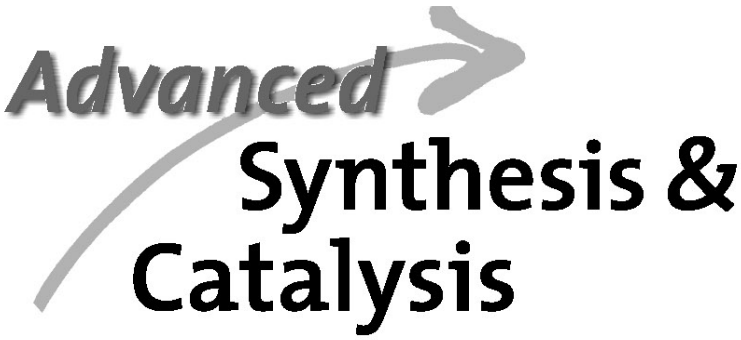

Supporting Information

Supporting Information for:

Highly Regioselective Copper(II)-mediated Bromoamination of Unfunctionalized Olefins: An Efficient Route to N-Heterocyclic Compounds

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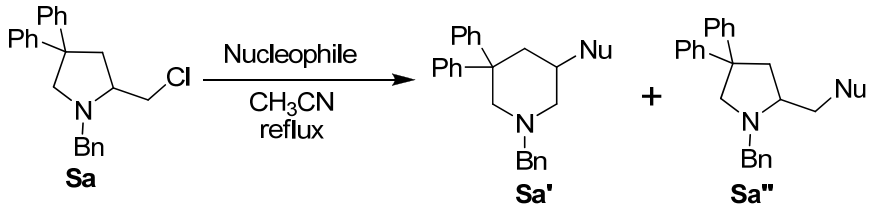
1. General information

Reactions were carried out using commercially available reagents in oven-dried apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 298 K using deuterated chloroform as solvent and TMS as the internal reference. Column chromatography was performed employing 200-300 mesh silica gel unless otherwise noted. Thin layer chromatography (TLC) was performed on silica gel GF_{254}. High resolution mass spectral analyses (HRMS) analyses were carried out with Varian FTICR-MS 7.0T. Unless otherwise indicated, starting materials and reagents used in reactions were purchased from J&K Chemicals (Beijing) or Aladdin Reagents (Shanghai) and were used as received without further purification.

2. Derivatization of Chloramination Product

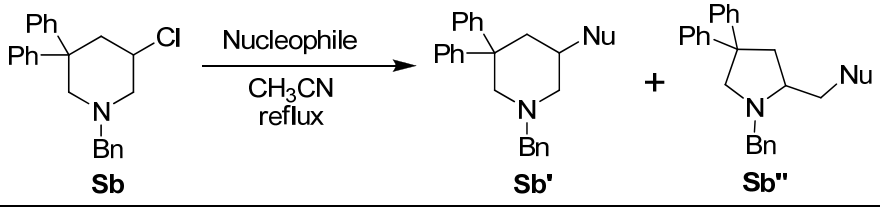
Table 1. Derivatization of N-benzyl-2-chloromethyl-4,4-diphenylpyrrolidine.



Entry	Nucleophile	**Sa'**[a]	**Sa''**[a]
1	$BnNH_2$	31	45
2	KOAc	43	32
3	NaN_3	36	32
4	NaCN	45	40
5	PhSNa	40	34

a: Isolated Yield.

Table 2. Derivatization of N-benzyl-3-chloro-5,5-diphenylpiperidine.

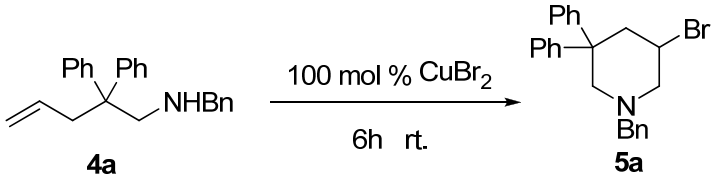


Entry	Nucleophile	**Sb'**[a]	**Sb''**[a]
1	$BnNH_2$	10	61
2	KOAc	14	68
3	NaN_3	13	78
4	NaCN	6	83
5	PhSNa	21	66

a: Isolated Yield.

3. Investigation of Solvent Effect

Table 3. Optimization of reaction conditions.

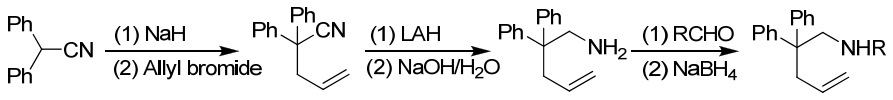


4a **5a**

Entry	solvent	Conversion [a]
1	Hexane	52
2	**CH_3CN**	**>99**
3	Acetone	56
4	$CHCl_3$	60
5	THF	79
6	Benzene	83
7	Toluene	80
8	Dioxane	87
9	DCE	88
10	DMSO	65
11	DMF	86
12[b]	CH_3CN	>99
13[c]	CH_3CN	>99
14[d]	CH_3CN	>99
15[e]	CH_3CN	50
16[f]	CH_3CN	31%
17[g]	CH_3CN	Unresolved complex mixture

a: Determined by crude NMR analysis. b: in the presence of 1 equiv. of K_2CO_3. c: in the presence of 1 equiv. of Cs_2CO_3. d: 50 mol% $CuBr_2$, 5 d, open air. e: 50 mol% $CuBr_2$, 5 d, under argon atmosphere. f: isolated yield, in the presence of 1 equiv. of TEMPO. g: N-benzyl-5-penten-1-amine was used as substrate.

4. Synthesis and Characterization of Aminoalkene Substrates [1]



S1 (93%) **S2** (85%)

4a R = Bn (86%)
4b R = 4-MeBn (81%)
4c R = 4-MeOBn (87%)
4d R = 4-FBn (82%)
4e R = 4-O_2NBn (83%)
4f R = *i*-Bu (92%)
4g R = *i*-Pr (89%)

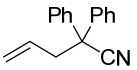
A solution of diphenylacetonitrile (9.65 g, 50 mmol) in DMF (20 mL) was added slowly to a suspension of NaH (1.32 g, 55 mmol) in DMF (50 mL) and the resulting

mixture was stirred at room temperature for 1 hour. The resulting bright yellow suspension was cooled to 0°C, treated with allyl bromide (6.66 g, 55 mmol), warmed to room temperature and stirred at room temperature for 12 hours. The resulting solution was poured into ice/water (200 mL) and was extracted with CH_2Cl_2 (3×100 mL). The combined organic layer was washed with water (2×50 mL), dried with $MgSO_4$, and concentrated to give 2,2-diphenyl-4-pentenenitrile (**S1**) (10.83 g, 93%), which was used in the subsequent step without further purification.

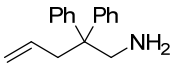
To a suspension of $LiAlH_4$ (1.52 g, 40 mmol) in THF (130 mL) was added **S1** (2.33 g, 10 mmol) at 0°C. The mixture was slowly warmed to room temperature and stirred overnight. The resulting suspension was cooled to 0°C and quenched by slow addition of 6 M NaOH (50 mL). The resulting mixture was extracted with CH_2Cl_2 (4×100 mL) and the combined ether extracts were dried ($MgSO_4$) and concentrated to give 2,2-diphenyl-diphenyl-4-pentenylamine (**S2**) (2.01g, 85%) as a pale yellow, viscous oil.

A solution of **S2** (1.19 g, 5 mmol) and benzaldehyde (0.54 g, 5.1mmol) in MeOH (20 mL) was stirred at room temperature for 5 h, then treated with $NaBH_4$ (0.29g, 7.5 mmol) and the mixture was stirred overnight. The resulting mixture was treated with water (50 mL), 1 M NaOH (20 mL) and then was extracted with CH_2Cl_2 (3×100 mL). The combined organic layer was dried ($MgSO_4$) and concentrated. The resulting oily residue was chromatographed to give **4a** (1.32 g, 86%) as a viscous oil.

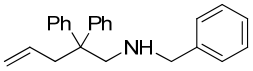
The N-substituted 4-penten-1-amines **4b-4g,** were synthesized via reductive amination of **S2** with the corresponding aldehydes or ketones via procedures similar to that used to synthesize **4a**.



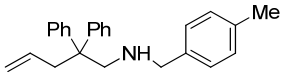
2,2-Diphenylpent-4-enenitrile (S1) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46-7.19 (m, 10H), 5.70 (ddt, *J*=17.1, 10.2, 7.0, 1H), 5.31-5.05 (m, 2H), 3.12 (d, *J*=7.0, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.81, 131.84, 128.90, 127.99, 127.10, 121.94, 120.43, 51.85, 43.98. Spectral data was consistent with the known aminoalkene.[1]



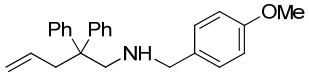
2,2-Diphenylpent-4-en-1-amine (S2) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37-6.91 (m, 10H), 5.51-5.27 (m, 1H), 5.17-4.83 (m, 2H), 3.31 (s, 2H), 2.92 (d, *J*=7.0, 2H), 0.77 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.33, 134.69, 128.24, 128.11, 126.10, 117.72, 51.50, 48.62, 41.17. Spectral data was consistent with the known aminoalkene.[1]



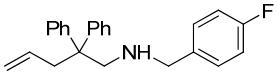
N-Benzyl-2,2-diphenylpent-4-en-1-amine (4a) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.21-7.07 (m, 15H), 5.40-5.12 (m, 1H), 4.86 (m, 2H), 3.64 (s, 2H), 3.12 (s, 2H), 2.96 (d, *J*=7.0, 2H), 0.91(brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.05, 140.92, 135.07, 128.40, 128.27, 128.17, 128.12, 126.91, 126.18, 117.87, 55.45, 54.37, 50.34, 41.81.Spectral data was consistent with the known aminoalkene.[1]



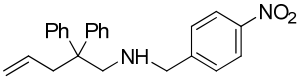
N-(4-Methylbenzyl)-2,2-diphenylpent-4-en-1-amine (4b) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.05 (m, 14H), 5.39-5.23 (m, 1H), 5.03-4.83 (m, 2H), 3.66 (s, 2H), 3.19 (s, 2H), 3.03 (d, *J*=7.1, 2H), 2.30 (s, 3H), 0.81 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.94, 137.76, 136.24, 135.00, 128.94, 128.15, 128.00, 127.91, 126.00, 118.23, 55.38, 53.99, 50.25, 41.72, 21.14. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{27}N$: 342.2222; found: 342.2220.



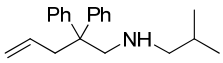
N-(4-Methoxybenzyl)-2,2-diphenylpent-4-en-1-amine (4c) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.07 (m, 12H), 6.80 (d, *J*=7.6, 2H), 5.33 (m, 1H), 4.93 (m, 2H), 3.77 (s, 3H), 3.64 (s, 2H), 3.18 (s, 2H), 3.02 (d, *J*=7.0, 2H), 0.98 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =158.58, 146.82, 134.95, 132.78, 129.08, 128.11, 127.97, 125.93, 117.70, 113.63, 55.28, 55.24, 53.61, 50.19, 41.69.Spectral data was consistent with the known aminoalkene.[2]



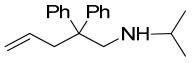
N-(4-Fluorobenzyl)-2,2-diphenylpent-4-en-1-amine (4d) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.20 (m, 12H), 7.01 (t, *J*=8.4, 2H), 5.50-5.32 (m, 1H), 5.00 (m, 2H), 3.73 (s, 2H), 3.24 (s, 2H), 3.09 (d, *J*=7.0, 2H), 0.95 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =163.14, 160.73, 146.84, 134.89, 129.50, 129.42, 128.11, 128.04, 126.07, 117.67, 115.09, 114.88, 55.26, 53.47, 50.20, 41.68.^{19}F NMR (376 MHz, $CDCl_3$) δ= -116.20. Spectral data was consistent with the known aminoalkene.[2]



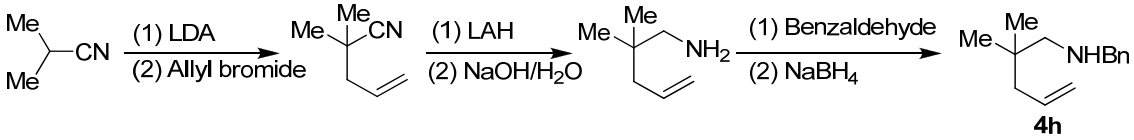
N-(4-Nitrobenzyl)-2,2-diphenylpent-4-en-1-amine (4e) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 4H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 4H), 5.44-5.23 (m, 1H), 5.00 (dd, *J* = 37.2, 13.6 Hz, 2H), 3.84 (s, 2H), 3.22 (s, 2H), 3.09 (d, *J* = 7.0 Hz, 2H). 0.96(brs,1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.57, 146.55, 134.73, 128.50, 128.10, 128.01, 126.57, 126.19, 123.49, 117.77, 55.38, 53.42, 50.14, 41.55. Spectral data was consistent with the known aminoalkene.[1]



N-Isobutyl-2,2-diphenylpent-4-en-1-amine(4f) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43-7.17 (m, 10H), 5.44 (dt, *J* = 17.1, 8.5 Hz, 1H), 5.05 (dd, *J* = 37.5, 13.3 Hz, 2H), 3.24 (s, 2H), 3.09 (d, *J* = 7.0 Hz, 2H), 2.39 (d, *J* = 6.8 Hz, 2H), 1.79-1.63 (m, 1H), 0.83 (d, *J* = 6.6 Hz, 6H), 0.47 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.06, 135.14, 128.13, 127.97, 125.96, 117.58, 58.52, 55.96, 50.21, 41.68, 27.85, 20.56.Spectral data was consistent with the known aminoalkene.[2]

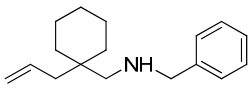


N-Isopropyl-2,2-diphenylpent-4-en-1-amine (4g) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19-7.03 (m, 10H), 5.28 (ddt, *J*=17.1, 10.0, 7.1, 1H), 4.99-4.70 (m, 2H), 3.11 (s, 2H), 2.91 (d, *J*=7.1, 2H), 2.54 (hept, *J*=6.2, 1H), 0.84 (d, *J*=6.3, 6H), 0.26 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.07, 135.02, 128.11, 127.93, 125.90, 117.55, 53.64, 49.97, 49.26, 41.61, 23.13. Spectral data was consistent with the known aminoalkene.[3]

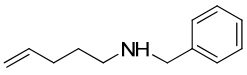


4h

N-Benzyl-2,2-dimethylpent-4-en-1-amine (4h) Isobutyronitrile (50 mmol) was added to a solution of LDA [generated in situ from *n*-BuLi and diisopropylamine (12.4 g,123 mmol) in THF (300 mL)] at -78°C and the mixture was stirred at this temperature for 1h. To the resulting solution was added allyl bromide (21.5 mL, 248 mmol). The solution was warmed to room temperature and was stirred overnight. CH_2Cl_2 (75 mL) was added and the resulting biphasic mixture was washed with water (3×100 mL), dried ($MgSO_4$), and carefully concentrated, due to the volatility of the cyanide, to give 2,2-dimethyl-4-pentenenitrile. Conversion of 2, 2-dimethyl-4-pentenenitrile to **4h** was accomplished in a manner similar to that employed for the conversion of **S2** to **4a-4g**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58-7.13 (m, 5H), 5.99-5.74 (m, 1H), 5.11 (d, *J* = 13.6 Hz, 2H), 3.88 (s, 2H), 2.47 (s, 2H), 2.13 (d, *J* = 7.4 Hz, 2H), 1.29 (s, 1H), 1.00 (d, *J* = 1.0 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.10, 135.68, 128.36, 128.05, 126.83, 116.86, 59.76, 54.80, 44.73, 34.46, 25.64. Spectral data was consistent with the known aminoalkene.[1]

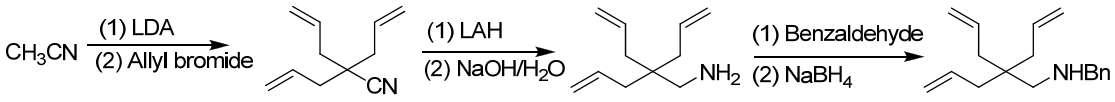


1-(1-Allylcyclohexyl)-N-benzylmethanamine (4i) Compound **4i** was synthesized employing procedure similar to that used to synthesize **4h** starting from cyclohexanenitrile**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.37-6.88 (m, 5H), 5.76 (ddd, *J* = 17.6, 10.1, 5.1 Hz, 1H), 5.08-4.87 (m, 2H), 3.76 (s, 2H), 2.41 (s, 2H), 2.11 (d, *J* = 7.5 Hz, 2H), 1.44-1.20 (m, 10H), 0.91 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =141.18, 135.43, 128.33, 128.10, 126.82, 116.74, 55.96, 54.76, 40.79, 36.77, 34.15, 26.57, 21.73. Spectral data was consistent with the known aminoalkene.[1]



N-Benzylpent-4-en-1-amine (4j) To a solution of benzylamine (5 mmol) and 5-bromo-1-pentene (1 mmol) in ethanol (30 mL) was added NaI (0.1 mmol,).The mixture was stirred overnight at 75 °C and the solvent was removed *in vacuo*. The resulting oily residue was chromatographed (Petroleum ether : Ethyl acetate= 5:1) to give **4j** (0.09g, 53%) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21-7.13 (m, 5H), 5.70 (m, 1H), 4.98-4.80 (m, 2H), 3.67 (s, 2H), 2.53 (t, *J*=7.2, 2H), 2.02 (brs, 1H), 2.01-1.95 (m, 2H), 1.58-1.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.24,

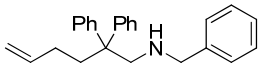
138.44, 128.41, 128.19, 126.97, 114.71, 53.93, 48.80, 31.56, 29.15. Spectral data was consistent with the known aminoalkene.[3]



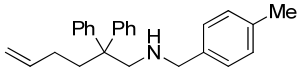
4k

2,2-diallyl-N-benzylpent-4-en-1-amine (4k)[4] A flask was charged with acetonitrile (30 mmol) and THF (50 mL). This solution was cooled to -78 °C. A solution of LDA (32 mmol) was added slowly to the acetonitrile solution. After 30 minutes of stirring at -78 °C, allyl bromide (32mmol) was added. The reaction mixture was warmed to room temperature with stirring for 1hour before being cooled to -78 °C again. Another equivalent of LDA solution was added, followed by 30 minutes of stirring, followed by the addition of another equivalent of allyl bromide. The reaction was again warmed to room temperature with stirring for 1 hour before being cooled to -78 °C. The third LDA solution was added, followed by 30 minutes of stirring, followed by the addition of a third equivalent of allyl bromide. Then the reaction was allowed to warm to room temperature with stirring overnight. CH_2Cl_2 (75 mL) was added and the resulting biphasic mixture was washed with water (3×100 mL), dried ($MgSO_4$), and concentrated to give 2,2-diallylpent-4-enenitrile. Conversion of 2,2-diallylpent-4-enenitrile to **4k** was accomplished in a manner similar to that employed for the conversion of **S2** to **4a-4g**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 6.93 (m, 5H), 6.06 – 5.52 (m, 3H), 4.96 (dd, *J* = 7.6, 6.9 Hz, 6H), 3.65 (s, 2H), 2.30 (s, 2H), 1.97 (d, *J* = 7.5 Hz, 6H), 1.11 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.05, 134.82, 128.31, 128.08, 126.82, 117.42, 54.78, 54.70, 40.16, 39.81. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{25}N$, 256.2065; found: 256.2061.

Compounds **6a-6g** was synthesized via procedures similar to that used to synthesize **4a-4i** starting from 4-bromo-1-butene.

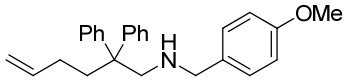


N-benzyl-2,2-diphenylhex-5-en-1-amine (6a) ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.34 – 7.09 (m, 15H), 5.75 (tt, *J* = 16.5, 6.4 Hz, 1H), 4.97 – 4.83 (m, 2H), 3.68 (s, 2H), 3.18 (s, 2H), 2.32 (dd, *J* = 9.9, 6.1 Hz, 2H), 1.64 (dd, *J* = 15.5 6.7 Hz, 2H), 1.64 (d, *J* = 5.2 Hz, 2H), 0.84 (brs, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.27, 139.32, 129.35, 128.40, 128.21, 128.16, 128.04, 127.88, 126.12, 114.31, 55.28, 50.40, 42.70, 36.42, 28.83.Spectral data was consistent with the known aminoalkene.[5]

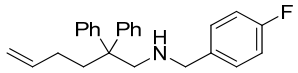


N-(4-methylbenzyl)-2,2-diphenylhex-5-en-1-amine (6b) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.03 (m, 14H), 5.76 (ddt, *J* = 16.8, 10.1, 6.5 Hz, 1H), 5.21 – 4.58 (m, 2H), 3.89 – 3.37 (m, 2H), 3.19 (s, 2H), 2.52 – 2.12 (m, 5H), 1.66 (dd, *J* = 15.4, 7.1 Hz, 2H), 1.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.04, 139.18, 136.29, 128.92, 128.06, 127.97, 127.95, 127.84, 125.93, 114.04, 55.15, 53.75, 50.27, 36.33,

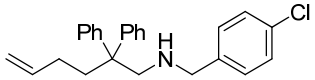
28.65, 21.07. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{29}N$, 356.2378; found: 356.2375.



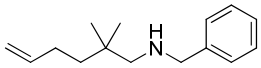
N-(4-methoxybenzyl)-2,2-diphenylhex-5-en-1-amine (6c) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 – 7.21 (m, 4H), 7.20 – 7.07 (m, 8H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.86 – 5.61 (m, 1H), 4.91 (dd, *J* = 23.7, 6.2 Hz, 2H), 3.77 (s, 3H), 3.65 (s, 2H), 3.18 (s, 2H), 2.37 – 2.25 (m, 2H), 1.72 – 1.60 (m, 2H), 1.31 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.08, 139.19, 129.01, 128.48, 128.05, 127.96, 126.55, 125.91, 114.04, 113.62, 55.25, 55.08, 53.42, 50.25, 36.32, 28.63. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{29}NO$, 372.2327; found: 372.2318.



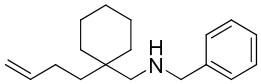
N-(4-fluorobenzyl)-2,2-diphenylhex-5-en-1-amine (6d) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 – 7.00 (m, 12H), 6.85 (t, *J* = 8.6 Hz, 2H), 5.66 (tt, *J* = 10.5, 6.5 Hz, 1H), 5.10 – 4.50 (m, 2H), 3.57 (s, 2H), 3.08 (s, 2H), 2.21 (dd, *J* = 22.0, 13.7 Hz, 2H), 1.55 (d, *J* = 7.8 Hz, 2H), 0.82 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =161.95, 159.53, 145.95, 138.03, 135.29, 135.26, 128.32, 128.25, 126.96, 126.94, 124.92, 114.01, 113.80, 113.06, 54.01, 52.18, 49.17, 35.16, 27.56. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -116.33.HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}FN$, 360.2128; found: 360.2121.



N-(4-chlorobenzyl)-2,2-diphenylhex-5-en-1-amine (6e) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 6.90 (m, 14H), 5.66 (ddt, *J* = 13.2, 10.2, 6.4 Hz, 1H), 4.81 (dd, *J* = 18.2, 9.1 Hz, 2H), 3.57 (s, 2H), 3.07 (s, 2H), 2.22 (dd, *J* = 10.0, 6.4 Hz, 2H), 1.55 (d, *J* = 5.3 Hz, 2H), 0.80 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =145.90, 138.14, 138.00, 131.30, 128.15, 127.27, 126.95, 124.94, 113.09, 54.05, 52.20, 49.18, 35.14, 27.57. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}ClN$, 376.1832; found: 376.1828.

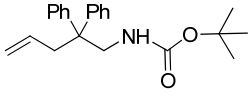


N-benzyl-2,2-dimethylhex-5-en-1-amine (6f). Compound **6f** was synthesized from isobutyronitrile and 4-bromobut-1-ene employing a procedure similar to that used to synthesize **4h**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.05 (m, 5H), 5.81 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 4.94 (dd, *J* = 23.2, 5.9 Hz, 2H), 3.79 (s, 2H), 2.36 (s, 2H), 2.01 – 1.92 (m, 2H), 1.37 – 1.31 (m, 2H), 1.15 (brs, 1H), 0.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.06, 139.74, 128.27, 127.96, 126.74, 113.78, 59.72, 54.72, 39.34, 33.93, 28.49, 25.62. Spectral data was consistent with the known aminoalkene.[5]

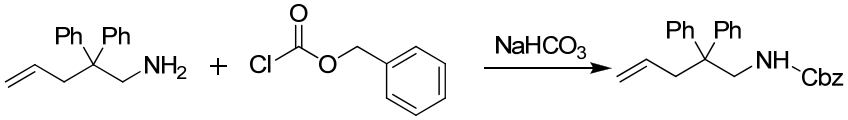


N-benzyl-1-(1-(but-3-enyl)cyclohexyl)methanamine (6g) Compound **6g** was synthesized from cyclohexanenitrile and 4-bromobut-1-ene employing a procedure similar to that used to synthesize **4i**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.00 (m, 5H), 5.90 – 5.70 (m, 1H), 4.94 (dd, *J* = 30.9, 13.6 Hz, 2H), 3.74 (d, *J* = 6.0 Hz, 2H),

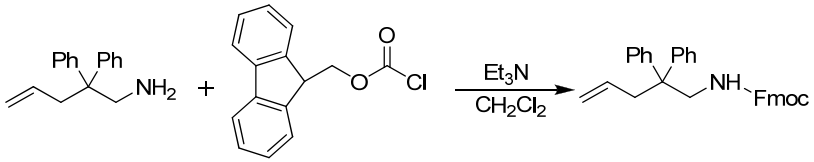
2.37 (dd, J = 6.4, 4.0 Hz, 2H), 1.85 (d, J = 6.4 Hz, 2H), 1.48 – 1.19 (m, 12H), 0.88 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.07, 139.91, 128.34, 128.09, 126.84, 113.88, 55.48, 54.74, 36.02, 35.15, 34.34, 27.61, 26.60, 21.68. Spectral data was consistent with the known aminoalkene.[5]



***tert*-Butyl 2,2-diphenylpent-4-enylcarbamate** To a solution of the 2,2-diphenylpent-4-en-1-amine (2 mmol) in THF (20 mL) at 0 ˚C was added Et_3N (12 mmol), followed by DMAP (about 0.01 g). To the reaction mixture was added di-*tert*-butyl dicarbonate (2.4 mmol) and the solution was stirred at this temperature for 6 h. At this time the reaction mixture was quenched with ice and water (30 mL) and extracted with CH_2Cl_2(3×30 mL). The combined organic phases were washed with brine (20 mL), dried ($MgSO_4$), and concentrated. Chromatography afforded a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31-7.16 (m, 10H), 5.42 (td, J = 16.4, 7.4 Hz, 1H), 5.07-4.82 (m, 2H), 4.14 (s, 1H), 3.85 (d, J = 5.4 Hz, 2H), 2.86 (d, J = 6.8 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.76, 145.50, 133.88, 128.24, 128.07, 126.40, 118.48, 79.01, 49.96, 47.18, 41.79, 28.83. Spectral data was consistent with the known aminoalkene.[6]

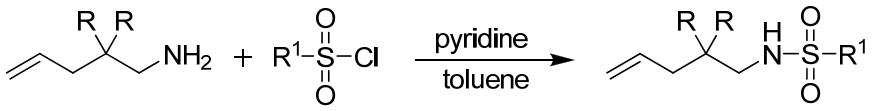


Benzyl 2,2-diphenylpent-4-enylcarbamate Benzyl chloroformate (2 mmol) was added slowly to a mixture of 2,2-diphenyl-4-pentenylamine (**S2**) (2 mmol) and $NaHCO_3$ (3 mmol) in ethanol/water (3:2, 20 mL) at room temperature. The resulting suspension was stirred for 1 h and treated with water (40 mL). The resulting mixture was extracted with CH_2Cl_2 (3×30 mL) and the combined CH_2Cl_2 extracts were dried ($MgSO_4$) and concentrated. Chromatography afforded the as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 – 7.36 (m, 9H), 7.34 – 7.26 (m, 6H), 5.69 – 5.53 (m, 1H), 5.17 (s, 2H), 5.14 – 5.10 (m, 2H), 4.59 (s, 1H), 4.09 (d, J = 6.0 Hz, 2H), 3.01 (d, J = 7.1 Hz, 2H). Spectral data was consistent with the known aminoalkene.[7]

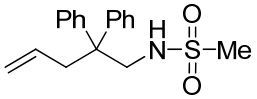


(9H-fluoren-9-yl)methyl 2,2-diphenylpent-4-enylcarbamate A solution of 9-fluorenylmethyl chloroformate (2 mmol), 2,2-diphenyl-4-pentenylamine (**S2**) (2.1 mmol), and Et_3N (3.5 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 h at room temperature, treated with water (30 mL), and extracted with CH_2Cl_2 (3×30 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), and concentrated under vacuum. Chromatography afforded the a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, J = 7.3 Hz, 2H), 7.41 (d, J = 7.1 Hz, 2H), 7.31 (t, J = 7.3 Hz, 2H), 7.27 – 7.07 (m, 12H), 5.50 – 5.30 (m, 1H), 5.02 – 4.76 (m, 2H), 4.26 (d, J = 6.5 Hz, 3H), 4.09 (d,

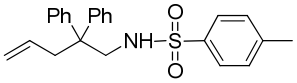
J = 6.5 Hz, 1H), 3.85 (d, J = 5.0 Hz, 2H), 2.76 (d, J = 6.7 Hz, 2H). Spectral data was consistent with the known aminoalkene.[7]



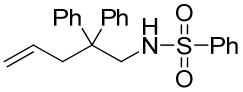
Compounds **8a-8k** were synthesized via reported procedures.[8] To a solution of alkeneamine (1.0 mmol) in 10 mL of dry toluene was added sulfonyl chloride (1.0 mmol) and pyridine (0.5 mL, 2 mmol). The mixture was stirred at 25 °C for 24 h, diluted with 5 mL of 1 N HCl and was extracted with Et_2O (3×30 mL). The combined organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting oily residue was chromatographed to give desired products.



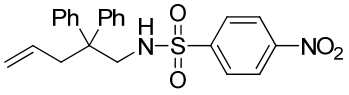
N-(2,2-diphenylpent-4-enyl)methanesulfonamide (**8a**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 – 6.75 (m, 10H), 5.41 – 5.20 (m, 1H), 5.09 – 4.80 (m, 2H), 4.02– 3.97 (d m, 1H), 3.69 (d, J = 6.6 Hz, 2H), 2.86 (d, J = 7.0 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.91, 133.49, 128.48, 127.95, 126.81, 119.05, 49.73, 49.69, 41.21, 39.78. Spectral data was consistent with the known aminoalkene.[9]



N-(2,2-Diphenylpent-4-enyl)-4-methylbenzenesulfonamide (**8b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, J=8.2, 2H), 7.39-7.13 (m, 8H), 7.08-7.00 (m, 4H), 5.35-5.14 (m, 1H), 5.01-4.86 (m, 2H), 3.88 (t, J=6.5, 1H), 3.52 (d, J=6.5, 2H), 2.89 (d, J=7.1, 2H), 2.41 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.54, 143.37, 136.33, 133.16, 129.68, 128.40, 127.71, 127.13, 126.70, 119.08, 49.45, 49.32, 41.27, 21.55. Spectral data was consistent with the known aminoalkene.[8]

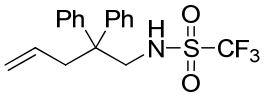


N-(2,2-diphenylpent-4-enyl)benzenesulfonamide (**8c**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (dd, J = 15.4, 7.5 Hz, 2H), 7.35 – 7.09 (m, 8H), 7.06 – 6.81 (m, 5H), 5.36 – 5.02 (m, 1H), 4.84 (d, J = 12.2 Hz, 2H), 3.82 (s, 1H), 3.47 (d, J = 6.4 Hz, 2H), 2.81 (d, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.50, 139.25, 133.09, 132.66, 129.11, 128.46, 127.75, 127.10, 126.79, 119.10, 49.44, 49.32, 41.26. Spectral data was consistent with the known aminoalkene.[9]

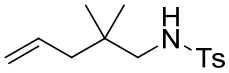


N-(2,2-diphenylpent-4-enyl)-4-nitrobenzenesulfonamide (**8d**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, J = 8.6 Hz, 2H), 7.76 (d, J = 8.6 Hz, 2H), 7.34 – 7.12 (m, 6H), 6.98 (d, J = 6.8 Hz, 4H), 5.23 – 5.13 (m, 1H), 5.01 – 4.72 (m, 2H), 4.02 (t, J = 6.1 Hz, 1H), 3.53 (d, J = 6.1 Hz, 2H), 2.82 (d, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

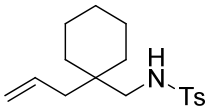
= 148.99, 144.16, 143.11, 131.89, 127.54, 127.26, 126.65, 125.97, 123.31, 118.24, 48.53, 48.47, 40.35. Spectral data was consistent with the known aminoalkene.[10]



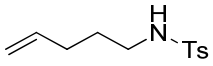
N-(2,2-diphenylpent-4-enyl)-1,1,1-trifluoromethanesulfonamide (**8e**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 6.79 (m, 10H), 5.41 – 5.19 (m, 1H), 5.01 – 4.88 (m, 2H), 4.32 (s, 1H), 3.83 (d, *J* = 5.0 Hz, 2H), 2.85 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.89, 132.68, 129.24, 128.74, 128.29, 127.79, 127.20, 119.65, 50.67, 49.73, 42.62, 40.98.^{19}F NMR (376 MHz, $CDCl_3$) δ = - 76.53. HRMS–ESI (*m/z*): M^+ calcd for $C_{18}H_{17}F_3NO_2S$, 369.1010; found: 369.1063.



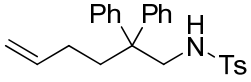
N-(2,2-dimethylpent-4-enyl)-4-methylbenzenesulfonamide (**8f**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 5.65 (ddt, *J* = 17.6, 10.3, 7.5 Hz, 1H), 5.06 – 4.75 (m, 2H), 4.66 (s, 1H), 2.60 (d, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 1.88 (d, *J* = 7.5 Hz, 2H), 0.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.29, 137.05, 134.29, 129.69, 127.07, 117.87, 52.86, 44.04, 34.12, 24.85, 21.51. Spectral data was consistent with the known aminoalkene.[8]



N-((1-allylcyclohexyl)methyl)-4-methylbenzenesulfonamide (**8g**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.80 – 5.47 (m, 1H), 5.09 – 4.79 (m, 2H), 4.48 (s, 1H), 2.67 (d, *J* = 6.9 Hz, 2H), 2.36 (s, 3H), 1.96 (d, *J* = 7.5 Hz, 2H), 1.46 – 1.09 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.26, 136.97, 134.13, 129.67, 127.07, 117.82, 49.44, 40.49, 36.35, 33.30, 25.99, 21.51, 21.25. Spectral data was consistent with the known aminoalkene.[8]

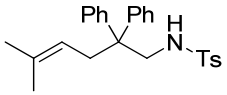


4-methyl-N-(pent-4-enyl)benzenesulfonamide (**8h**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.61 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 (d, *J* = 5.2 Hz, 1H), 4.96 – 4.77 (m, 2H), 2.84 (dd, *J* = 13.5, 6.8 Hz, 2H), 2.34 (s, 2H), 1.95 (q, *J* = 7.1 Hz, 3H), 1.53 – 1.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.31, 137.30, 137.02, 129.69, 127.09, 115.43, 42.60, 30.62, 28.65, 21.49.Spectral data was consistent with the known aminoalkene.[8]

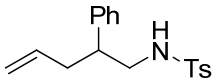


N-(2,2-diphenylhex-5-enyl)-4-methylbenzenesulfonamide (**8i**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.3 Hz, 2H), 7.18 – 6.86 (m, 12H), 5.64 – 5.46 (m, 1H), 4.78 (dd, *J* = 11.6, 6.3 Hz, 2H), 3.91 (t, *J* = 6.4 Hz, 1H), 3.47 (d, *J* = 6.5 Hz, 2H), 2.29 (s, 3H), 2.14 – 2.02 (m, 2H), 1.56 (dd, *J* = 15.8, 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.91, 143.46, 138.31, 129.79, 128.48, 127.80, 127.14, 126.72, 126.63, 114.63,

49.69, 49.49, 35.95, 28.33, 21.56. Spectral data was consistent with the known aminoalkene.[9]



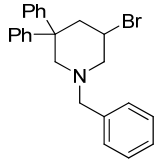
4-methyl-N-(5-methyl-2,2-diphenylhex-4-enyl)benzenesulfonamide (8j) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.08 (m, 8H), 6.98 (dd, *J* = 8.1, 1.3 Hz, 4H), 4.65 (t, *J* = 7.2 Hz, 1H), 3.77 (t, *J* = 6.1 Hz, 1H), 3.43 (d, *J* = 6.3 Hz, 2H), 2.73 (d, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 1.47 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.76, 143.37, 136.17, 135.50, 129.66, 128.31, 127.93, 127.16, 126.62, 118.51, 50.16, 49.73, 35.57, 25.95, 21.52, 17.89. Spectral data was consistent with the known aminoalkene.[11]



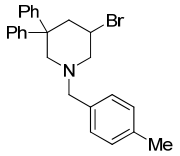
4-methyl-N-(2-phenylpent-4-enyl)benzenesulfonamide (8k) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.11 (m, 5H), 6.95 (d, *J* = 7.0 Hz, 2H), 5.52 (ddt, *J* = 14.0, 10.2, 7.0 Hz, 1H), 4.90 (dd, *J* = 26.8, 18.0 Hz, 2H), 4.20 (s, 1H), 3.33 – 3.12 (m, 1H), 3.04 – 2.84 (m, 1H), 2.78 – 2.62 (m, 1H), 2.39 – 2.30 (m, 3H), 2.30 – 2.17 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.39, 140.99, 136.93, 135.41, 129.70, 128.88, 127.72, 127.18, 127.09, 117.04, 47.76, 45.29, 38.03, 21.53. Spectral data was consistent with the known aminoalkene.[3]

5. General Procedures for Bromoamination

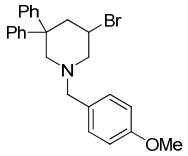
The reaction was carried out in open air system. To a 100 mL flask was added 1 mmol alkenylamine, 1equiv. $CuBr_2$ and 20 mL of CH_3CN. The reaction mixture was stirred at room temperature for a specified period. Then 30 mL of CH_2Cl_2 was added and the reaction mixture was washed with EDTA (25 mL × 3), dried over $MgSO_4$ and was concentrated to give an oil. In most of the reactions, the product obtained was NMR pure; further silica gel chromatography was not necessary.



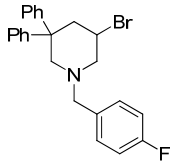
1-benzyl-5-bromo-3,3-diphenylpiperidine (5a) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26 – 6.98 (m, 15H), 3.87 (ddd, *J* = 15.3, 8.0, 4.0 Hz, 1H), 3.49 (q, *J* = 13.2 Hz, 3H), 3.18 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.01 (d, *J* = 12.5 Hz, 1H), 2.40 (t, *J* = 12.4 Hz, 1H), 2.30-2.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.36, 144.80, 137.63, 129.37, 128.71, 128.45, 128.19, 127.54, 126.48, 126.06, 62.57, 62.00, 49.23, 46.80, 45.52. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{24}BrN$, 406.1170; found: 406.1161.



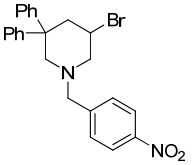
5-bromo-1-(4-methylbenzyl)-3,3-diphenylpiperidine (5b) White solid. M.p. = 135-137°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 6.89 (m, 15H), 4.09 – 3.79 (m, 1H), 3.54 (d, *J* = 12.4 Hz, 1H), 3.49 (s, 2H), 3.20 (dd, *J* = 10.5, 4.3 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.42 (t, *J* = 12.4 Hz, 1H), 2.28 (s, 3H), 2.29 – 2.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.41, 144.87, 137.07, 134.50, 129.34, 129.11, 128.75, 128.44, 128.16, 126.48, 126.46, 126.02, 62.29, 61.98, 61.92, 49.22, 46.85, 45.59, 21.32. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}BrN$, 420.1327; found: 420.1226.



5-bromo-1-(4-methoxybenzyl)-3,3-diphenylpiperidine (5c) White solid. M.p. = 88-91°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 6.92 (m, 12H), 6.78 (d, *J* = 7.7 Hz, 2H), 3.87 (t, *J* = 11.3 Hz, 1H), 3.71 (s, 3H), 3.51 (d, *J* = 12.1 Hz, 1H), 3.44 (s, 2H), 3.21 – 3.16 (m, 1H), 3.01 (d, *J* = 12.3 Hz, 1H), 2.40 (t, *J* = 12.4 Hz, 1H), 2.30 – 2.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.00, 147.37, 144.80, 130.52, 129.27, 128.68, 128.41, 128.14, 127.80, 126.44, 125.99, 113.73, 61.97, 61.88, 61.74, 55.34, 49.17, 46.81, 45.59. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}BrNO$, 436.1276; found: 436.1263.

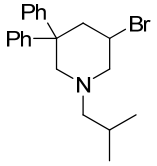


5-bromo-1-(4-fluorobenzyl)-3,3-diphenylpiperidine (5d) White solid. M.p. = 104-107°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 6.62 (m, 14H), 3.83 (dtt, *J* = 18.5, 10.8, 3.8 Hz, 1H), 3.48 (t, *J* = 9.1 Hz, 1H), 3.44 (s, 2H), 3.14 (dd, *J* = 10.4, 4.1 Hz, 1H), 3.01 (d, *J* = 12.6 Hz, 1H), 2.39 (t, *J* = 12.4 Hz, 1H), 2.30 – 2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.50, 161.06, 147.27, 144.69, 133.37, 133.35, 130.88, 130.80, 128.60, 128.48, 128.23, 126.53, 126.45, 126.11, 115.39, 115.17, 61.98, 61.90, 61.71, 49.21, 46.75, 45.32. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -114.95. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{23}BrFN$, 424.1076; found: 424.1078.

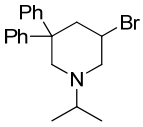


5-bromo-1-(4-nitrobenzyl)-3,3-diphenylpiperidine (5e) White solid. M.p. = 149-151°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.29 – 7.06(m, 8H), 7.04(d, *J* = 7.3 Hz, 2H), 3.92 (tt, *J* = 11.9, 4.0 Hz, 1H), 3.66 – 3.50 (m, 3H), 3.12 (dd, *J* = 10.2, 4.6 Hz, 1H), 3.06 (d, *J* = 12.8 Hz, 1H), 2.43 –

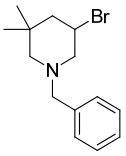
2.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.34, 145.82, 144.40, 143.27, 128.60, 127.39, 127.26, 127.20, 125.49, 125.23, 125.14, 122.59, 61.15, 60.80, 60.51, 48.11, 45.34, 43.56. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{23}BrN_2O_2$, 451.1021; found: 451.1010.



