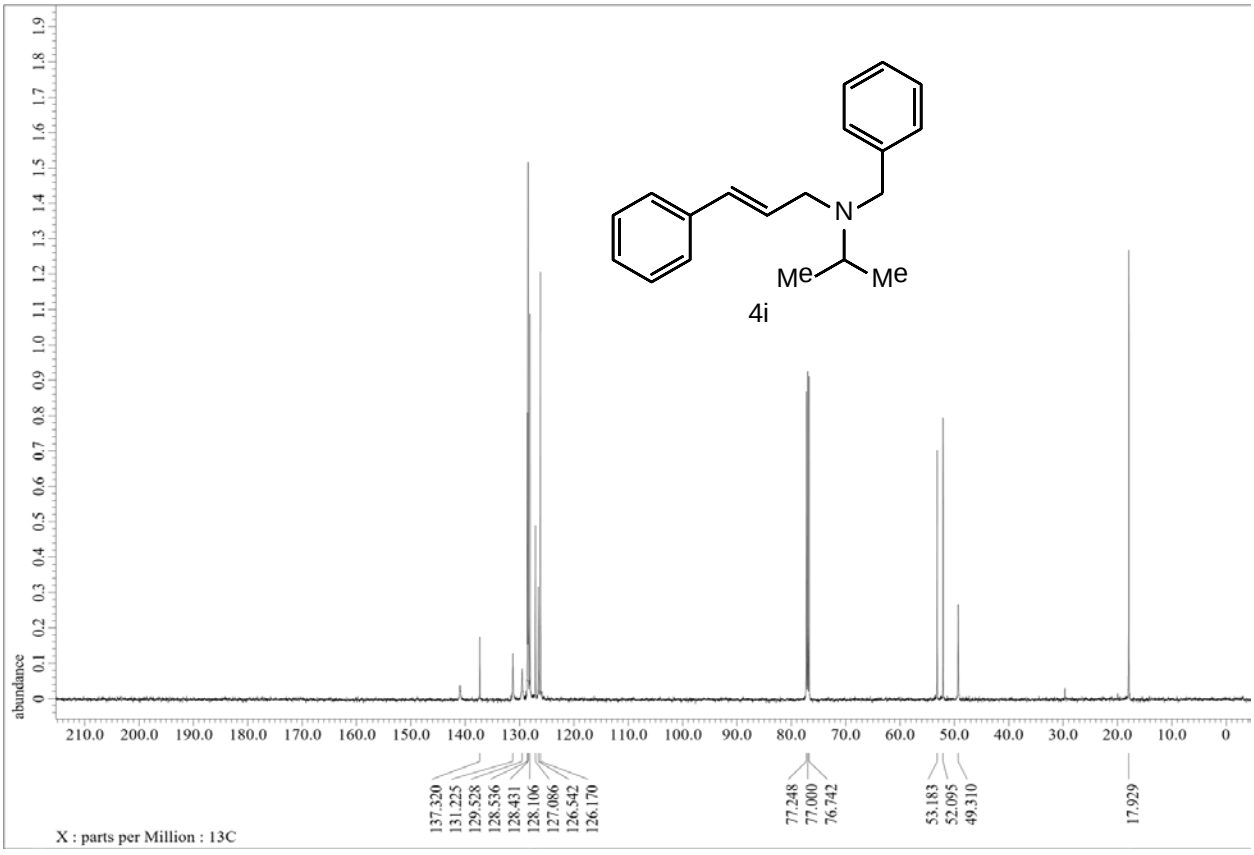
^{13}C NMR (125 MHz, $CDCl_3$)



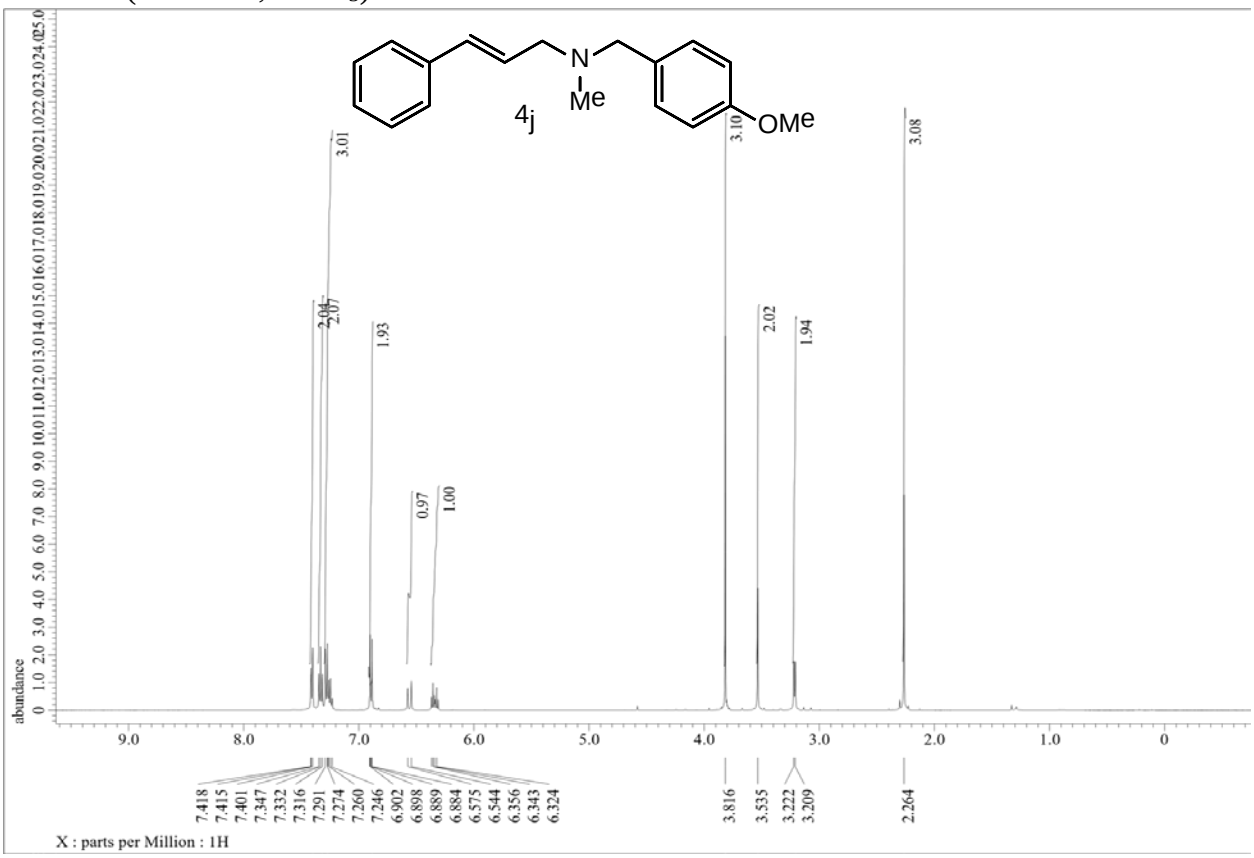
^{1}H NMR (500 MHz, $CDCl_3$)



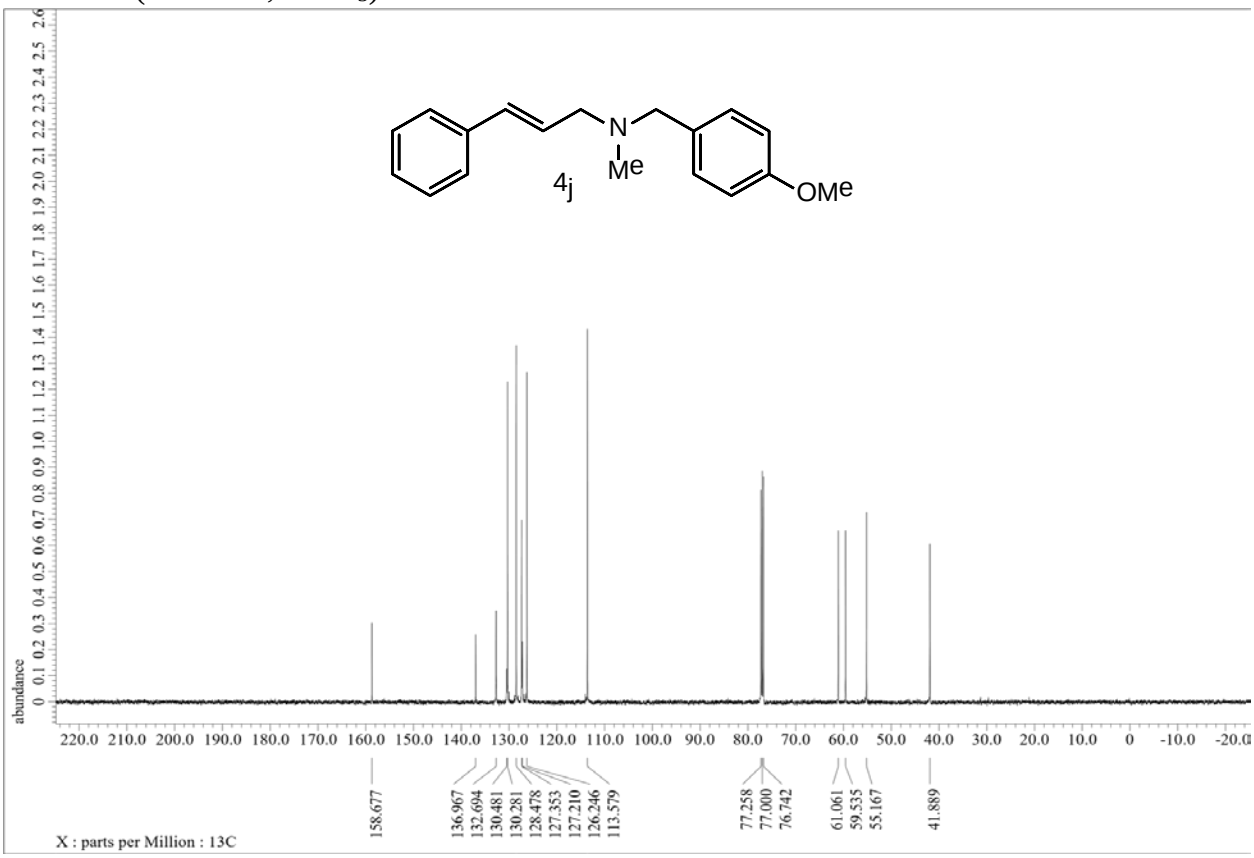
^{13}C NMR (125 MHz, $CDCl_3$)