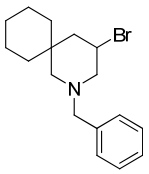
5-bromo-1-isobutyl-3,3-diphenylpiperidine (5f) White solid. M.p. = 83-85°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.31 (m, 2H), 7.21 – 7.04 (m, 8H), 3.93 – 3.82 (m, 1H), 3.50 (d, *J* = 12.2 Hz, 1H), 3.23 – 3.18 (m, 1H), 3.00 – 2.92 (m, 1H), 2.41 (t, *J* = 12.3 Hz, 1H), 2.21 – 2.14 (m, 2H), 2.09 (dd, *J* = 5.1, 2.5 Hz, 2H), 1.86 – 1.70 (m, 1H), 0.86 (d, *J* = 4.4 Hz, 3H), 0.84 (d, *J* = 4.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.55, 145.17, 128.82, 128.38, 128.02, 126.46, 126.38, 125.91, 66.68, 63.58, 62.16, 49.26, 46.98, 45.86, 25.66, 21.19, 20.91. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{26}BrN$, 372.1327; found: 372.1313.



5-bromo-1-isopropyl-3,3-diphenylpiperidine (5g) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.24 (m, 10H),4.04 – 3.89 (m, 1H), 3.69 (d, *J*=12.1, 1H), 3.32 (d, *J*=6.3, 1H), 3.18 – 3.07 (m, 2H), 2.63 – 2.40 (m, 3H), 1.25 (d, *J*=6.6, 3H), 1.22 (d, *J*=6.6, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 144.3, 127.5, 127.3, 127.0, 125.4, 125.3, 124.8, 56.7, 56.1, 53.6, 53.5, 47.0, 45.4, 16.8, 16.5. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{24}BrN$, 358.1170; found: 358.1167.

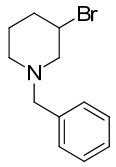


1-benzyl-5-bromo-3,3-dimethylpiperidine (5h) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.29 – 7.16 (m, 5H), 4.16 (ddd, *J* = 15.7, 10.0, 4.5 Hz, 1H), 3.48 (d, *J* = 13.4 Hz, 1H), 3.35 (d, *J* = 13.4 Hz, 1H), 3.15 (d, *J* =6.6 Hz, 1H), 2.35 (d, *J* = 11.1 Hz, 1H), 2.07 (t, *J* = 10.8 Hz, 1H), 1.99 – 1.94 (m, 1H),1.70 (d, *J* = 11.0 Hz, 1H), 1.46 (t, *J* = 12.5 Hz, 1H), 0.99 (s, 3H), 0.80 (s, 3H). **^{13}**C NMR (100 MHz, $CDCl_3$) δ = 137.44, 127.61, 127.21, 126.01, 63.41, 61.37, 61.20, 48.23, 45.35, 33.36, 28.23, 23.83. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{14}H_{20}BrN$, 282.0857; found: 282.0854.

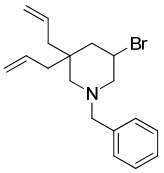


2-benzyl-4-bromo-2-azaspiro[5.5]undecane (5i) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 – 7.15 (m, 5H), 4.17 (tt, *J* = 12.0, 4.4 Hz, 1H), 3.48 (d, *J* = 13.4 Hz, 1H), 3.35

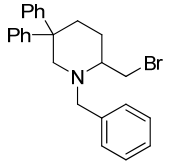
(dd, *J* = 13.4, 5.4 Hz, 1H), 3.15 (dd, *J* = 10.5, 4.3 Hz, 1H), 2.65 (d, *J* = 11.3 Hz, 1H), 2.19 (dd, *J* = 11.0, 1.8 Hz, 1H), 2.12 (t, *J* = 10.8 Hz, 1H), 1.57 (d, *J* = 11.3 Hz, 2H), 1.36 – 1.08 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.56, 127.54, 127.18, 125.98, 62.11, 61.28, 45.29, 37.31, 36.07, 31.65, 25.56, 20.50, 20.47. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{24}BrN$, 322.1170; found: 322.1168.



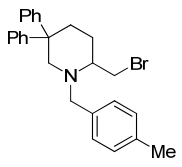
1-benzyl-3-bromopiperidine (5j) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 – 7.02 (m, 5H), 4.05 (ddd, *J* = 13.7, 9.6, 4.0 Hz, 1H), 3.46 (s, 2H), 3.01 (d, *J* = 9.7 Hz, 1H), 2.66 (d, *J* = 11.2 Hz, 1H), 2.28 (t, *J* = 10.4 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.04 (t, *J* = 9.9 Hz, 1H), 1.77 – 1.50 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.84, 127.95, 127.23, 126.10, 61.60, 60.76, 51.77, 47.34, 34.63, 24.85. Spectral data was consistent with the known compound.[12]



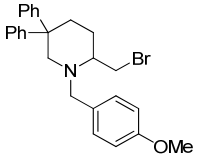
3,3-diallyl-1-benzyl-5-bromopiperidine (5k) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 – 6.91 (m, 5H), 5.74 – 5.56 (m, 2H), 5.12 – 4.87 (m, 4H), 3.49 – 3.34 (m, 2H), 3.11 (ddd, *J* = 25.1, 10.5, 4.4 Hz, 1H), 2.51 (d, *J* = 11.5 Hz, 1H), 2.28 – 2.18 (m, 2H), 2.07 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.91 – 1.79 (m, 2H), 1.73 (d, *J* = 11.3 Hz, 1H), 1.54 – 1.42 (m, 1H), 1.31 – 1.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.27, 133.10, 132.22, 127.78, 127.25, 126.12, 117.20, 116.93, 61.34, 61.29, 60.12, 44.77, 44.06, 41.82, 39.14, 36.95. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{14}BrN$, 334.1170; found: 334.1165.



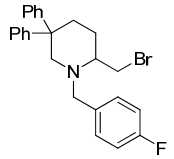
1-benzyl-2-(bromomethyl)-5,5-diphenylpiperidine (7a) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 – 7.13 (m, 15H), 4.09 (d, *J* = 13.1 Hz, 1H), 3.69 – 3.58 (m, 2H), 3.35 (dd, *J* = 17.1, 12.9 Hz, 2H), 2.75 (s, 1H), 2.63 (d, *J* = 12.4 Hz, 1H), 2.50 (d, *J* = 13.0 Hz, 1H), 2.39 – 2.18 (m, 1H), 1.86 – 1.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.79, 146.52, 138.41, 129.54, 129.25, 128.31, 128.27, 128.06, 127.79, 127.20, 125.88, 125.63, 60.46, 60.08, 58.95, 46.31, 34.66, 33.10, 26.32. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}BrN$, 420.1327; found: 420.1225.



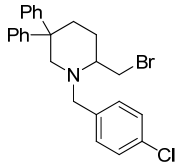
2-(bromomethyl)-1-(4-methylbenzyl)-5,5-diphenylpiperidine（**7b**）Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 – 7.01 (m, 14H), 3.98 (d, *J* = 13.1 Hz, 1H), 3.57 (d, *J* = 4.9 Hz, 2H), 3.30 (dd, *J* = 12.4, 1.2 Hz, 1H), 3.24 (d, *J* = 13.1 Hz, 1H), 2.67 (td, *J* = 8.9, 4.7 Hz, 1H), 2.56 (d, *J* = 12.4 Hz, 1H), 2.47 – 2.38 (m, 1H), 2.36 (s, 3H), 2.28 – 2.19 (m, 1H), 1.79 – 1.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.82, 146.59, 136.82, 135.21, 129.40, 128.91, 128.31, 127.99, 127.73, 127.21, 125.80, 125.56, 60.35, 59.97, 58.60, 46.29, 34.56, 33.07, 26.26, 21.18. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{28}BrN$, 434.1483; found: 4354.1478.



2-(bromomethyl)-1-(4-methoxybenzyl)-5,5-diphenylpiperidine (7c) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.08 (m, 6H), 7.06 – 6.96 (m, 4H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.90 (d, *J* = 13.0 Hz, 1H), 3.75 (s, 3H), 3.56 – 3.45 (m, 2H), 3.22 (d, *J* = 12.4 Hz, 1H), 3.14 (d, *J* = 13.0 Hz, 1H), 2.65 – 2.55 (m, 1H), 2.47 (d, *J* = 12.4 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.22 – 2.10 (m, 1H), 1.70 – 1.60 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.88, 147.81, 146.56, 130.61, 130.32, 128.29, 128.00, 127.73, 127.19, 125.80, 125.55, 113.59, 60.32, 59.77, 58.13, 55.28, 46.27, 34.58, 33.08, 26.28. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{26}H_{28}BrNO$, 450.1433; found: 450.1420.

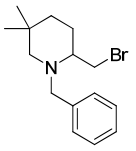


2-(bromomethyl)-1-(4-fluorobenzyl)-5,5-diphenylpiperidine (7d) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (dd, *J* = 8.2, 5.8 Hz, 2H), 7.30 – 7.22 (m, 6H), 7.20 – 7.05 (m, 6H), 4.06 (d, *J* = 13.1 Hz, 1H), 3.67 (dd, *J* = 10.6, 6.8 Hz, 1H), 3.60 (dd, *J* = 10.6, 2.5 Hz, 1H), 3.35 (dd, *J* = 12.3, 1.1 Hz, 1H), 3.26 (d, *J* = 13.1 Hz, 1H), 2.80 – 2.68 (m, 1H), 2.60 (d, *J* = 12.3 Hz, 1H), 2.50 (dt, *J* = 7.9, 3.5 Hz, 1H), 2.36 – 2.26 (m, 1H), 1.87 – 1.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.12, 161.68, 148.43, 147.09, 134.83, 134.80, 131.77, 131.70, 128.95, 128.81, 128.52, 127.82, 126.65, 126.38, 115.89, 115.68, 61.14, 60.67, 58.72, 46.98, 35.35, 33.83, 27.08. 19F NMR (376 MHz, $CDCl_3$) δ = -115.52. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{25}BFrN$, 438.1233; found: 438.1227.

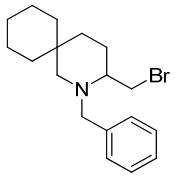


2-(bromomethyl)-1-(4-chlorobenzyl)-5,5-diphenylpiperidine (7e) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (s, 4H), 7.24 – 7.15 (m, 6H), 7.14 – 7.06 (m, 4H), 3.99 (d, *J* = 13.3 Hz, 1H), 3.59 (dd, *J* = 10.6, 6.7 Hz, 1H), 3.53 (dd, *J* = 10.6, 2.7 Hz, 1H), 3.29 (dd, *J* = 12.3, 1.4 Hz, 1H), 3.21 (d, *J* = 13.3 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.55 (d, *J* =

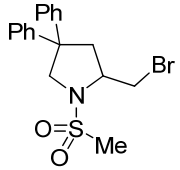
12.3 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.31 – 2.20 (m, 1H), 1.79 – 1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.63, 146.27, 136.97, 133.01, 130.75, 128.38, 128.19, 128.07, 127.79, 127.05, 125.91, 125.65, 60.50, 60.16, 58.14, 46.27, 34.51, 33.08, 26.36. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{25}BrClN$, 454.0937; found: 454.0934.



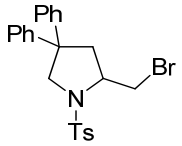
1-benzyl-2-(bromomethyl)-5,5-dimethylpiperidine (7f) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.20 (m, 1H), 3.97 (d, *J* = 13.5 Hz, 1H), 3.66 (dd, *J* = 10.6, 6.5 Hz, 1H), 3.52 (dd, *J* = 10.6, 2.0 Hz, 1H), 3.19 (d, *J* = 13.5 Hz, 1H), 2.49 (s, 1H), 2.32 (d, *J* = 11.3 Hz, 1H), 1.91 (ddd, *J* = 13.2, 11.1, 4.3 Hz, 1H), 1.80 (d, *J* = 11.4 Hz, 1H), 1.72 – 1.62 (m, 1H), 1.46 – 1.36 (m, 1H), 1.28 – 1.17 (m, 1H), 0.93 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.61, 128.49, 128.13, 126.74, 62.38, 60.56, 57.96, 35.77, 35.29, 30.61, 28.07, 26.60, 25.50. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{15}H_{22}BrN$, 296.1014; found: 296.1013.



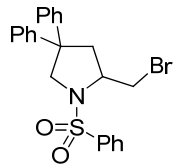
2-benzyl-3-(bromomethyl)-2-azaspiro[5.5]undecane (7g) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 – 7.09 (m, 5H), 3.97 (d, *J* = 13.4 Hz, 1H), 3.67 (dd, *J* = 10.6, 6.4 Hz, 1H), 3.51 (dd, *J* = 10.6, 1.9 Hz, 1H), 3.15 (d, *J* = 13.4 Hz, 1H), 2.50 (d, *J* = 11.3 Hz, 2H), 1.95 – 1.84 (m, 1H), 1.79 (d, *J* = 11.5 Hz, 1H), 1.69 – 1.49 (m, 2H), 1.47 – 1.11 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.73, 128.53, 128.10, 126.75, 61.23, 57.98, 36.85, 35.59, 33.68, 32.92, 26.81, 25.85, 21.58, 21.55. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{26}BrN$, 336.1327; found: 336.1325.



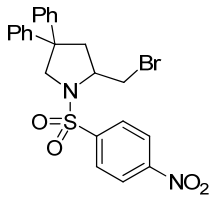
2-(bromomethyl)-1-(methylsulfonyl)-4,4-diphenylpyrrolidine (**9a**) White solid. M.p. = 143-145°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 6.91 (m, 10H), 4.22 (dd, *J* = 11.0, 1.7 Hz, 1H), 4.09 (d, *J* = 11.0 Hz, 1H), 3.97 (ddd, *J* = 14.7, 7.9, 2.6 Hz, 1H), 3.68 (dd, *J* = 10.1, 2.9 Hz, 1H), 3.35 (dd, *J* = 10.1, 8.3 Hz, 1H), 3.15 (ddd, *J* = 13.3, 6.9, 1.6 Hz, 1H), 2.53 (dd, *J* = 13.4, 8.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.60, 144.12, 129.01, 128.81, 127.22, 126.92, 126.84, 126.46, 59.85, 59.49, 53.25, 42.69, 36.72, 36.58. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{20}BrNO_2S$, 394.0476; found: 394.0468**.**



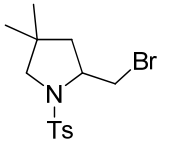
2-(bromomethyl)-4,4-diphenyl-1-tosylpyrrolidine (**9b**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 8.0 Hz, 2H), 7.25 – 6.85 (m, 12H), 4.33 (d, *J* = 10.2 Hz, 1H), 3.96 – 3.81 (m, 1H), 3.72 (dd, *J* = 9.7, 3.1 Hz, 1H), 3.63 (d, *J* = 10.2 Hz, 1H), 2.86 (t, *J* = 9.9 Hz, 1H), 2.67 (qd, *J* = 13.2, 6.5 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 144.70, 144.44, 143.76, 133.82, 129.85, 128.77, 128.70, 127.45, 126.84, 126.61, 126.56, 126.36, 60.08, 58.87, 52.29, 42.04, 35.90, 21.59. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{24}BrNO_2S$, 470.0789; found: 470.0789. Spectral data was consistent with the known compound.[13]



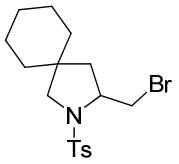
2-(bromomethyl)-4,4-diphenyl-1-(phenylsulfonyl)pyrrolidine (**9c**) White solid. M.p. = 162-163°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 – 7.64 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.17 (m, 4H), 7.16 – 6.98 (m, 6H), 4.32 (d, *J* = 10.2 Hz, 1H), 3.94 – 3.80 (m, 1H), 3.80 – 3.60 (m, 2H), 2.89 (t, *J* = 9.9 Hz, 1H), 2.78 – 2.57 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 144.55, 144.34, 137.10, 132.91, 129.18, 128.76, 128.71, 127.39, 126.86, 126.76, 126.59, 126.30, 60.03, 58.81, 52.30, 42.11, 35.69. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{22}BrNO_2S$, 456.0633; found: 456.0625.



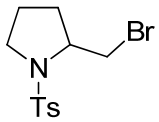
2-(bromomethyl)-1-(4-nitrophenylsulfonyl)-4,4-diphenylpyrrolidine (**9d**) White solid. M.p. = 165-167°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.29 – 6.91 (m, 10H), 4.26 (d, *J* = 10.8 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.96 (ddd, *J* = 10.3, 7.9, 2.9 Hz, 1H), 3.79 (dd, *J* = 10.1, 2.9 Hz, 1H), 3.31 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.00 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.50 (dd, *J* = 13.5, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ =149.93, 144.50, 143.49, 143.30, 128.82, 128.76, 128.10, 126.99, 126.78, 126.41, 126.33, 124.20, 60.09, 59.99, 52.77, 42.48, 36.16. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{21}BrN_2O_4S$, 501.0484; found: 501.0464.



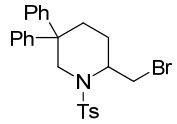
2-(bromomethyl)-4,4-dimethyl-1-tosylpyrrolidine (9f) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.86 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.80 (ddd, *J* = 15.9, 8.3, 3.0 Hz, 1H), 3.45 (t, *J* = 9.1 Hz, 1H), 3.10 (q, *J* = 10.9 Hz, 2H), 2.36 (s, 3H), 1.81 (dd, *J* = 12.9, 7.2 Hz, 1H), 1.63 (dd, *J* = 12.9, 8.2 Hz, 1H), 0.98 (s, 3H), 0.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=143.73, 134.88, 129.73, 127.53, 61.88, 60.02, 45.86, 37.52, 37.47, 26.09, 25.79, 21.56. Spectral data was consistent with the known compound.[14]



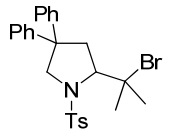
3-(bromomethyl)-2-tosyl-2-azaspiro[4.5]decane (**9g**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 3.86 (dd, *J* = 9.7, 3.0 Hz, 1H), 3.73 (ddd, *J* = 16.1, 8.4, 3.0 Hz, 1H), 3.46 – 3.40 (m, 1H), 3.27 (d, *J* = 10.9 Hz, 1H), 3.07 (d, *J* = 10.9 Hz, 1H), 2.36 (s, 3H), 1.86 (dt, *J* = 49.9, 24.9 Hz, 1H), 1.56 (dd, *J* = 13.1, 8.4 Hz, 1H), 1.35 – 0.98 (m, 8H), 0.73 (ddd, *J* = 13.0, 9.2, 3.8 Hz, 1H), 0.64 – 0.53 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.69, 134.75, 129.70, 127.49, 59.29, 59.09, 44.08, 41.43, 37.72, 36.16, 34.01, 25.77, 23.69, 22.79, 21.54. Spectral data was consistent with the known compound.[14]



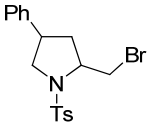
2-(bromomethyl)-1-tosylpyrrolidine (**9h**) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 3.75 (ddd, *J* = 11.6, 7.6, 3.6 Hz, 1H), 3.68 (dd, *J* = 9.9, 3.1 Hz, 1H), 3.42 – 3.35 (m, 1H), 3.29 (t, *J* = 9.7 Hz, 1H), 3.08 (dt, *J* = 9.9, 7.1 Hz, 1H), 2.36 (s, 3H), 1.90 – 1.81 (m, 1H), 1.76 (dt, *J* = 18.7, 5.9 Hz, 1H), 1.67 (ddd, *J* = 12.4, 7.6, 4.2 Hz, 1H), 1.56 – 1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.87, 133.98, 129.87, 127.51, 60.37, 49.83, 36.15, 30.26, 23.80, 21.55. Spectral data was consistent with the known compound.[14]



2-(bromomethyl)-5,5-diphenyl-1-tosylpiperidine (**9i**) White solid. M.p. = 134-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.21 – 7.06 (m, 10H), 4.54 (d, *J* = 13.4 Hz, 1H), 4.03 – 3.94 (m, 1H), 3.45 (t, *J* = 10.8 Hz, 1H), 3.26 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.08 (d, *J* = 13.4 Hz, 1H), 2.40 (dd, *J* = 14.1, 2.4 Hz, 1H), 2.33 (s, 3H), 2.17 (td, *J* = 14.0, 2.9 Hz, 1H), 2.07 (dd, *J* = 14.2, 1.8 Hz, 1H), 1.59 (t, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.86, 142.76, 142.24, 135.54, 128.84, 127.54, 127.44, 126.77, 126.43, 125.61, 125.29, 125.10, 52.09, 47.55, 44.56, 27.61, 27.37, 20.74, 20.52. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}BrNO_2S$, 484.0946; found: 484.0937.

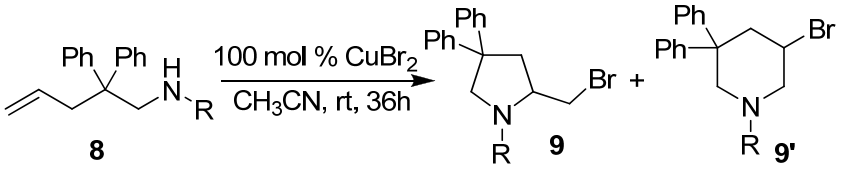


2-(2-bromopropan-2-yl)-4,4-diphenyl-1-tosylpyrrolidine (9j) White solid. M.p. = 89-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.21 (dt, *J* = 12.3, 6.3 Hz, 3H), 7.17 – 7.11 (m, 5H), 7.01 (d, *J* = 8.1 Hz, 2H), 5.16 (dd, *J* = 13.8, 2.6 Hz, 1H), 4.09 (dd, *J* = 13.0, 3.7 Hz, 1H), 3.55 (d, *J* = 13.8 Hz, 1H), 3.15 (dt, *J* = 14.0, 3.2 Hz, 1H), 2.65 (t, *J* = 13.5 Hz, 1H), 2.28 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.11, 143.12, 142.78, 140.10, 129.49, 129.02, 128.71, 127.93, 127.20, 126.79, 126.61, 125.96, 61.82, 58.17, 49.97, 48.80, 42.98, 27.87, 21.42, 16.29. HRMS–ESI (m/z): [M+H]+ calcd for $C_{26}H_{28}BrNO_2S$, 498.1102; found: 498.1101.



2-(bromomethyl)-4-phenyl-1-tosylpyrrolidine (9k) White solid. M.p. = 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.10 (m, 3H), 7.06 – 6.96 (m, 2H), 3.90 (tt, *J* = 16.5, 8.1 Hz, 1H), 3.82 – 3.75 (m, 2H), 3.52 (dd, *J* = 9.7, 8.4 Hz, 1H), 3.30 (t, *J* = 11.4 Hz, 1H), 2.57 (ddd, *J* = 18.4, 11.6, 7.0 Hz, 1H), 2.46 – 2.33 (m, 4H), 1.92 (td, *J* = 12.3, 9.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.04, 138.83, 134.90, 130.03, 128.73, 127.52, 127.26, 127.01, 60.51, 55.66, 43.10, 39.09, 37.57, 21.62. S–ESI (m/z): [M+H]+ calcd for $C_{18}H_{20}BrNO_2S$, 393.0476; found: 394.0476.

Table 4. Bromoamination of carbamate substrates.

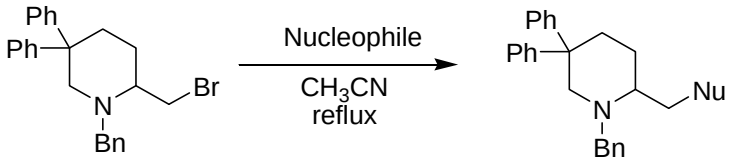


Entry	R	Conversion [a]	Selectivity(**9**:**9**')[a]
1	Boc	>99	1.1:1
2	Cbz	90	1:0.8
3	Fmoc	>99	1:1

a: Determined by ^{1}H NMR analysis.

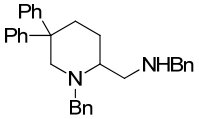
6. Derivatization of Bromoamination Product

6.1 Nucleophilic substitution reaction of 7a

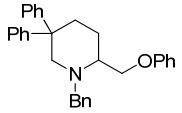


7a **10-15**

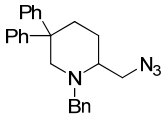
1-benzyl-2-(bromomethyl)-5,5-diphenylpiperidine (**7a**) was dissolved in 20 ml of acetonitrile, the nucleophile of interest was added, and the reaction mixture was heated to reflux overnight. Then 30 mL of CH_2Cl_2 was added and reaction mixture was washed with water, dried over $MgSO_4$, and concentrated. The resulting residue was isolated by silica gel chromatography.



N-benzyl-1-(1-benzyl-5,5-diphenylpiperidin-2-yl)methanamine (**10**) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 6.72 (m, 20H), 3.98 (d, *J* = 13.3 Hz, 1H), 3.68 – 3.60 (m, 2H), 3.34 (dd, *J* = 12.2, 1.7 Hz, 1H), 3.04 (d, *J* = 13.3 Hz, 1H), 2.80 (dd, *J* = 11.9, 5.6 Hz, 1H), 2.70 (dd, *J* = 11.9, 2.8 Hz, 1H), 2.40 (d, *J* = 10.1 Hz, 2H), 2.33 (d, *J* = 12.3 Hz, 1H), 2.13 – 1.98 (m, 1H), 1.84 (brs, 1H), 1.71 – 1.56 (m,2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.50, 146.24, 140.26, 139.03, 129.40, 128.51, 128.35, 128.17, 128.05, 128.02, 127.77, 127.05, 126.92, 126.90, 125.80, 125.43, 61.48, 60.88, 58.94, 54.24, 46.28, 34.28, 29.74, 26.68.HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{32}H_{34}N_2$, 477.2800; found: 477.2797.

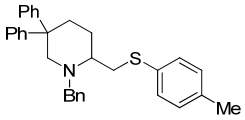


1-benzyl-2-(phenoxymethyl)-5,5-diphenylpiperidine (**11**) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.64 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 3H), 7.23 – 6.97 (m, 12H), 6.75 (t, *J* = 9.1 Hz, 2H), 4.18 – 4.04 (m, 2H), 3.92 – 3.80 (m, 1H), 3.31 (t, *J* = 13.9 Hz, 2H), 2.81 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.50 (d, *J* = 12.4 Hz, 1H), 2.43 (dd, *J* = 13.1, 2.4 Hz, 1H), 2.22 – 2.12 (m, 1H), 1.78 (ddd, *J* = 13.3, 6.0, 3.4 Hz, 1H), 1.53 – 1.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.79, 148.11, 139.21, 132.43, 130.09, 129.46, 128.35, 128.31, 128.13, 128.05, 127.78, 127.09, 125.52, 120.75, 114.57, 70.34, 61.10, 60.15, 59.70, 46.28, 33.80, 26.38.HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{31}H_{31}NO$, 434.2484; found: 434.2477.

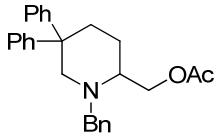


2-(azidomethyl)-1-benzyl-5,5-diphenylpiperidine (**12**) White solid. M.p. = 80-83°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 – 6.48 (m, 15H), 4.00 (d, *J* = 13.4 Hz, 1H), 3.37

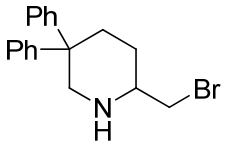
(d, *J* = 5.1 Hz, 2H), 3.29 (dd, *J* = 12.4, 1.5 Hz, 1H), 3.20 (d, *J* = 13.4 Hz, 1H), 2.51 (td, *J* = 8.9, 4.8 Hz, 1H), 2.42 (d, *J* = 12.4 Hz, 1H), 2.39 – 2.37 (m, 1H), 2.23 – 2.03 (m, 1H), 1.77 – 1.60 (m, 1H), 1.46 (ddd, *J* = 16.5, 13.0, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.96, 146.20, 138.51, 129.31, 129.23, 128.35, 128.29, 128.08, 127.83, 127.77, 127.28, 127.03, 125.89, 125.61, 60.99, 60.33, 59.40, 52.81, 46.28, 33.58, 26.44. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{25}H_{26}N_4$, 383.2236; found: 383.2233.



1-benzyl-5,5-diphenyl-2-(p-tolylthiomethyl)piperidine (**13**) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 6.57 (m, 19H), 3.97 (d, *J* = 13.2 Hz, 1H), 3.27 – 3.07 (m, 3H), 3.02 (dd, *J* = 12.3, 8.2 Hz, 1H), 2.64 (s, 1H), 2.50 (d, *J* = 12.3 Hz, 1H), 2.31 (s, 1H), 2.20 (s, 3H), 2.16 – 2.06 (m, 1H), 1.67 (ddd, *J* = 21.7, 10.9, 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.96, 146.90, 138.86, 136.01, 133.61, 130.05, 129.73, 129.56, 128.25, 128.23, 128.04, 127.89, 127.39, 127.22, 125.81, 125.65, 60.20, 59.40, 59.10, 46.39, 36.05, 33.26, 26.78, 21.10. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{32}H_{33}NS$, 464.2412; found: 464.2404.



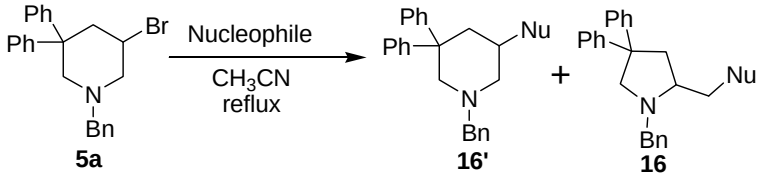
(1-benzyl-5,5-diphenylpiperidin-2-yl)methyl acetate (**14**) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 6.80 (m, 15H), 4.20 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.12 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.02 (d, *J* = 13.4 Hz, 1H), 3.28 (d, *J* = 12.5 Hz, 1H), 3.22 (d, *J* = 13.4 Hz, 1H), 2.59 (dt, *J* = 33.6, 16.8 Hz, 1H), 2.45 (d, *J* = 12.5 Hz, 1H), 2.39 (d, *J* = 13.1 Hz, 1H), 2.19 – 2.09 (m, 1H), 1.94 (s, 3H), 1.71 – 1.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.97, 147.99, 146.43, 138.85, 135.96, 129.43, 129.23, 128.34, 128.28, 128.18, 128.06, 127.77, 127.12, 125.85, 125.55, 65.57, 60.80, 59.47, 46.26, 42.64, 33.56, 25.92, 21.01. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{27}H_{29}NO_2$, 400.2277; found: 400.2276.



2-(Bromomethyl)-5,5-diphenylpiperidine (15) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 – 6.84 (m, 10H), 4.03 (dd, *J* = 13.1, 2.8 Hz, 1H), 3.50 (dd, *J* = 10.0, 4.1 Hz, 1H), 3.36 (dd, *J* = 10.0, 7.3 Hz, 1H), 3.18 (d, *J* = 13.1 Hz, 1H), 3.04 (ddd, *J* = 14.3, 7.0, 3.5 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.31 (td, *J* = 13.3, 3.5 Hz, 1H), 1.81 – 1.73 (m, 1H), 1.41 (ddd, *J* = 24.3, 13.2, 3.3 Hz, 1H), 1.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.24, 144.61, 128.50, 128.37, 128.30, 126.48, 126.05, 125.89, 57.18, 55.35, 45.39, 38.70, 34.97, 27.50. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{20}BrN$, 330.0857; found: 330.0850.

6.2 Nucleophilic substitution reaction of 5a

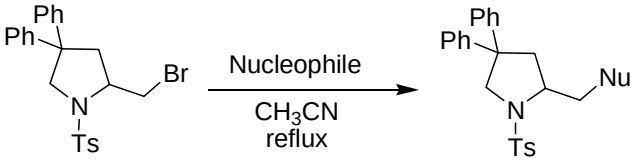
Table 5. Nucleophilic substitution of **5a**.



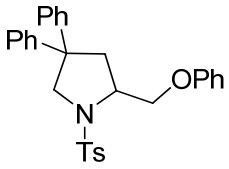
5a **16'** **16**

Entry	Nucleophile	**16'**	**16**
1	$BnNH_2$	24	49
2	KOAc	30	50
3	NaN_3	24	60
4	NaCN	17	65
5	PhSNa	37	45

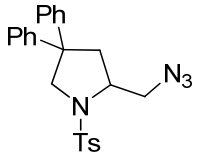
6.3 Nucleophilic substitution reaction of 15b



9b **17-20**

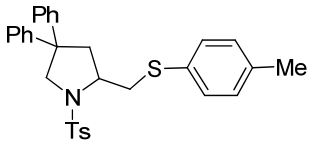


2-(Phenoxymethyl)-4,4-diphenyl-1-tosylpyrrolidine (**17**) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.00 (m, 15H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.27 (d, *J* = 10.1 Hz, 1H), 4.21 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.73 (d, *J* = 10.1 Hz, 1H), 3.49 (t, *J* = 9.1 Hz, 1H), 2.73 (dd, J = 13.0, 5.3 Hz, 1H), 2.66 (dd, J = 13.0, 7.9 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.27, 145.04, 144.83, 143.44, 134.24, 129.68, 129.39, 128.65, 128.62, 127.38, 126.73, 126.64, 126.49, 126.46, 120.88, 114.49, 68.96, 58.37, 57.93, 52.57, 40.84, 21.49. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{29}NO_3S$, 484.1946; found: 484.1935.

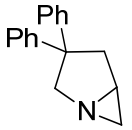


2-(Azidomethyl)-4,4-diphenyl-1-tosylpyrrolidine (**18**) White solid. M.p. = 171-172°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (t, *J* = 8.4 Hz, 2H), 7.26 – 6.94 (m, 14H), 4.34 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.91 – 3.78 (m, 1H), 3.74 – 3.67 (m, 1H), 3.65 – 3.57 (m, 1H), 2.92 – 2.52 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ=144.65, 144.46, 143.70, 129.80, 129.78, 128.74, 128.66, 127.44, 127.38, 126.81, 126.59, 126.33, 60.06, 58.82, 52.26, 42.05, 35.79, 21.53. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{24}N_4O_2S$, 433.1698; found: 433.1688.

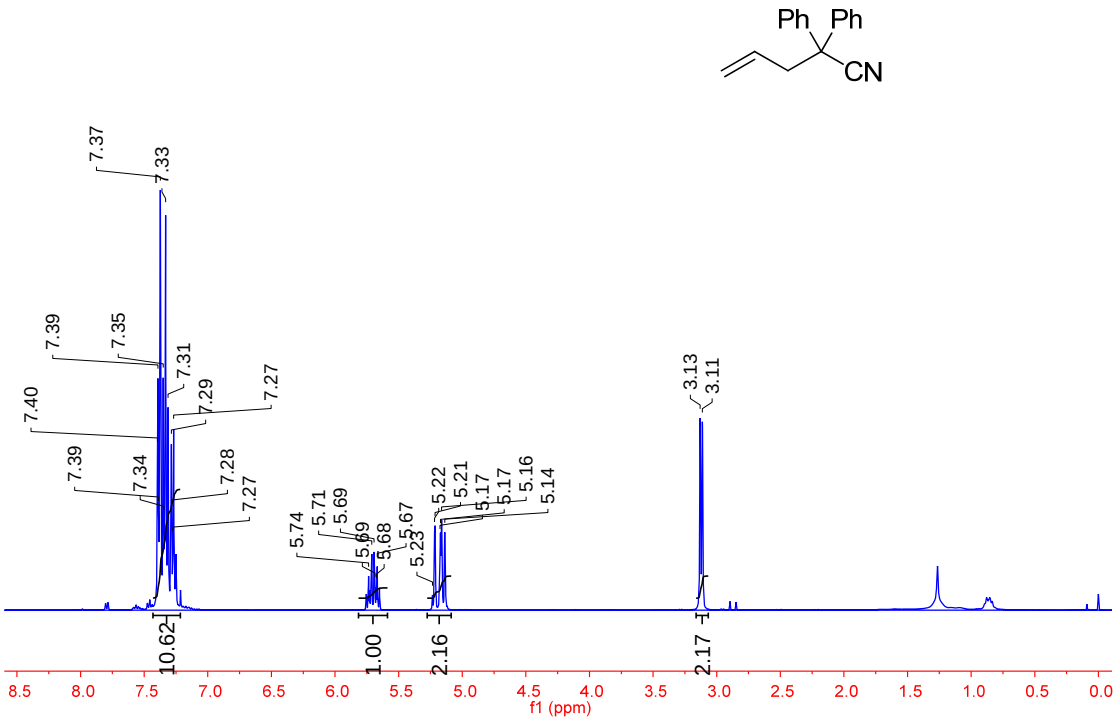


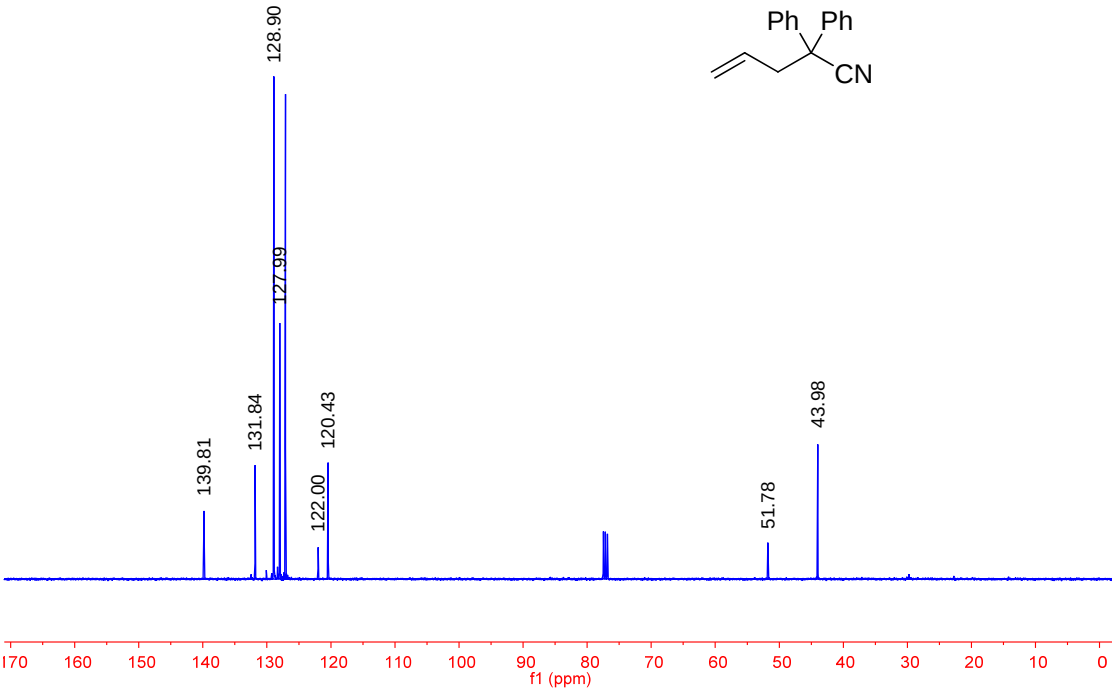
4,4-diphenyl-2-(p-tolylthiomethyl)-1-tosylpyrrolidine (**19**) White solid. M.p. = 134-136°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.17 (m, 6H), 7.11 – 6.91 (m, 10H), 4.41 (d, *J* = 10.1 Hz, 1H), 3.67 – 3.49 (m, 2H), 3.37 (d, *J* = 10.1 Hz, 1H), 2.59 (qd, *J* = 13.0, 6.0 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.14 (dd, *J* = 13.4, 11.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.97, 143.45, 136.49, 133.15, 131.27, 130.53, 129.87, 129.64, 128.69, 128.61, 127.59, 126.84, 126.67, 126.48, 126.40, 58.68, 52.19, 41.80, 38.65, 21.55, 21.14. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{31}H_{31}NO_2S_2$, 514.1874; found: 514.1863.

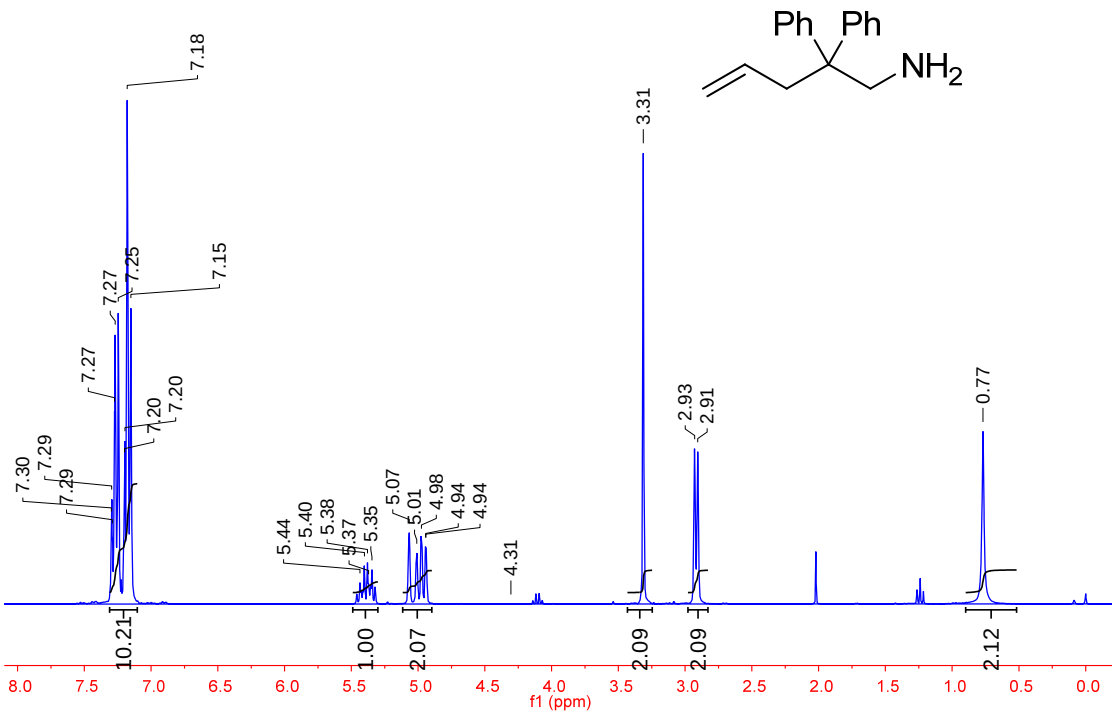


3,3-Diphenyl-1-azabicyclo[3.1.0]hexane (20) Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 6.95 (m, 10H), 4.33 (d, J = 10.0 Hz, 1H), 3.67 (d, J = 10.0 Hz, 1H), 3.59 (dd, J = 10.0, 3.2 Hz, 1H), 3.42 (qd, J = 8.4, 3.1 Hz, 1H), 3.17 (t, J = 9.5 Hz, 1H), 2.89 (dd, J = 13.4, 8.4 Hz, 1H), 2.37 (dd, J = 13.4, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.19, 146.69, 137.52, 130.30, 128.62, 128.38, 127.03, 126.96, 75.70, 73.48, 52.72, 43.10, 33.43. HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{17}N$, 236.1439; found: 236.1432.

7. Copies of NMR Spectra



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5.35
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5.01
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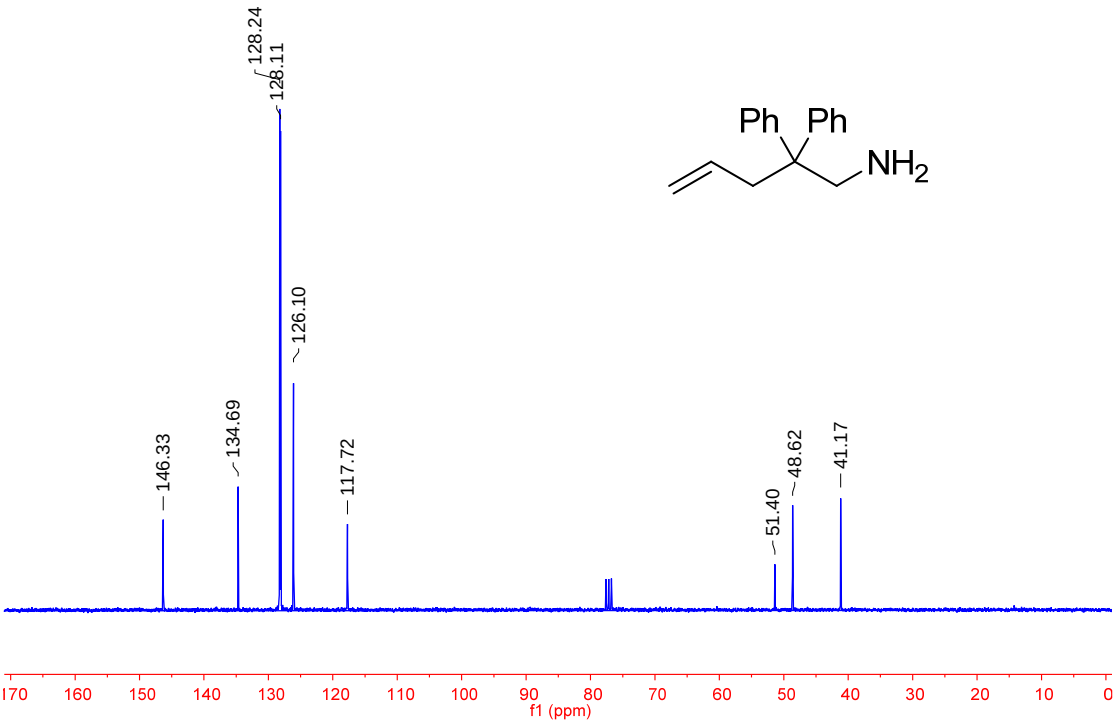
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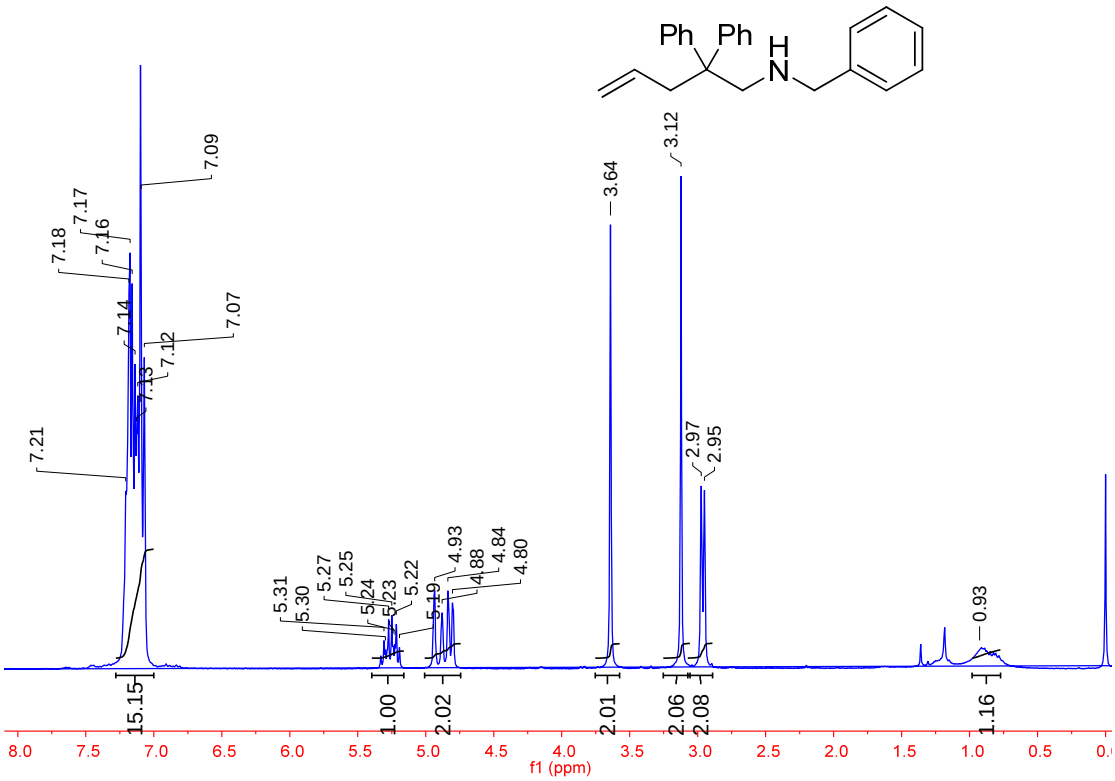
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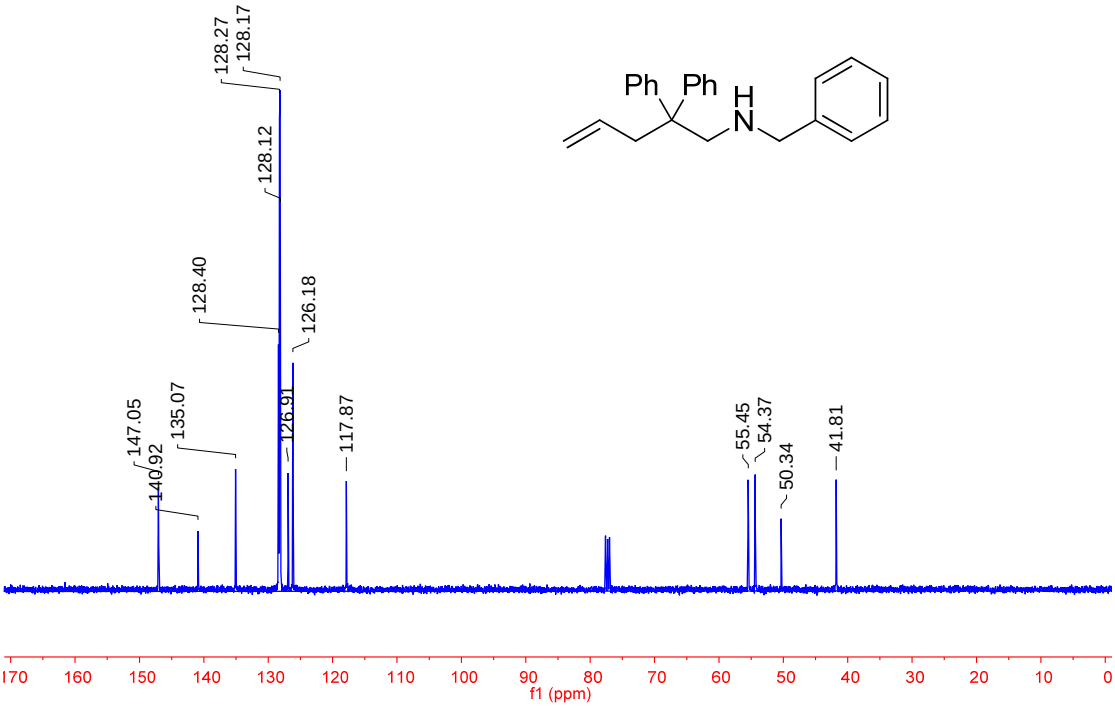
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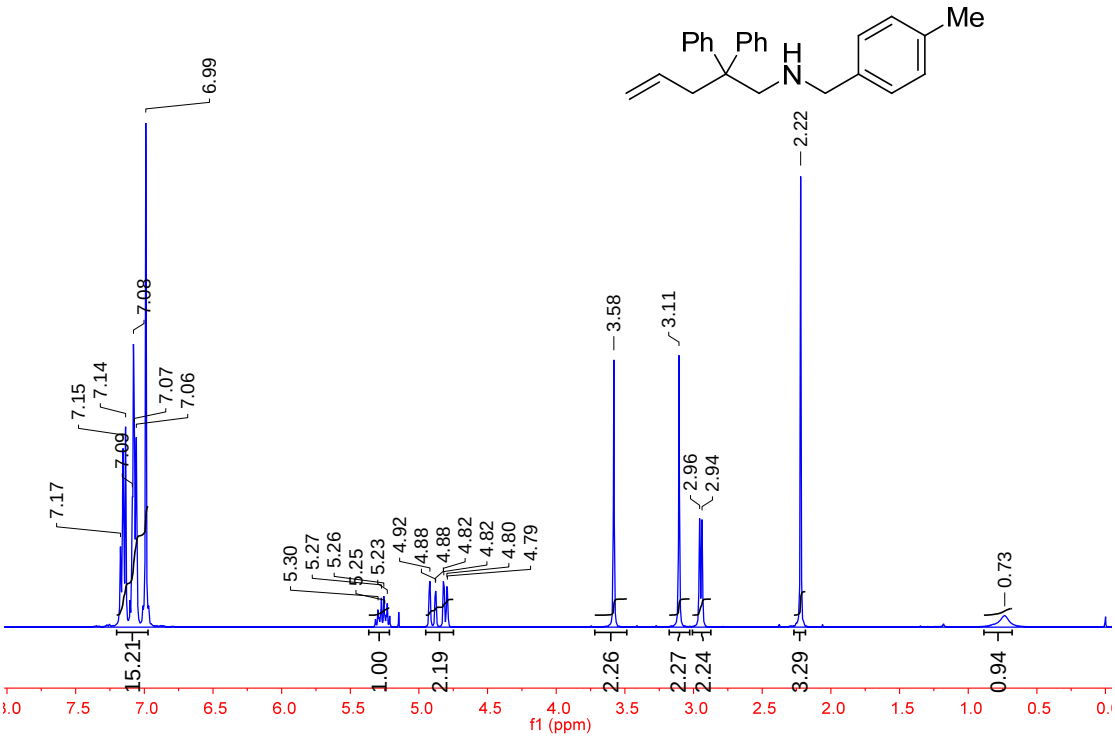
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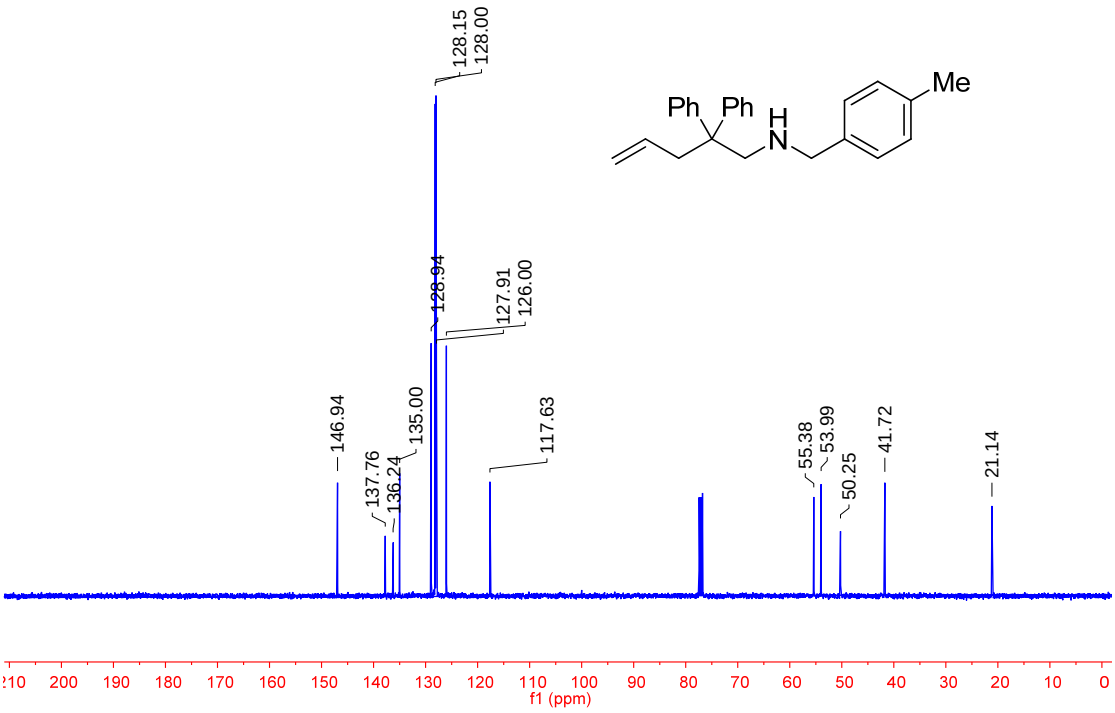
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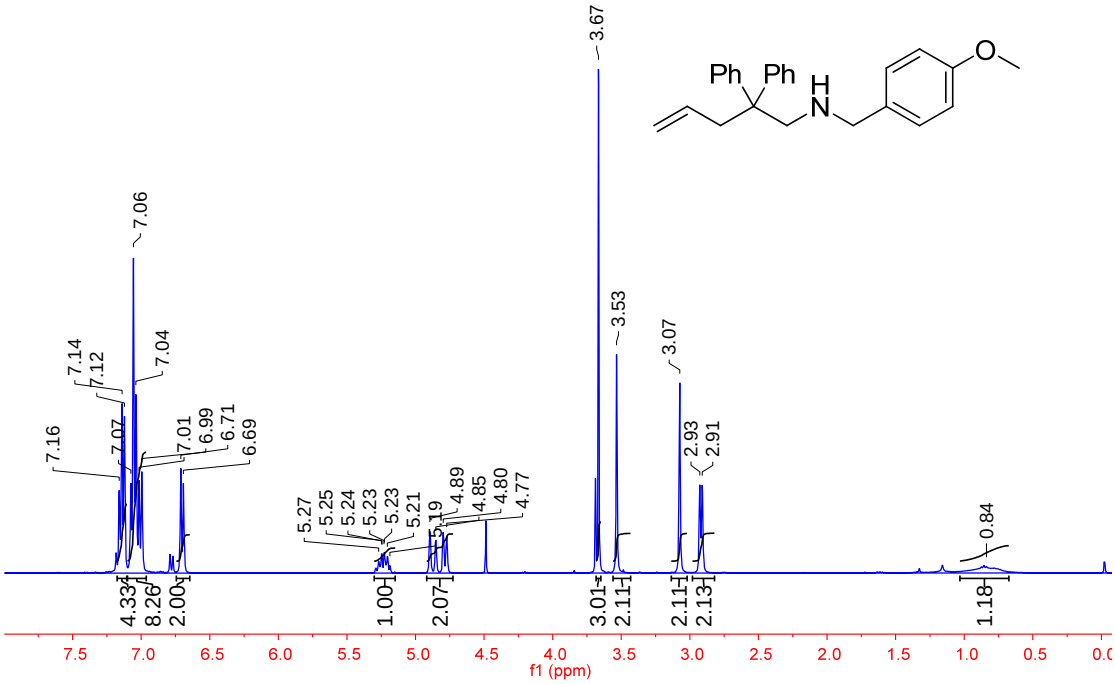
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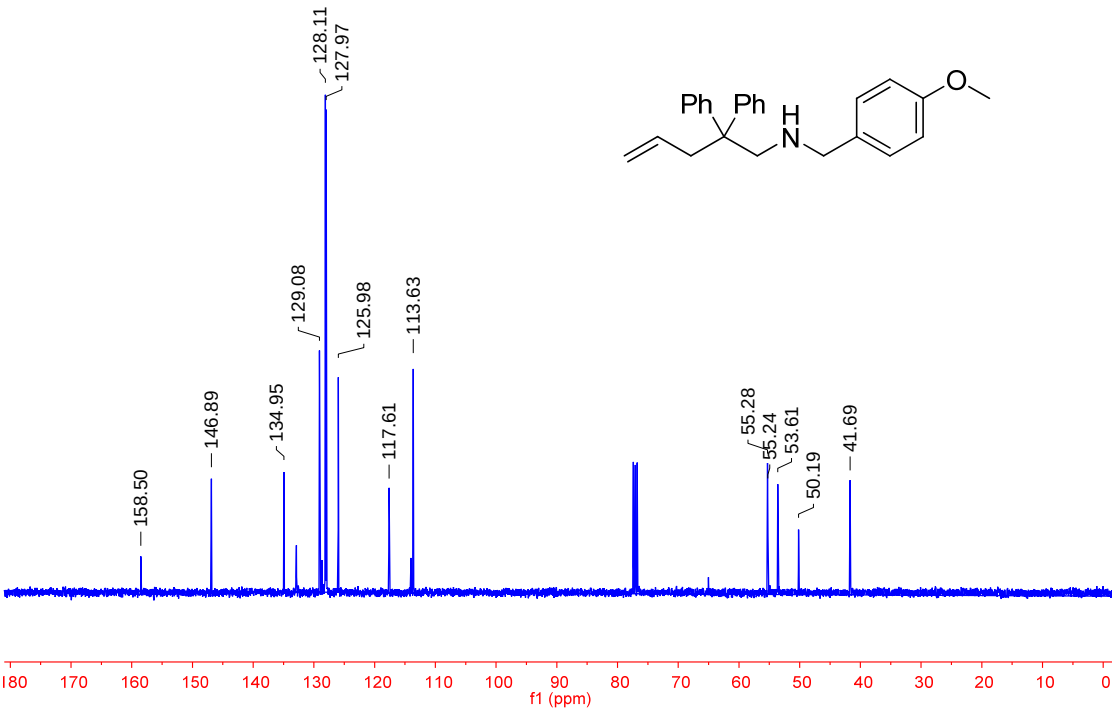
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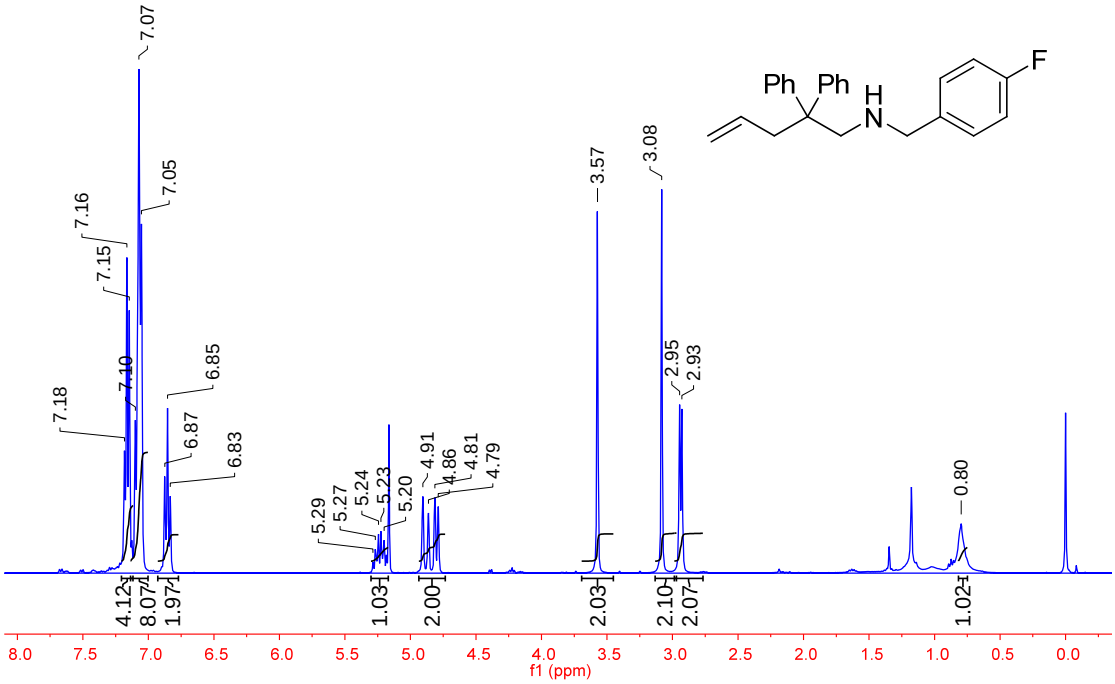
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4.12
8.07
1.97
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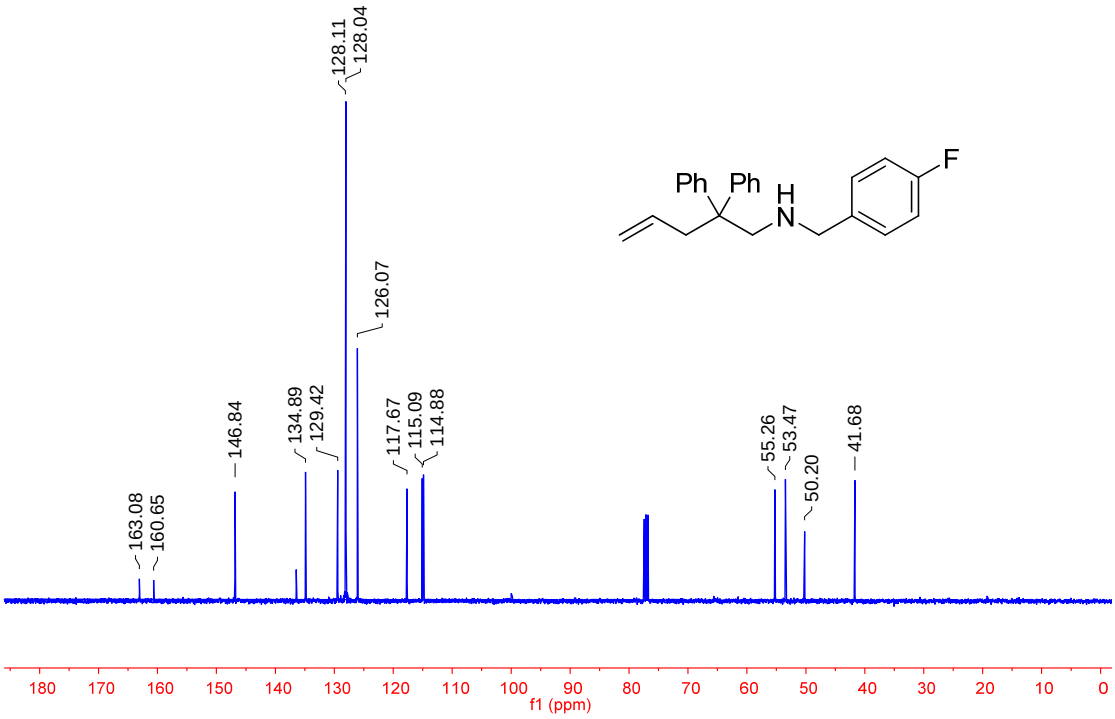
2.00
2.03
2.10
2.07
1.02
Ph
Ph
H
N
F
f1 (ppm)


128.11
128.04
126.07
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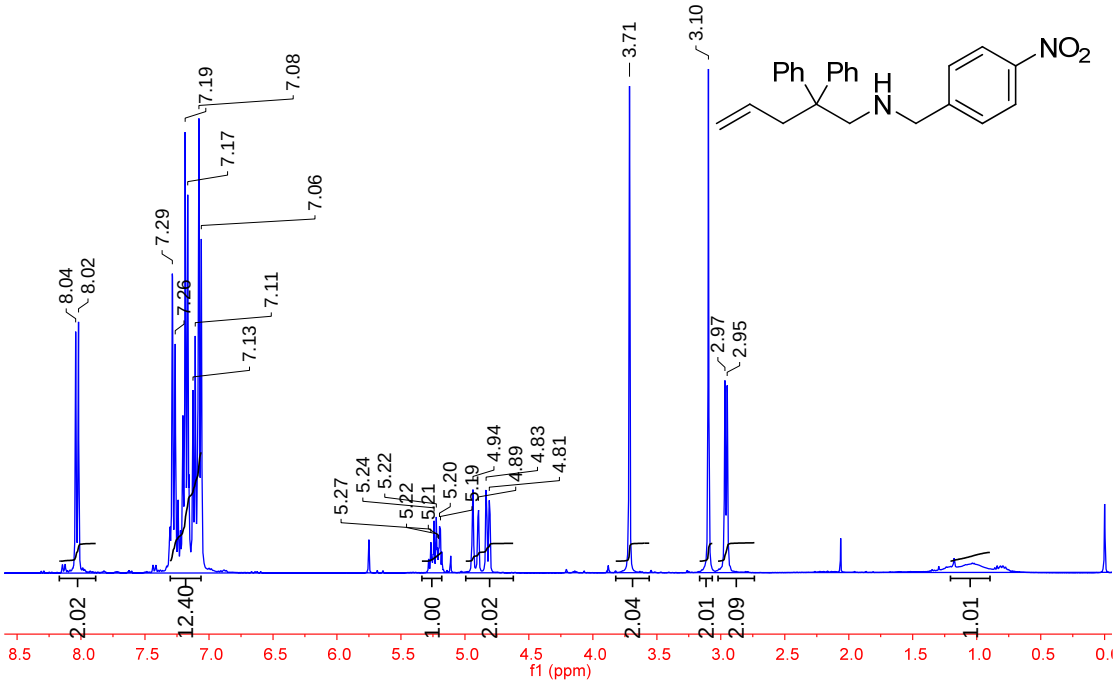
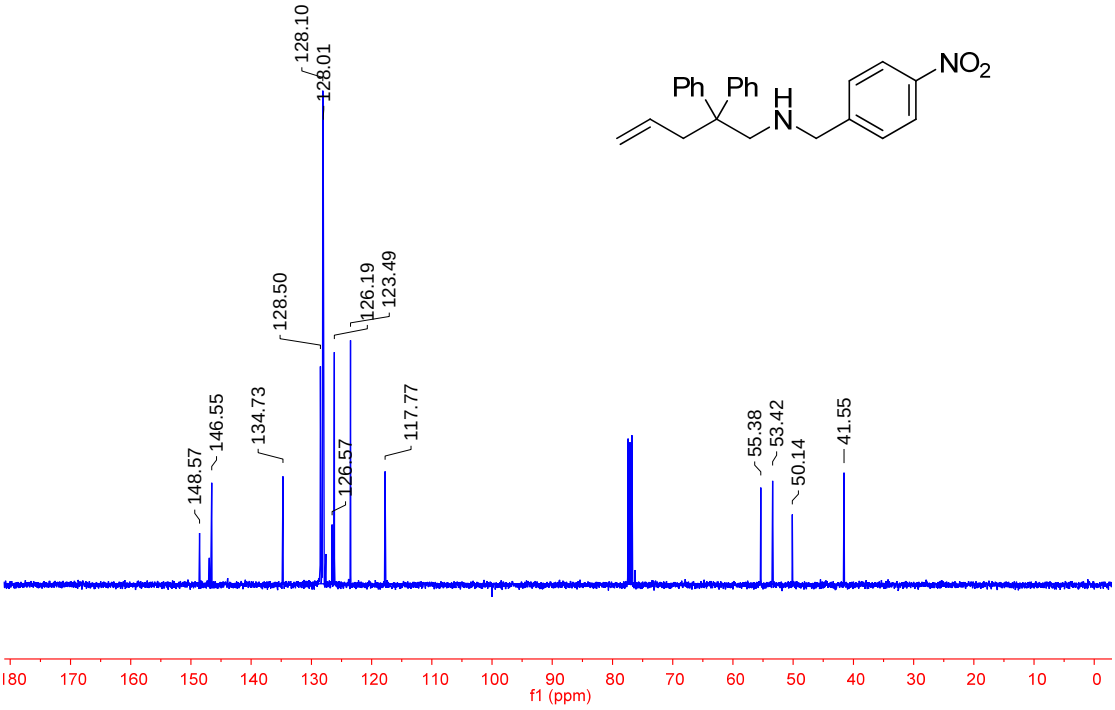
134.89
129.42
117.67
115.09
114.88
163.08
160.65
55.26
53.47
50.20
41.68
Ph
Ph
H
N
F
f1 (ppm)


Ph
Ph
H
N
NO2
8.04
8.02
7.29
7.26
7.19
7.17
7.13
7.11
7.08
7.06
5.27
5.24
5.22
5.21
5.20
5.19
4.94
4.89
4.83
4.81
3.71
3.10
2.97
2.95
2.02
12.40
1.00
2.02
2.04
2.01
2.09
1.01
f1 (ppm)


Ph
Ph
H
N
NO2
128.10
128.01
128.50
126.19
123.49
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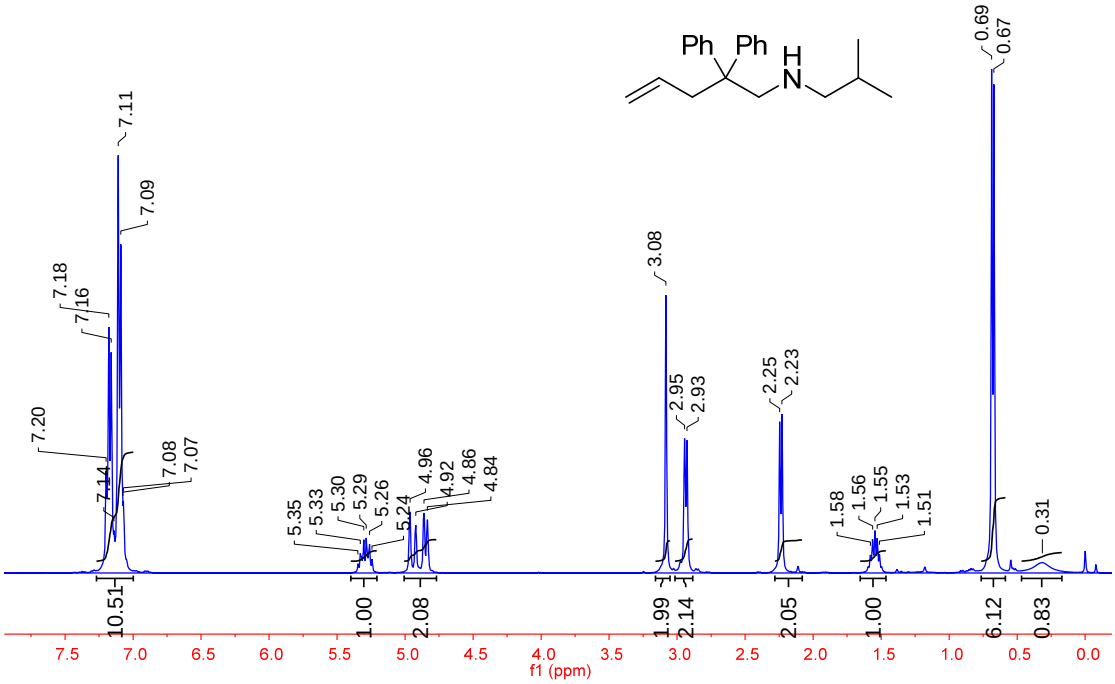
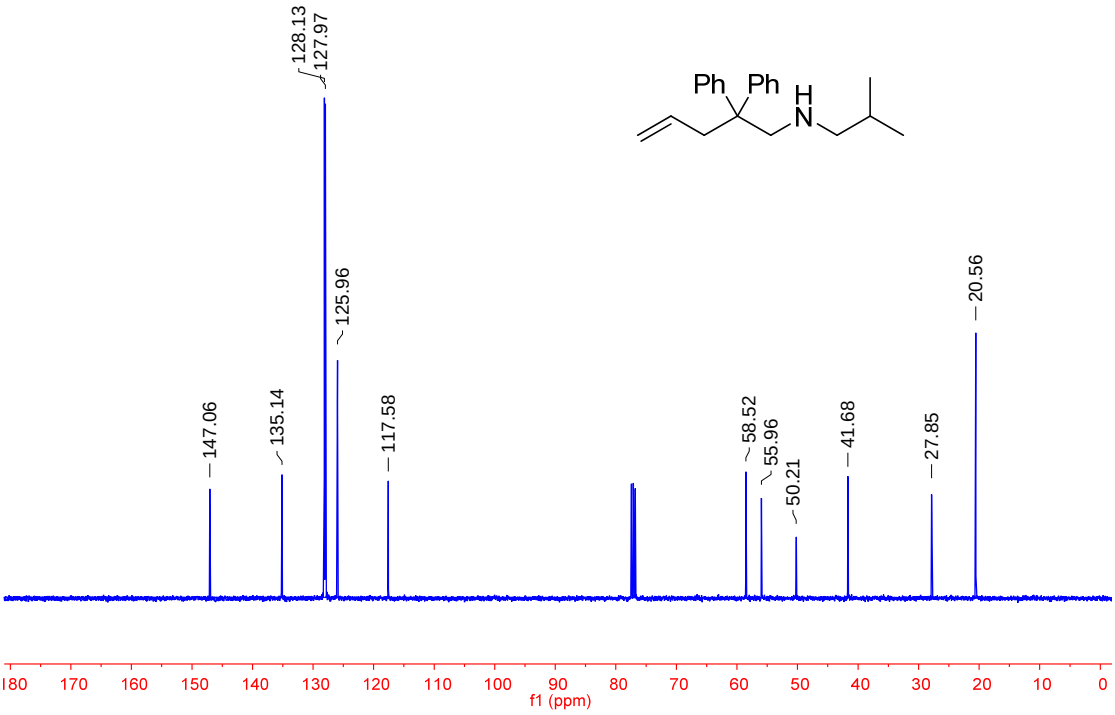
146.55
134.73
126.57
117.77
55.38
53.42
50.14
41.55
f1 (ppm)


Ph Ph
H
N
7.20
7.18
7.16
7.14
7.11
7.09
7.08
7.07
5.35
5.33
5.30
5.29
5.26
5.24
4.96
4.92
4.86
4.84
3.08
2.95
2.93
2.25
2.23
1.58
1.56
1.55
1.53
1.51
0.69
0.67
0.31
10.51
1.00
2.08
1.99
2.14
2.05
1.00
6.12
0.83
f1 (ppm)


Ph Ph
H
N
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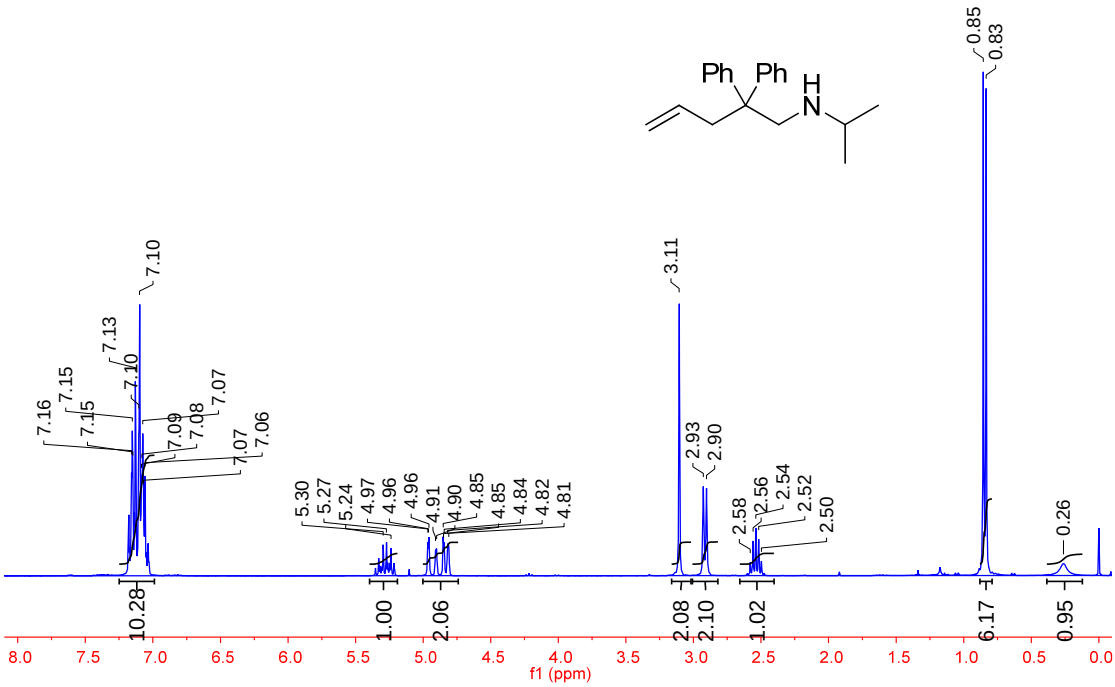
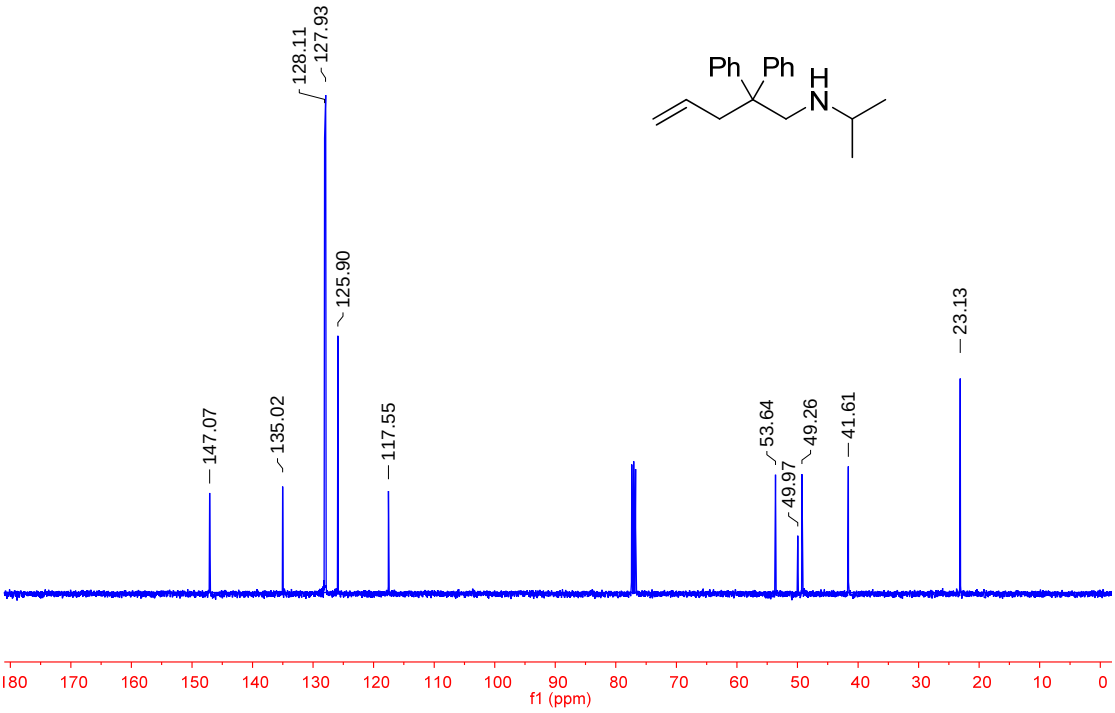
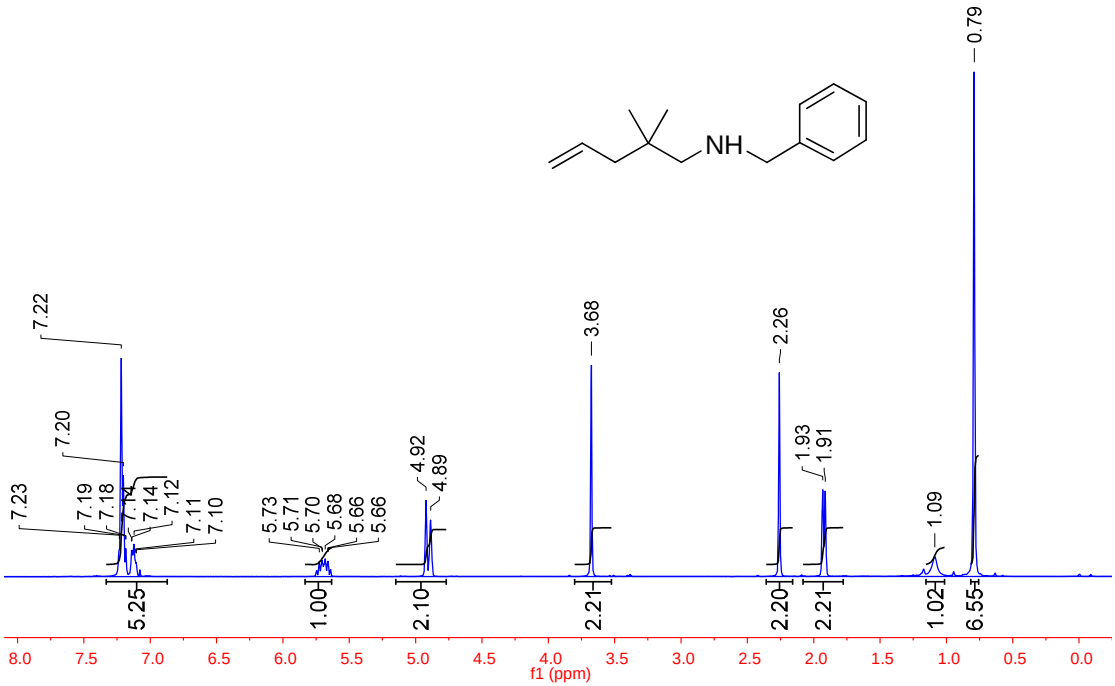
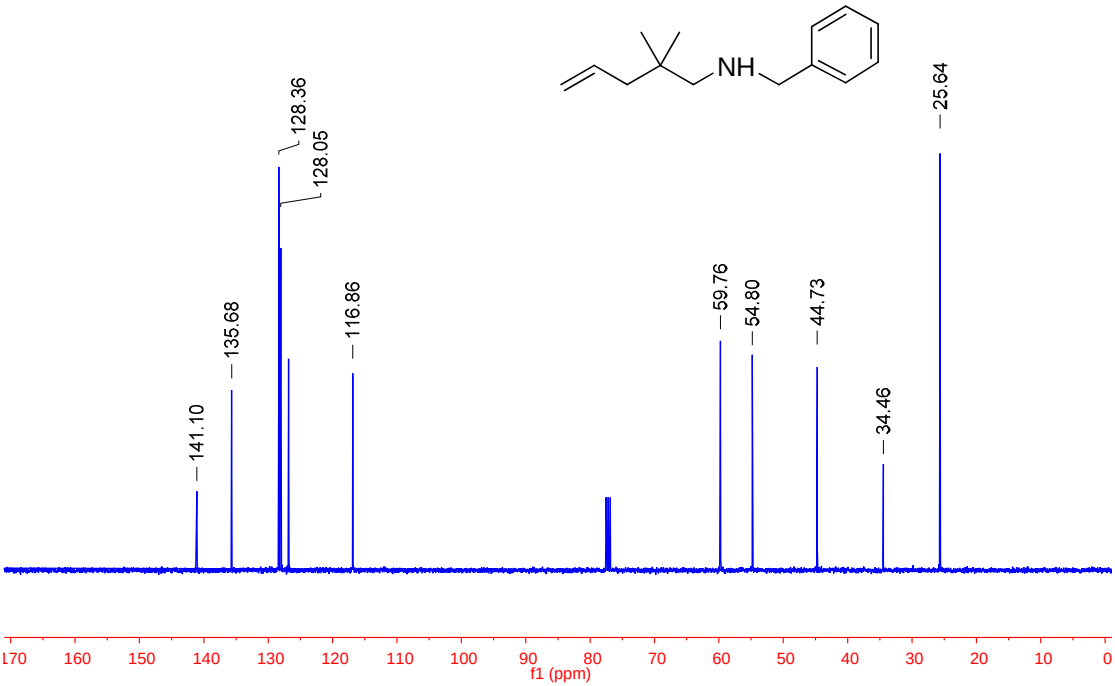
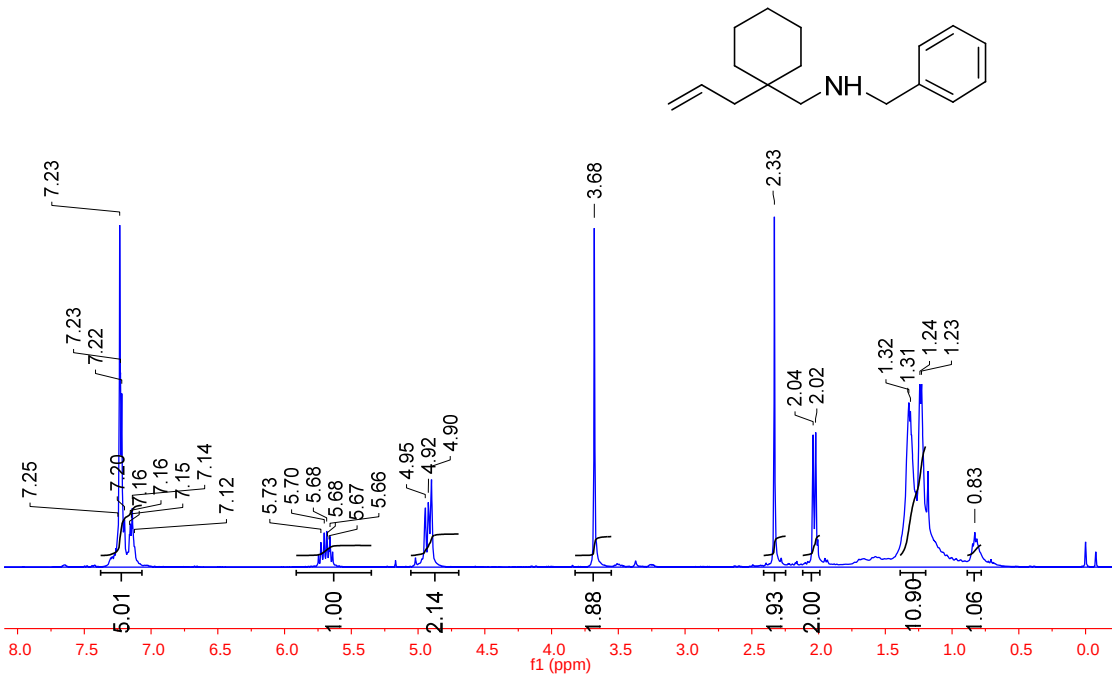
127.97
125.96
147.06
135.14
117.58
58.52
55.96
50.21
41.68
27.85
20.56
f1 (ppm)