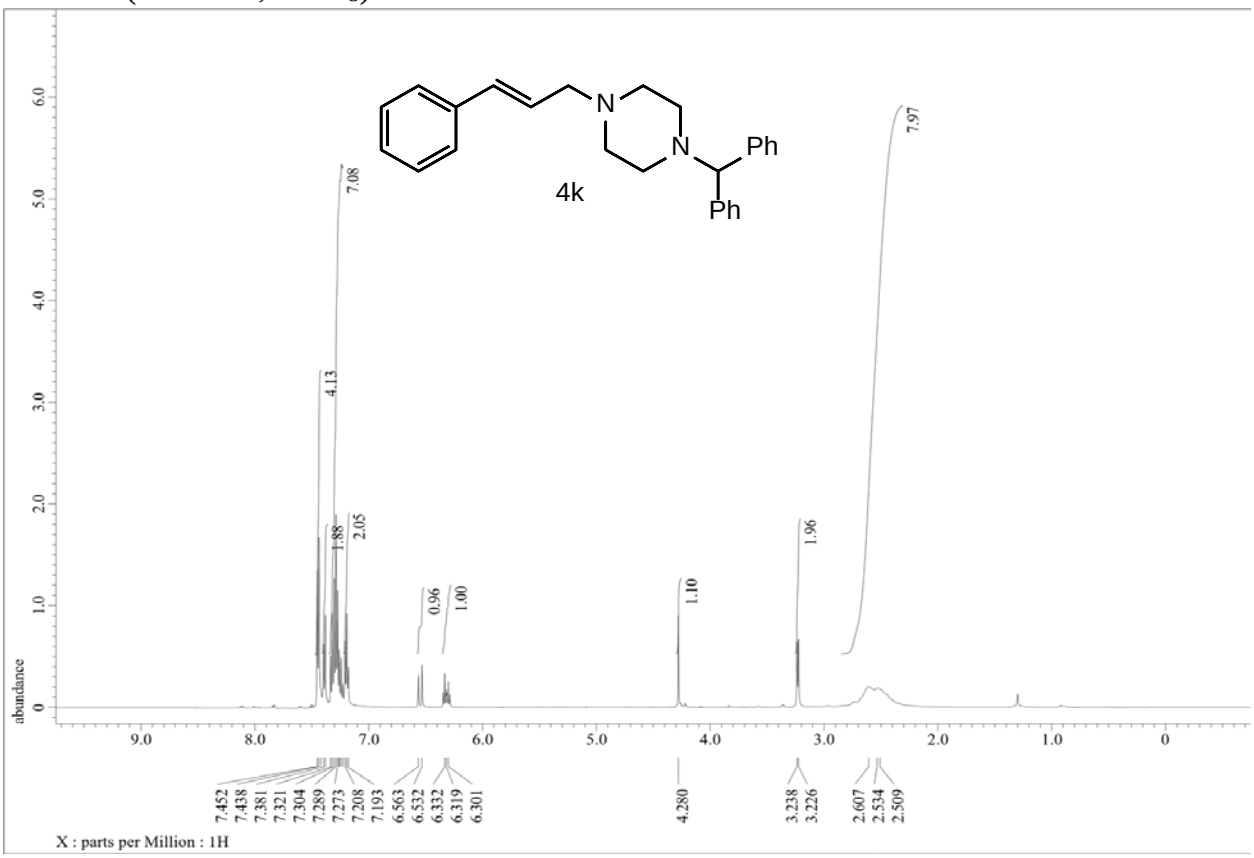
^{1}H NMR (500 MHz, $CDCl_3$)



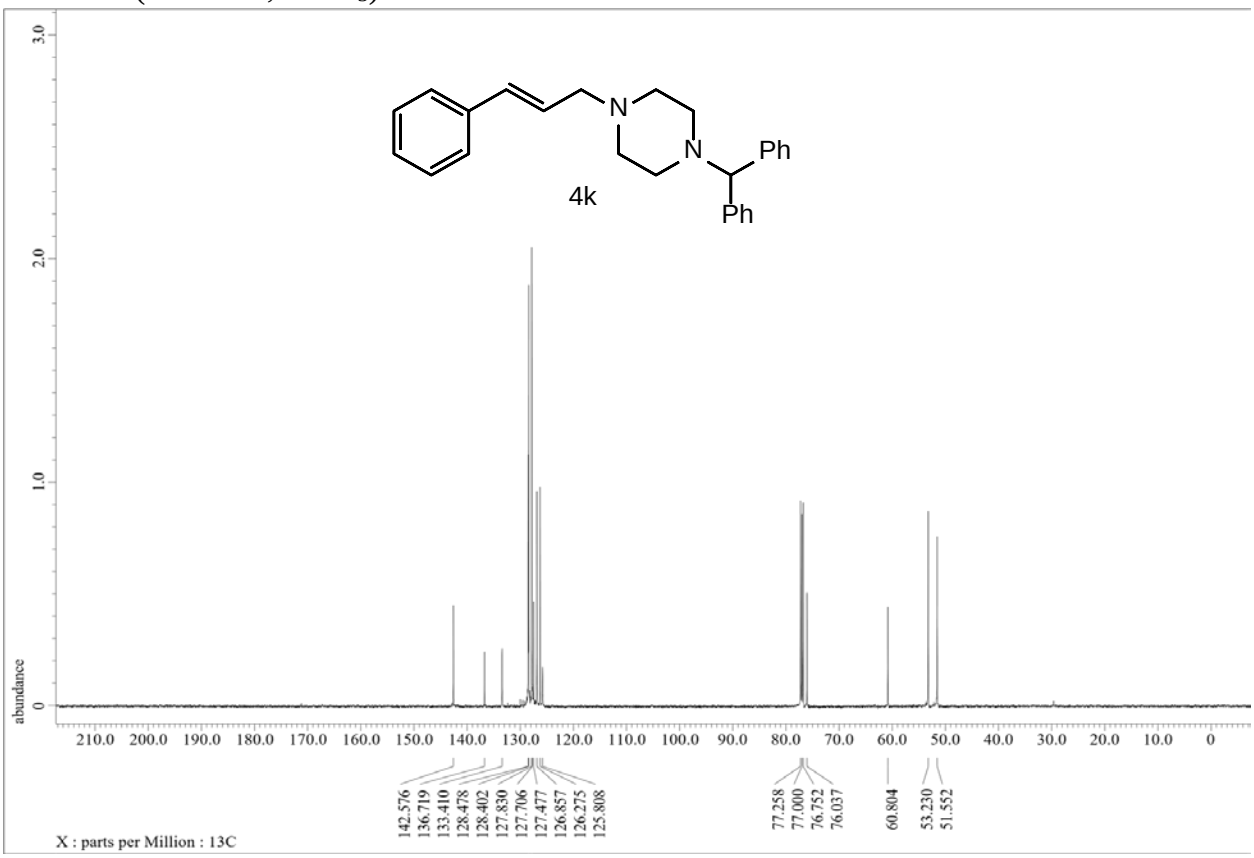
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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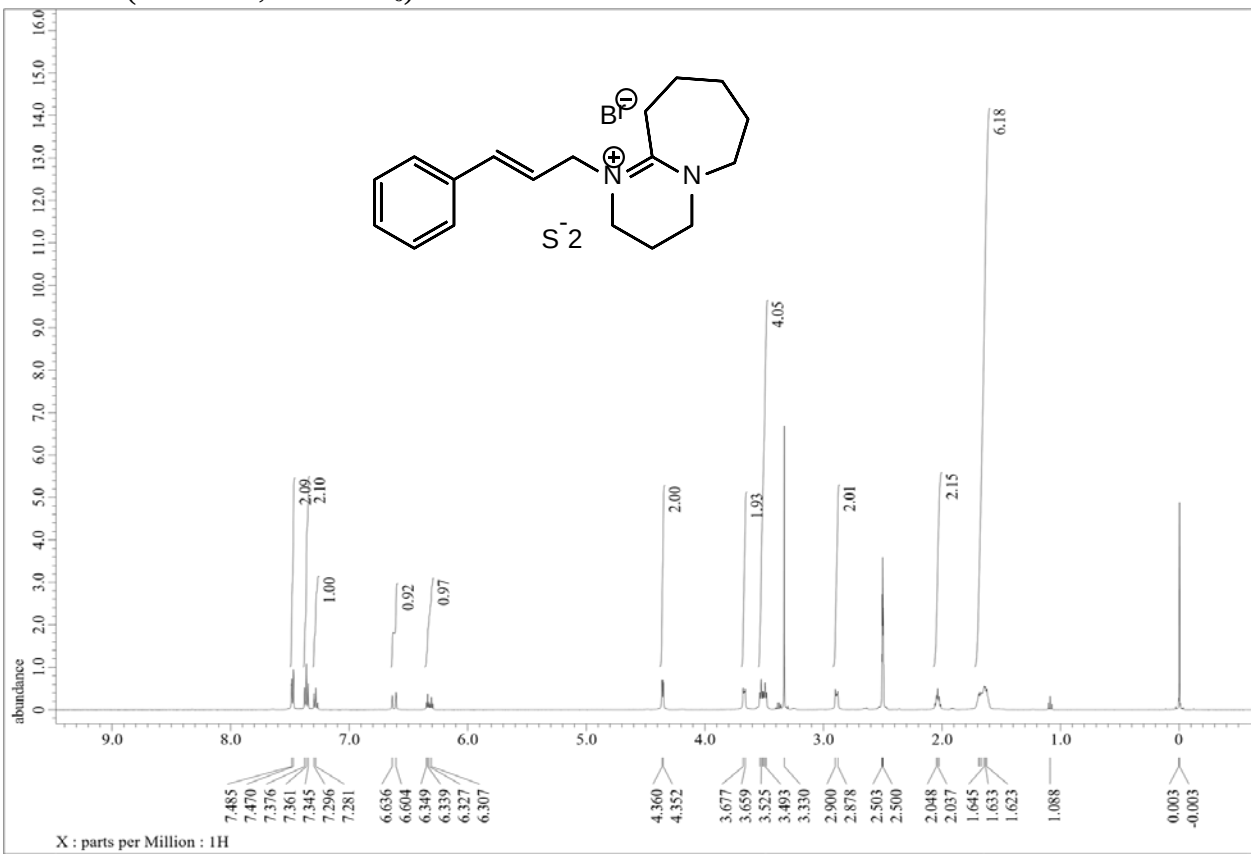
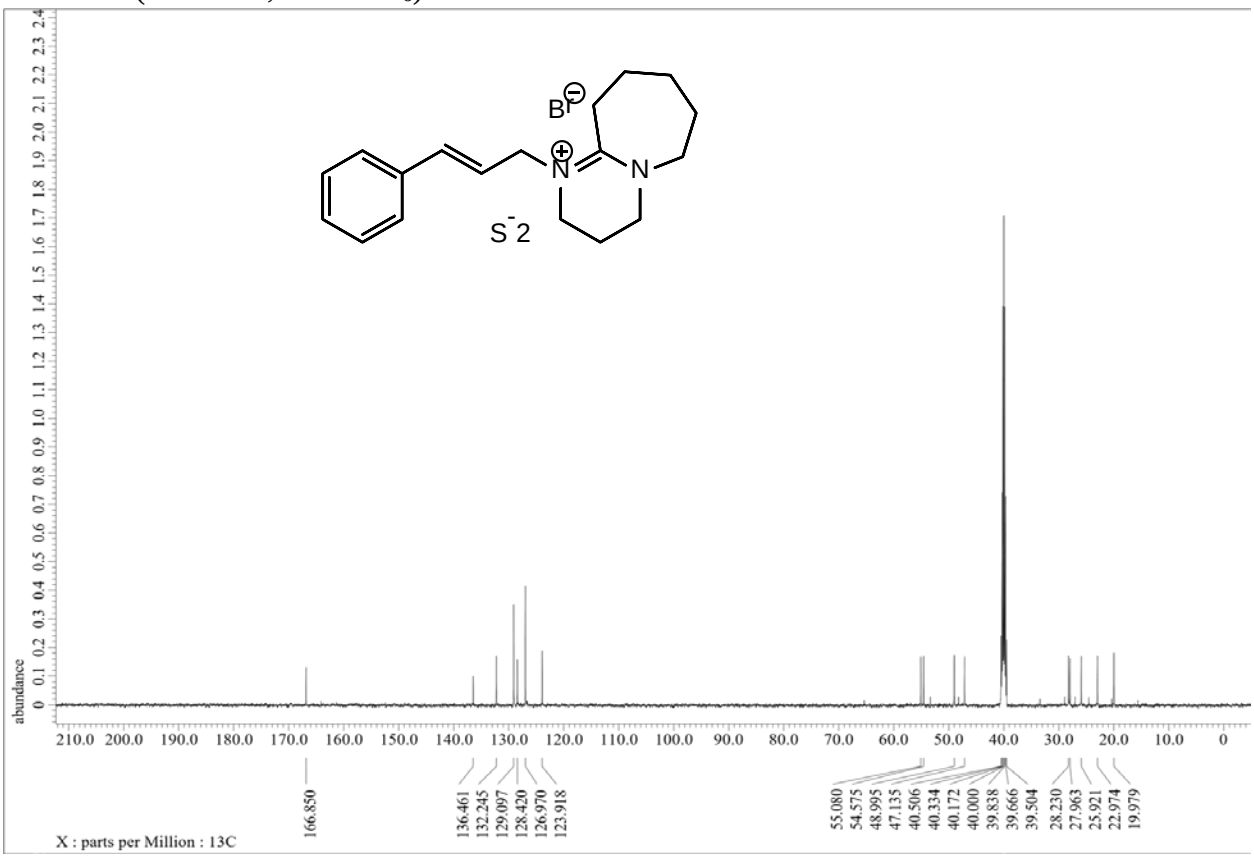
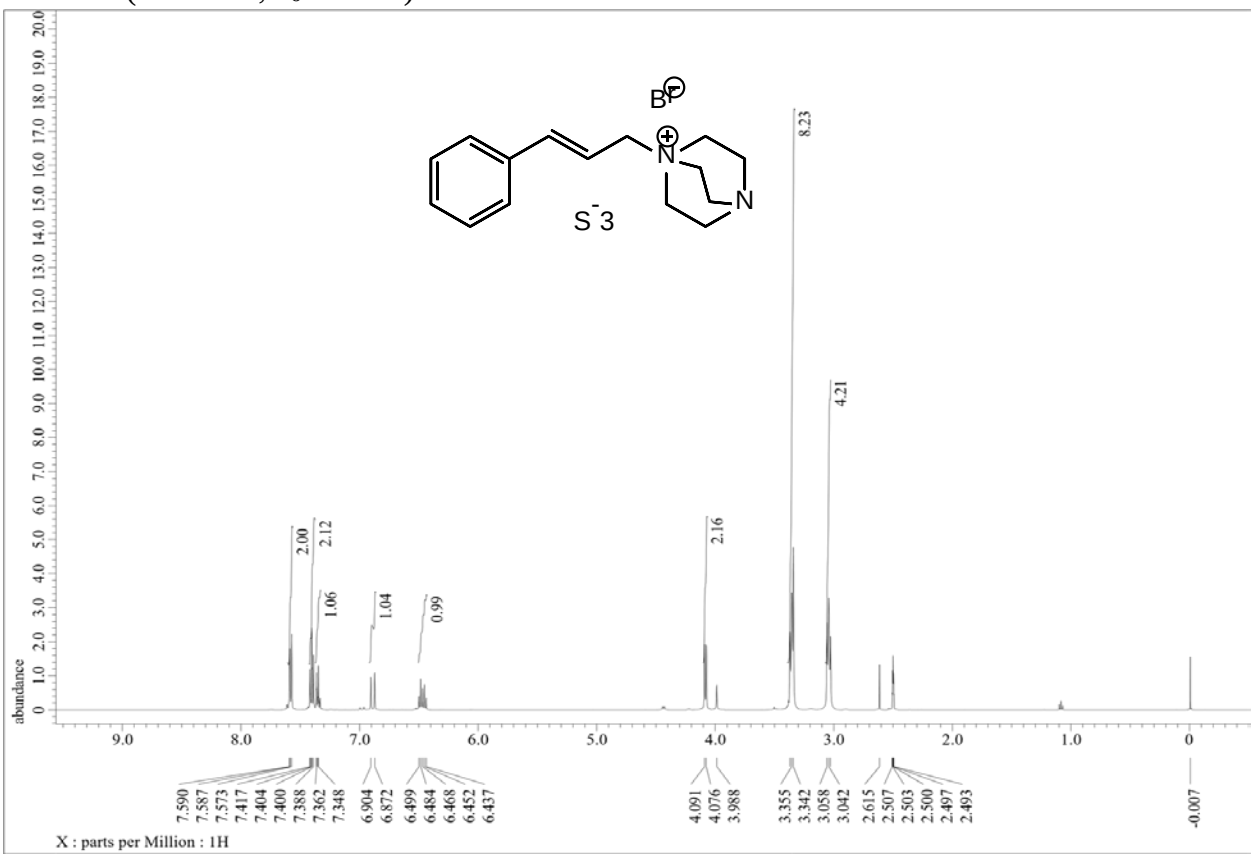