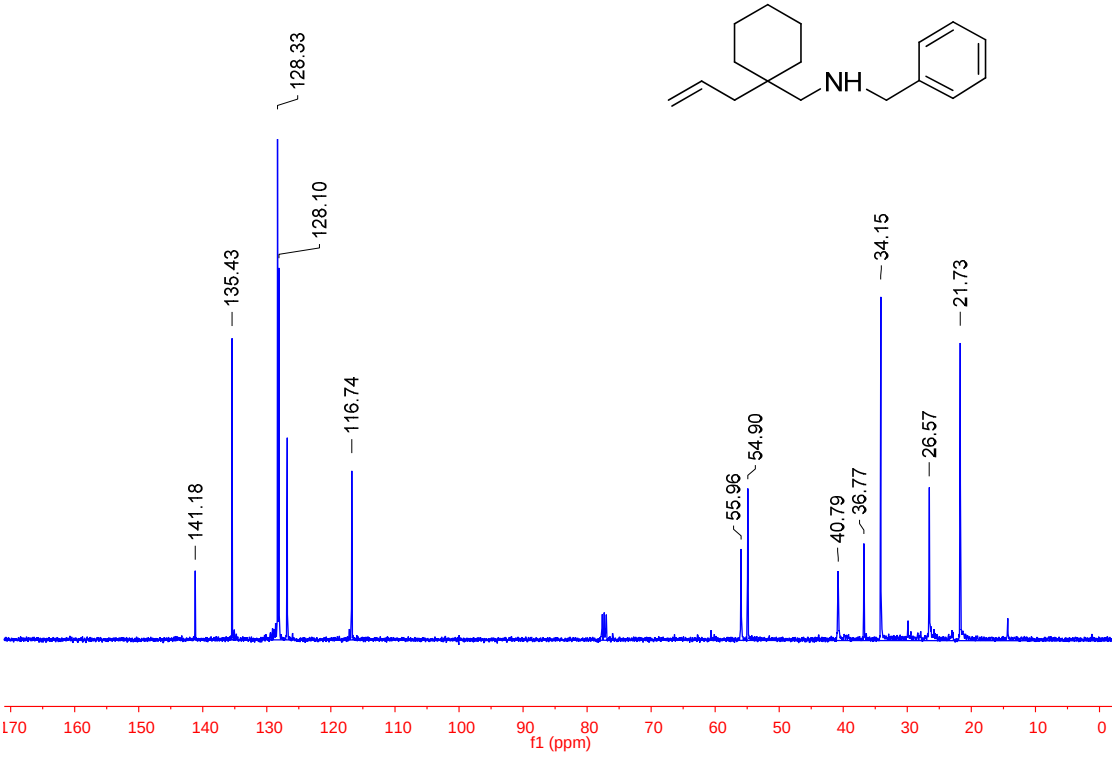

Ph Ph
H
N
7.16
7.15
7.15
7.13
7.10
7.10
7.09
7.08
7.07
7.07
7.06
5.30
5.27
5.24
4.97
4.96
4.96
4.91
4.90
4.85
4.85
4.84
4.82
4.81
3.11
2.93
2.90
2.58
2.56
2.54
2.52
2.50
0.85
0.83
0.26
10.28
1.00
2.06
2.08
2.10
1.02
6.17
0.95
f1 (ppm)

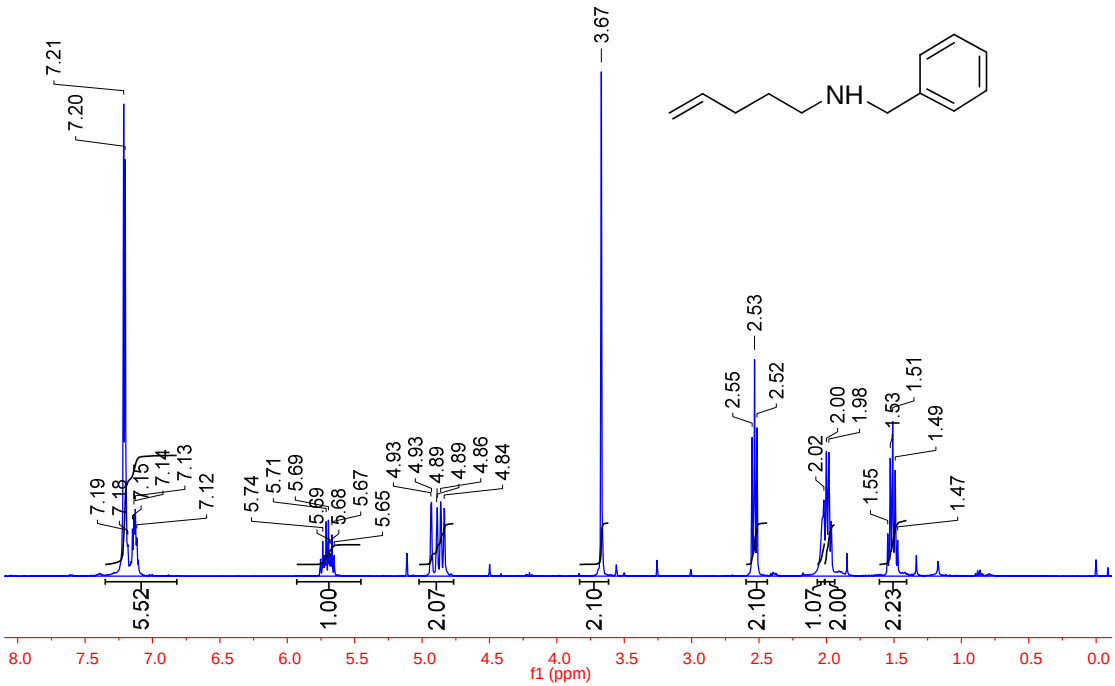

Ph Ph
H
N
128.11
127.93
125.90
147.07
135.02
117.55
53.64
49.97
49.26
41.61
23.13
f1 (ppm)

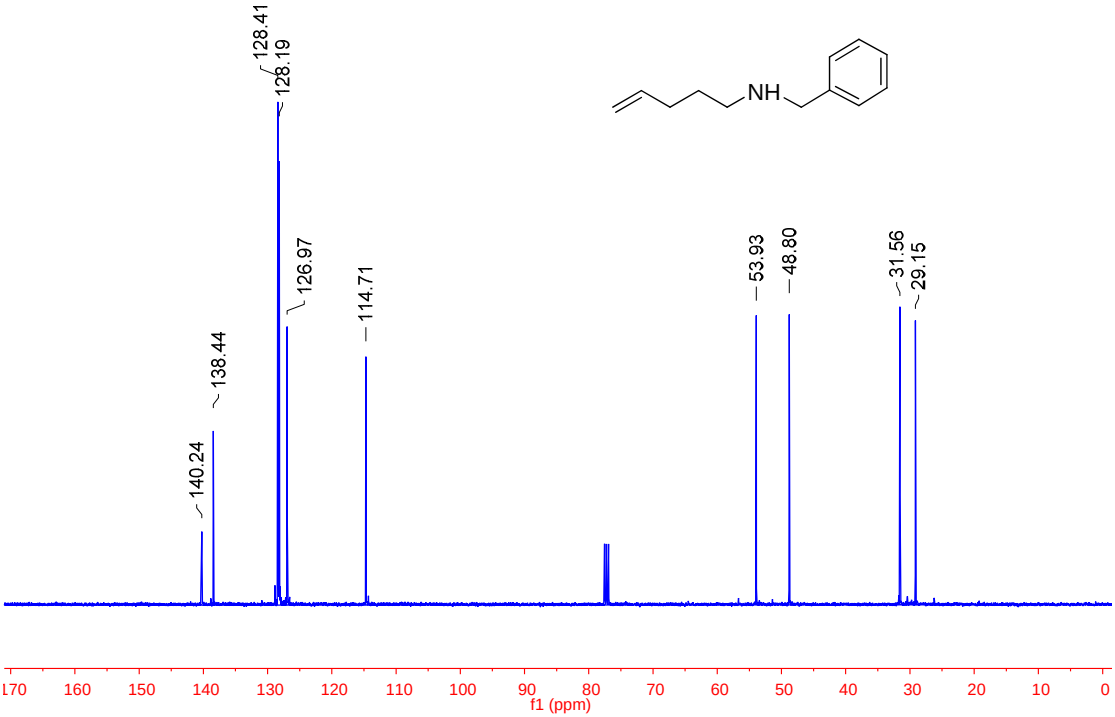

NH
0.79
7.22
7.20
7.23
7.19
7.18
7.14
7.14
7.12
7.11
7.10
5.73
5.71
5.70
5.68
5.66
5.66
4.92
4.89
3.68
2.26
1.93
1.91
1.09
5.25
1.00
2.10
2.21
2.20
2.21
1.02
6.55
f1 (ppm)


NH
128.36
128.05
25.64
141.10
135.68
116.86
59.76
54.80
44.73
34.46
f1 (ppm)


NH
7.23
7.23
7.22
7.25
7.20
7.16
7.15
7.14
7.12
5.73
5.70
5.68
5.68
5.67
5.66
4.95
4.92
4.90
3.68
2.33
2.04
2.02
1.32
1.31
1.24
1.23
0.83
5.01
1.00
2.14
1.88
1.93
2.00
10.90
1.06
f1 (ppm)


NH
128.33
128.10
135.43
116.74
141.18
55.96
54.90
40.79
36.77
34.15
26.57
21.73
f1 (ppm)


7.21
7.20
7.19
7.18
7.15
7.14
7.13
7.12
5.74
5.71
5.69
5.68
5.67
5.65
4.93
4.89
4.89
4.86
4.84
3.67
2.55
2.53
2.52
2.02
2.00
1.98
1.55
1.53
1.51
1.49
1.47
NH
5.52
1.00
2.07
2.10
2.10
1.07
2.00
2.23
f1 (ppm)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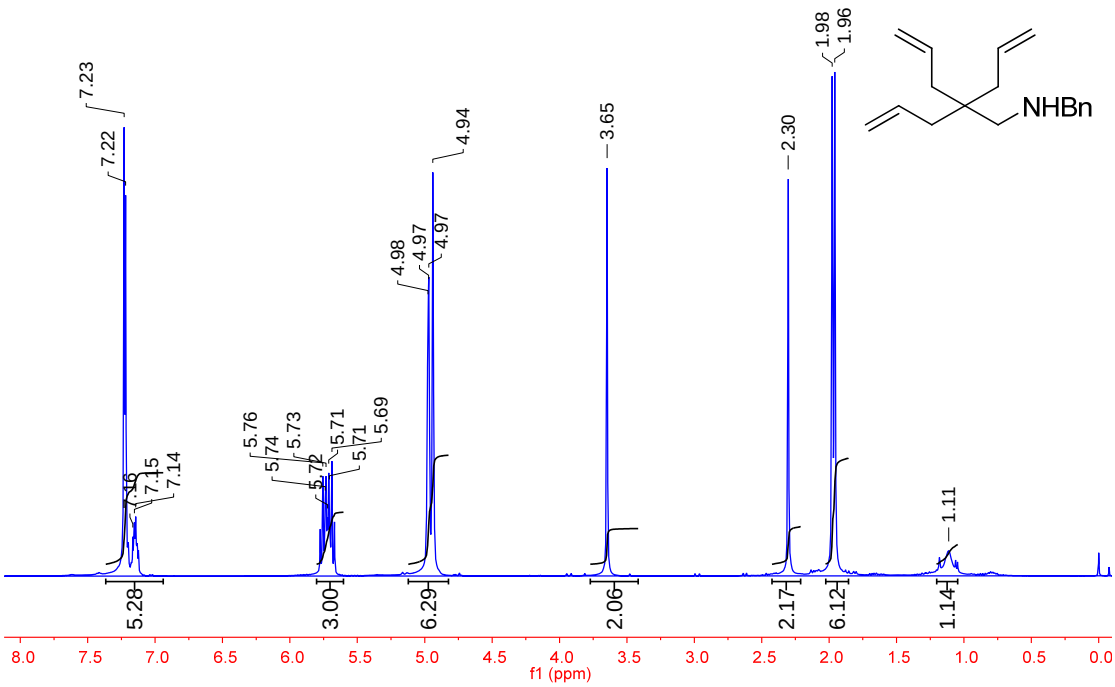
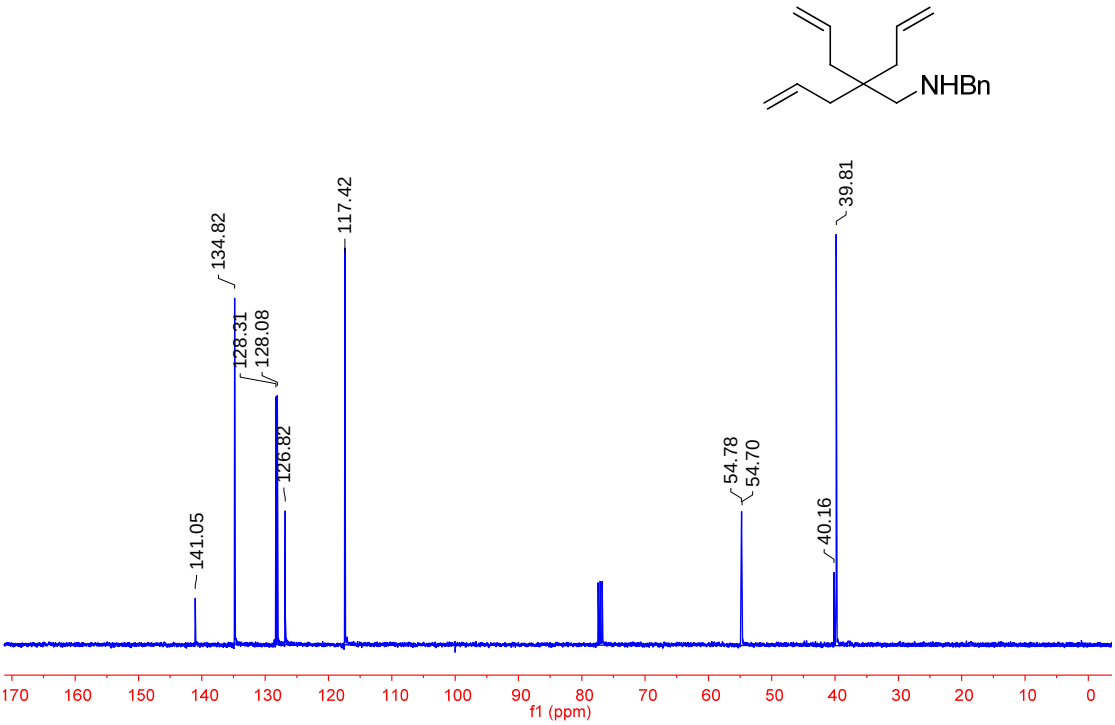
128.19
126.97
114.71
140.24
138.44
53.93
48.80
31.56
29.15
NH
f1 (ppm)


7.23
7.22
7.16
7.15
7.14
5.76
5.74
5.73
5.72
5.71
5.71
5.69
4.98
4.97
4.97
4.94
3.65
2.30
1.98
1.96
1.11
NHBn
5.28
3.00
6.29
2.06
2.17
6.12
1.14
f1 (ppm)


NHBn
141.05
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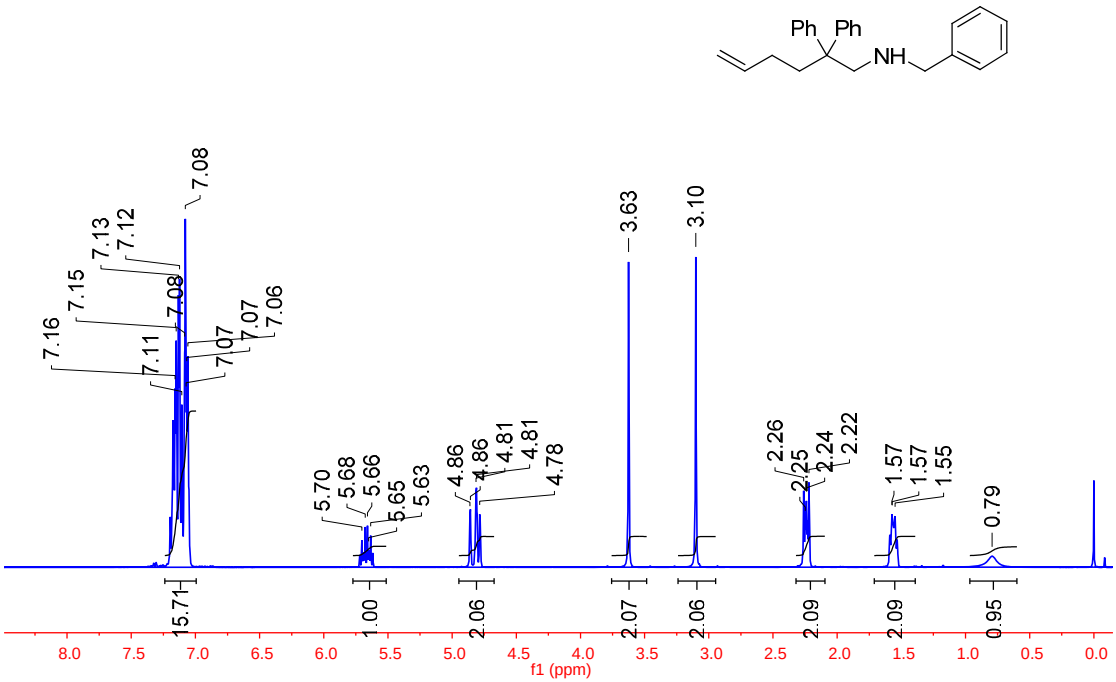
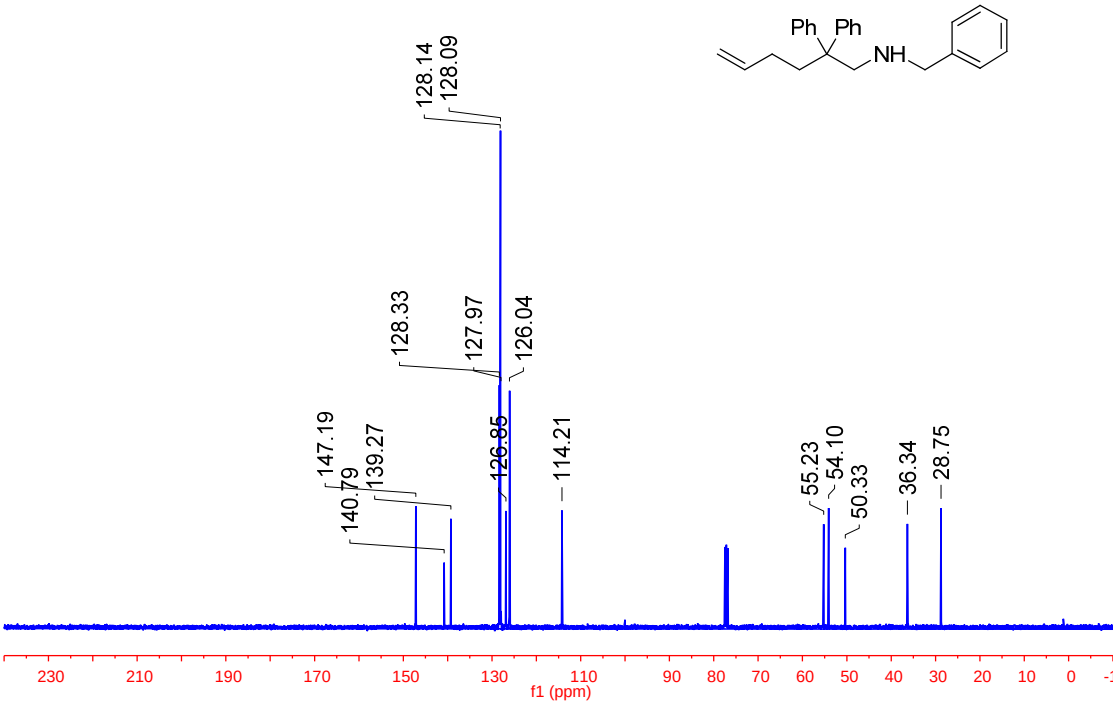
128.31
128.08
126.82
117.42
54.78
54.70
40.16
39.81
f1 (ppm)


Ph
Ph
NH
7.08
7.13
7.12
7.15
7.09
7.16
7.07
7.06
7.11
7.07
3.63
3.10
5.70
5.68
5.66
5.65
5.63
4.86
4.86
4.81
4.81
4.78
2.26
2.25
2.24
2.22
1.57
1.57
1.55
0.79
15.71
1.00
2.06
2.07
2.06
2.09
2.09
0.95
f1 (ppm)


Ph
Ph
NH
128.14
128.09
128.33
127.97
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147.19
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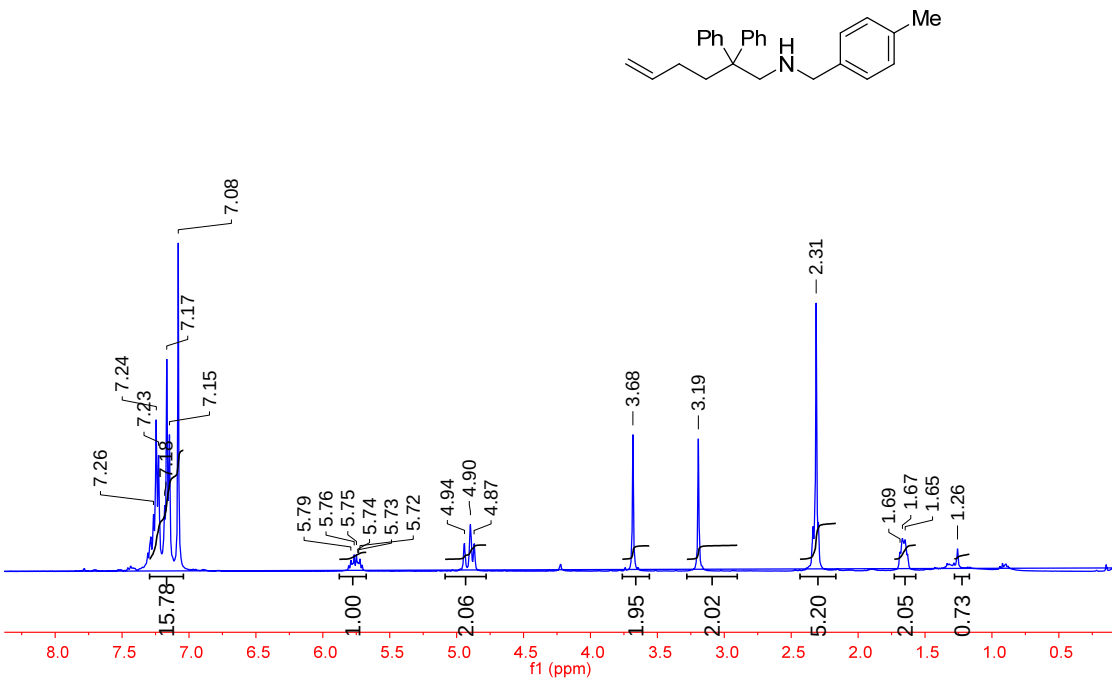
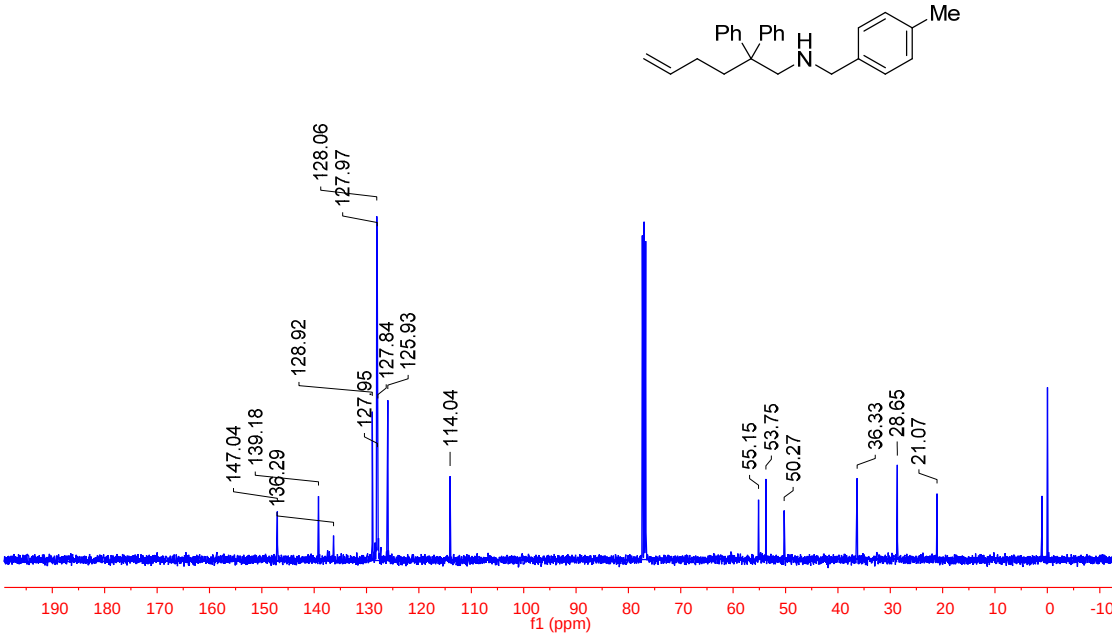
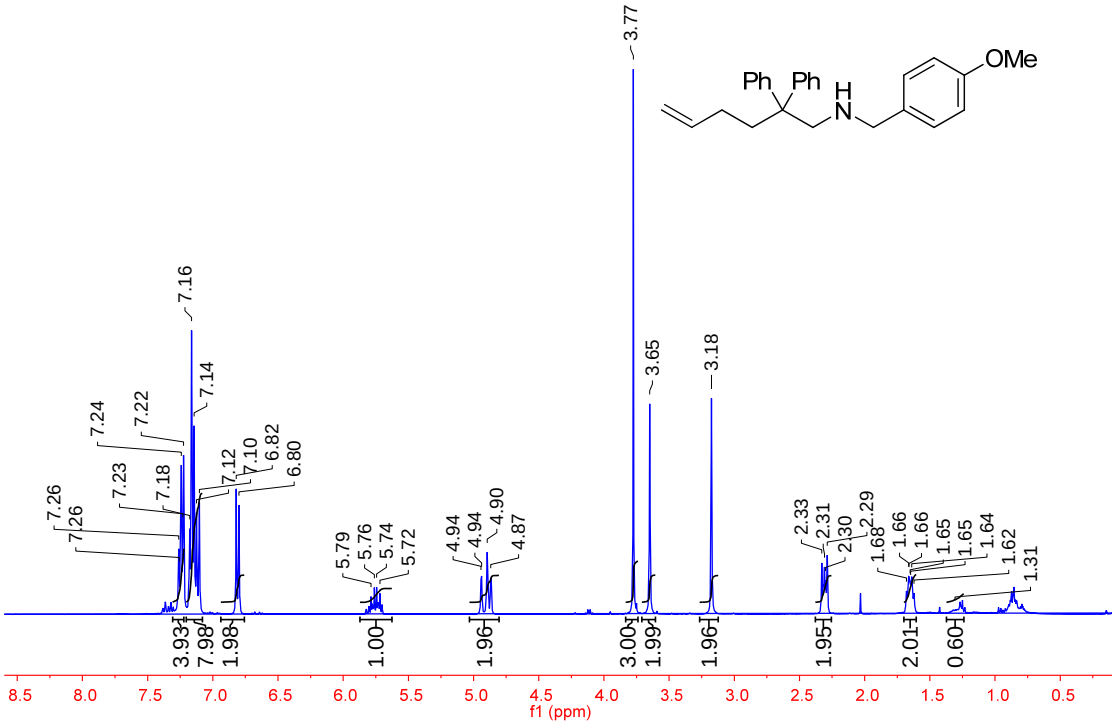
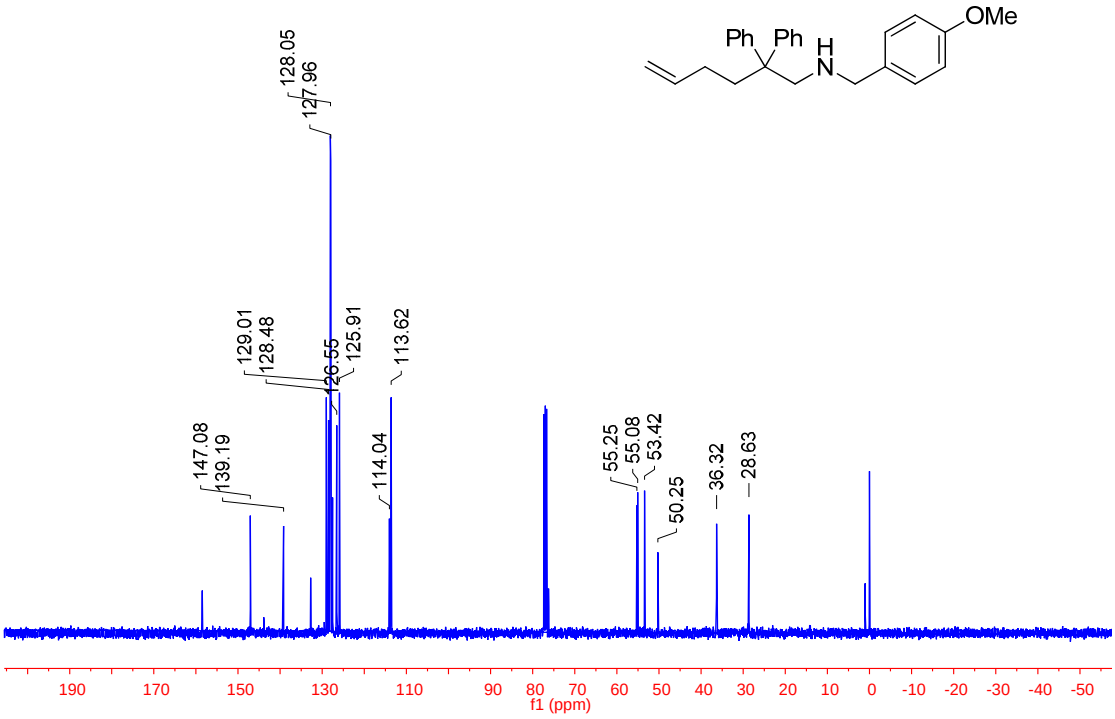
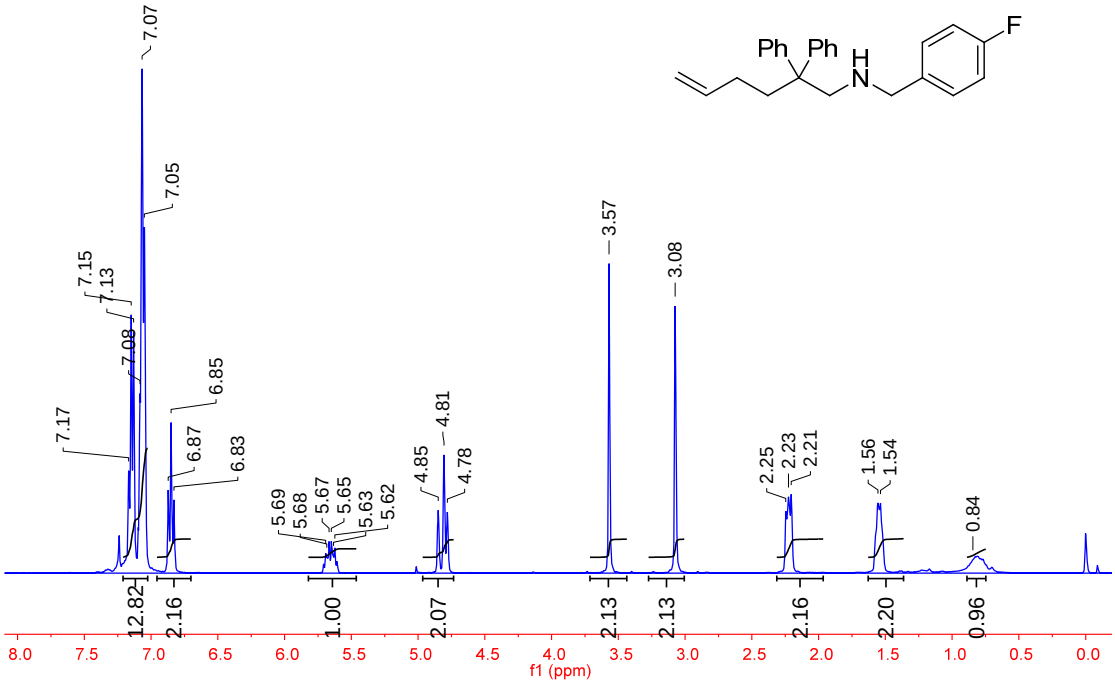
140.79
126.85
114.21
55.23
54.10
50.33
36.34
28.75
f1 (ppm)

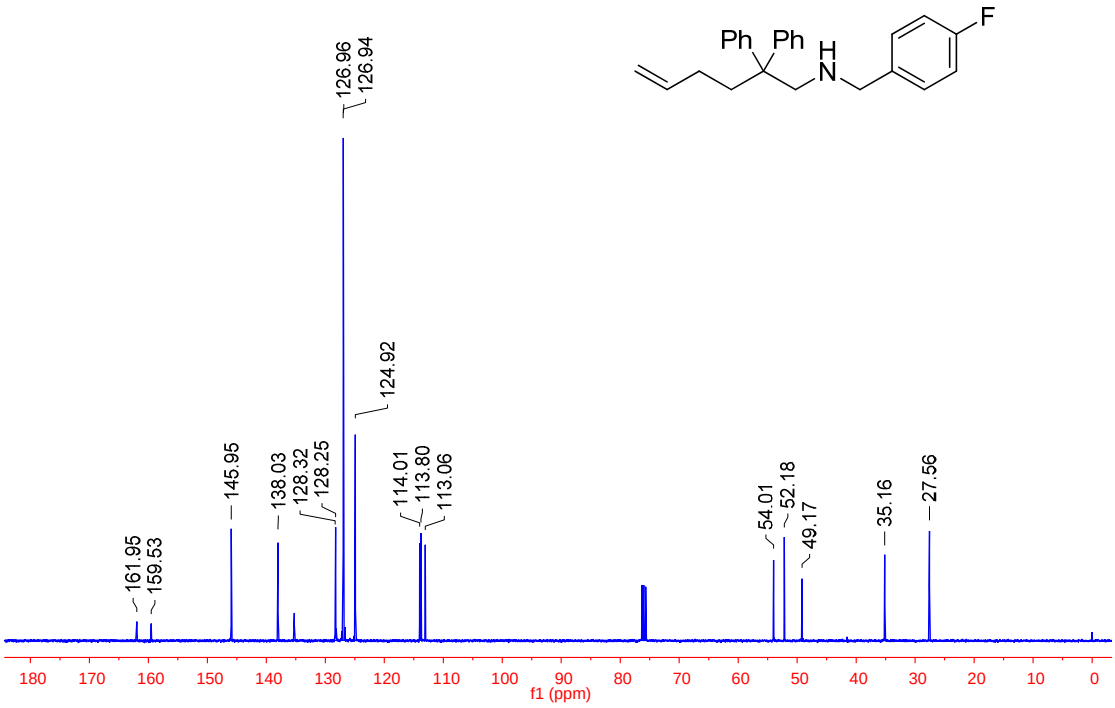

Ph
Ph
H
N
Me
7.08
7.17
7.24
7.23
7.18
7.15
7.26
5.79
5.76
5.75
5.74
5.73
5.72
4.94
4.90
4.87
3.68
3.19
2.31
1.69
1.67
1.65
1.26
15.78
1.00
2.06
1.95
2.02
5.20
2.05
0.73
f1 (ppm)


Ph
Ph
H
N
Me
128.06
127.97
128.92
127.84
125.93
127.95
114.04
147.04
139.18
136.29
55.15
53.75
50.27
36.33
28.65
21.07
f1 (ppm)


Ph
Ph
H
N
OMe
3.77
7.16
7.14
7.24
7.22
7.23
7.18
7.12
7.10
6.82
6.80
7.26
7.26
5.79
5.76
5.74
5.72
4.94
4.94
4.90
4.87
3.65
3.18
2.33
2.31
2.30
2.29
1.68
1.66
1.66
1.65
1.65
1.64
1.62
1.31
3.93
7.98
1.98
1.00
1.96
3.00
1.99
1.96
1.95
2.01
0.60
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph
Ph
H
N
OMe
128.05
127.96
129.01
128.48
126.55
125.91
113.62
147.08
139.19
114.04
55.25
55.08
53.42
50.25
36.32
28.63
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


Ph
Ph
H
N
F
7.07
7.05
7.15
7.13
7.08
7.17
6.85
6.87
6.83
5.69
5.68
5.67
5.65
5.63
5.62
4.85
4.81
4.78
3.57
3.08
2.25
2.23
2.21
1.56
1.54
0.84
12.82
2.16
1.00
2.07
2.13
2.13
2.16
2.20
0.96
f1 (ppm)


Ph
Ph
H
N
F
126.96
126.94
124.92
145.95
138.03
128.32
128.25
114.01
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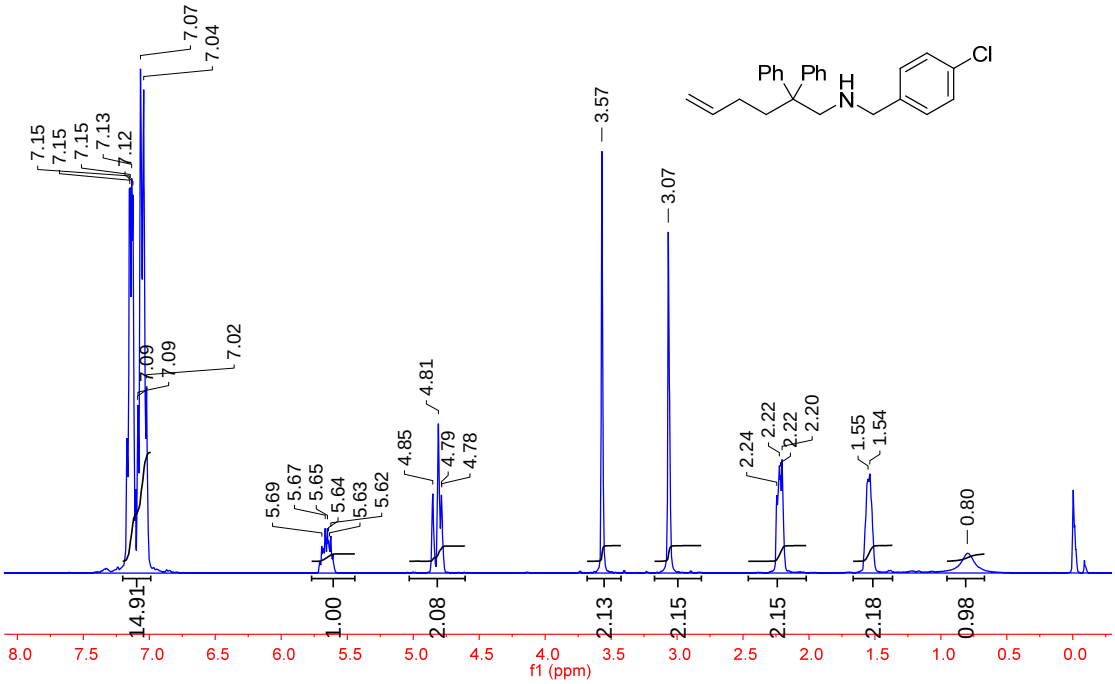
113.06
161.95
159.53
54.01
52.18
49.17
35.16
27.56
f1 (ppm)


Ph
Ph
H
N
Cl
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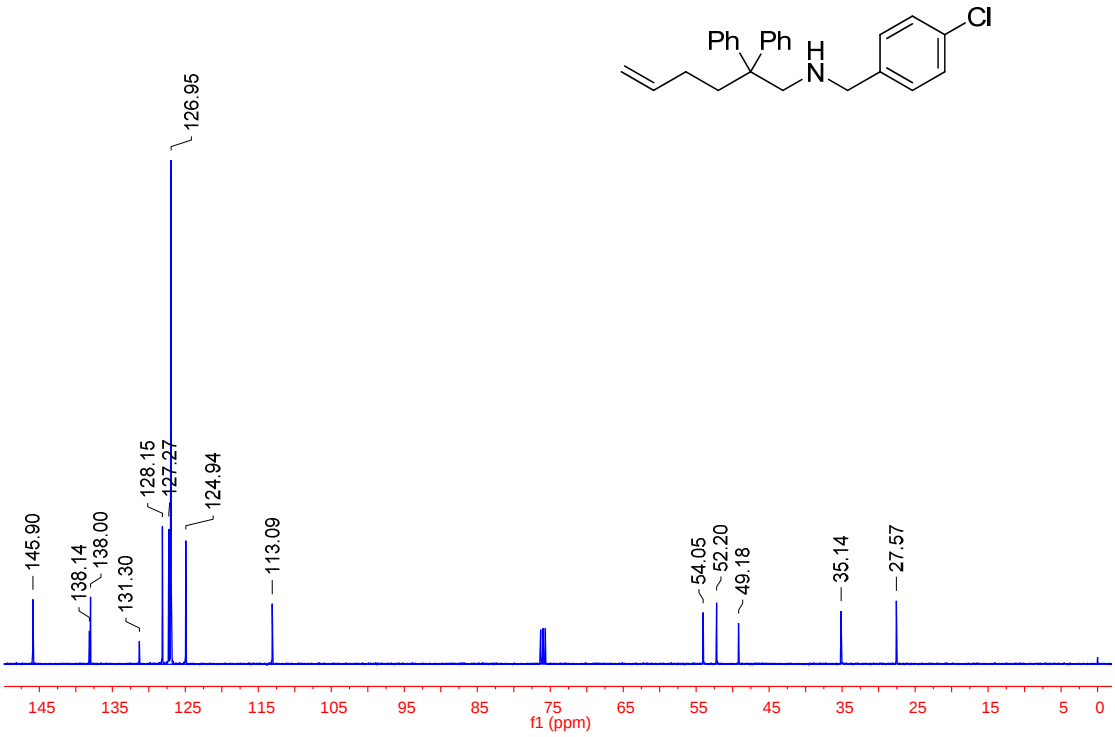
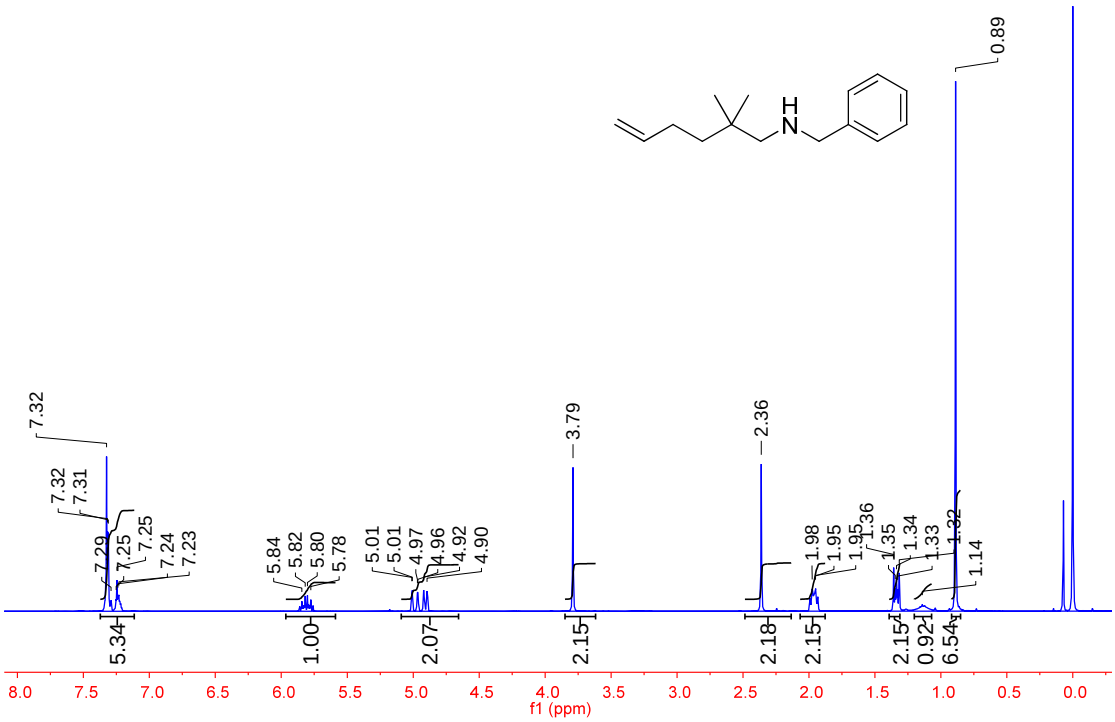
7.15
7.15
7.13
7.12
7.07
7.04
7.09
7.09
7.02
5.69
5.67
5.65
5.64
5.63
5.62
4.85
4.81
4.79
4.78
3.57
3.07
2.24
2.22
2.22
2.20
1.55
1.54
0.80
14.91
1.00
2.08
2.13
2.15
2.15
2.18
0.98
f1 (ppm)


Ph
Ph
H
N
Cl
126.95
128.15
127.27
124.94
145.90
138.14
138.00
131.30
113.09
54.05
52.20
49.18
35.14
27.57
f1 (ppm)


7.32
7.32
7.31
7.29
7.25
7.25
7.24
7.23
5.84
5.82
5.80
5.78
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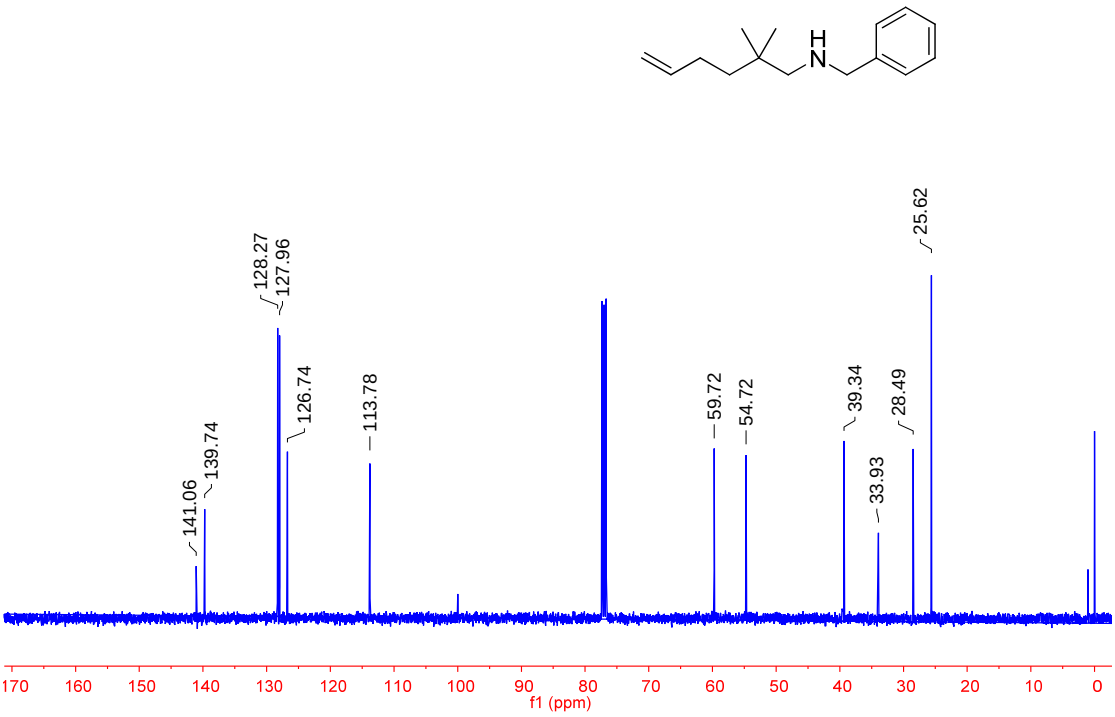
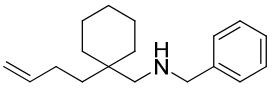
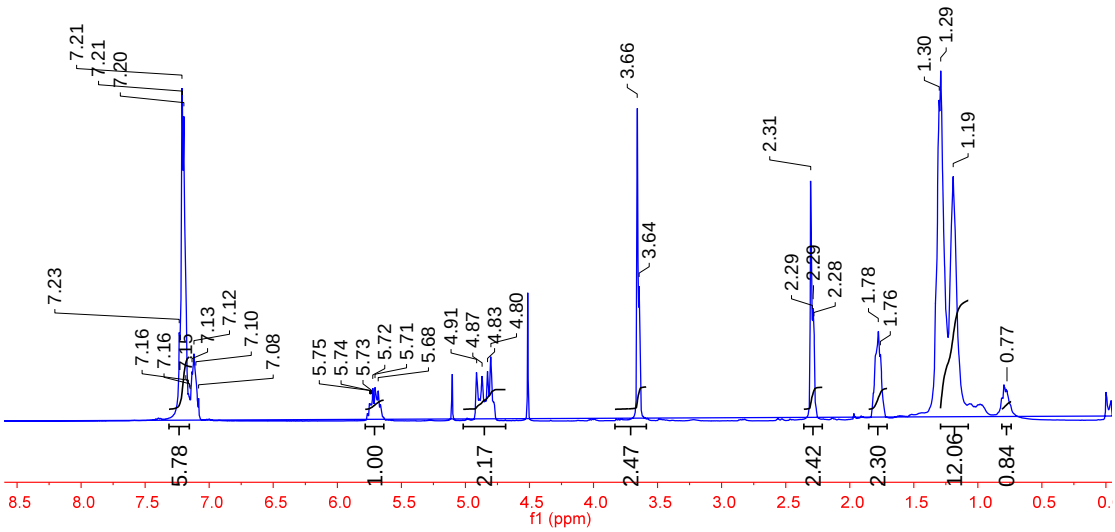
5.01
4.97
4.96
4.92
4.90
3.79
2.36
1.98
1.95
1.95
1.36
1.35
1.34
1.33
1.32
1.14
0.89
5.34
1.00
2.07
2.15
2.18
2.15
2.15
0.92
6.54
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.06
139.74
128.27
127.96
126.74
113.78
59.72
54.72
39.34
33.93
28.49
25.62
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)




7.21
7.21
7.20
7.23
7.16
7.16
7.15
7.13
7.12
7.10
7.08
5.75
5.74
5.73
5.72
5.71
5.68
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4.87
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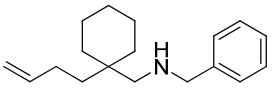
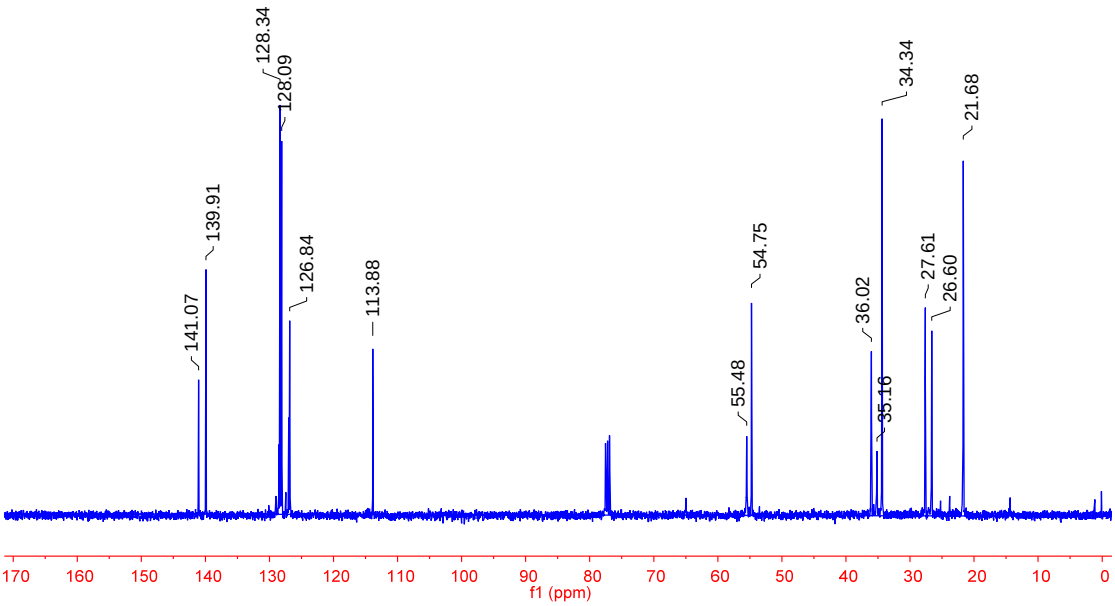
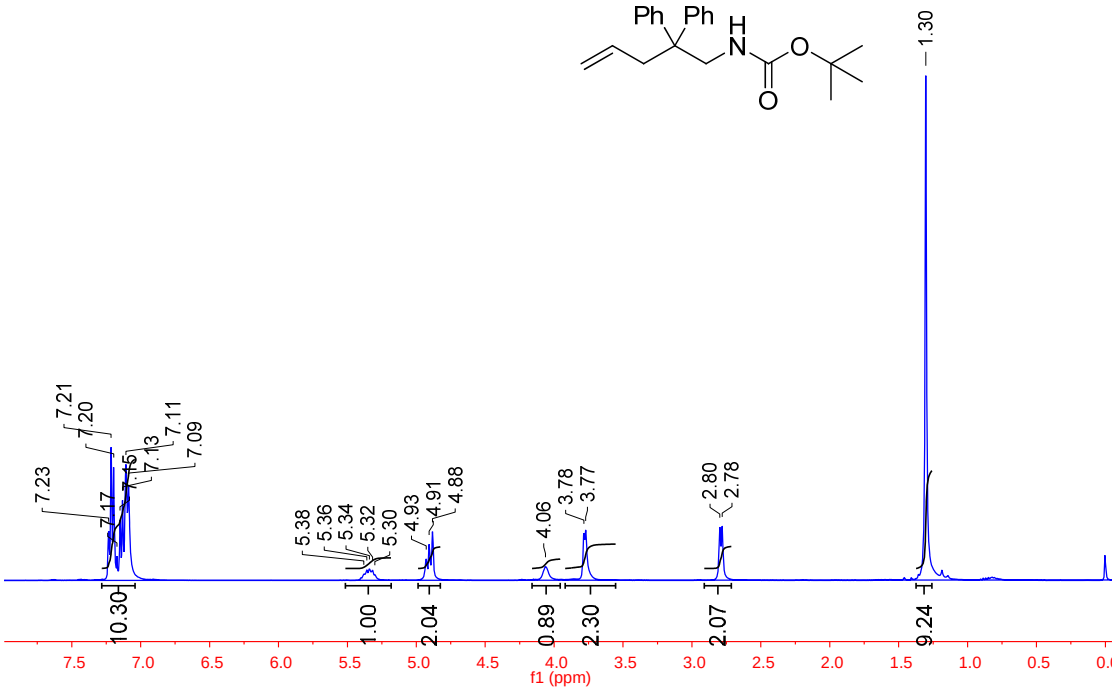
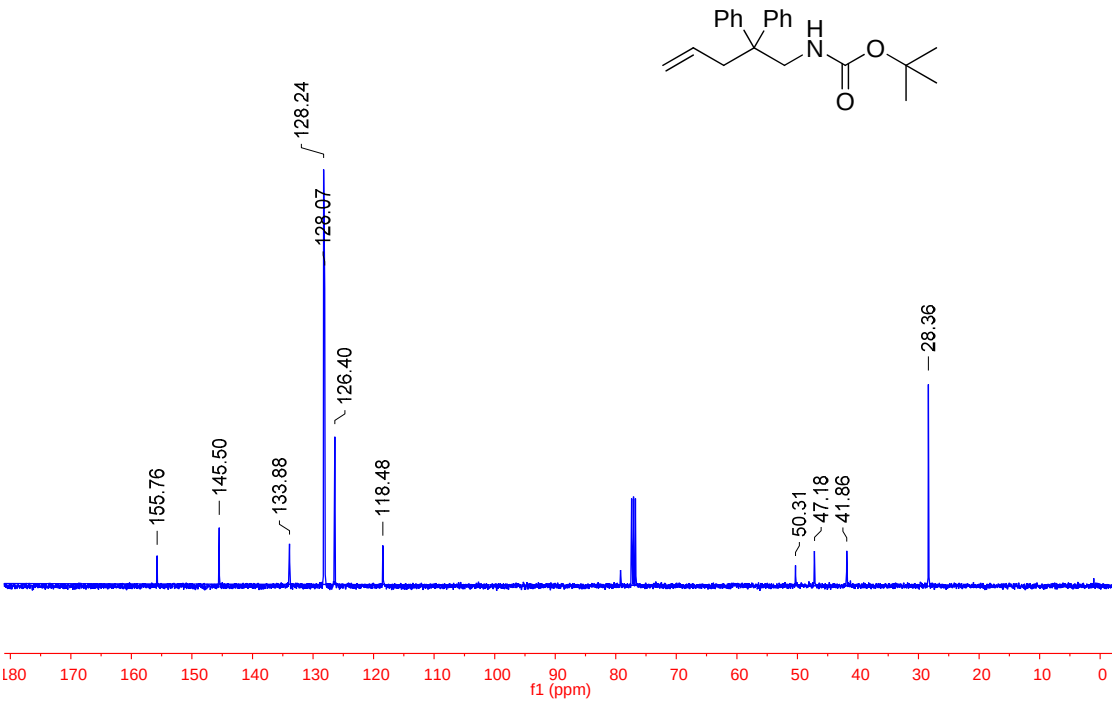
4.80
3.66
3.64
2.31
2.29
2.29
2.28
1.78
1.76
1.30
1.29
1.19
0.77
5.78
1.00
2.17
2.47
2.42
2.30
12.06
0.84
f1 (ppm)




128.34
128.09
139.91
126.84
141.07
113.88
54.75
55.48
34.34
36.02
35.16
27.61
26.60
21.68
f1 (ppm)


Ph
Ph
H
N
O
O
7.23
7.21
7.20
7.17
7.15
7.13
7.11
7.09
5.38
5.36
5.34
5.32
5.30
4.93
4.91
4.88
4.06
3.78
3.77
2.80
2.78
1.30
10.30
1.00
2.04
0.89
2.30
2.07
9.24
f1 (ppm)


Ph
Ph
H
N
O
O
128.24
128.07
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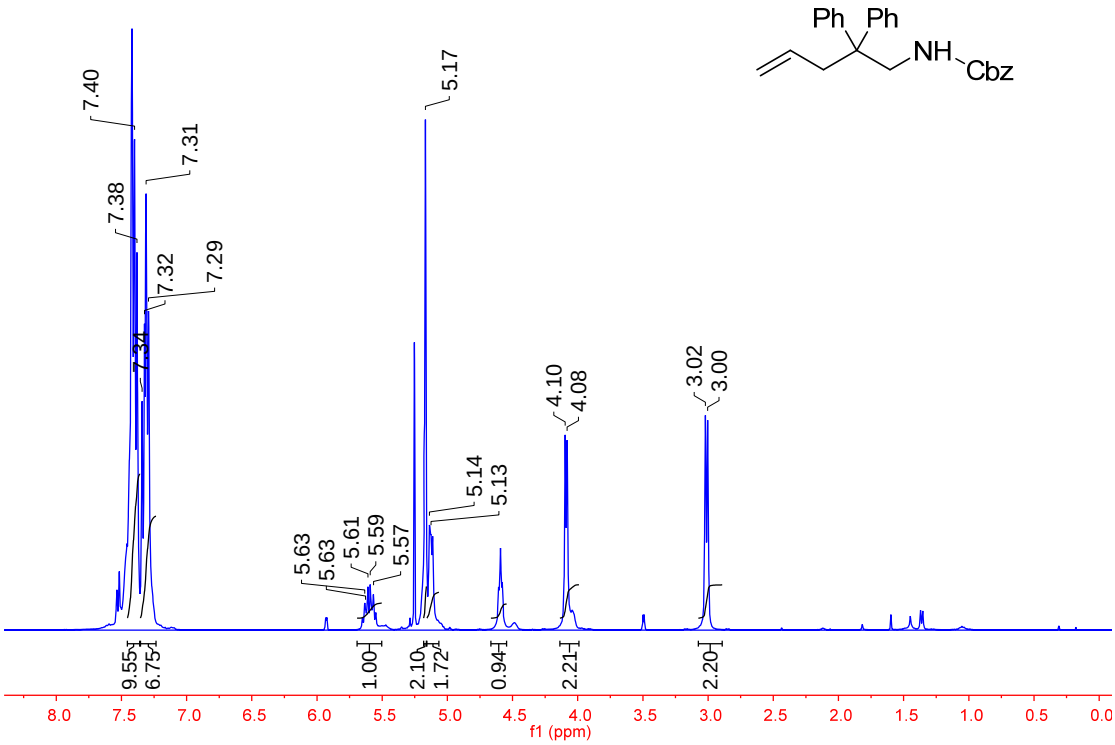
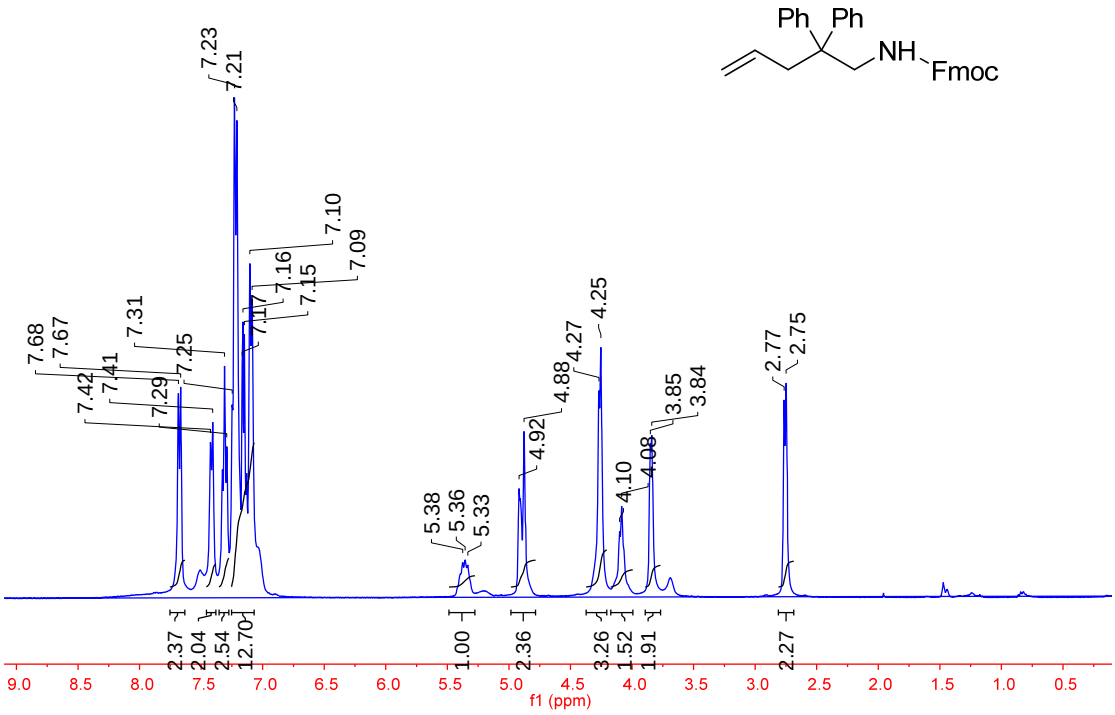
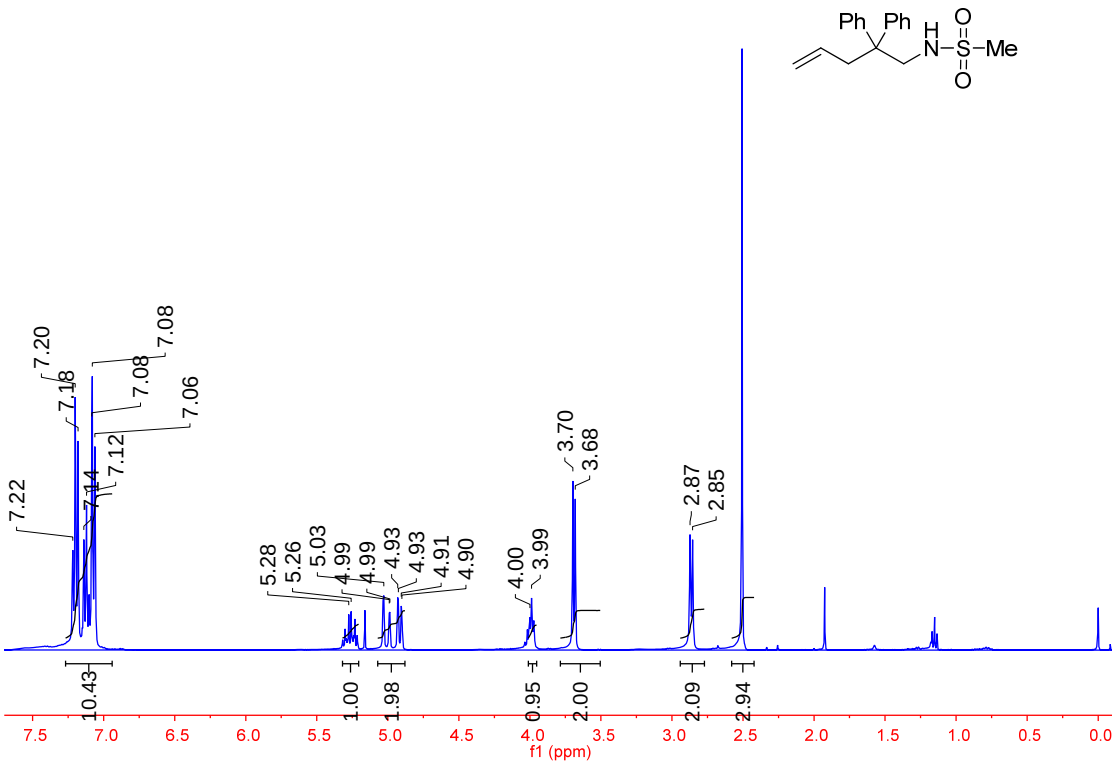
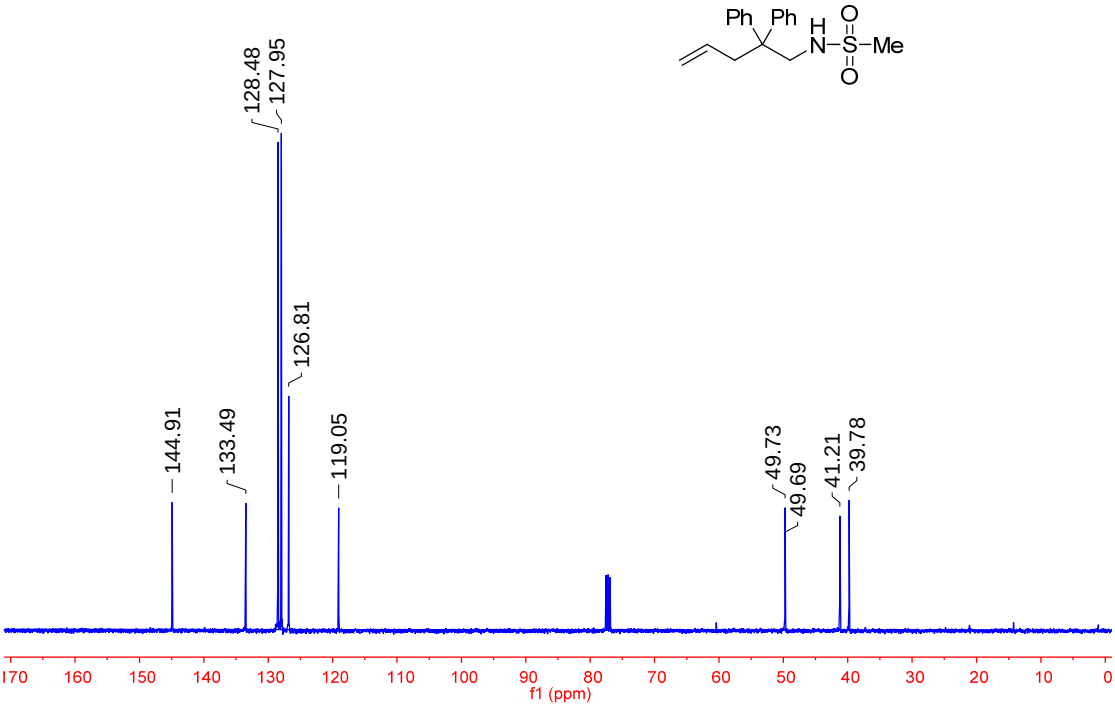
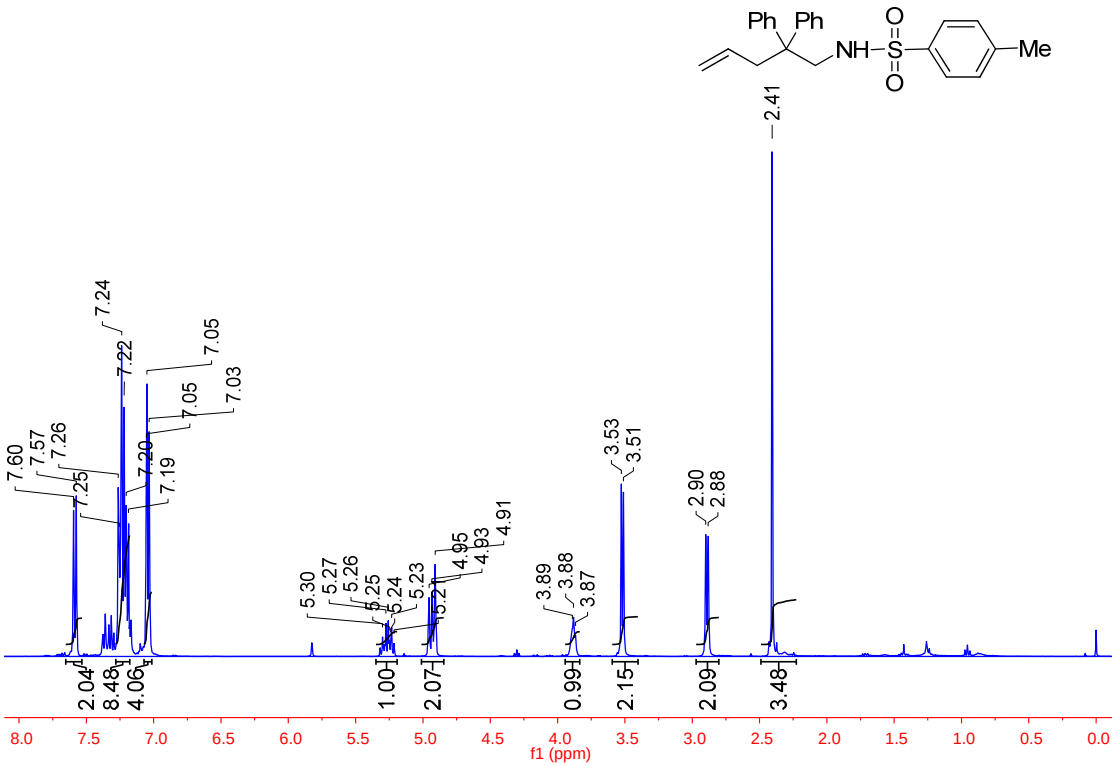
155.76
145.50
133.88
118.48
50.31
47.18
41.86
28.36
f1 (ppm)

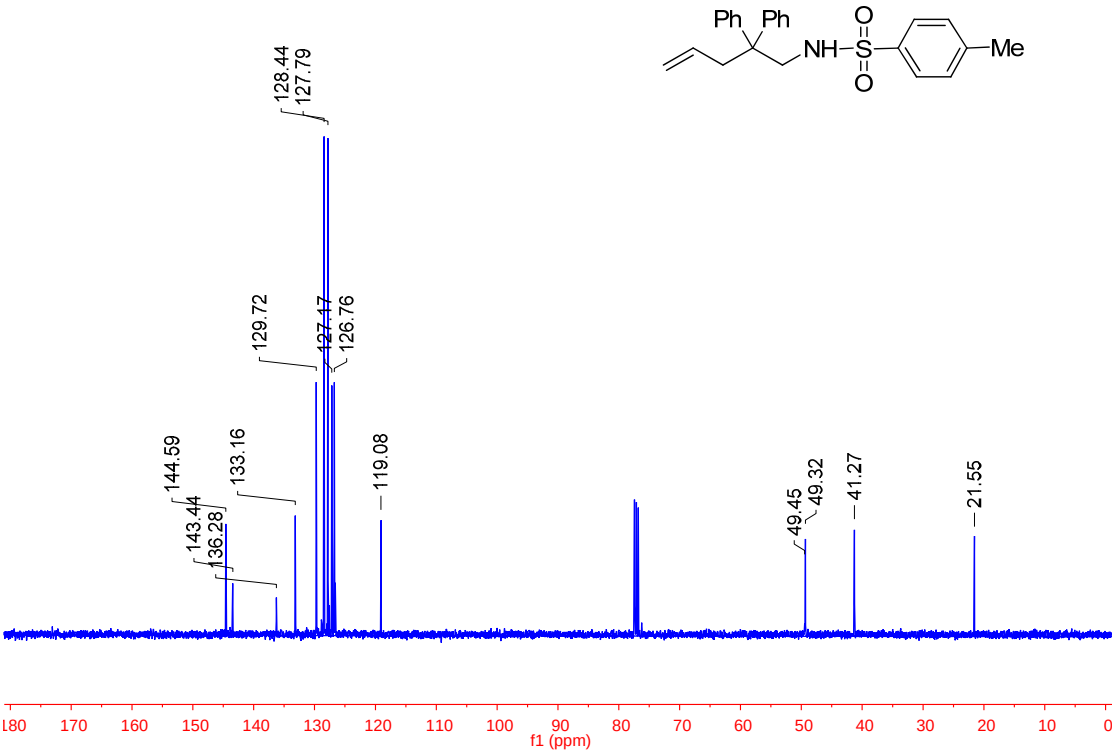

Ph
Ph
NH
Cbz
7.40
7.38
7.31
7.32
7.29
7.34
5.17
5.63
5.63
5.61
5.59
5.57
5.14
5.13
4.10
4.08
3.02
3.00
9.55
6.75
1.00
2.10
1.72
0.94
2.21
2.20
f1 (ppm)

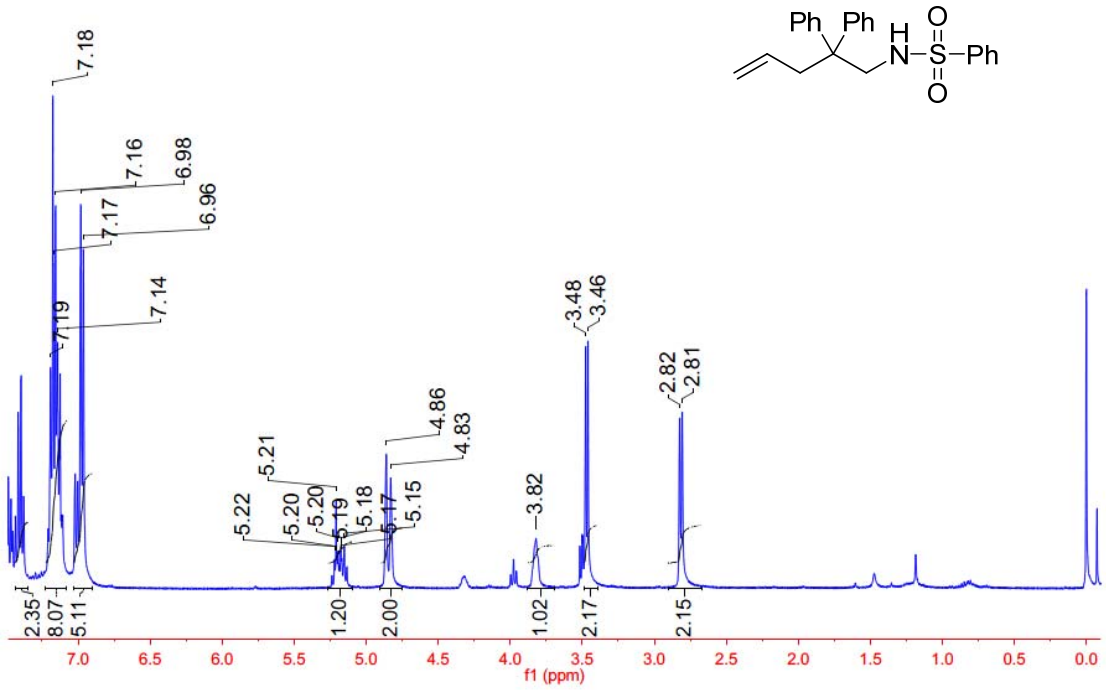

Ph
Ph
NH
Fmoc
7.23
7.21
7.10
7.09
7.16
7.15
7.17
7.68
7.67
7.31
7.25
7.42
7.41
7.29
4.25
4.27
4.88
4.92
4.10
4.08
3.85
3.84
2.77
2.75
5.38
5.36
5.33
2.37
2.04
2.54
12.70
1.00
2.36
3.26
1.52
1.91
2.27
f1 (ppm)

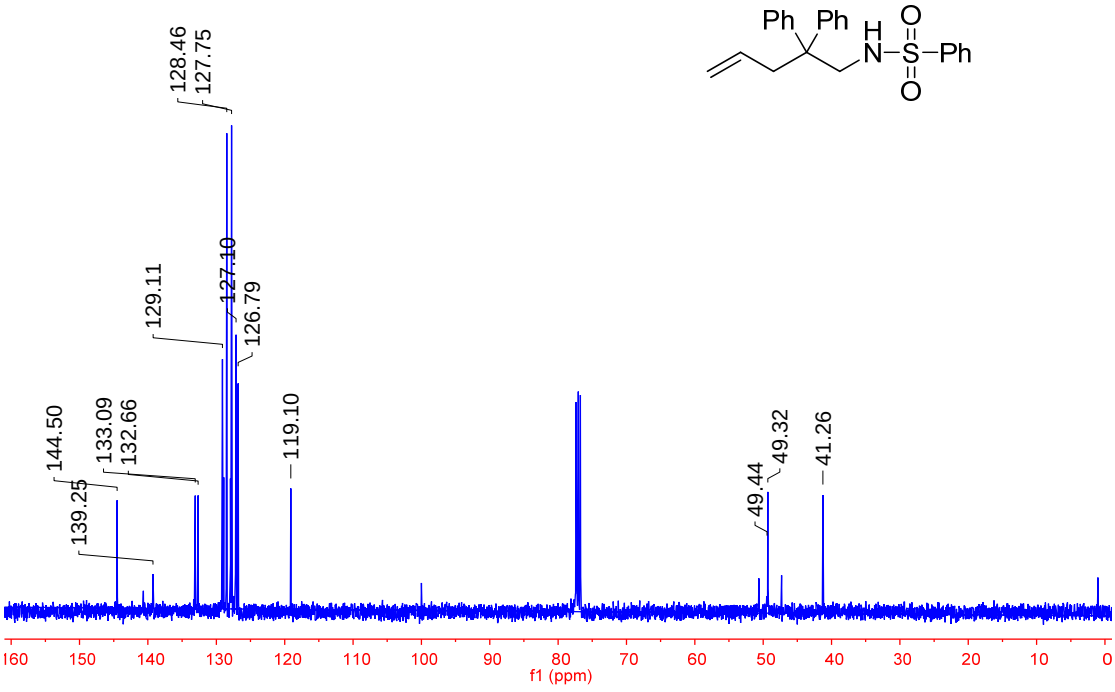

Ph
Ph
H
N
S
O
O
Me
7.22
7.20
7.18
7.14
7.12
7.08
7.08
7.06
5.28
5.26
5.03
4.99
4.99
4.93
4.93
4.91
4.90
4.00
3.99
3.70
3.68
2.87
2.85
10.43
1.00
1.98
0.95
2.00
2.09
2.94
f1 (ppm)