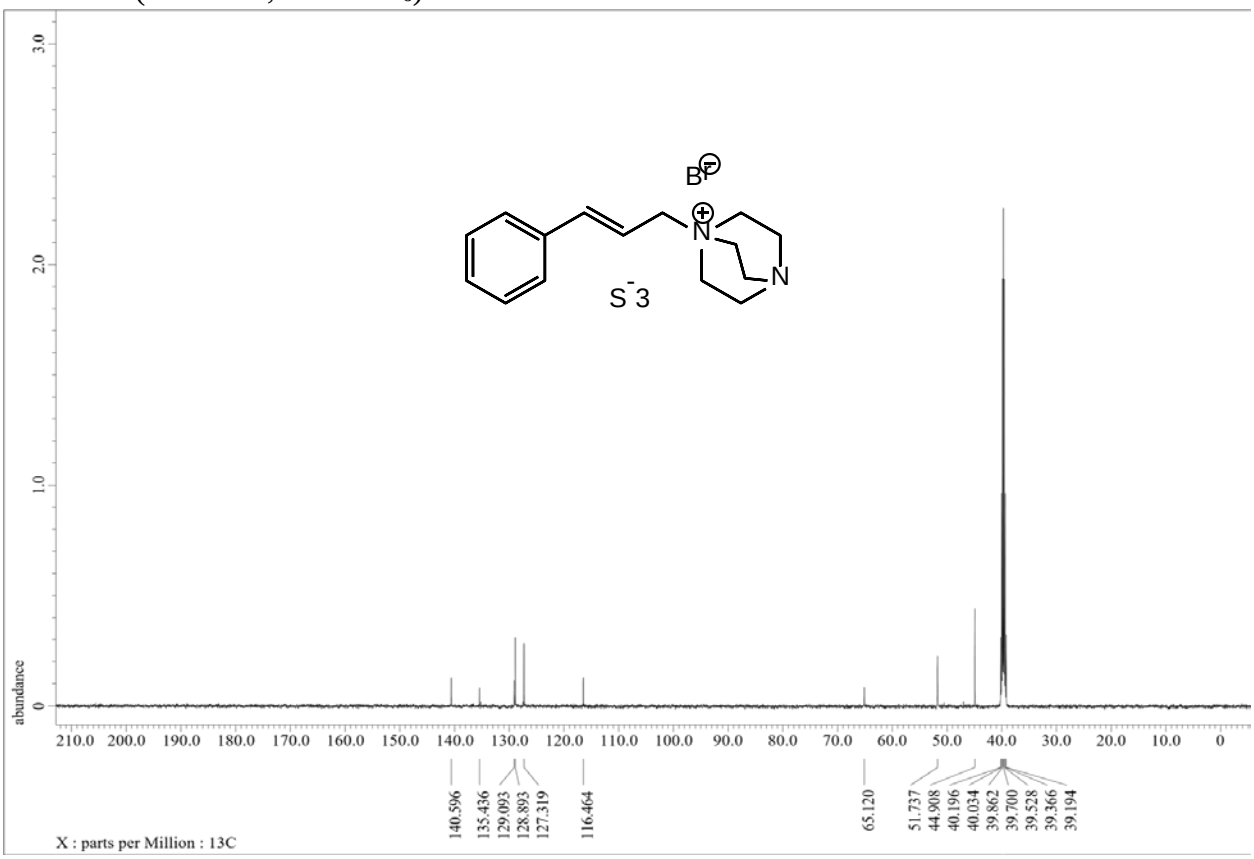
^{13}C NMR (125 MHz, DMSO-d_6)



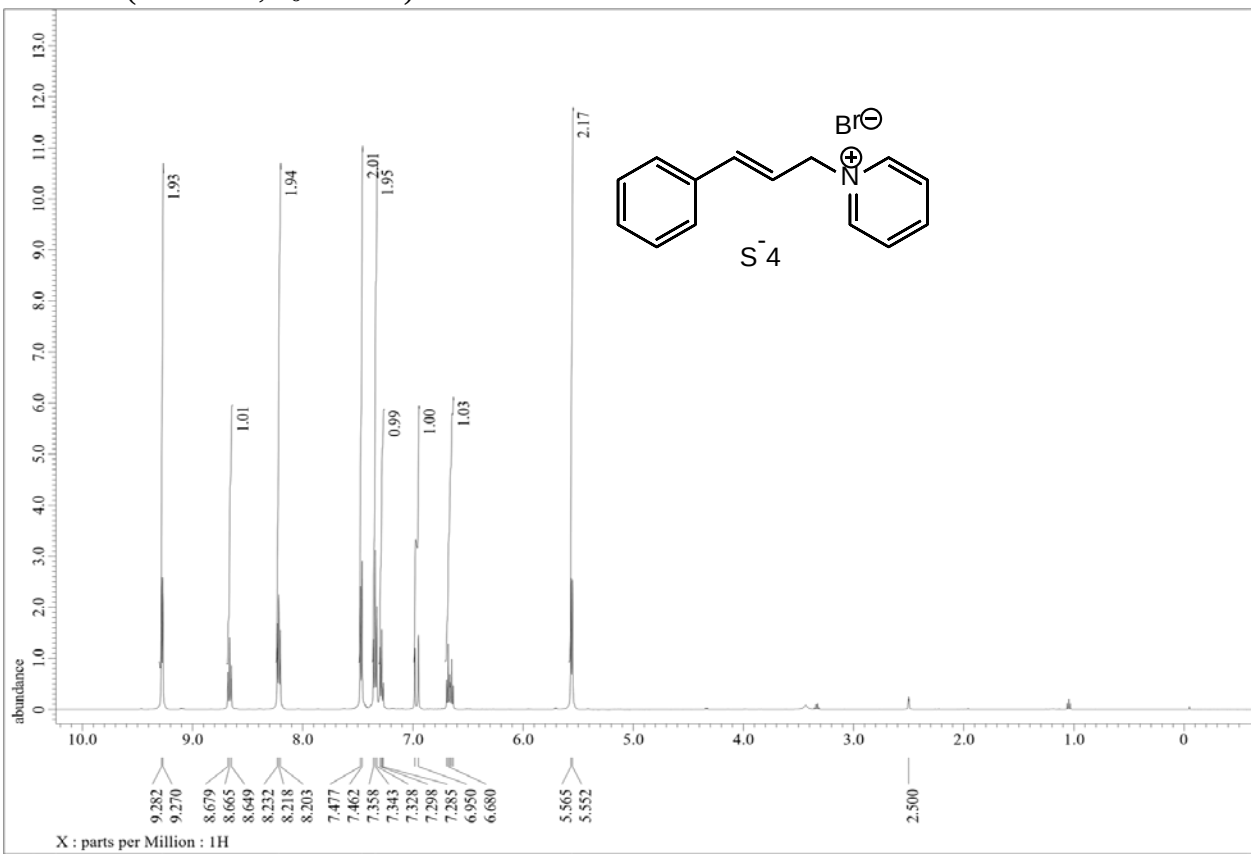
^{1}H NMR (500 MHz, d_6-DMSO)