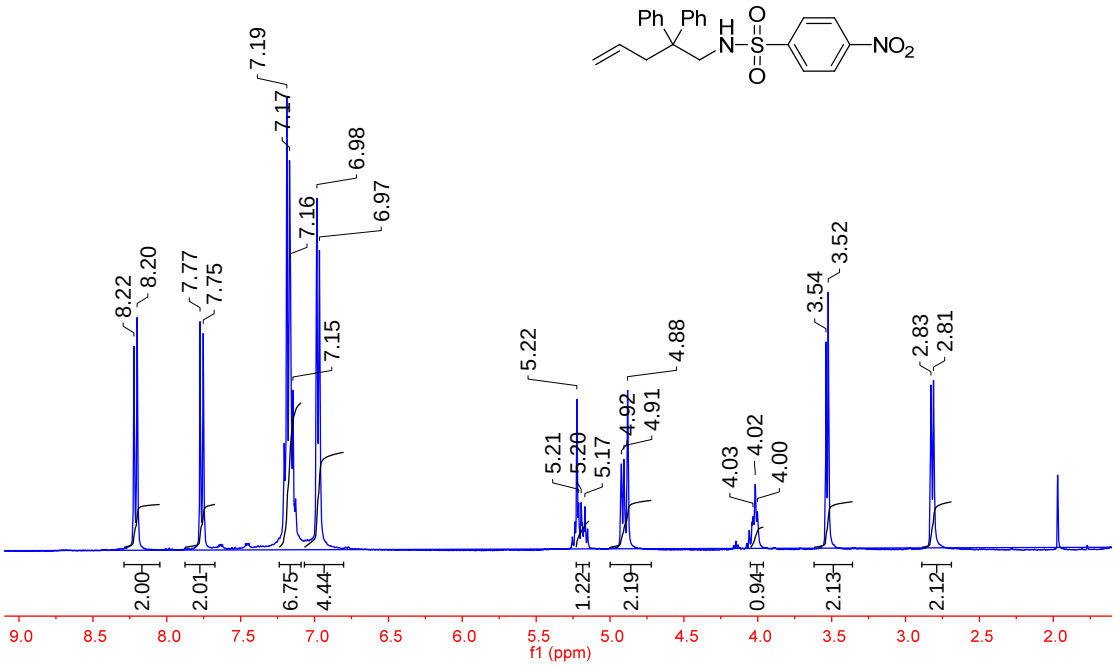

Ph
Ph
H
N
S
O
O
Me
128.48
127.95
126.81
144.91
133.49
119.05
49.73
49.69
41.21
39.78
f1 (ppm)

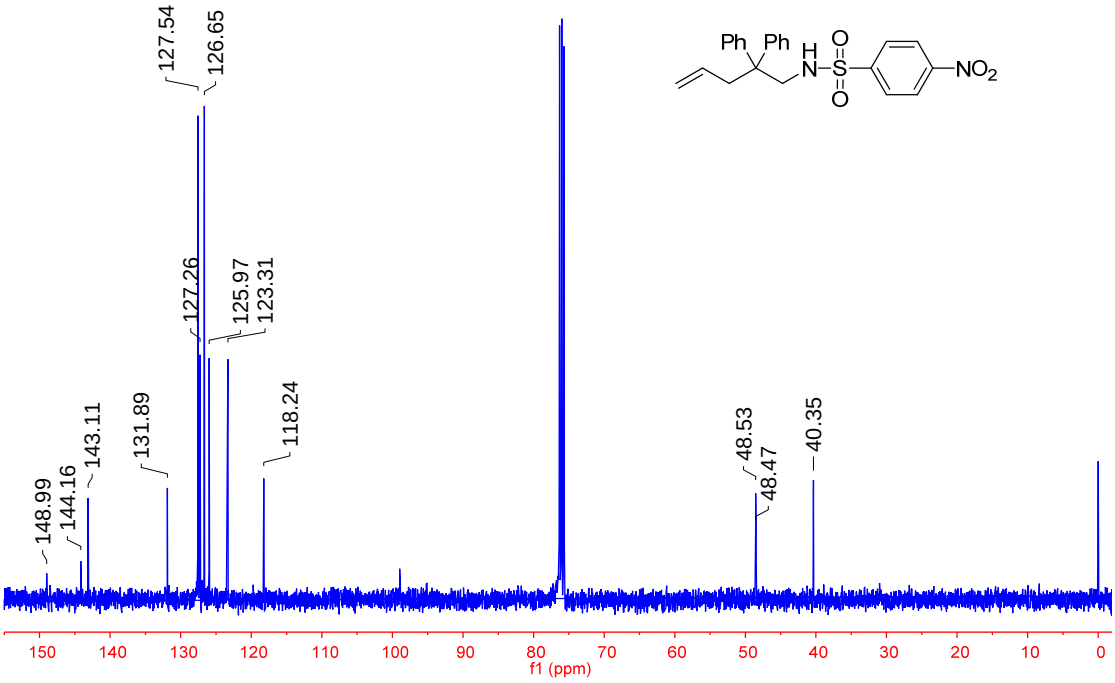

Ph Ph
NH
S
O
O
Me
7.60
7.57
7.26
7.25
7.24
7.22
7.20
7.19
7.05
7.05
7.03
5.30
5.27
5.26
5.25
5.24
5.23
5.21
4.95
4.93
4.91
3.89
3.88
3.87
3.53
3.51
2.90
2.88
2.41
2.04
8.48
4.06
1.00
2.07
0.99
2.15
2.09
3.48
f1 (ppm)

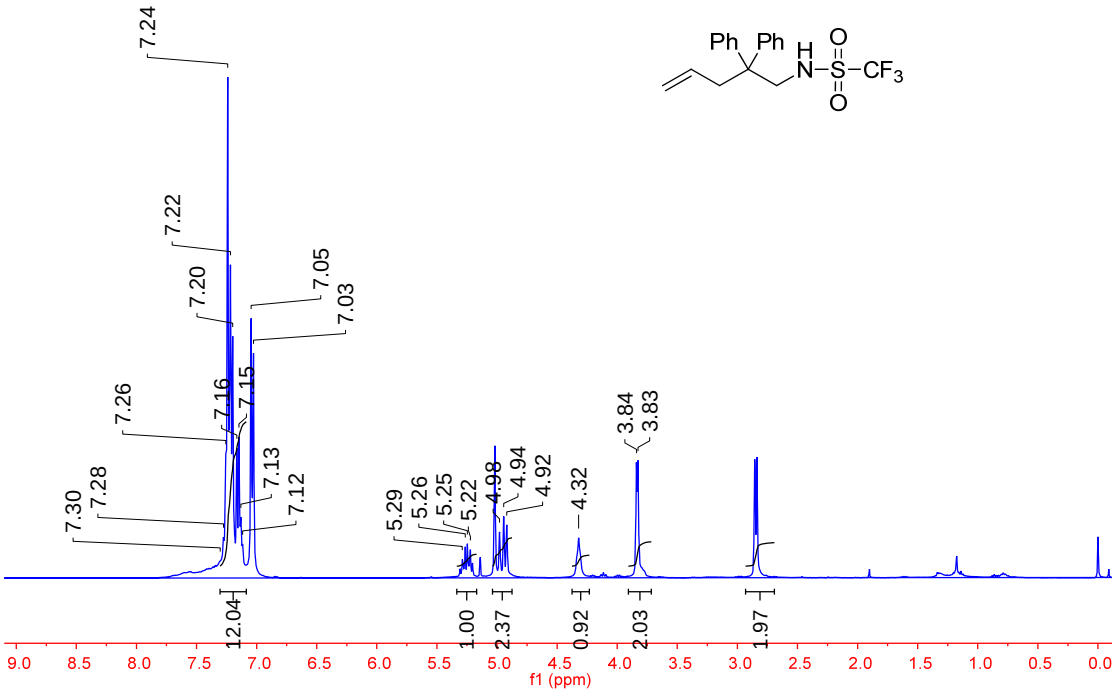

Ph Ph
NH
S
O
O
Me
128.44
127.79
129.72
127.47
126.76
144.59
143.44
136.28
133.16
119.08
49.45
49.32
41.27
21.55
f1 (ppm)

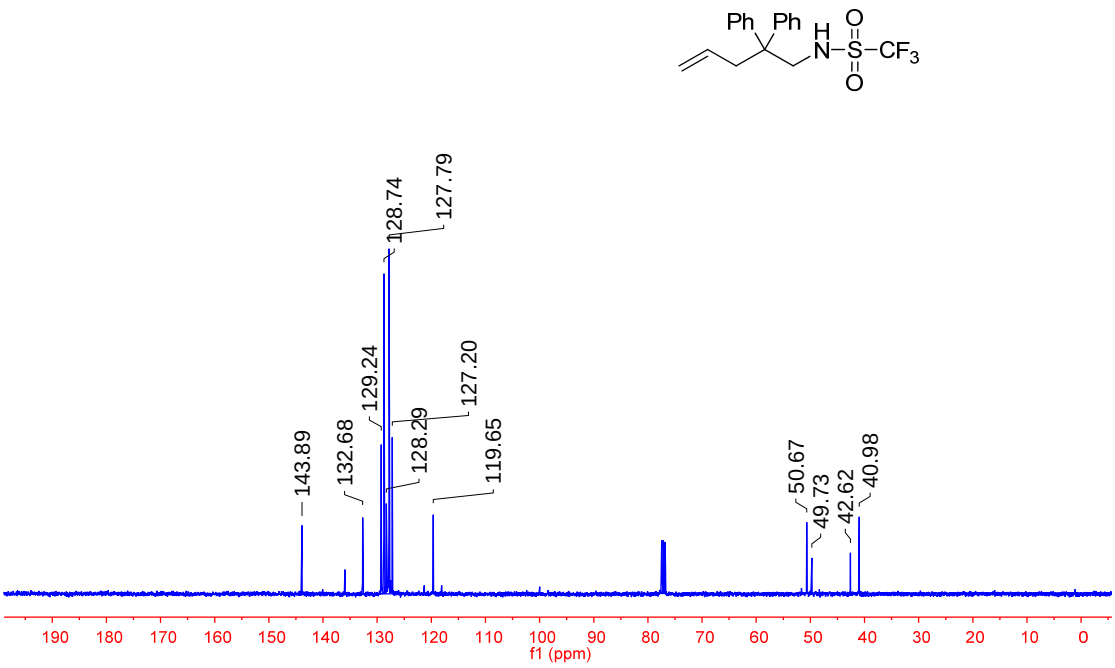

Ph Ph
H
N–S–Ph
O
O
7.18
7.16
6.98
7.17
6.96
7.14
7.19
3.48
3.46
2.82
2.81
4.86
4.83
5.21
5.22
5.20
5.20
5.19
5.18
5.17
5.15
3.82
2.35
8.07
5.11
1.20
2.00
1.02
2.17
2.15
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph Ph
H
N–S–Ph
O
O
128.46
127.75
129.11
127.10
126.79
144.50
133.09
132.66
119.10
139.25
49.44
49.32
41.26
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Ph
H
N
S
O
O
O
NO2
8.22
8.20
7.77
7.75
7.19
7.17
7.16
6.98
6.97
7.15
5.22
5.21
5.20
5.17
4.92
4.91
4.88
4.03
4.02
4.00
3.54
3.52
2.83
2.81
2.00
2.01
6.75
4.44
1.22
2.19
0.94
2.13
2.12
f1 (ppm)


Ph
Ph
H
N
S
O
O
O
NO2
127.54
126.65
127.26
125.97
123.31
118.24
148.99
144.16
143.11
131.89
48.53
48.47
40.35
f1 (ppm)


7.24
7.22
7.20
7.05
7.03
7.26
7.16
7.15
7.13
7.12
7.30
7.28
5.29
5.26
5.25
5.22
4.98
4.94
4.92
4.32
3.84
3.83
12.04
1.00
2.37
0.92
2.03
1.97
f1 (ppm)


143.89
132.68
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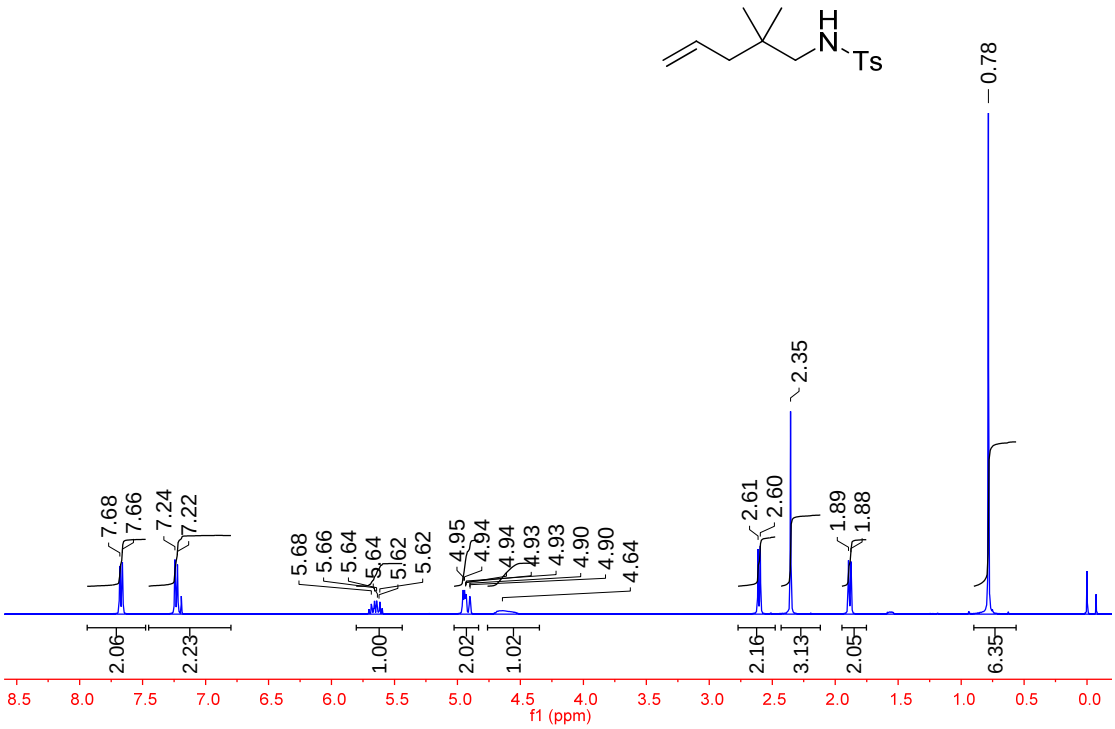
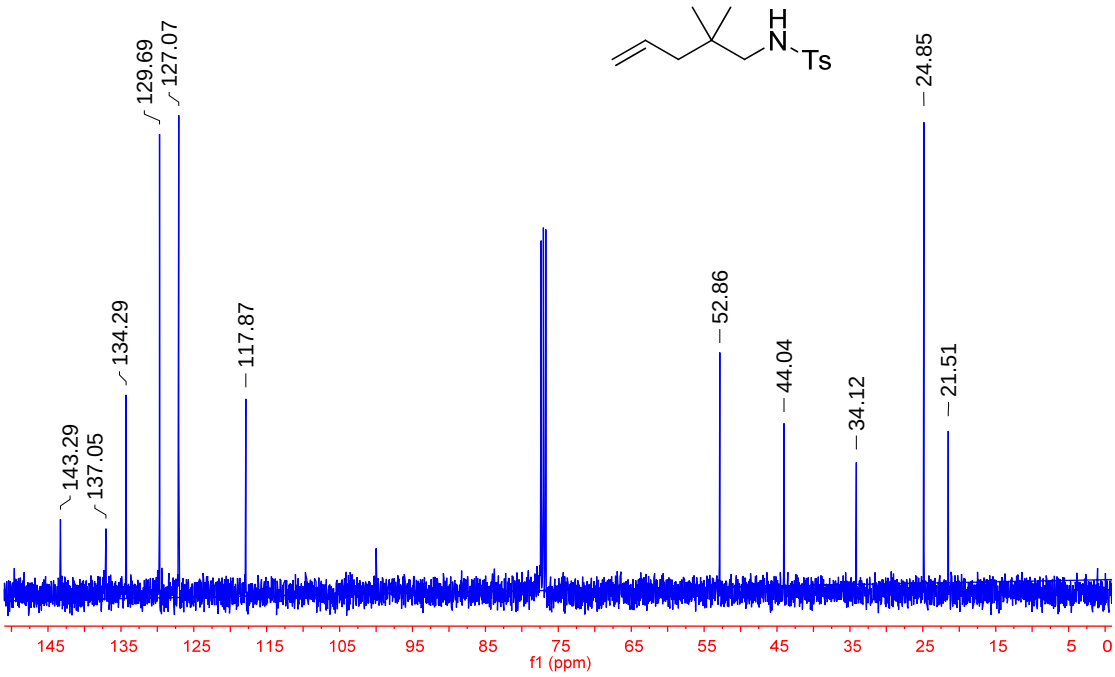
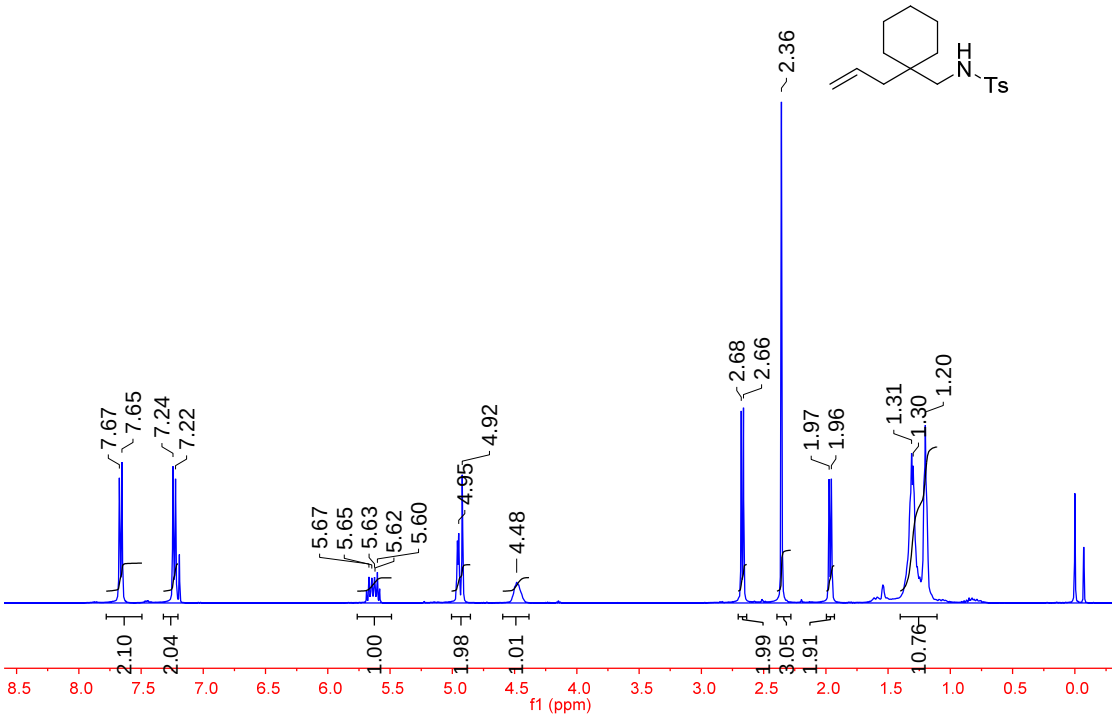
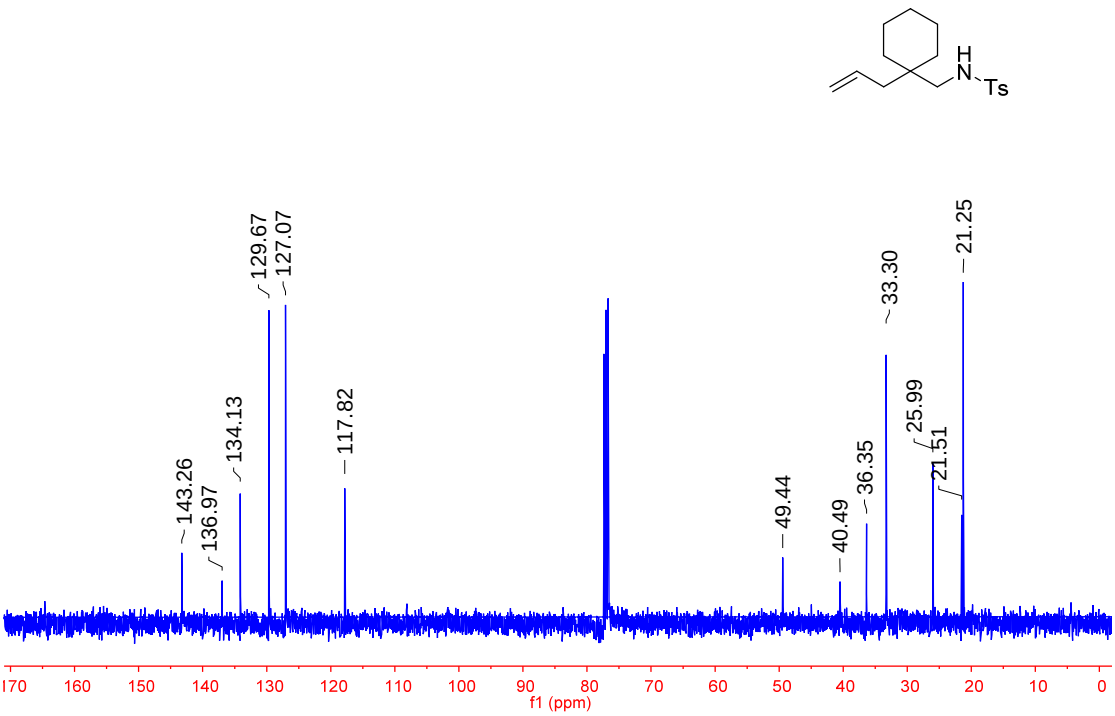
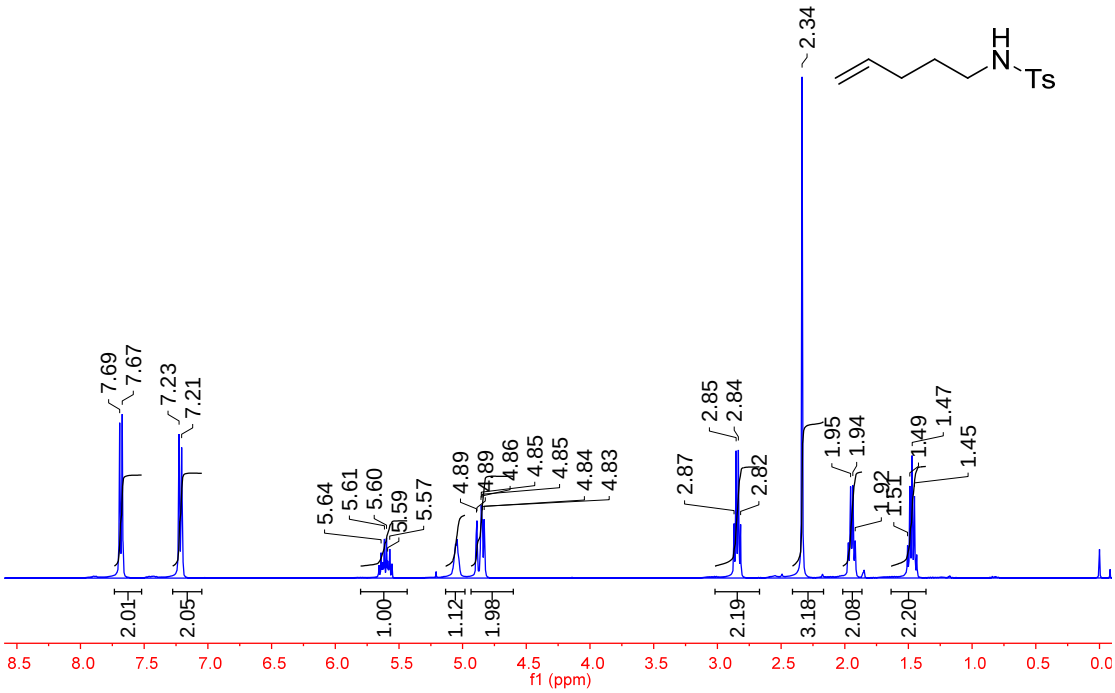
128.74
128.29
127.79
127.20
119.65
50.67
49.73
42.62
40.98
f1 (ppm)

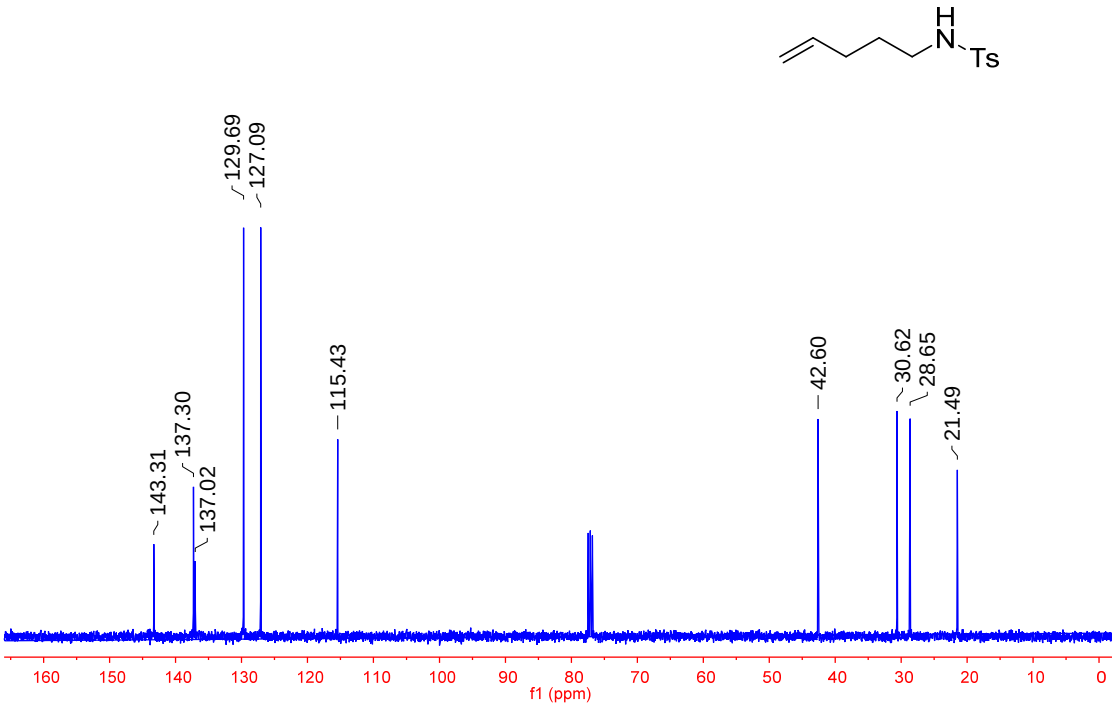

H
N
Ts
0.78
2.35
7.68
7.66
7.24
7.22
5.68
5.66
5.64
5.64
5.62
5.62
4.95
4.94
4.94
4.93
4.93
4.90
4.90
4.64
2.61
2.60
1.89
1.88
2.06
2.23
1.00
2.02
1.02
2.16
3.13
2.05
6.35
f1 (ppm)

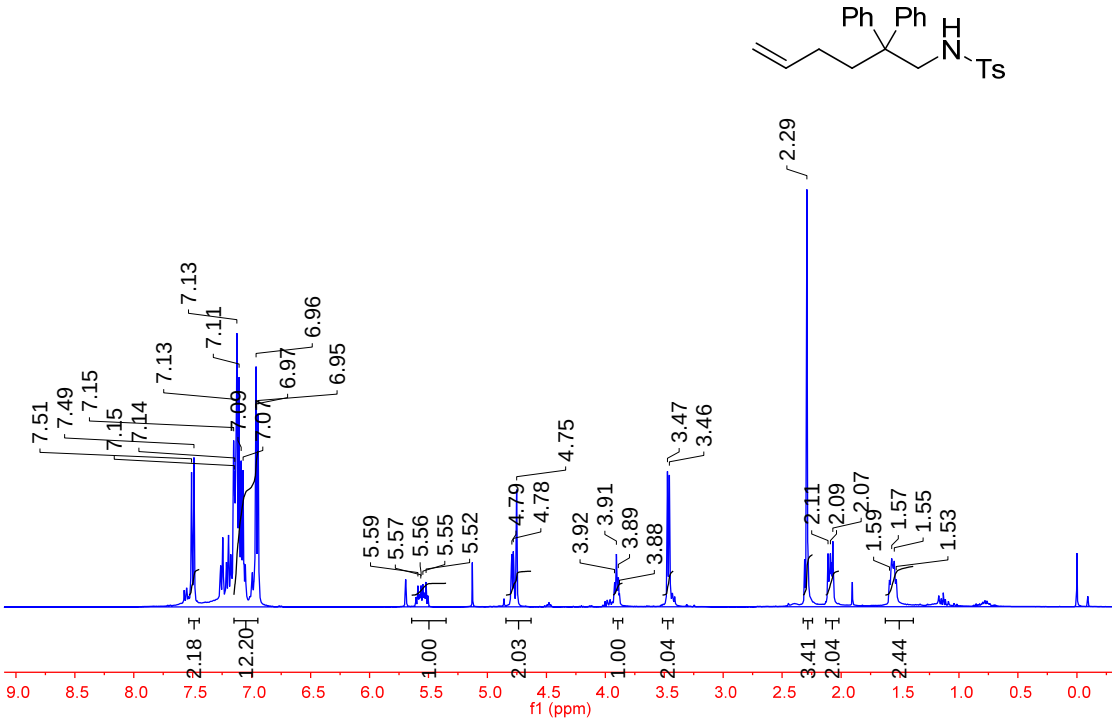

H
N
Ts
129.69
127.07
143.29
137.05
134.29
117.87
52.86
44.04
34.12
24.85
21.51
f1 (ppm)

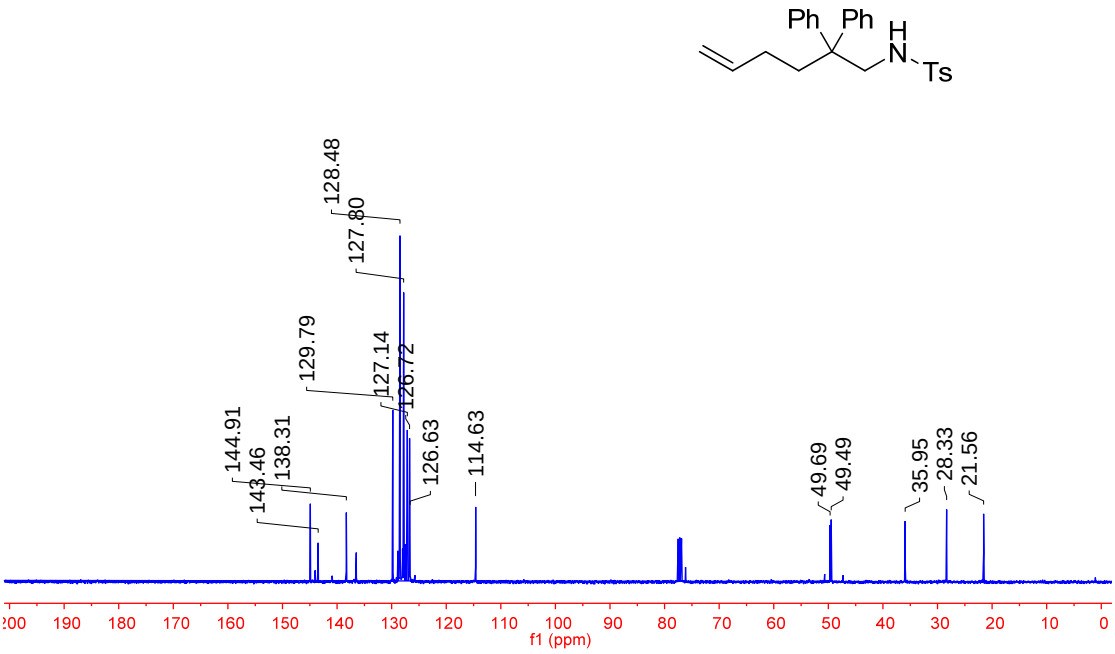

NH
Ts
2.36
7.67
7.65
7.24
7.22
5.67
5.65
5.63
5.62
5.60
4.95
4.92
4.48
2.68
2.66
1.97
1.96
1.31
1.30
1.20
2.10
2.04
1.00
1.98
1.01
1.99
3.05
1.91
10.76
f1 (ppm)

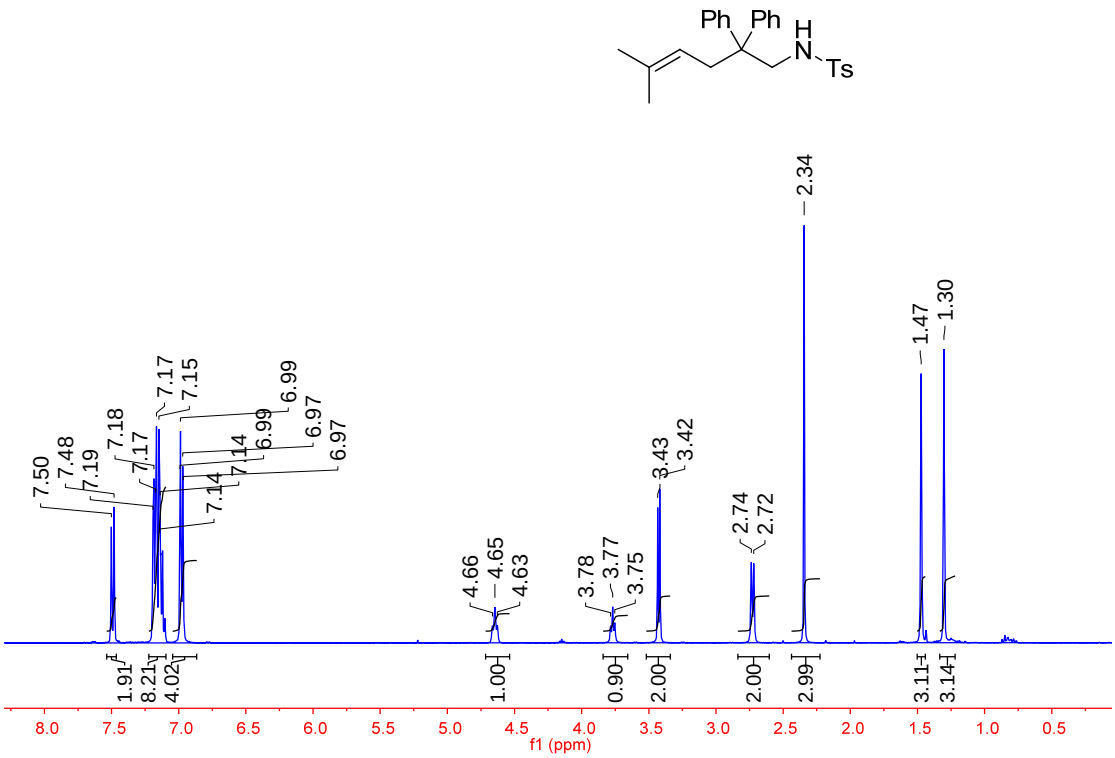

NH
Ts
143.26
136.97
134.13
129.67
127.07
117.82
49.44
40.49
36.35
33.30
25.99
21.51
21.25
f1 (ppm)

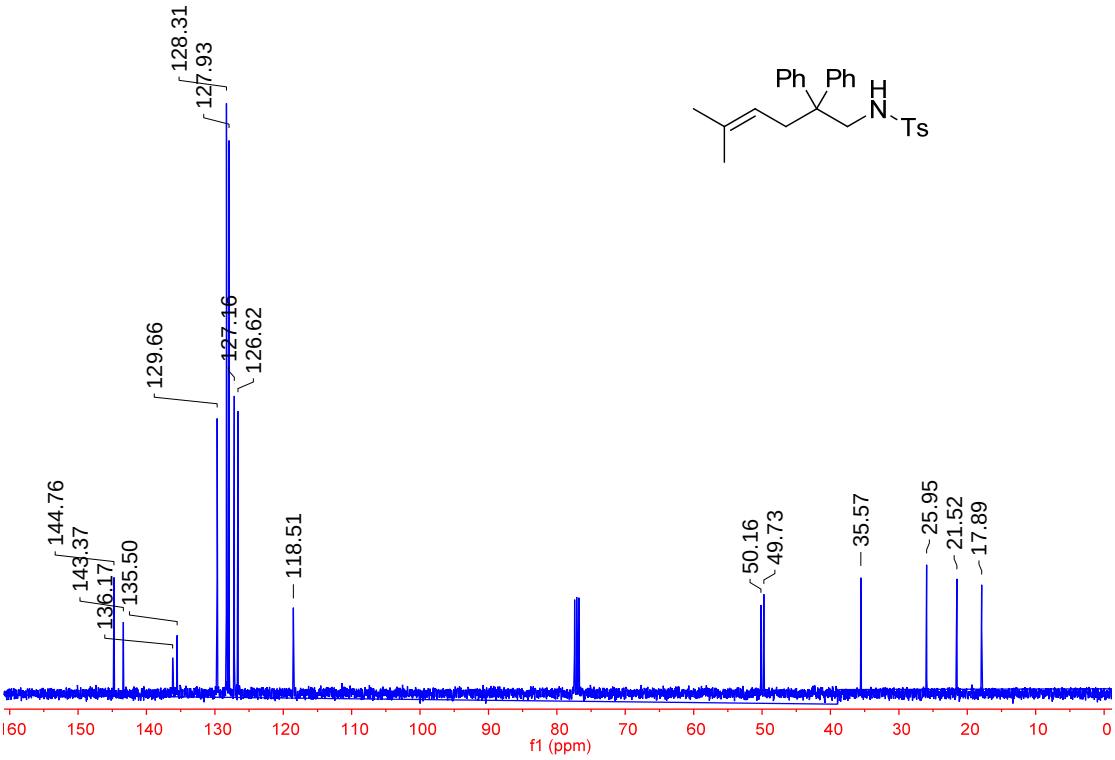

2.34
H
N
Ts
7.69
7.67
7.23
7.21
5.64
5.61
5.60
5.59
5.57
4.89
4.89
4.86
4.85
4.85
4.84
4.83
2.87
2.85
2.84
2.82
1.95
1.94
1.92
1.51
1.49
1.47
1.45
2.01
2.05
1.00
1.12
1.98
2.19
3.18
2.08
2.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

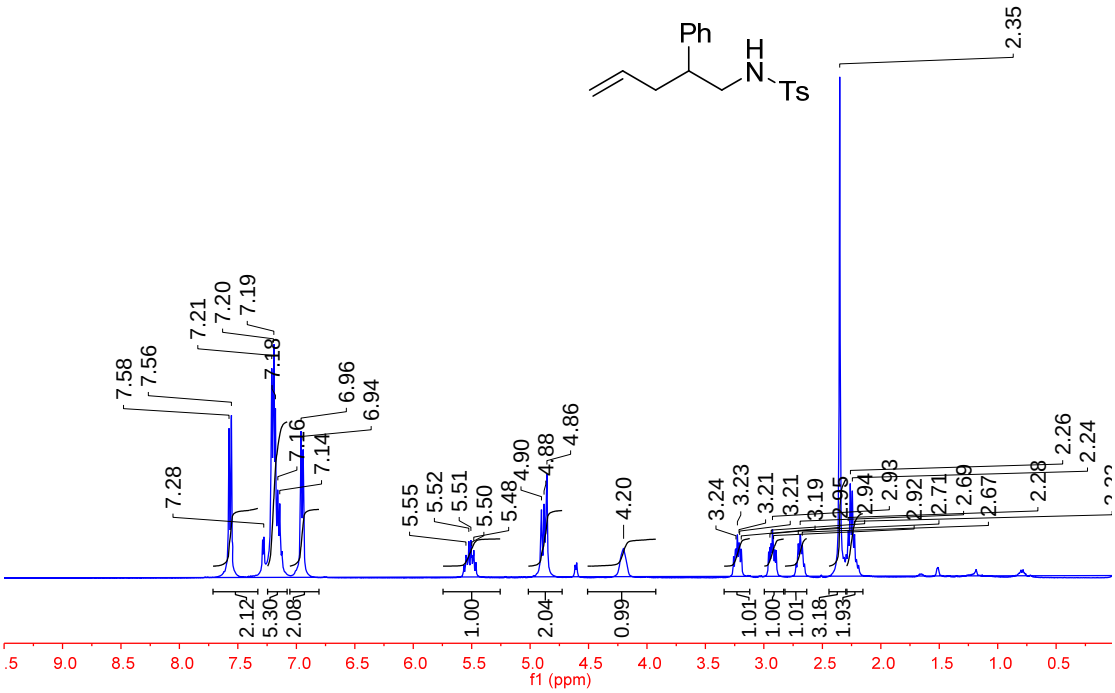

H
N
Ts
129.69
127.09
143.31
137.30
137.02
115.43
42.60
30.62
28.65
21.49
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

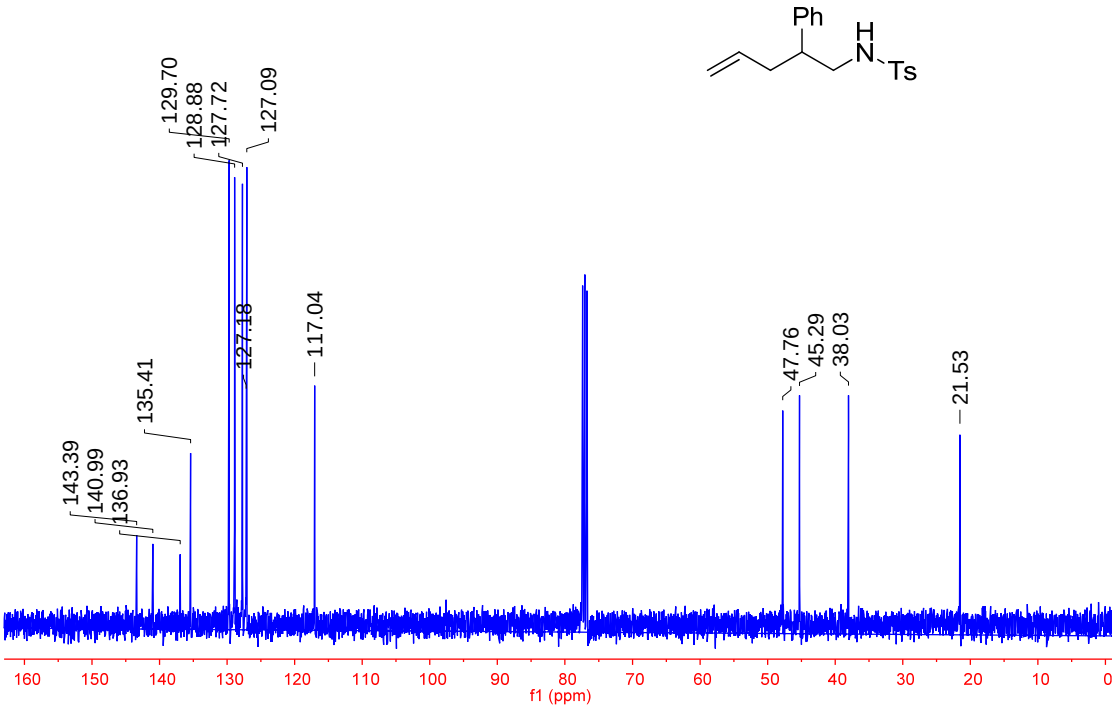

Ph
Ph
H
N
Ts
7.51
7.49
7.15
7.15
7.14
7.13
7.13
7.11
7.09
7.07
6.97
6.96
6.95
5.59
5.57
5.56
5.55
5.52
4.79
4.78
4.75
3.92
3.91
3.89
3.88
3.47
3.46
2.29
2.11
2.09
2.07
1.59
1.57
1.55
1.53
2.18
12.20
1.00
2.03
1.00
2.04
3.41
2.04
2.44
f1 (ppm)