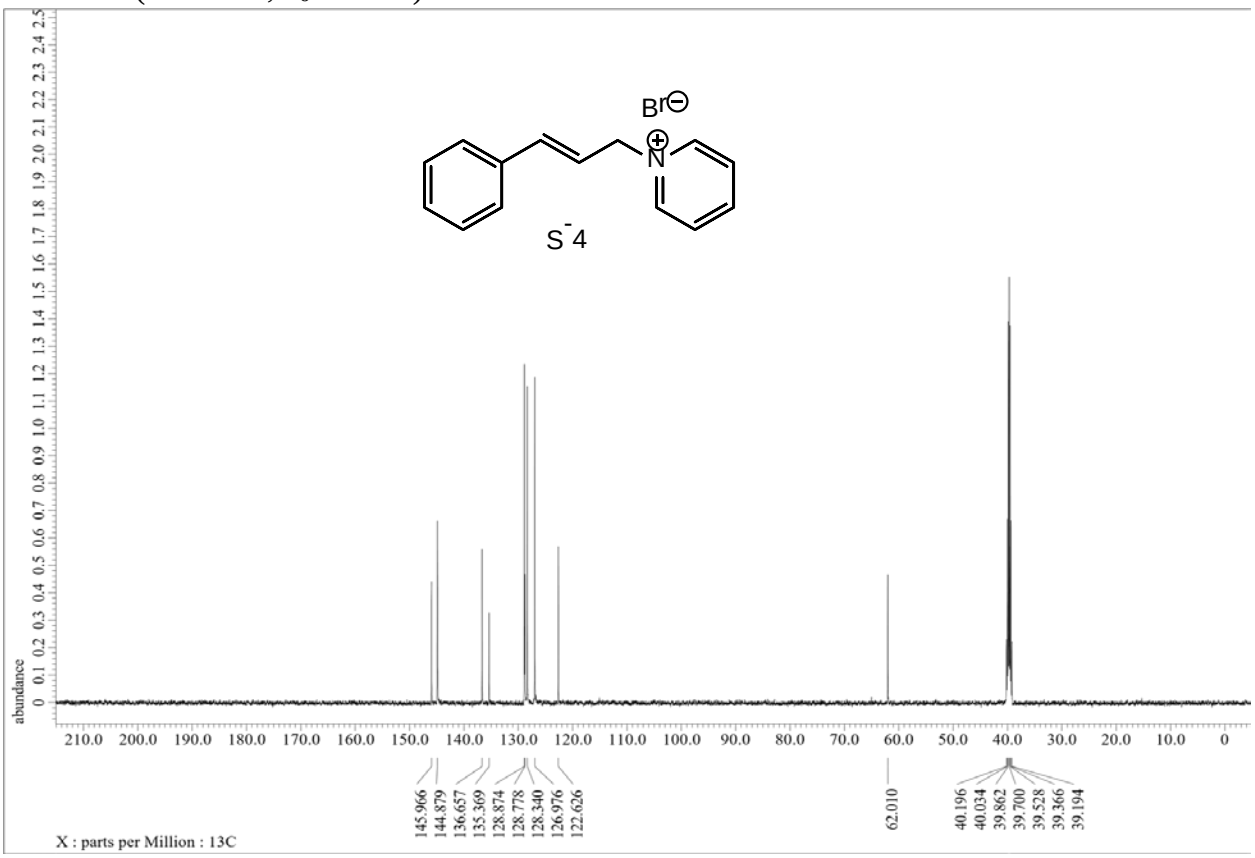
^{13}C NMR (125 MHz, DMSO-d_6)



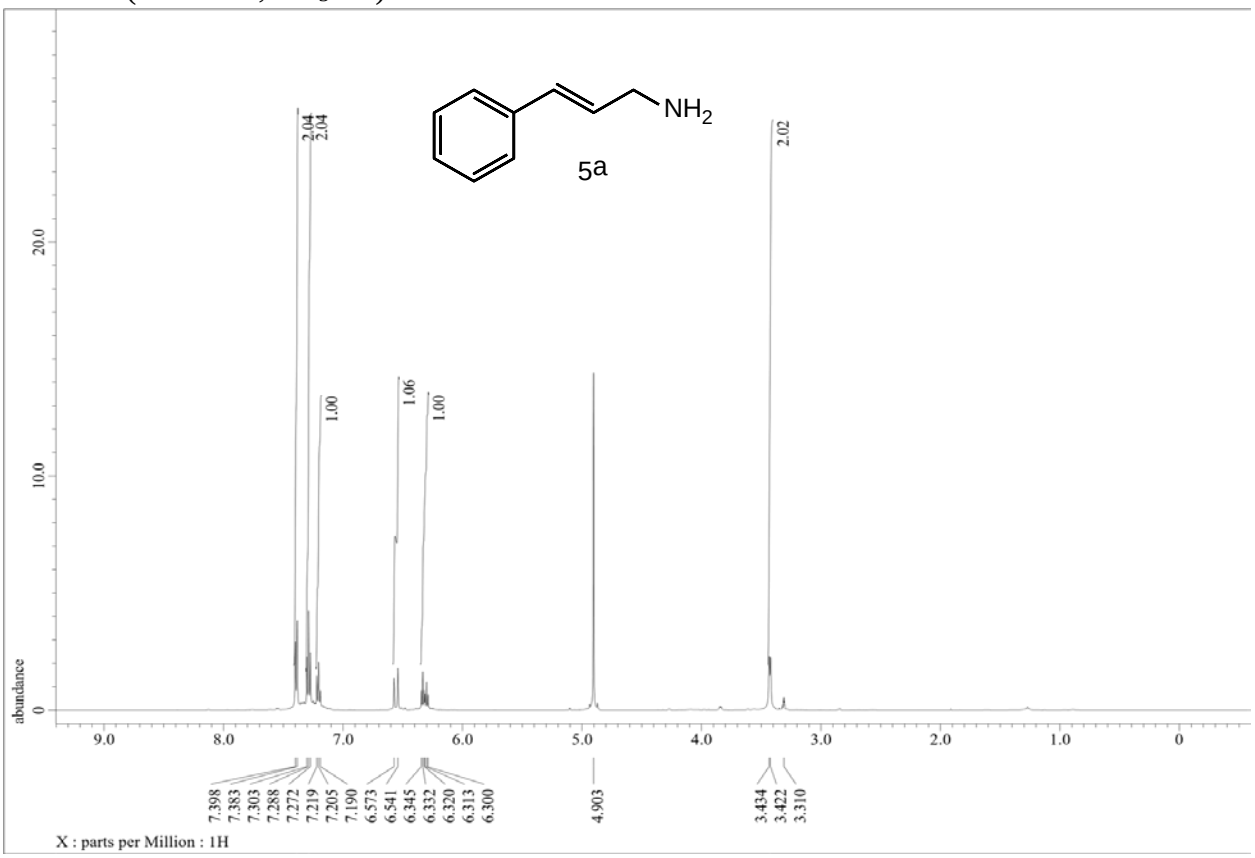
^{1}H NMR (500 MHz, d_6-DMSO)



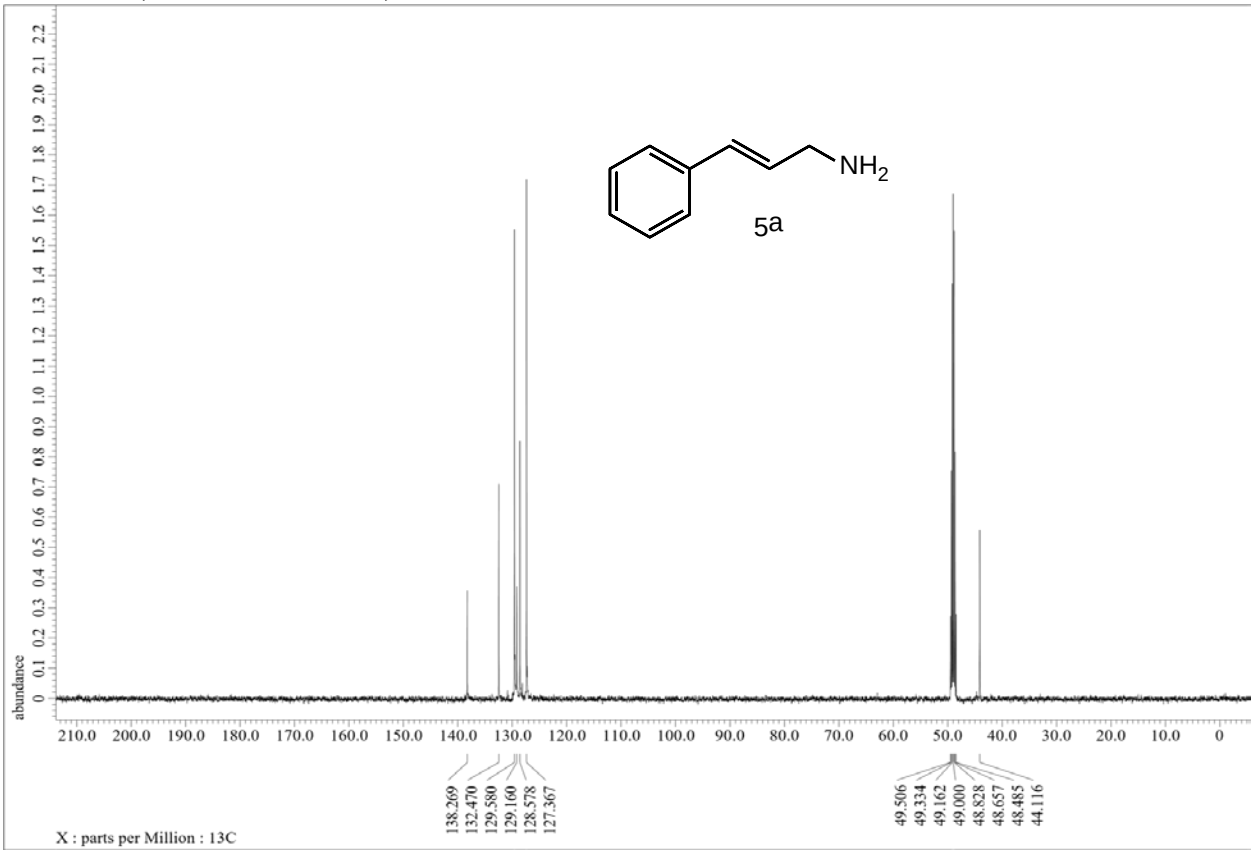
^{13}C NMR (125 MHz, d_6-DMSO)



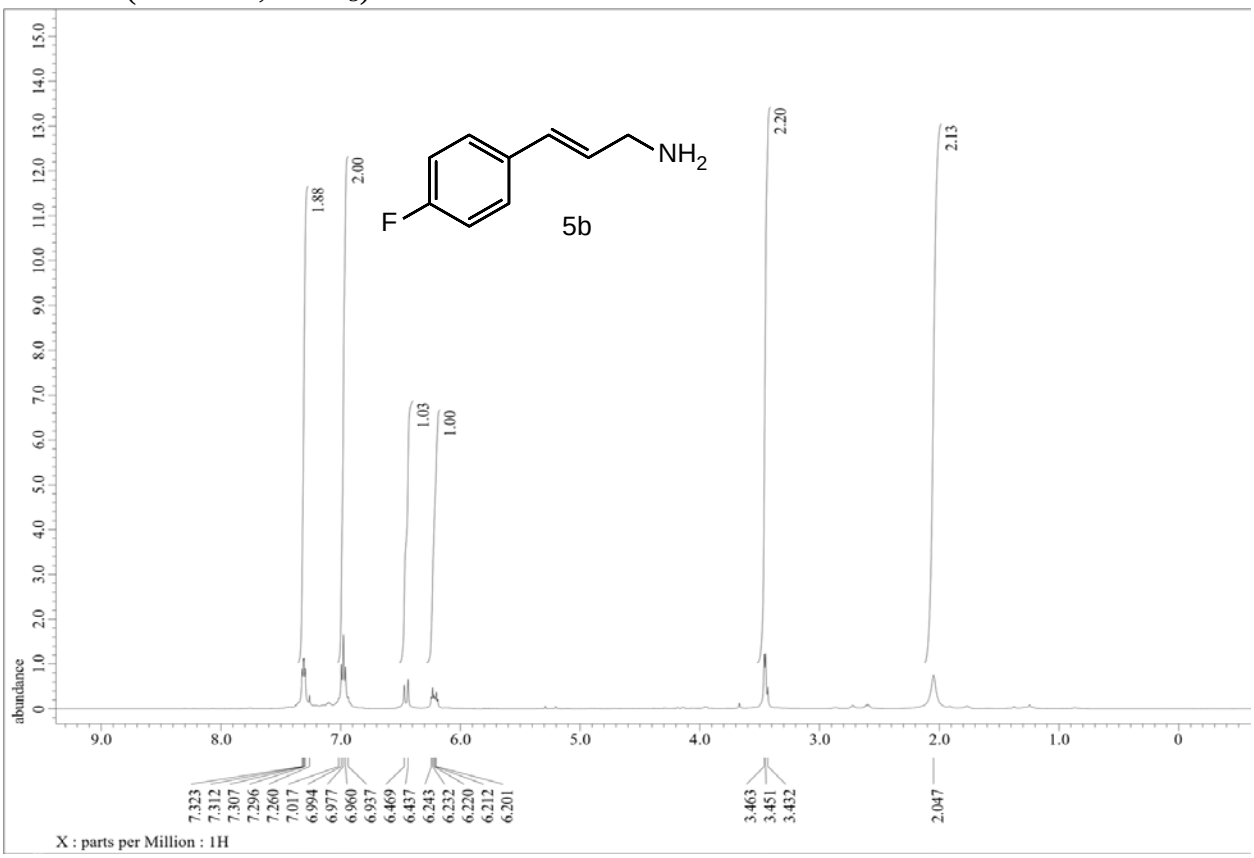
^{1}H NMR (500 MHz, CD_3OD)



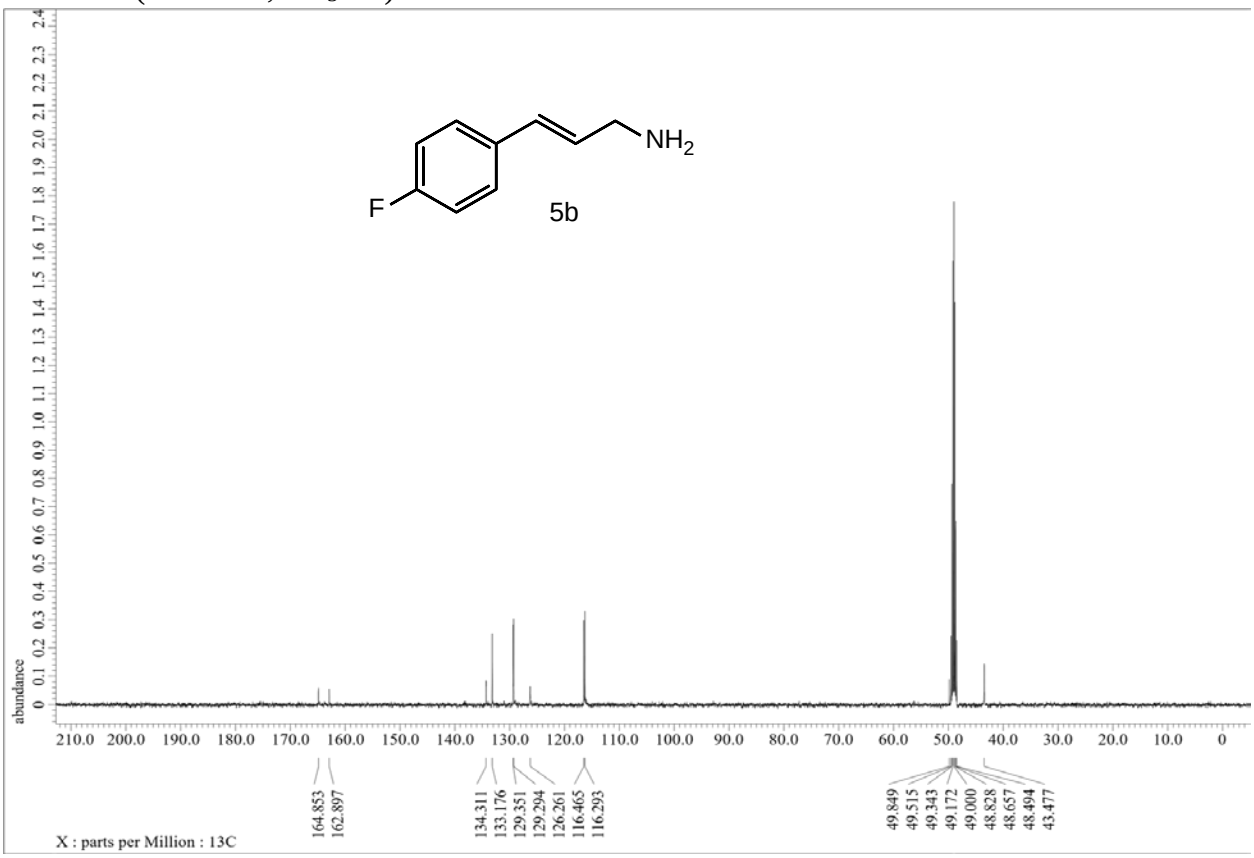
^{13}C NMR (125 MHz, CD_3OD)



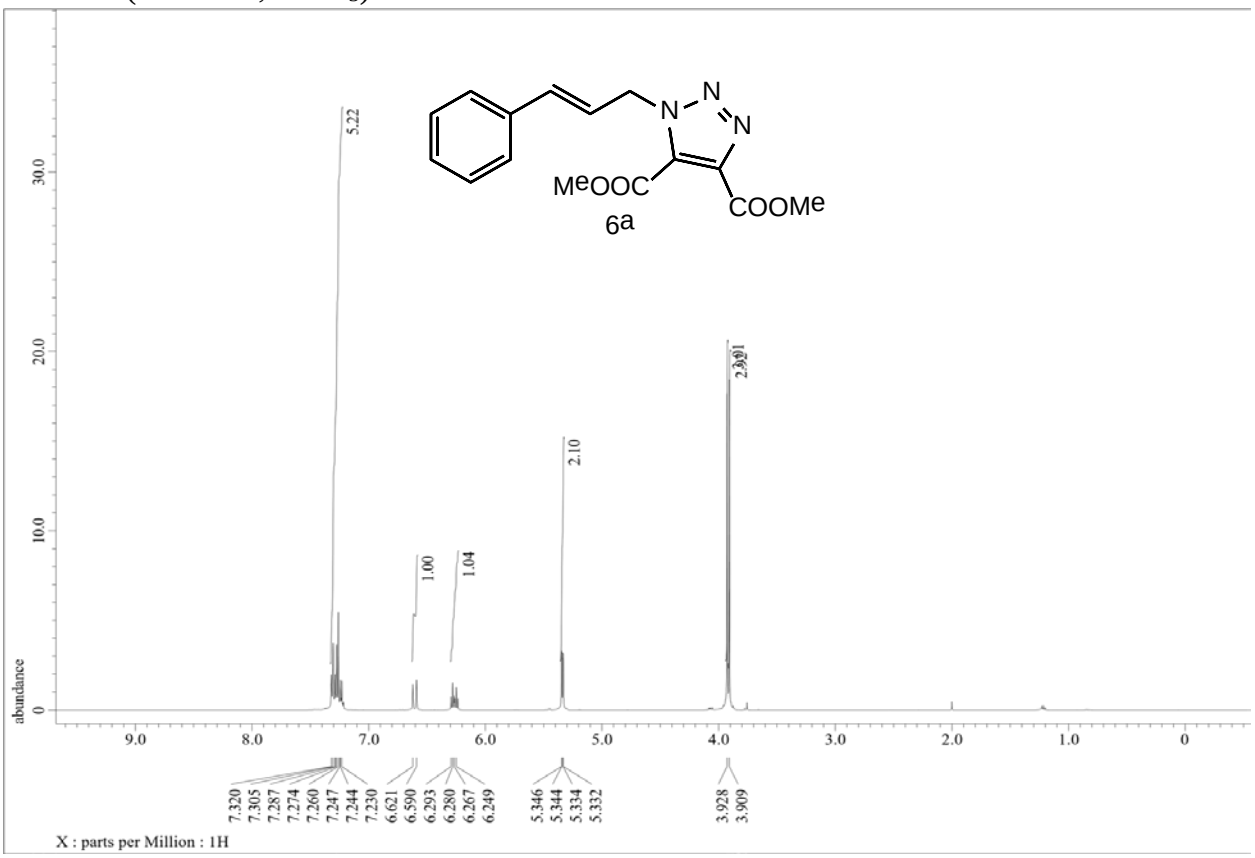
^{1}H NMR (500 MHz, $CDCl_3$)