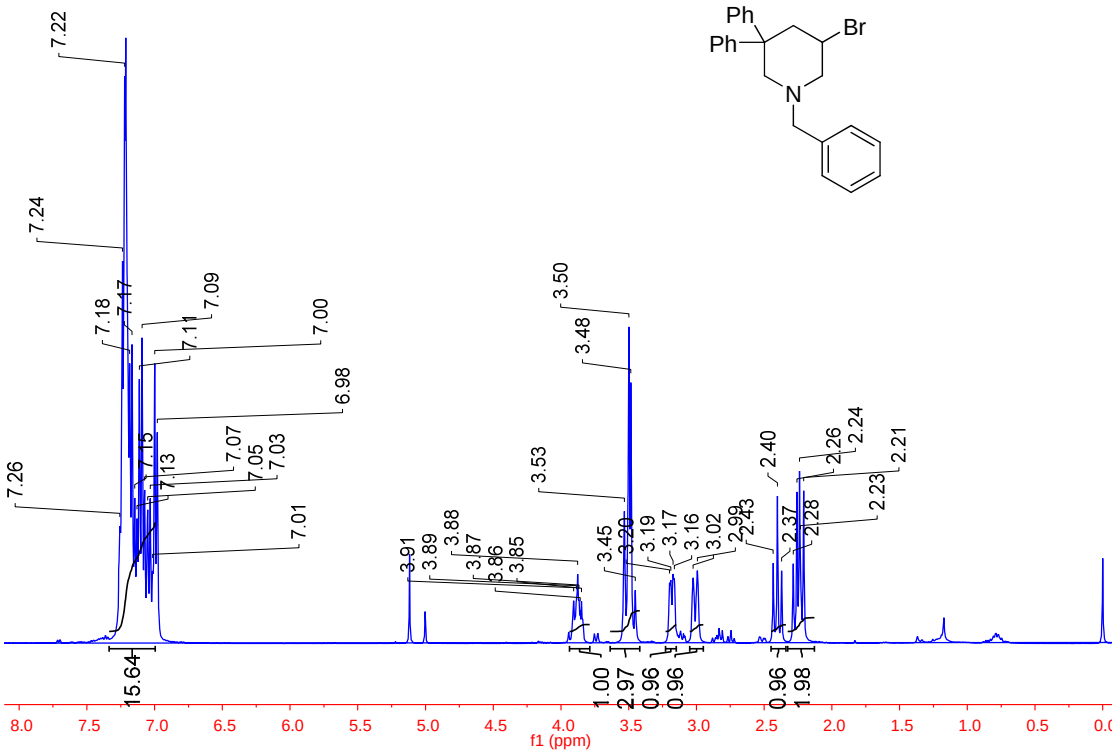

Ph
Ph
H
N
Ts
128.48
127.80
129.79
127.14
126.72
126.63
114.63
144.91
143.46
138.31
49.69
49.49
35.95
28.33
21.56
f1 (ppm)

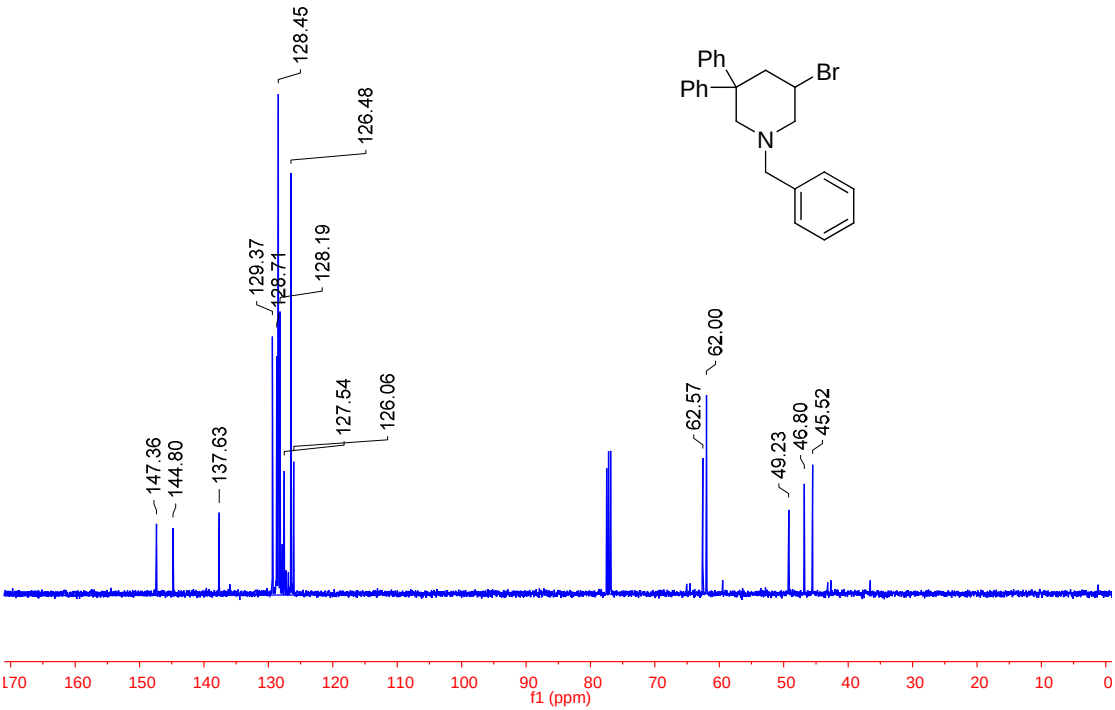

Ph
Ph
H
N
Ts
7.50
7.48
7.19
7.18
7.17
7.17
7.15
7.14
7.14
6.99
6.99
6.97
6.97
4.66
4.65
4.63
3.78
3.77
3.75
3.43
3.42
2.74
2.72
2.34
1.47
1.30
1.91
8.21
4.02
1.00
0.90
2.00
2.00
2.99
3.11
3.14
f1 (ppm)


Ph
Ph
H
N
Ts
128.31
127.93
129.66
127.16
126.62
144.76
143.37
136.17
135.50
118.51
50.16
49.73
35.57
25.95
21.52
17.89
f1 (ppm)


Ph
H
N
Ts
2.35
7.58
7.56
7.28
7.21
7.20
7.19
7.18
7.16
7.14
6.96
6.94
5.55
5.52
5.51
5.50
5.48
4.90
4.88
4.86
4.20
3.24
3.23
3.21
3.21
3.19
2.95
2.94
2.93
2.92
2.71
2.69
2.67
2.28
2.26
2.24
2.12
5.30
2.08
1.00
2.04
0.99
1.01
1.00
1.01
3.18
1.93
f1 (ppm)


Ph
H
N
Ts
129.70
128.88
127.72
127.09
127.18
117.04
135.41
143.39
140.99
136.93
47.76
45.29
38.03
21.53
f1 (ppm)


Ph
Ph
Br
N
7.22
7.24
7.18
7.17
7.09
7.11
7.00
6.98
7.26
7.15
7.13
7.07
7.05
7.03
7.01
3.50
3.48
3.53
3.91
3.89
3.88
3.87
3.86
3.85
3.45
3.20
3.19
3.17
3.16
3.02
2.99
2.43
2.40
2.37
2.28
2.26
2.24
2.23
2.21
15.64
1.00
2.97
0.96
0.96
0.96
1.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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Ph
Br
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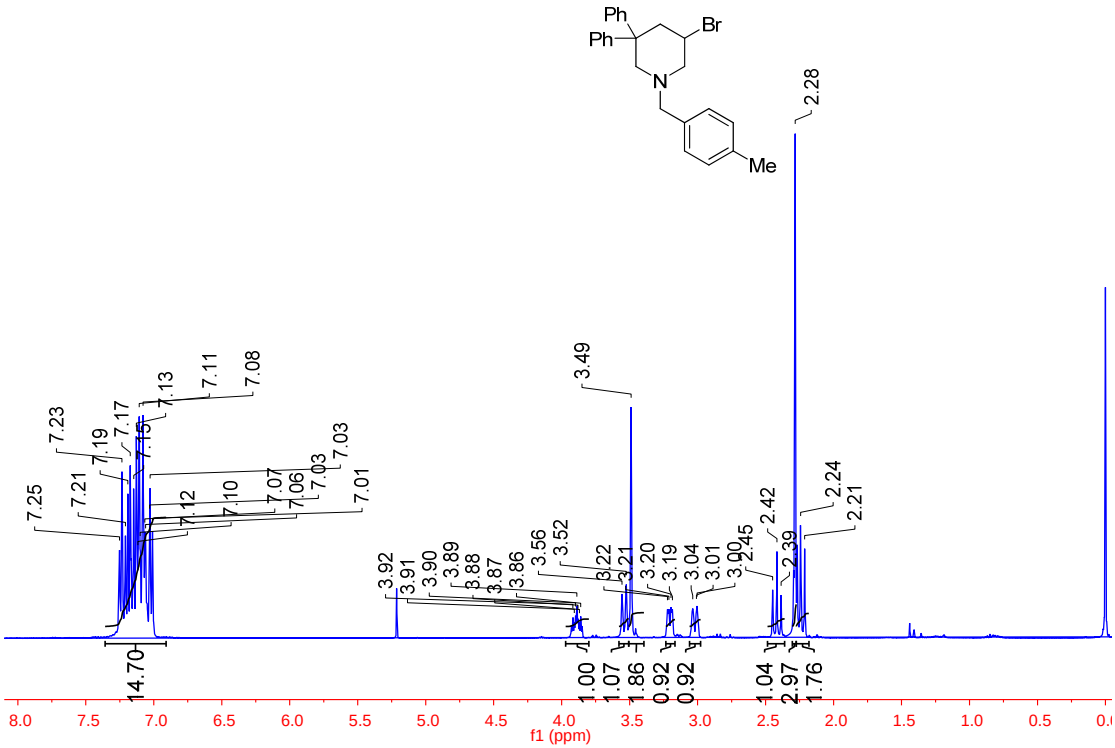
127.54
126.06
147.36
144.80
137.63
62.00
62.57
49.23
46.80
45.52
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Ph
Br
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Me
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7.25
7.23
7.21
7.19
7.17
7.15
7.13
7.12
7.11
7.10
7.08
7.07
7.06
7.03
7.03
7.01
3.92
3.91
3.90
3.89
3.88
3.87
3.86
3.56
3.52
3.22
3.21
3.20
3.19
3.04
3.01
3.00
2.45
2.42
2.39
2.24
2.21
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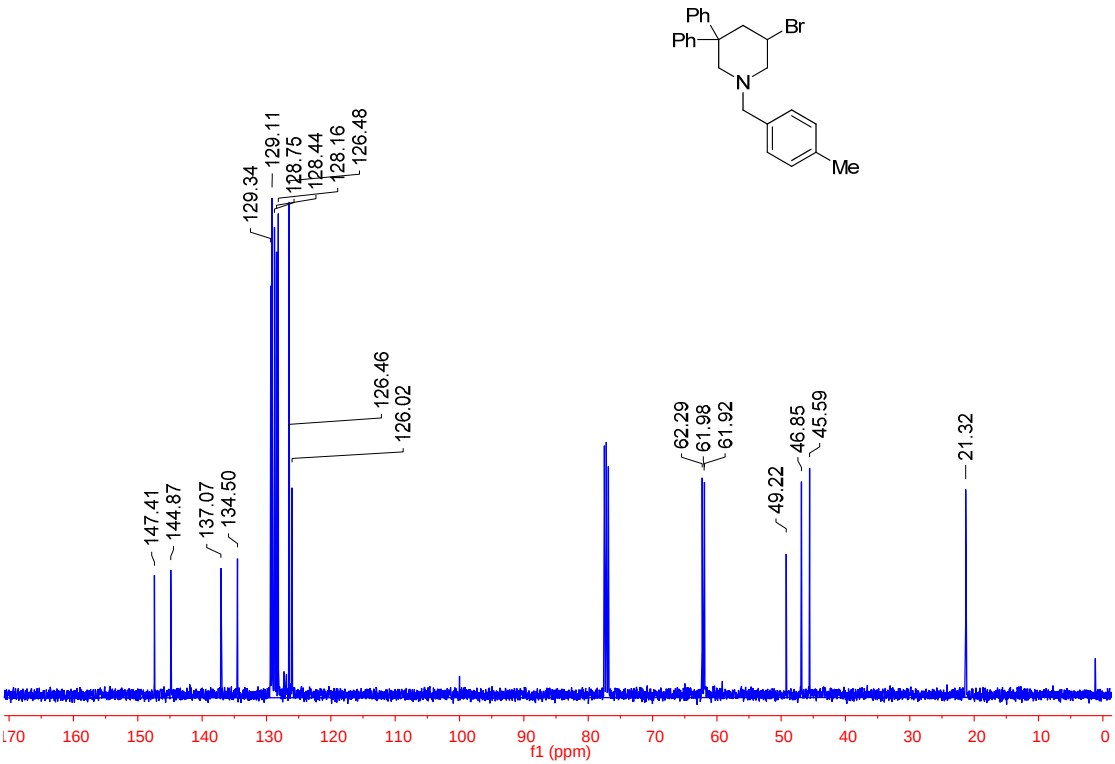
1.07
1.86
0.92
0.92
1.04
2.97
1.76
f1 (ppm)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Me
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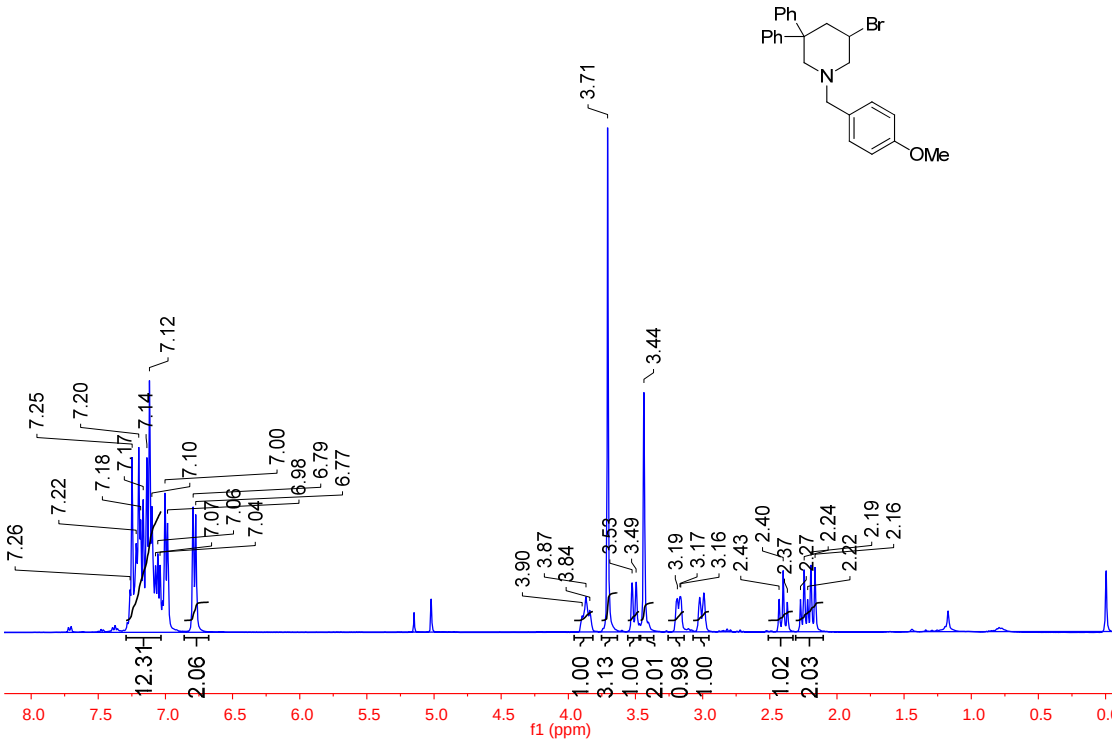
61.92
49.22
46.85
45.59
21.32
f1 (ppm)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Ph
Br
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OMe
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7.18
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7.14
7.12
7.10
7.07
7.06
7.04
7.00
6.98
6.79
6.77
3.90
3.87
3.84
3.71
3.53
3.49
3.44
3.19
3.17
3.16
2.43
2.40
2.37
2.27
2.24
2.22
2.19
2.16
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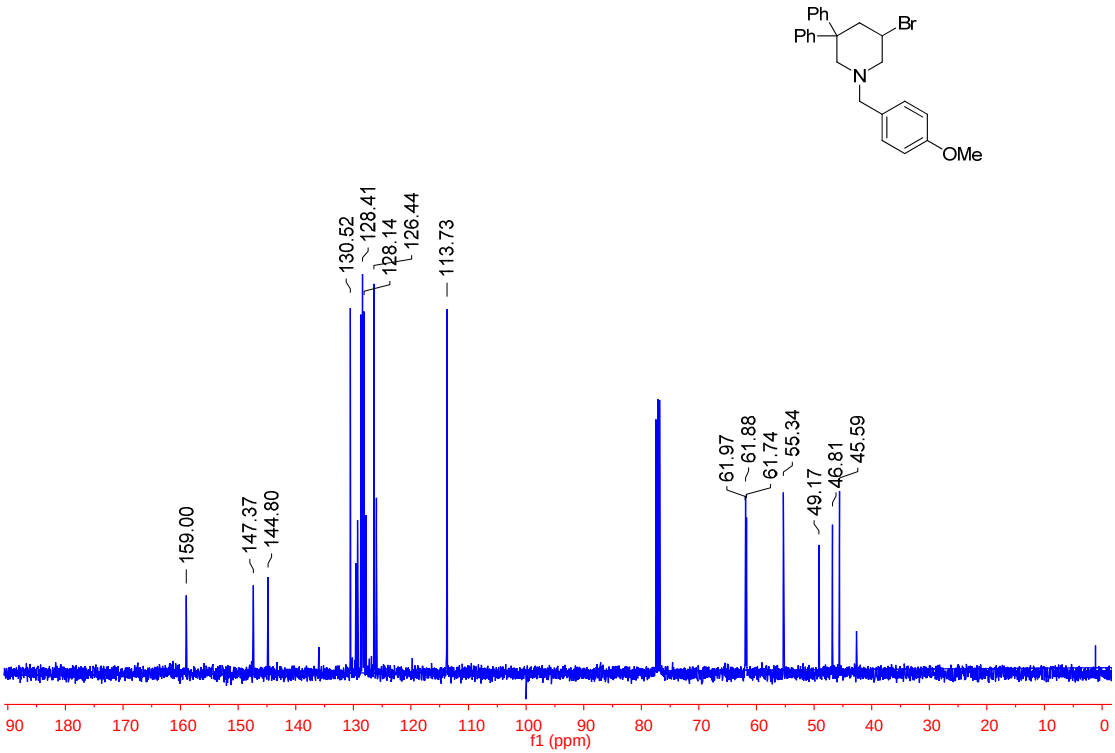
3.13
1.00
2.01
0.98
1.00
1.02
2.03
f1 (ppm)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Ph
Br
N
OMe
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147.37
144.80
130.52
128.41
128.14
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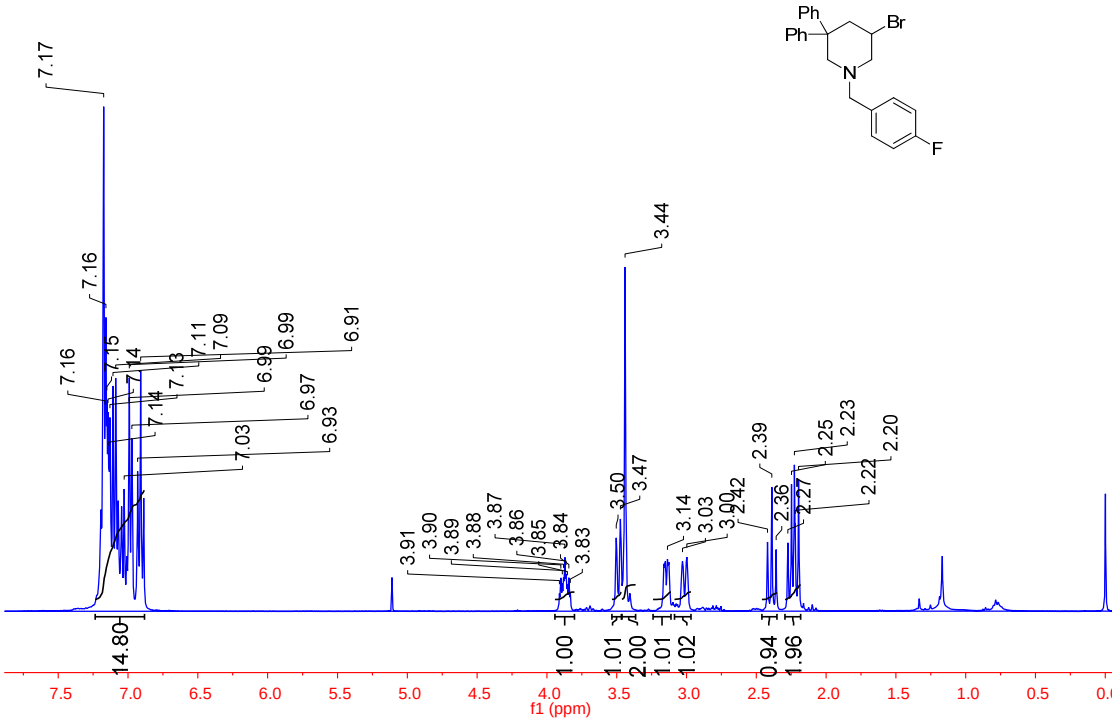
113.73
61.97
61.88
61.74
55.34
49.17
46.81
45.59
f1 (ppm)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Ph
Br
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F
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7.16
7.15
7.14
7.13
7.11
7.09
6.99
6.99
6.91
6.97
6.93
7.14
7.03
3.91
3.90
3.89
3.88
3.87
3.86
3.85
3.84
3.83
3.50
3.47
3.44
3.14
3.03
3.00
2.42
2.39
2.36
2.27
2.25
2.23
2.22
2.20
14.80
1.00
1.01
2.00
1.01
1.02
0.94
1.96
7.5
7.0
6.5
6.0
5.5
5.0
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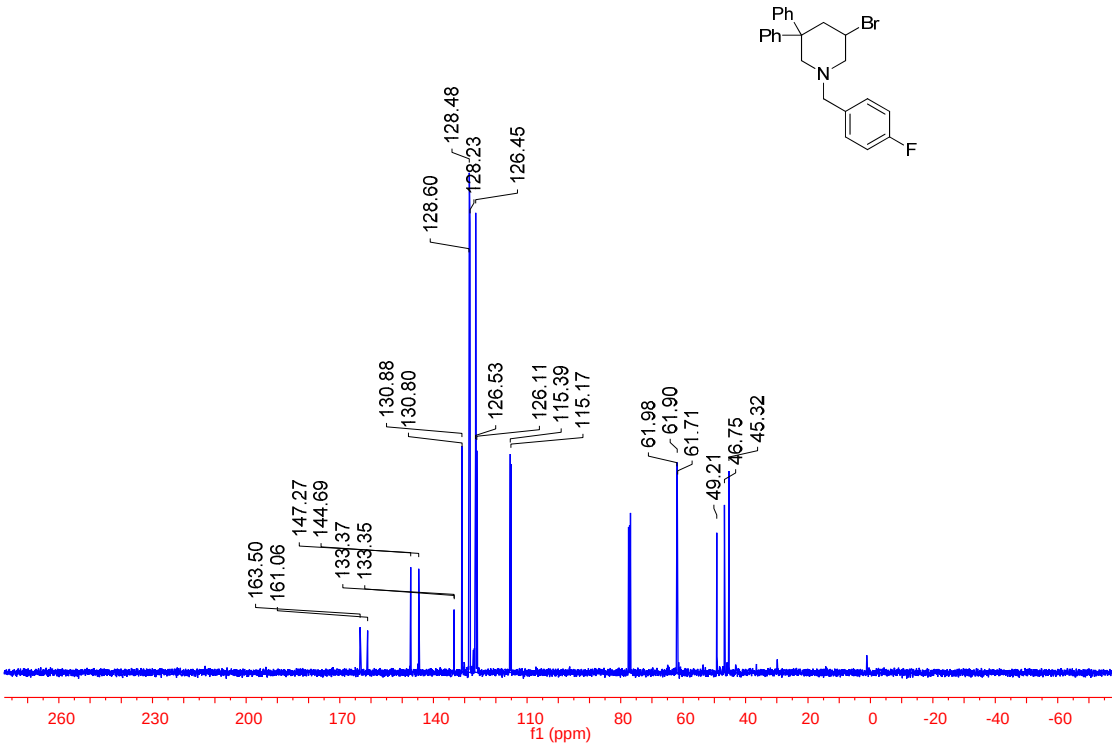
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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Ph
Br
N
F
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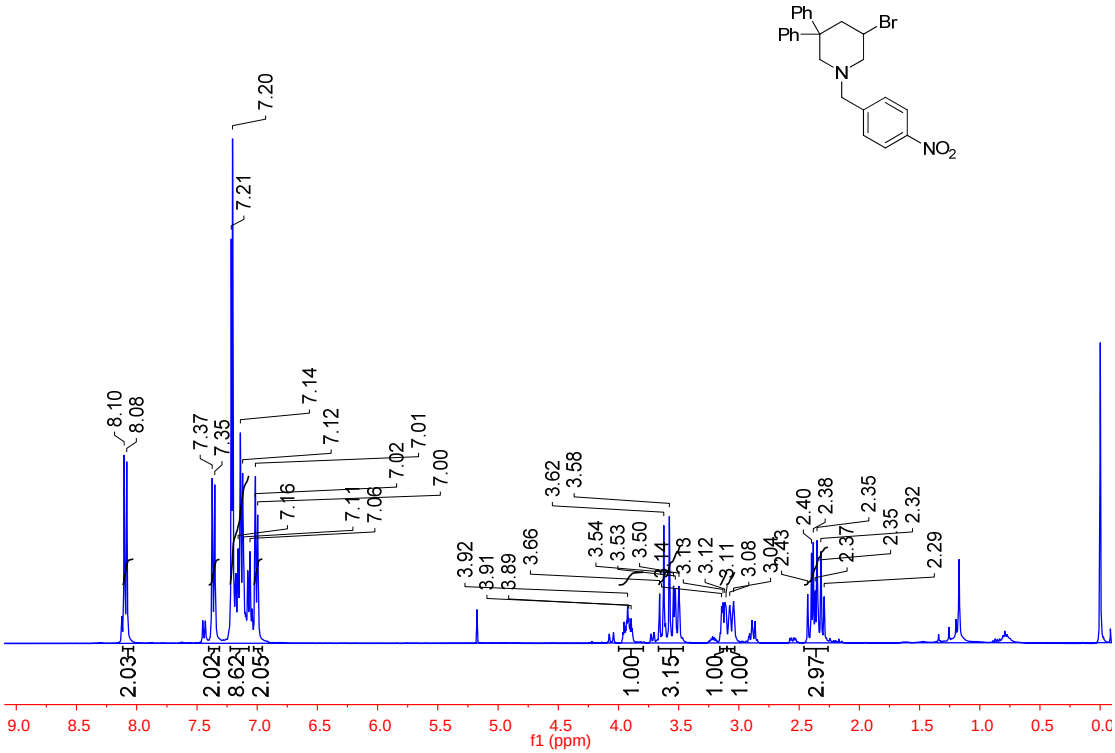
128.23
126.45
128.60
130.88
130.80
126.53
126.11
115.39
115.17
61.98
61.90
61.71
46.75
45.32
49.21
147.27
144.69
133.37
133.35
163.50
161.06
260
230
200
170
140
110
80
60
40
20
0
-20
-40
-60
f1 (ppm)


Ph
Ph
Br
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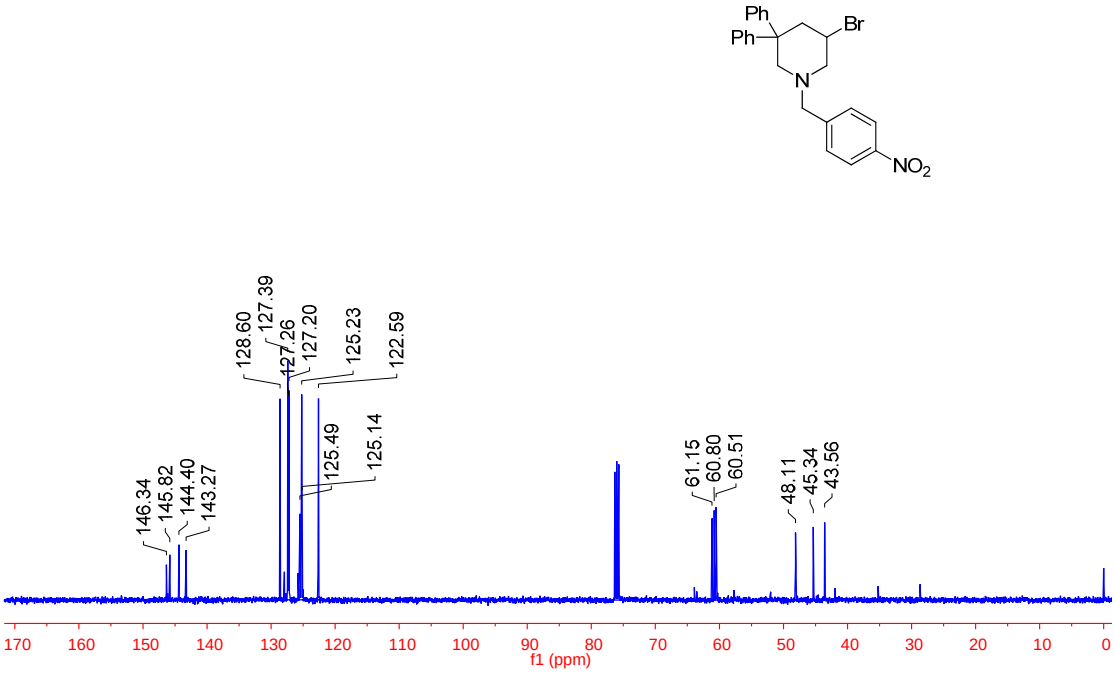
7.21
8.10
8.08
7.37
7.35
7.14
7.12
7.02
7.01
7.00
7.16
7.11
7.06
3.62
3.58
3.92
3.91
3.89
3.66
3.54
3.53
3.50
3.18
3.12
3.11
3.08
3.04
2.43
2.40
2.38
2.35
2.37
2.35
2.32
2.29
2.03
2.02
8.62
2.05
1.00
3.15
1.00
1.00
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
Ph
Br
N
NO2
128.60
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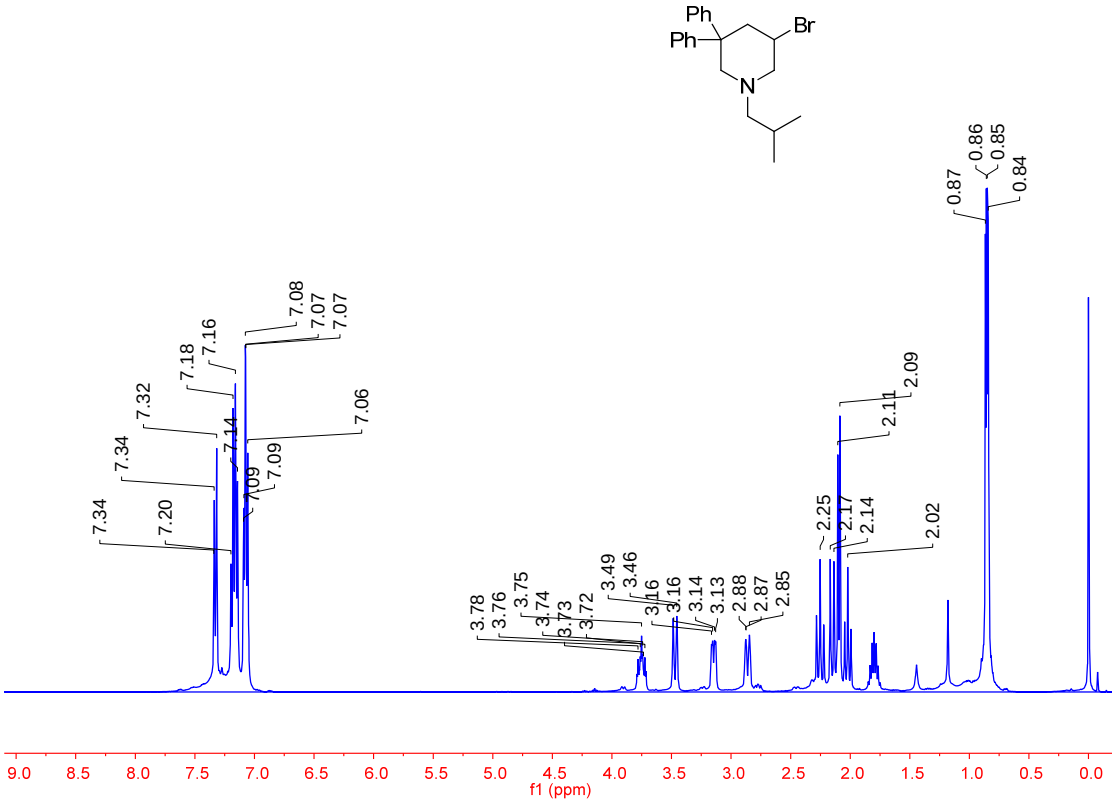
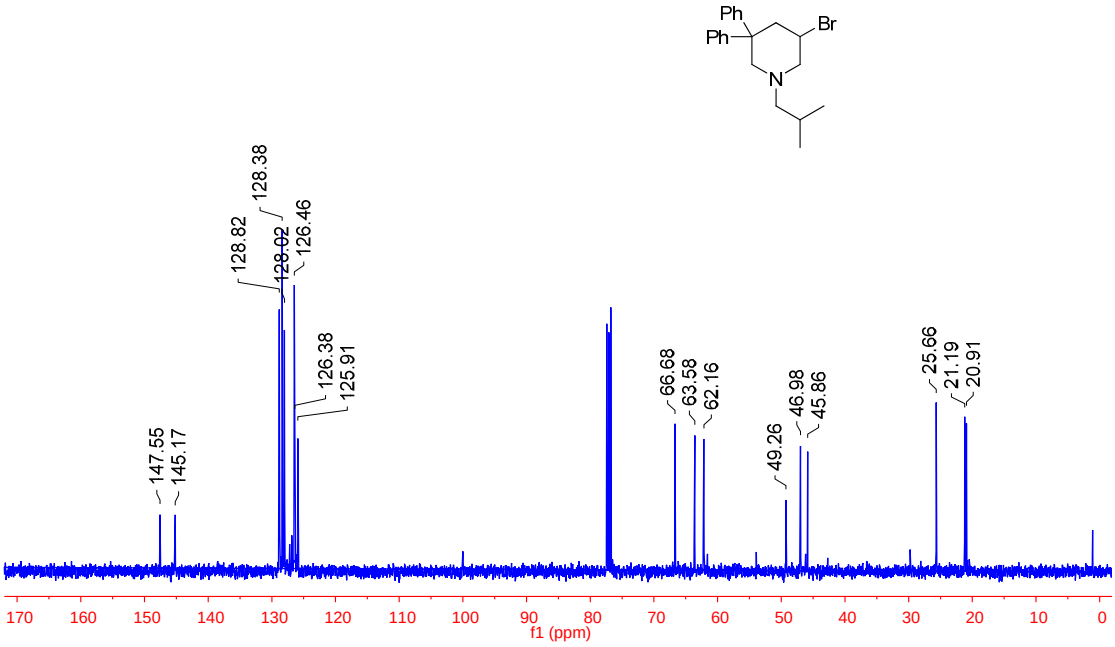
127.26
127.20
125.23
122.59
125.49
125.14
146.34
145.82
144.40
143.27
61.15
60.80
60.51
48.11
45.34
43.56
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Br
N
0.87
0.86
0.85
0.84
2.09
2.11
2.25
2.17
2.14
2.02
7.08
7.07
7.07
7.18
7.16
7.32
7.06
7.34
7.14
7.09
7.09
7.34
7.20
3.78
3.76
3.75
3.74
3.73
3.72
3.49
3.46
3.16
3.14
3.13
2.88
2.87
2.85
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Ph
Ph
Br
N
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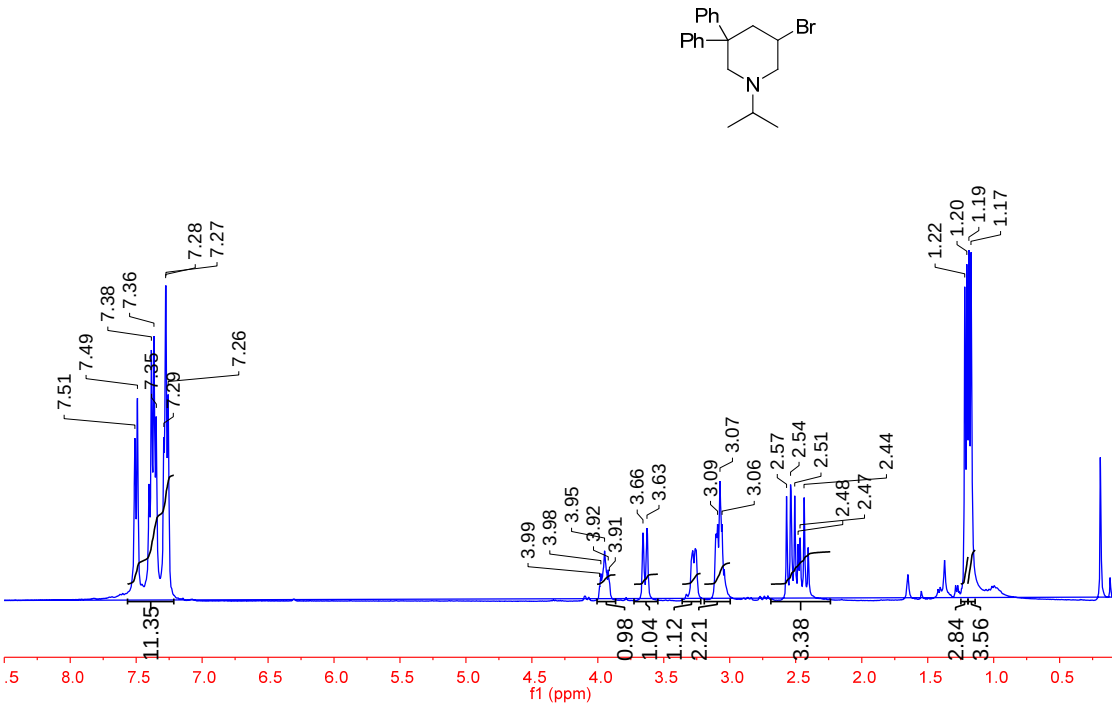
128.82
128.02
126.46
126.38
125.91
147.55
145.17
66.68
63.58
62.16
49.26
46.98
45.86
25.66
21.19
20.91
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Br
N
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7.49
7.38
7.36
7.35
7.29
7.28
7.27
7.26
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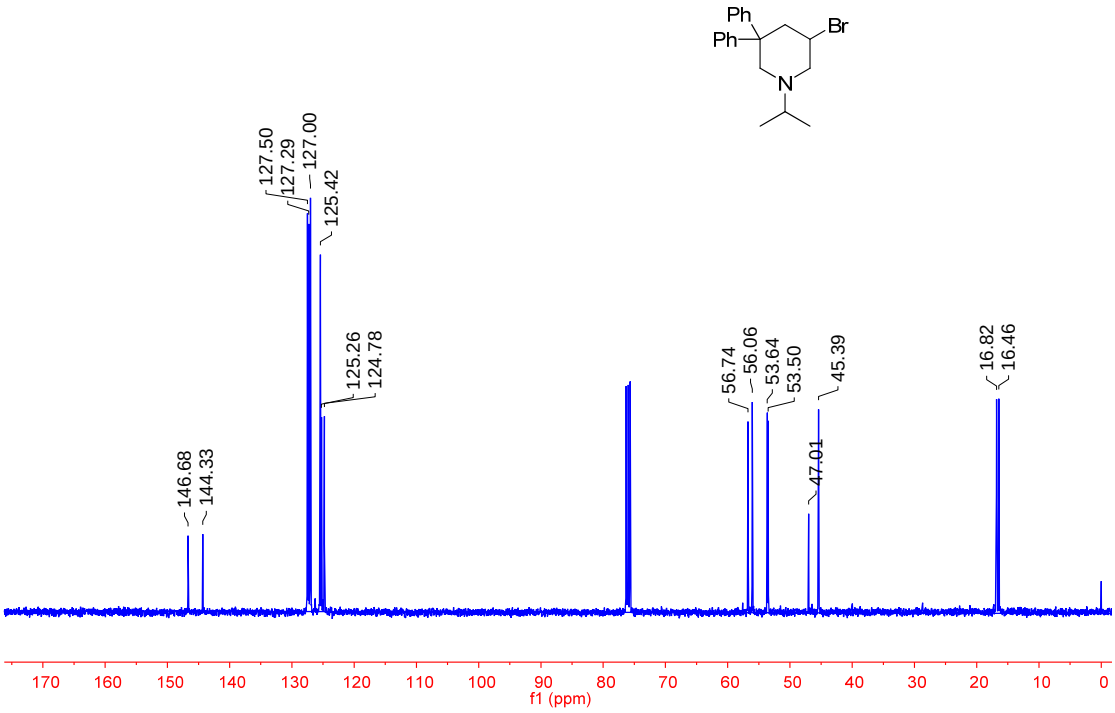
3.98
3.95
3.92
3.91
3.66
3.63
3.09
3.07
3.06
2.57
2.54
2.51
2.48
2.47
2.44
1.22
1.20
1.19
1.17
11.35
0.98
1.04
1.12
2.21
3.38
2.84
3.56
f1 (ppm)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Ph
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56.74
56.06
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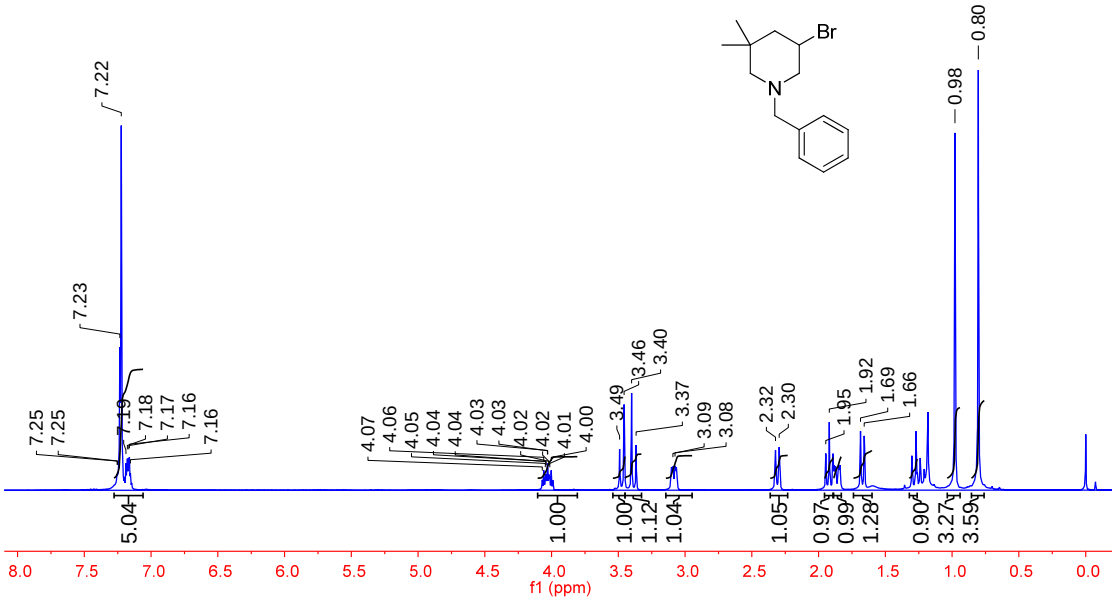
53.50
47.01
45.39
16.82
16.46
f1 (ppm)