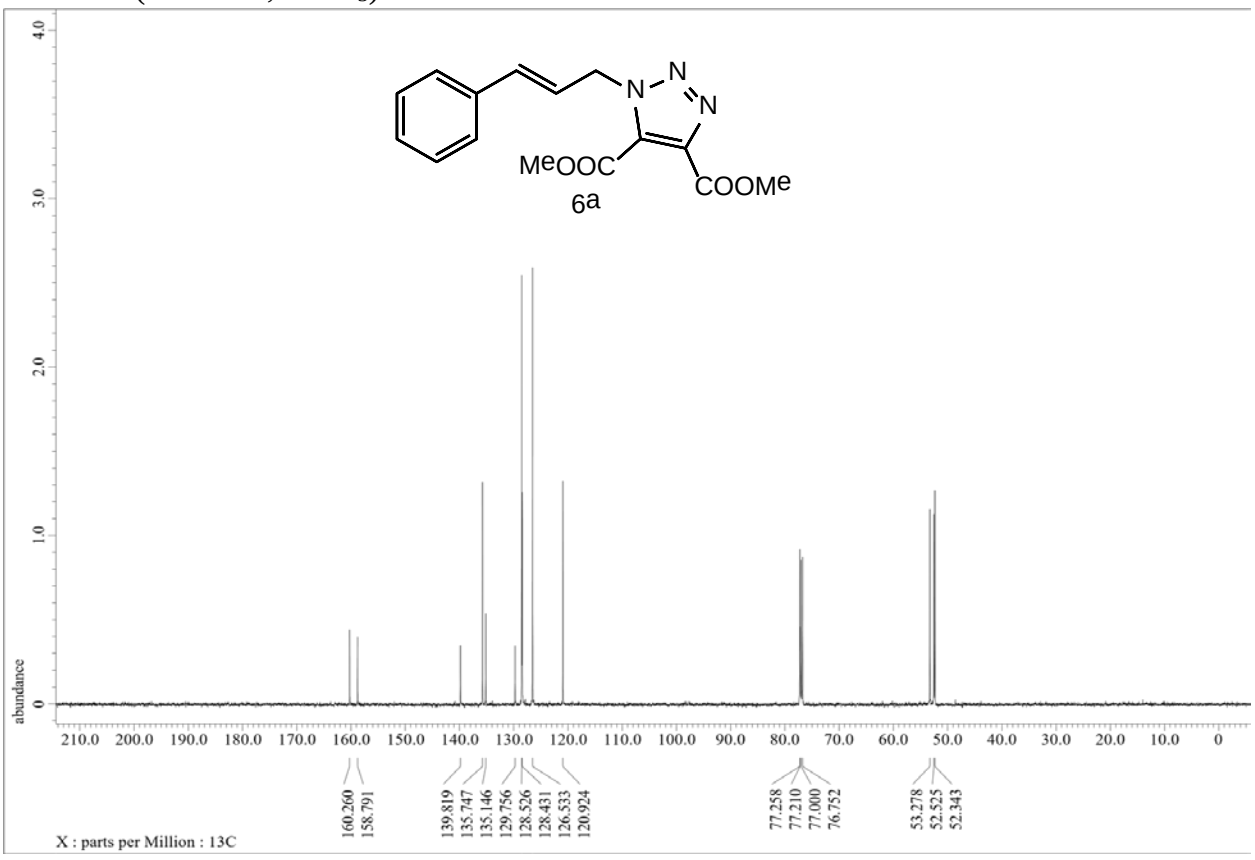
^{13}C NMR (125 MHz, *C*D_3OD)



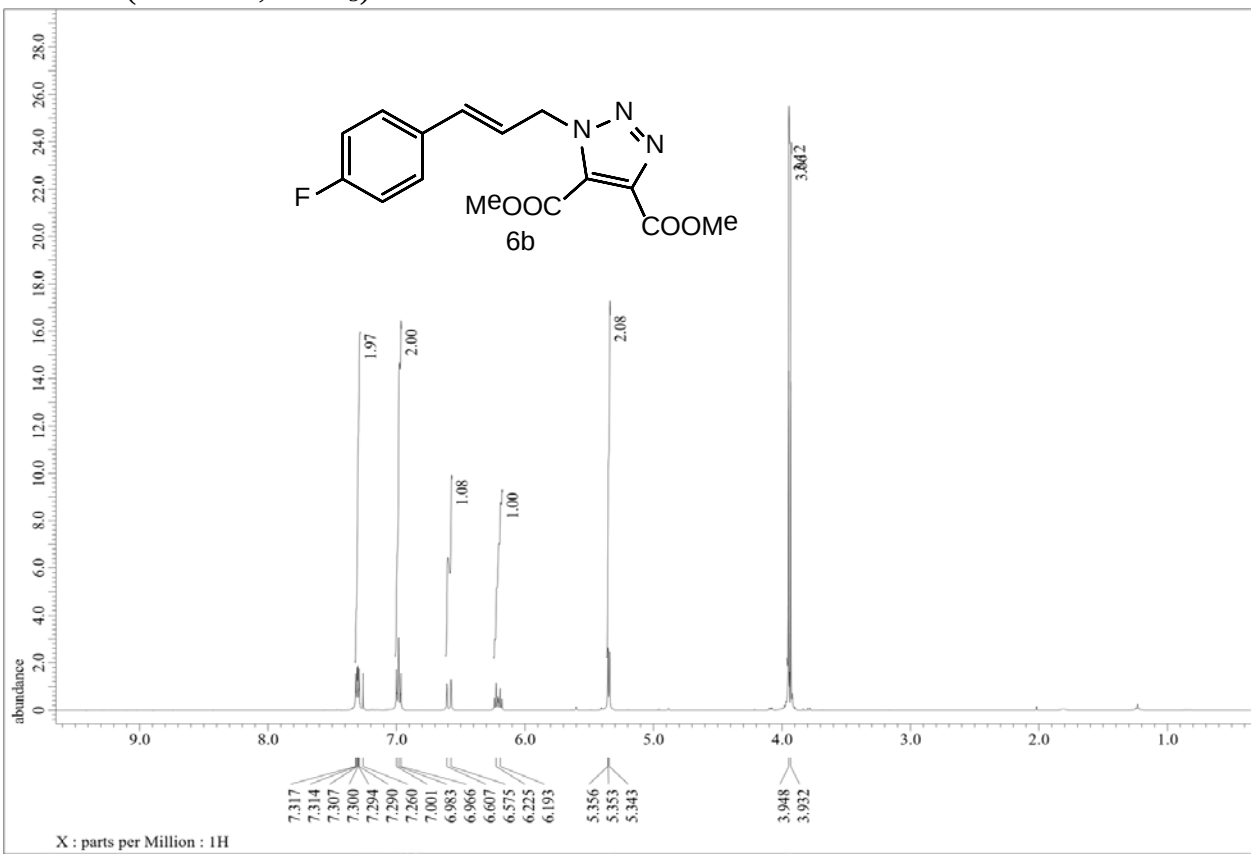
^{1}H NMR (500 MHz, $CDCl_3$)



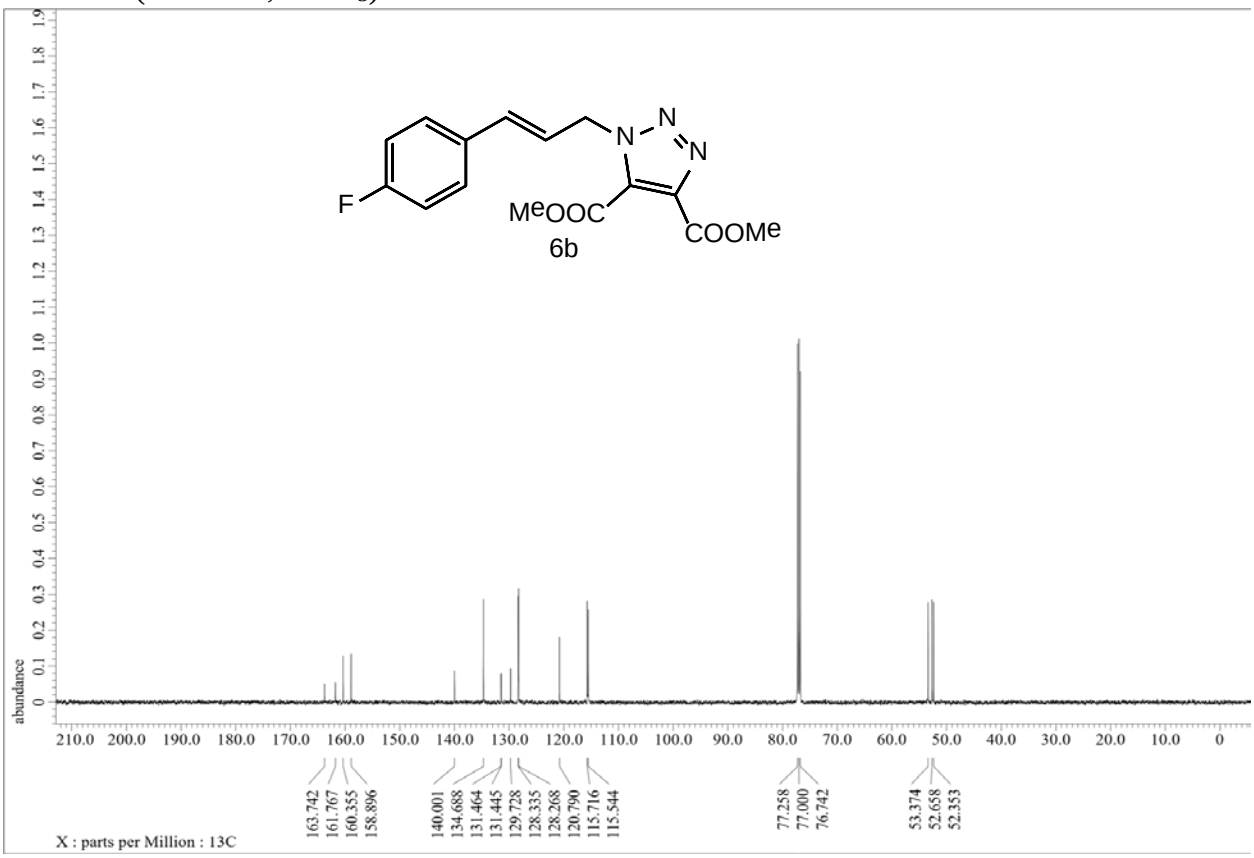
^{13}C NMR (125 MHz, $CDCl_3$)



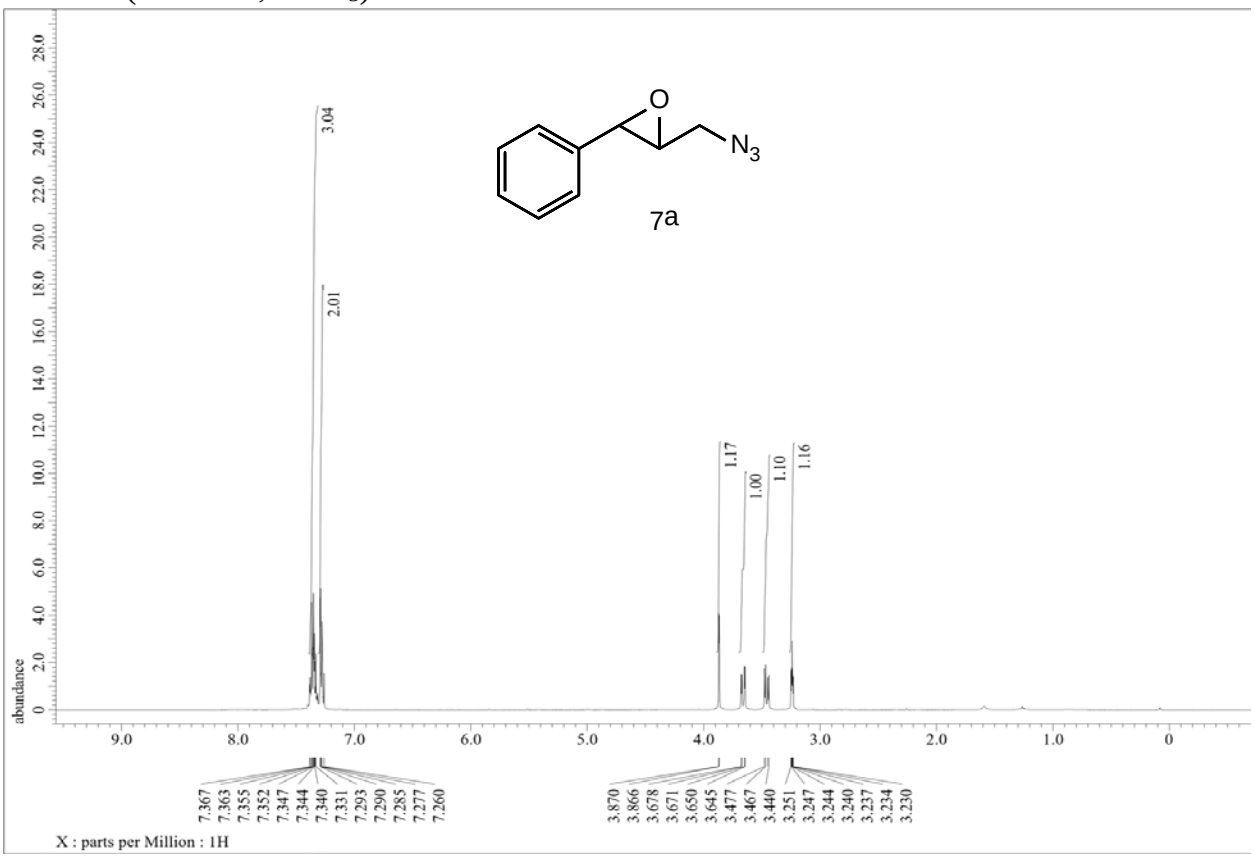
^{1}H NMR (500 MHz, $CDCl_3$)



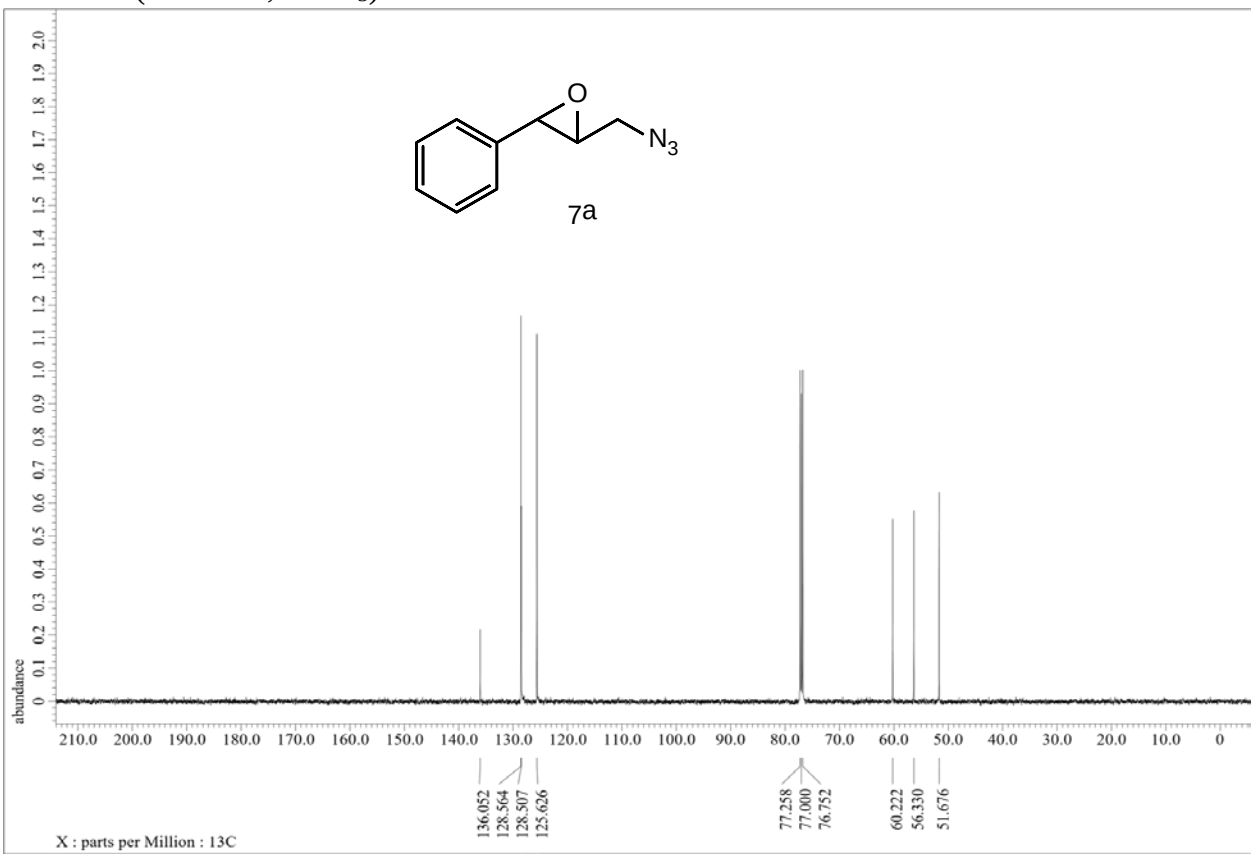
^{13}C NMR (125 MHz, $CDCl_3$)



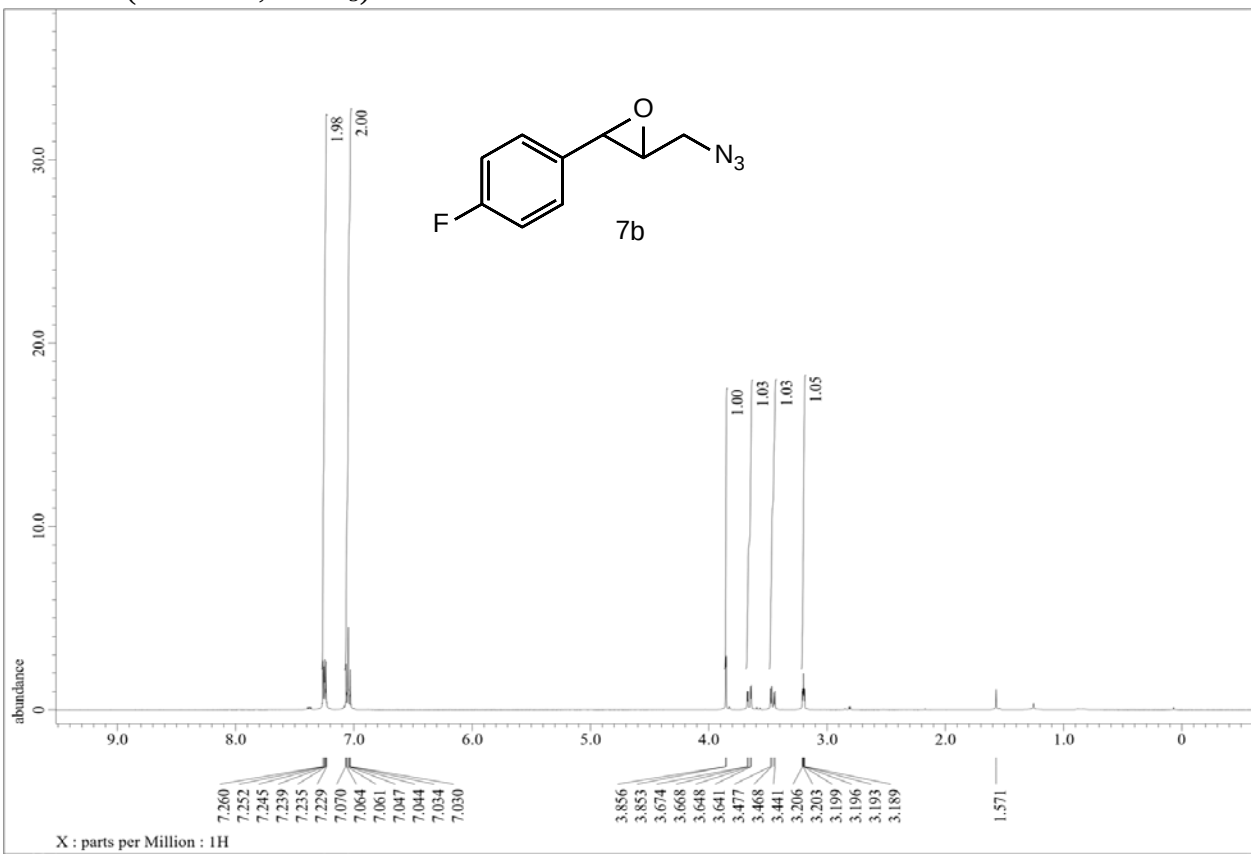
^{1}H NMR (500 MHz, $CDCl_3$)



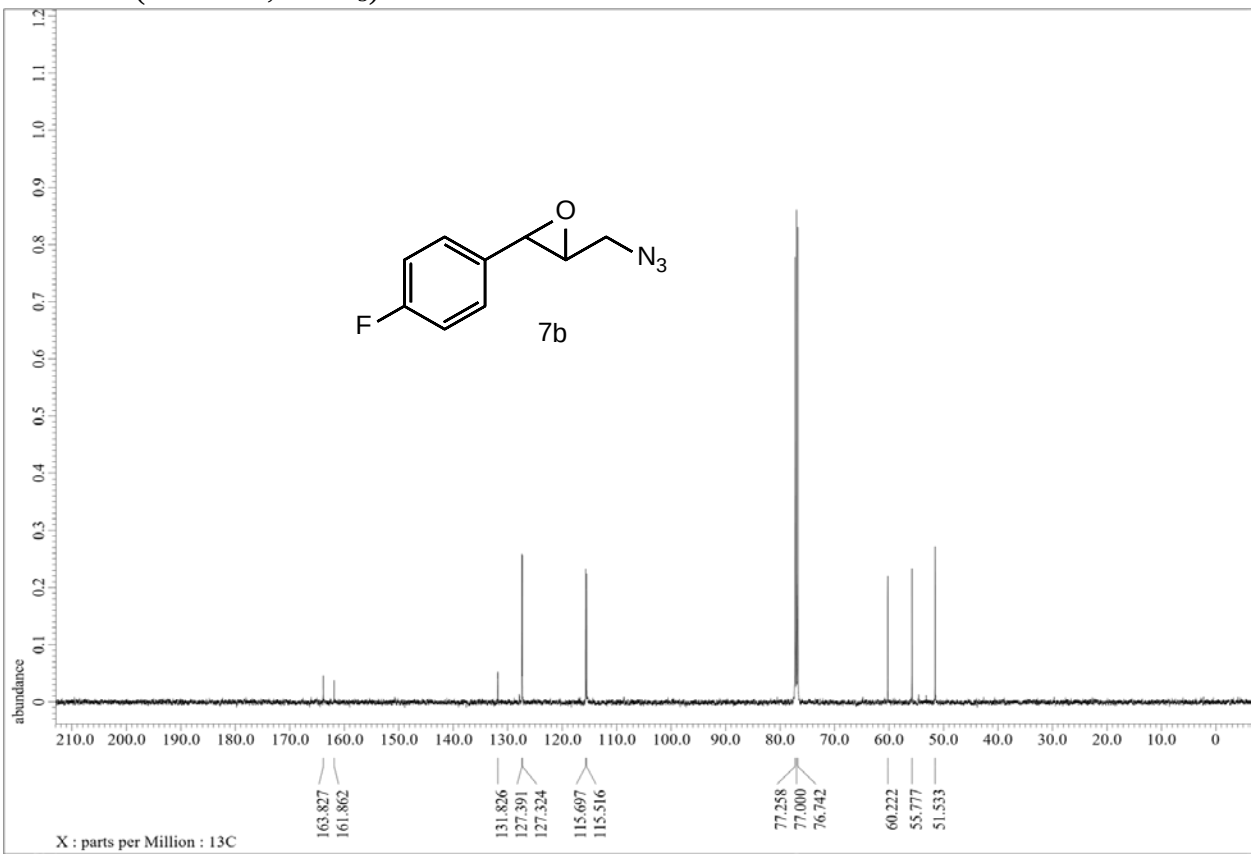
^{13}C NMR (125 MHz, $CDCl_3$)



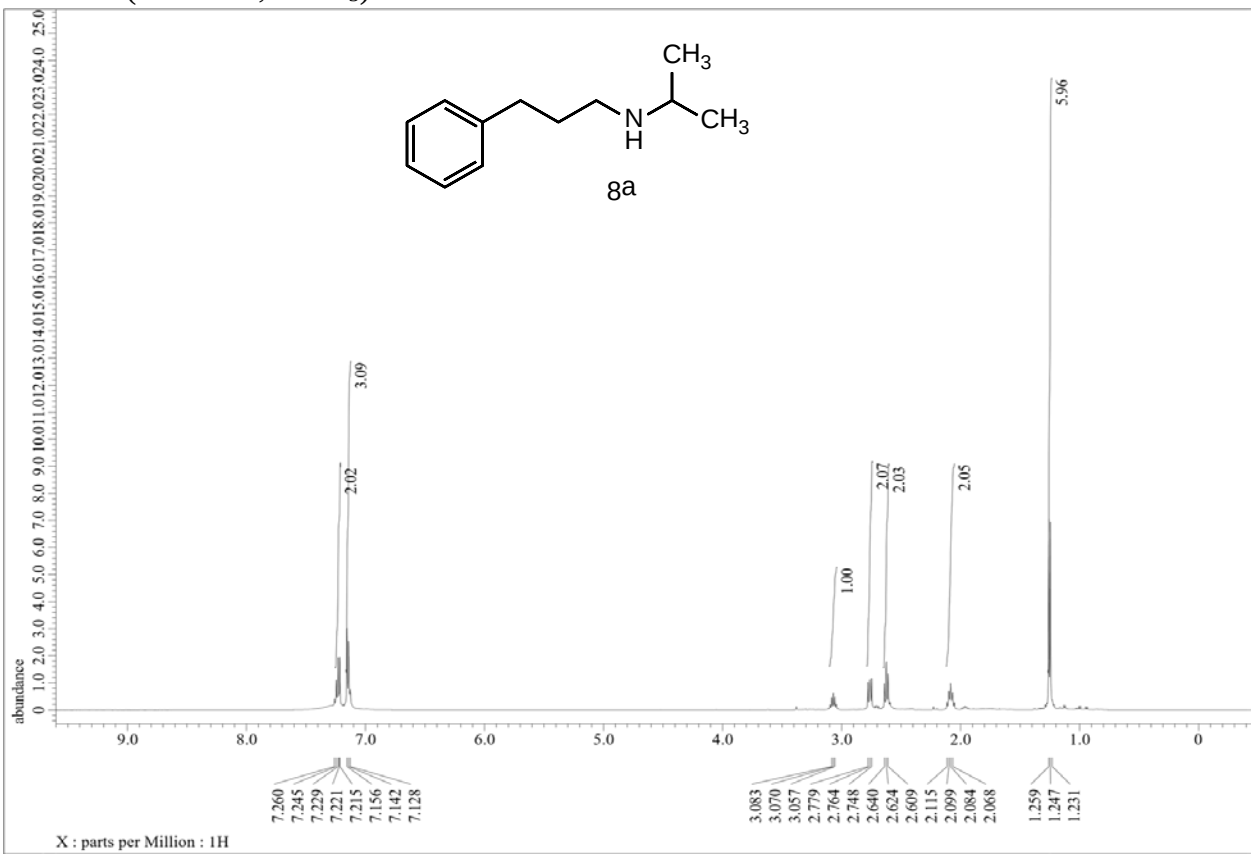
^{1}H NMR (500 MHz, $CDCl_3$)



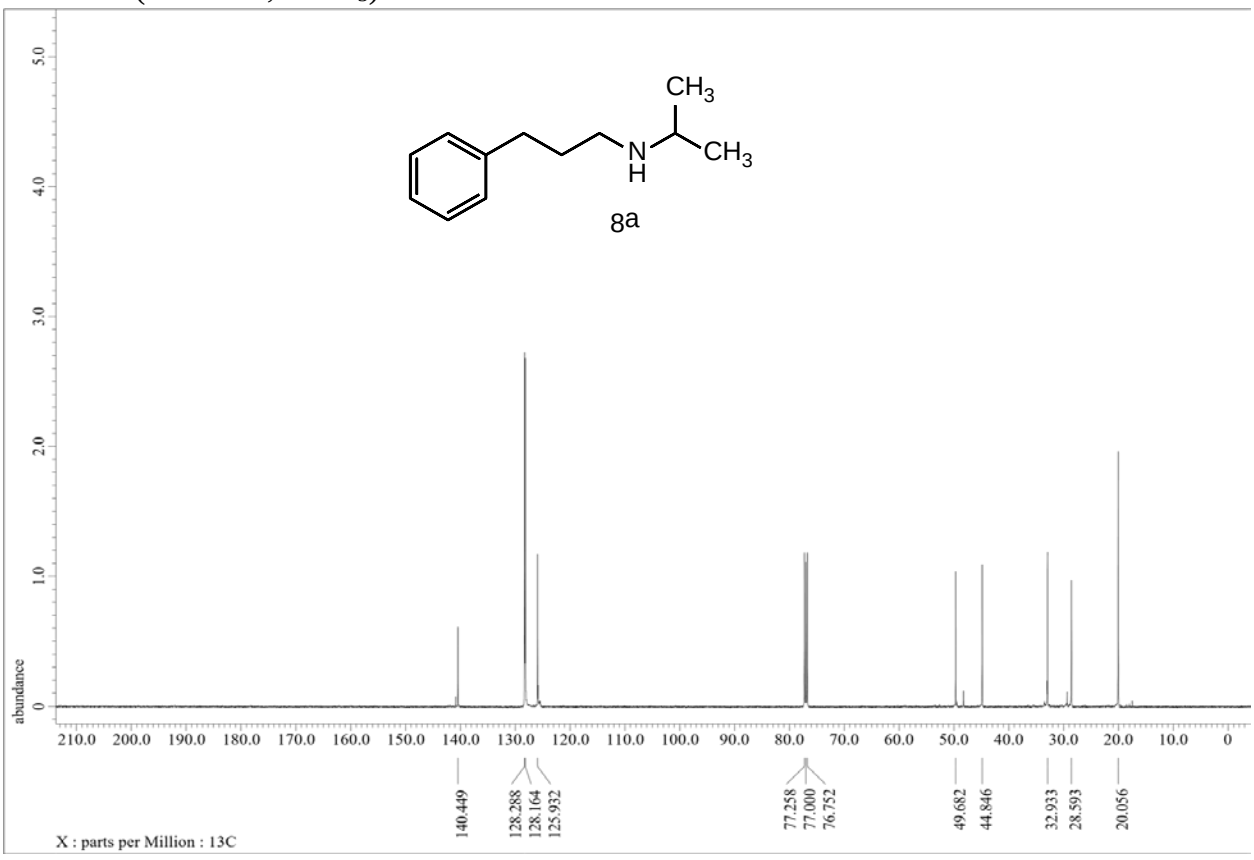
^{13}C NMR (125 MHz, $CDCl_3$)



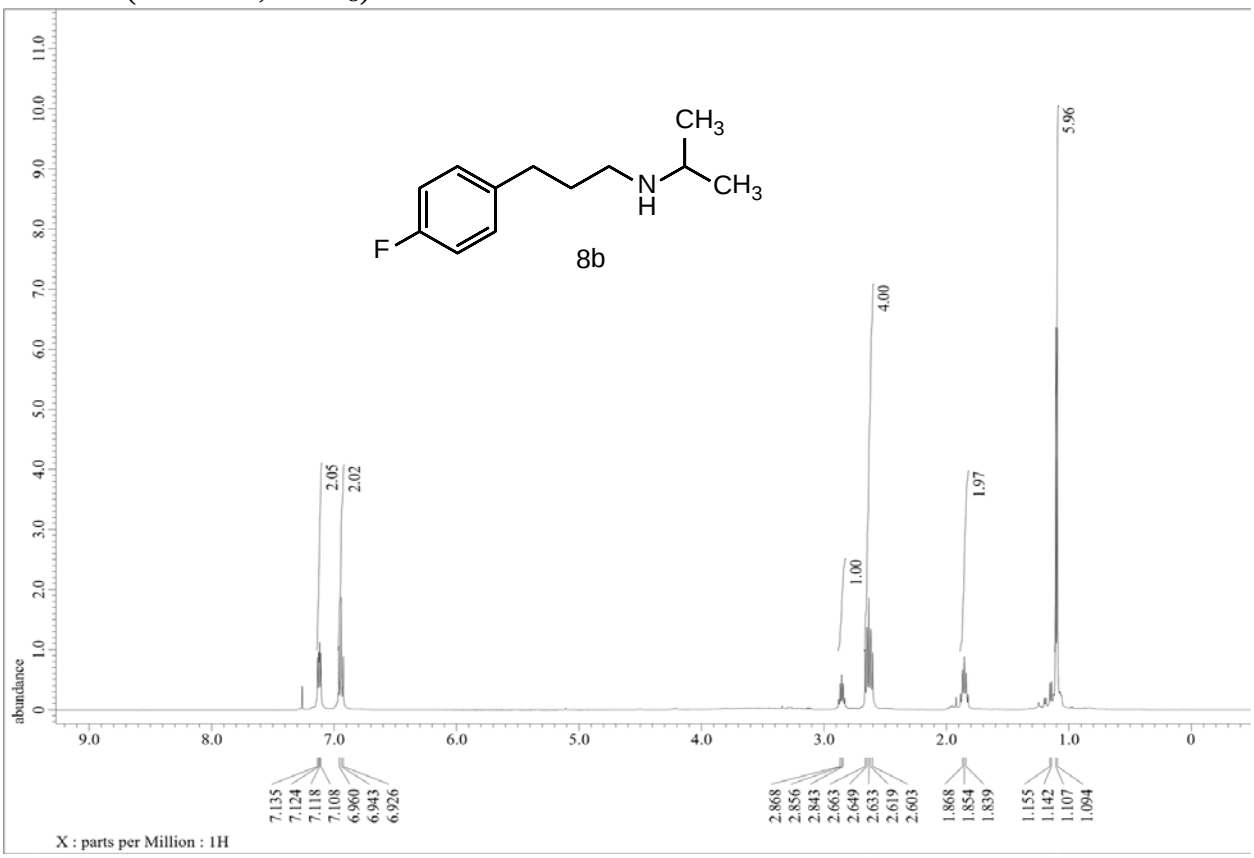
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)