Br
N
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7.23
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7.25
7.19
7.18
7.17
7.16
7.16
4.07
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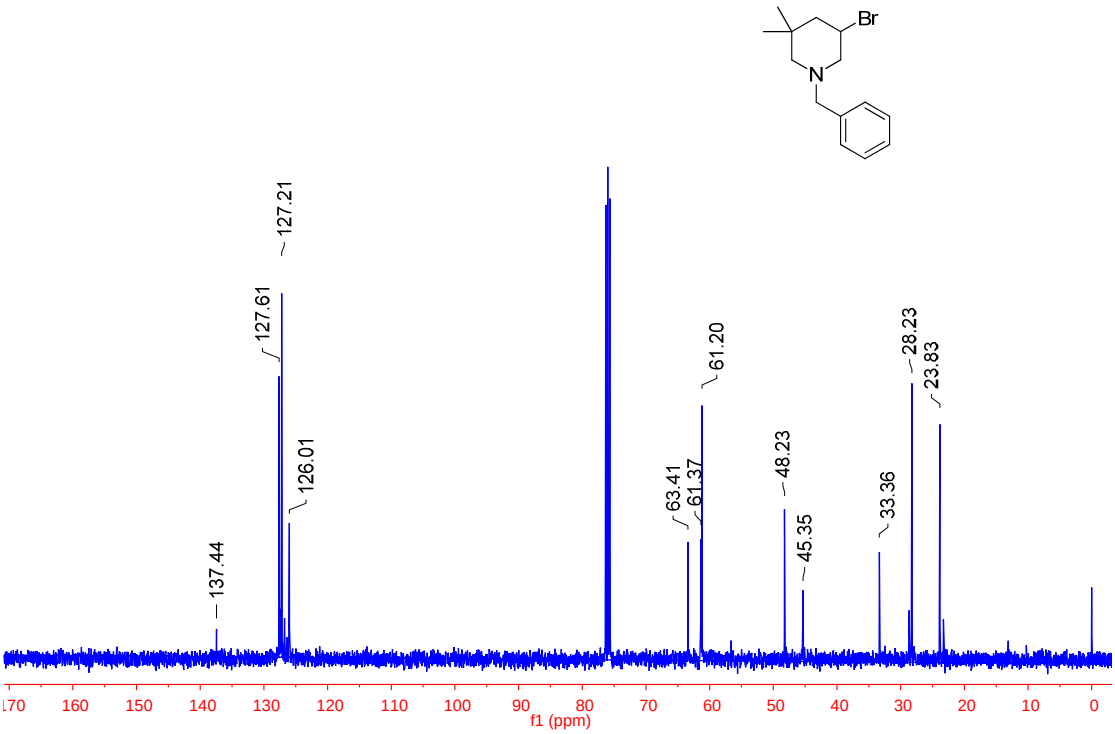
4.05
4.04
4.04
4.03
4.03
4.02
4.02
4.01
4.00
3.49
3.46
3.40
3.37
3.09
3.08
2.32
2.30
1.95
1.92
1.69
1.66
0.98
0.80
5.04
1.00
1.00
1.12
1.04
1.05
0.97
0.99
1.28
0.90
3.27
3.59
f1 (ppm)


Br
N
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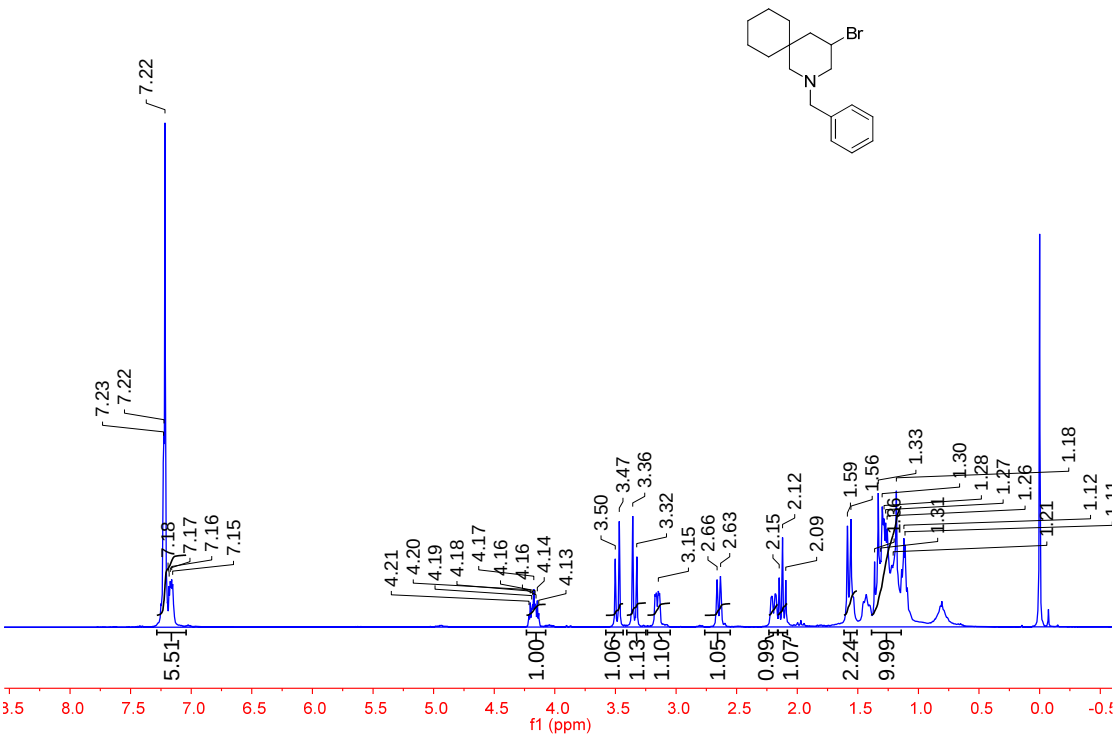
63.41
61.37
61.20
48.23
45.35
33.36
28.23
23.83
f1 (ppm)


Br
N
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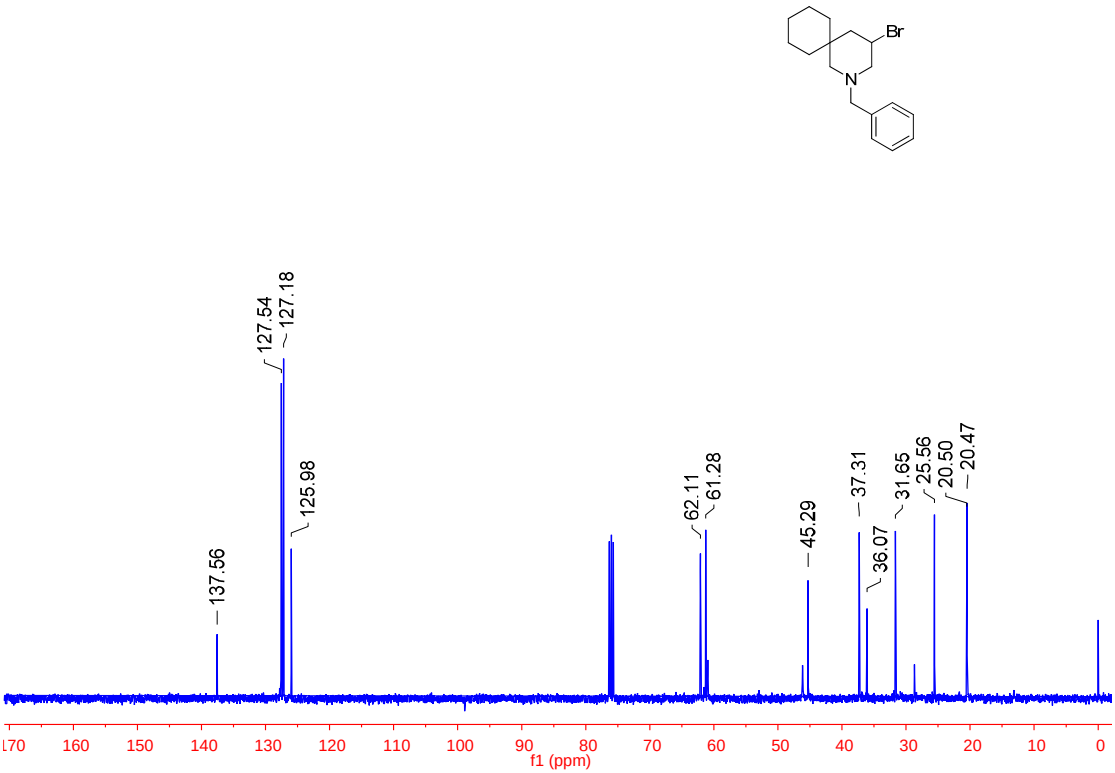
7.23
7.22
7.18
7.17
7.16
7.15
4.21
4.20
4.19
4.18
4.17
4.16
4.14
4.13
3.50
3.47
3.36
3.32
3.15
2.66
2.63
2.15
2.12
2.09
1.59
1.56
1.33
1.30
1.28
1.27
1.26
1.21
1.18
1.12
5.51
1.00
1.06
1.13
1.10
1.05
0.99
1.07
2.24
9.99
f1 (ppm)


Br
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127.18
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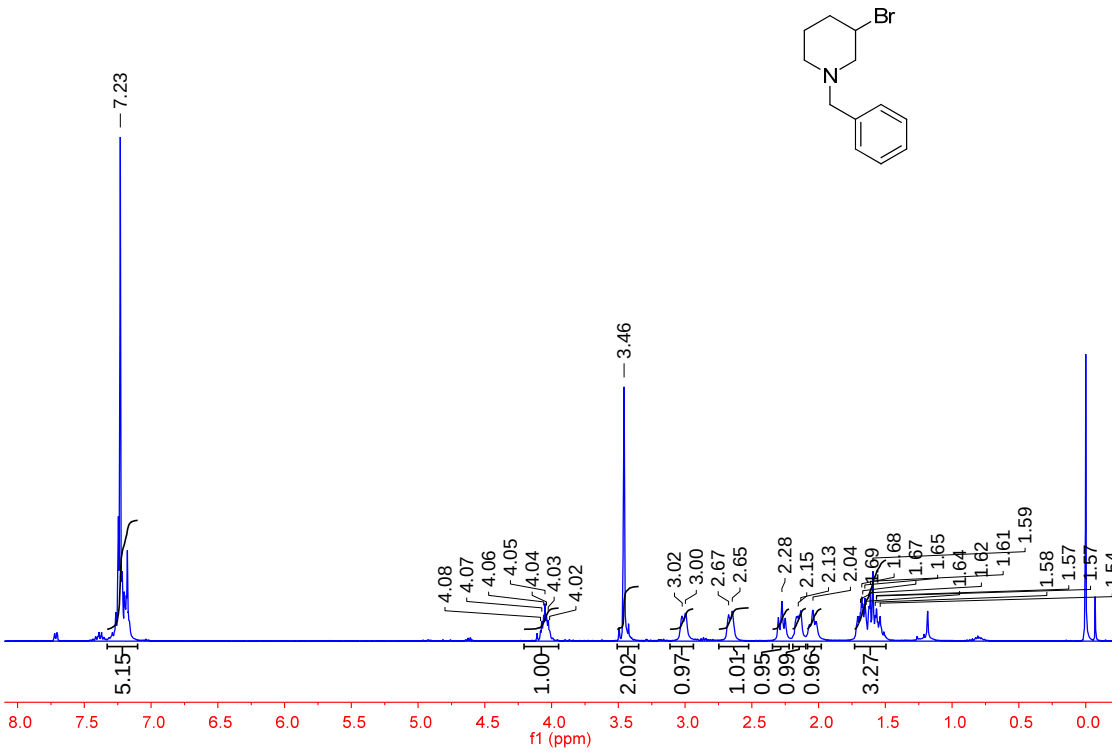
61.28
45.29
37.31
36.07
31.65
25.56
20.50
20.47
f1 (ppm)


Br
N
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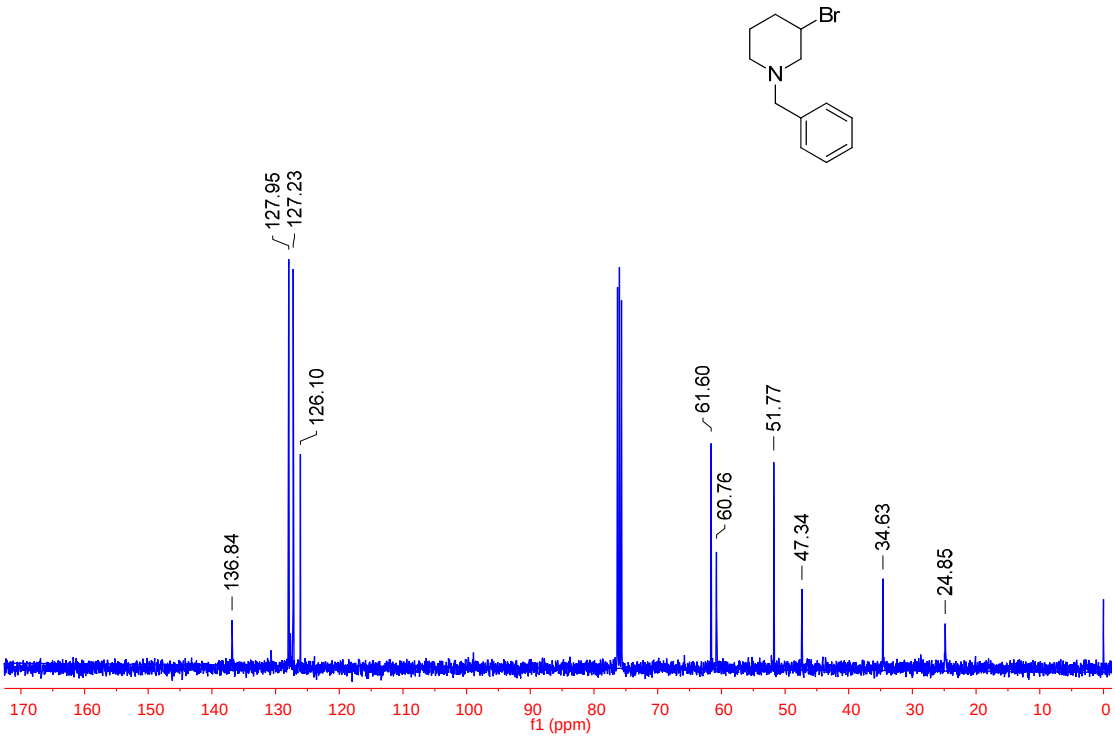
4.08
4.07
4.06
4.05
4.04
4.03
4.02
3.46
3.02
3.00
2.67
2.65
2.28
2.15
2.13
2.04
1.69
1.68
1.67
1.65
1.64
1.62
1.61
1.59
1.58
1.57
5.15
1.00
2.02
0.97
1.01
0.95
0.99
0.96
3.27
f1 (ppm)


Br
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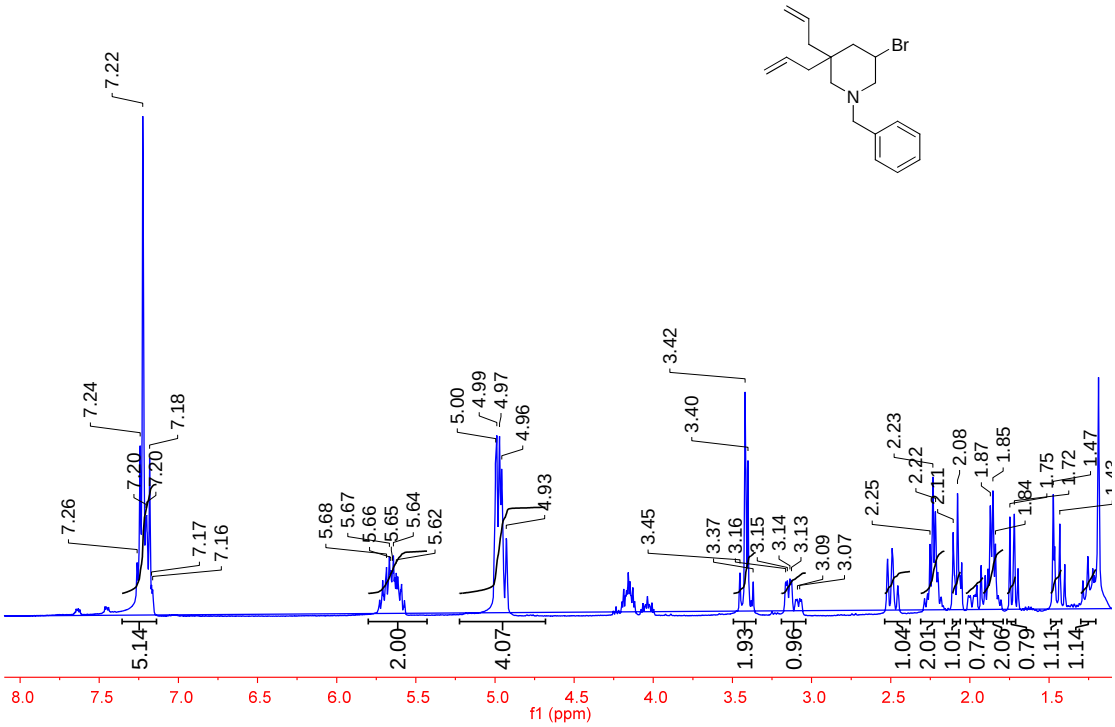
126.10
136.84
61.60
60.76
51.77
47.34
34.63
24.85
f1 (ppm)


Br
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7.26
7.20
7.20
7.18
7.17
7.16
5.68
5.67
5.66
5.65
5.64
5.62
5.00
4.99
4.97
4.96
4.93
3.42
3.40
3.45
3.37
3.16
3.15
3.14
3.13
3.09
3.07
2.25
2.23
2.22
2.11
2.08
1.87
1.85
1.84
1.75
1.72
1.47
5.14
2.00
4.07
1.93
0.96
1.04
2.01
1.01
0.74
2.06
0.79
1.11
1.14
8.0
7.5
7.0
6.5
6.0
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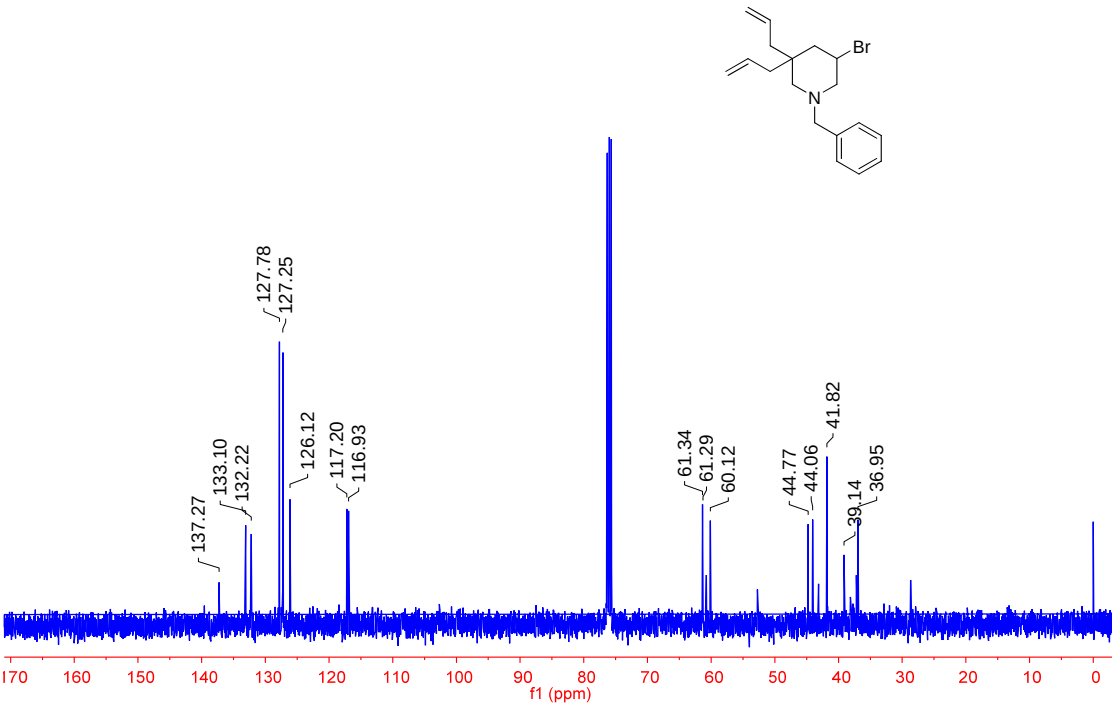
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


Br
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127.25
126.12
117.20
116.93
61.34
61.29
60.12
44.77
44.06
41.82
39.14
36.95
170
160
150
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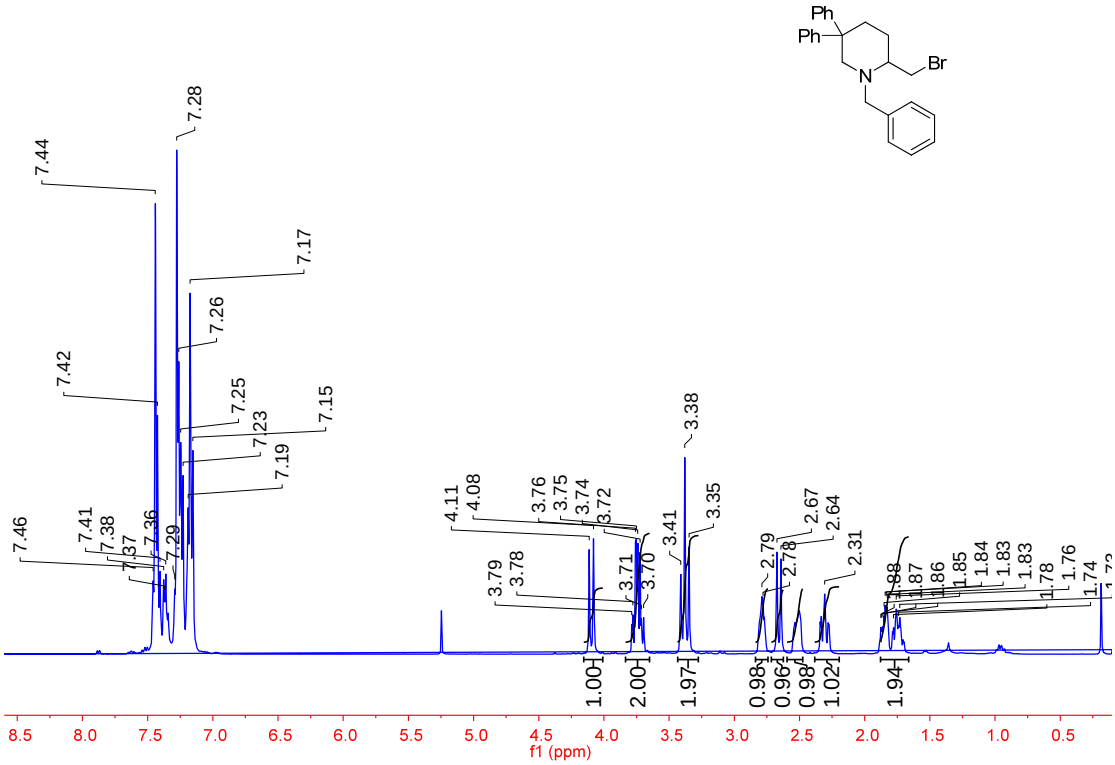
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Ph
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Br
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7.26
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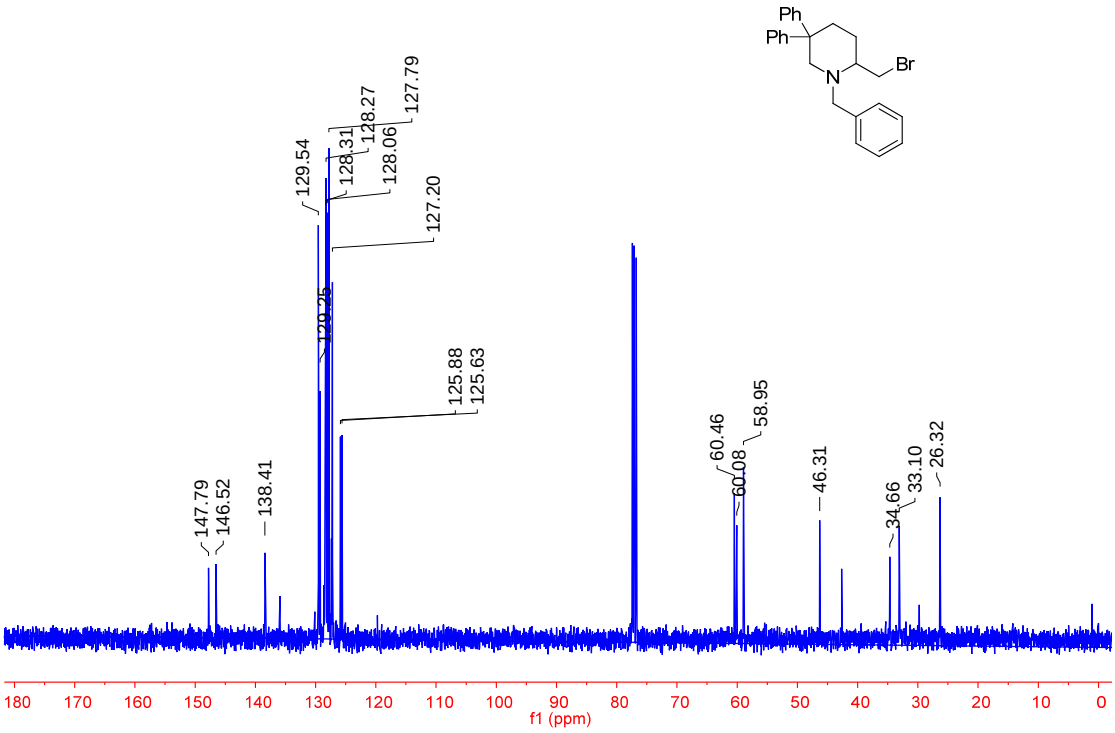
7.25
7.23
7.15
7.19
7.46
7.41
7.38
7.37
7.36
7.29
4.11
4.08
3.76
3.75
3.74
3.72
3.38
3.41
3.35
3.79
3.78
3.71
3.70
2.79
2.78
2.67
2.64
2.31
1.88
1.87
1.86
1.85
1.84
1.83
1.78
1.76
1.74
1.00
2.00
1.97
0.98
0.96
0.98
1.02
1.94
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph
Ph
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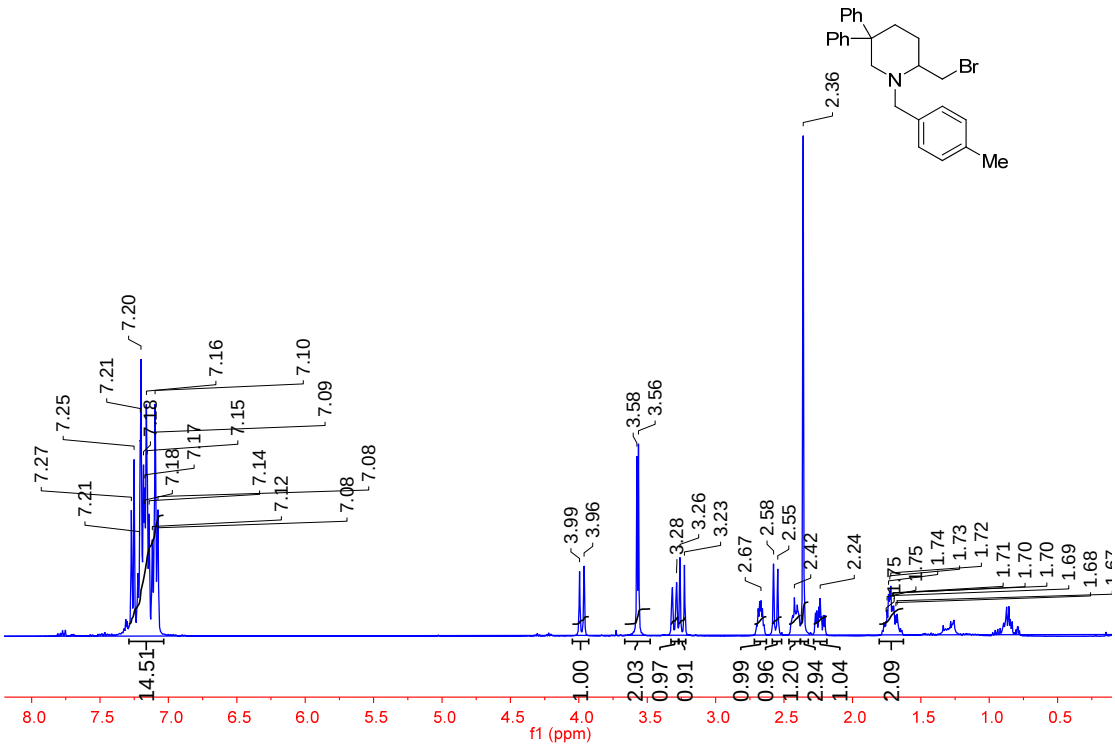
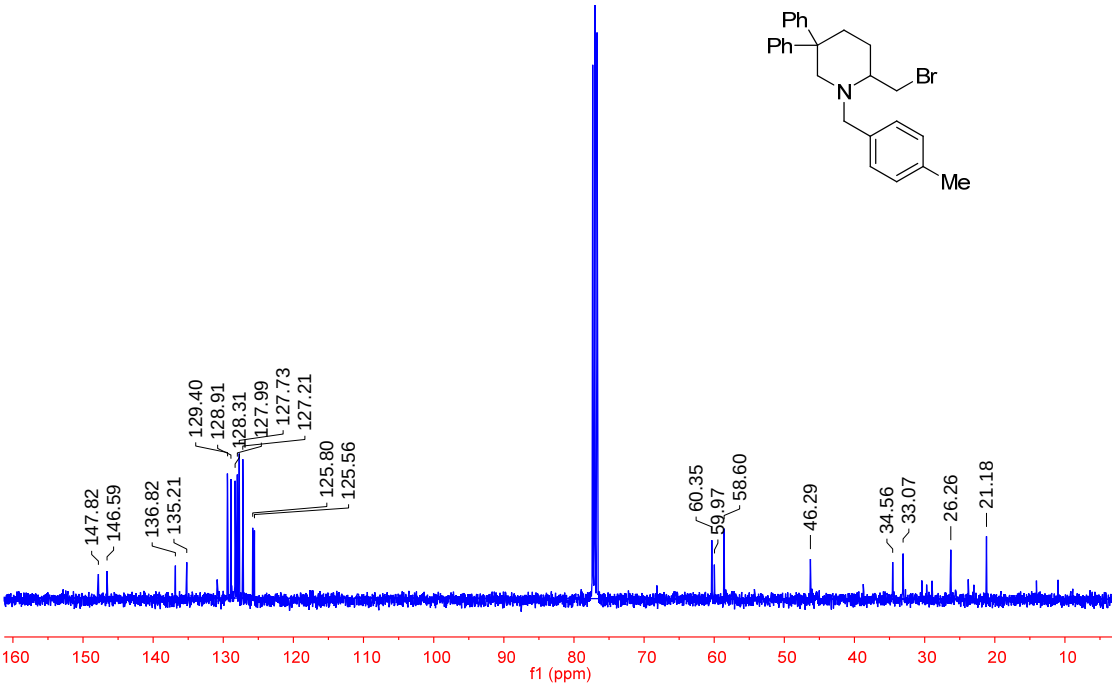
Br
129.54
128.31
128.27
128.06
127.79
127.20
129.25
125.88
125.63
147.79
146.52
138.41
60.46
60.08
58.95
46.31
34.66
33.10
26.32
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
N
Br
Me
2.36
7.20
7.21
7.16
7.10
7.25
7.18
7.09
7.15
7.27
7.17
7.18
7.14
7.08
7.21
7.12
7.08
3.58
3.56
3.99
3.96
3.28
3.26
3.23
2.67
2.58
2.55
2.42
2.24
1.75
1.74
1.73
1.72
1.71
1.70
1.70
1.69
1.68
14.51
1.00
2.03
0.97
0.91
0.99
0.96
1.20
2.94
1.04
2.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Ph
Ph
N
Br
Me
147.82
146.59
136.82
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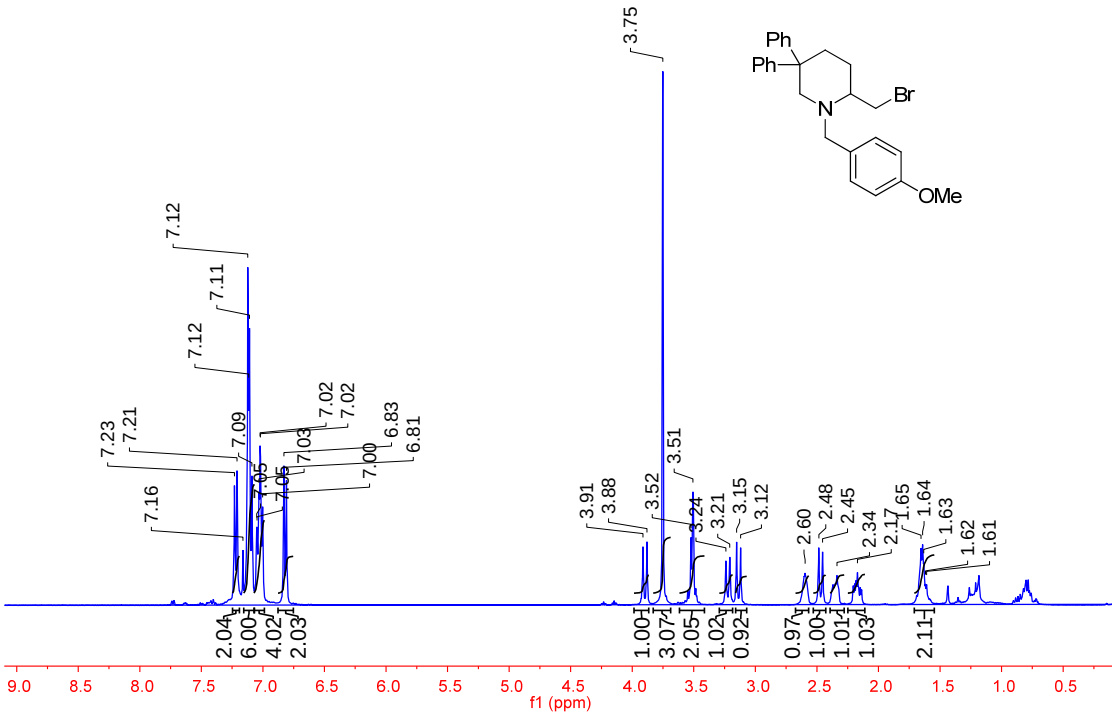
129.40
128.91
128.31
127.99
127.73
127.21
125.80
125.56
60.35
59.97
58.60
46.29
34.56
33.07
26.26
21.18
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
Ph
N
Br
OMe
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7.11
7.12
7.23
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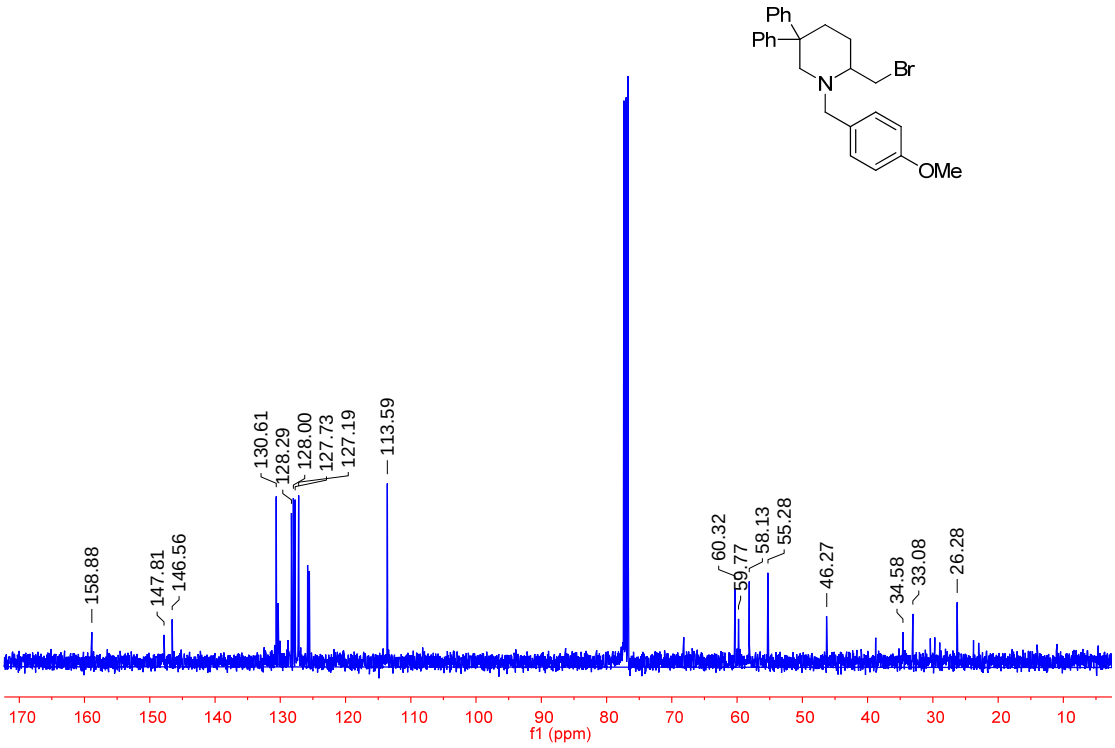
7.09
7.02
7.02
6.83
6.81
7.03
7.00
7.05
7.05
7.16
3.91
3.88
3.52
3.51
3.24
3.21
3.15
3.12
2.60
2.48
2.45
2.34
2.17
1.65
1.64
1.63
1.62
1.61
2.04
6.00
4.02
2.03
1.00
3.07
2.05
1.02
0.92
0.97
1.00
1.01
1.03
2.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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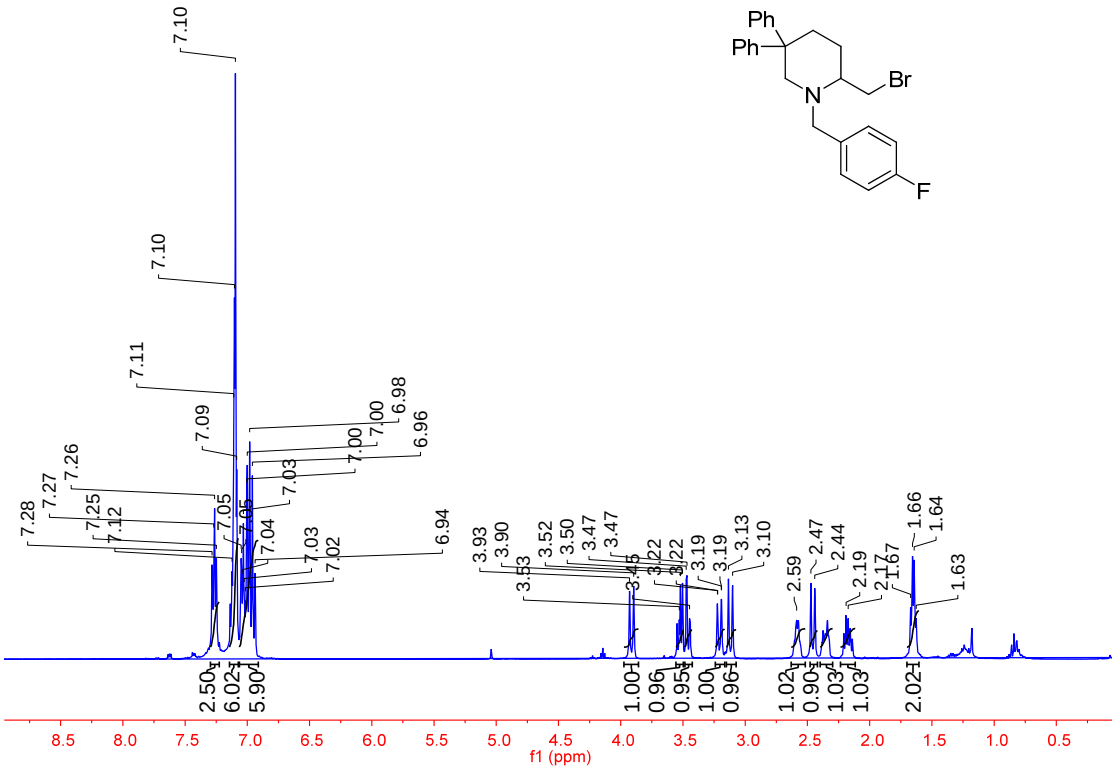
Ph
N
Br
OMe
158.88
147.81
146.56
130.61
128.29
128.00
127.73
127.19
113.59
60.32
59.77
58.13
55.28
46.27
34.58
33.08
26.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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Ph
N
Br
F
7.10
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7.09
7.00
6.98
6.96
7.26
7.27
7.28
7.25
7.12
7.05
7.04
7.03
7.02
6.94
3.93
3.90
3.53
3.52
3.50
3.47
3.45
3.22
3.19
3.13
3.10
2.59
2.47
2.44
2.19
2.17
1.67
1.66
1.64
1.63
2.50
6.02
5.90
1.00
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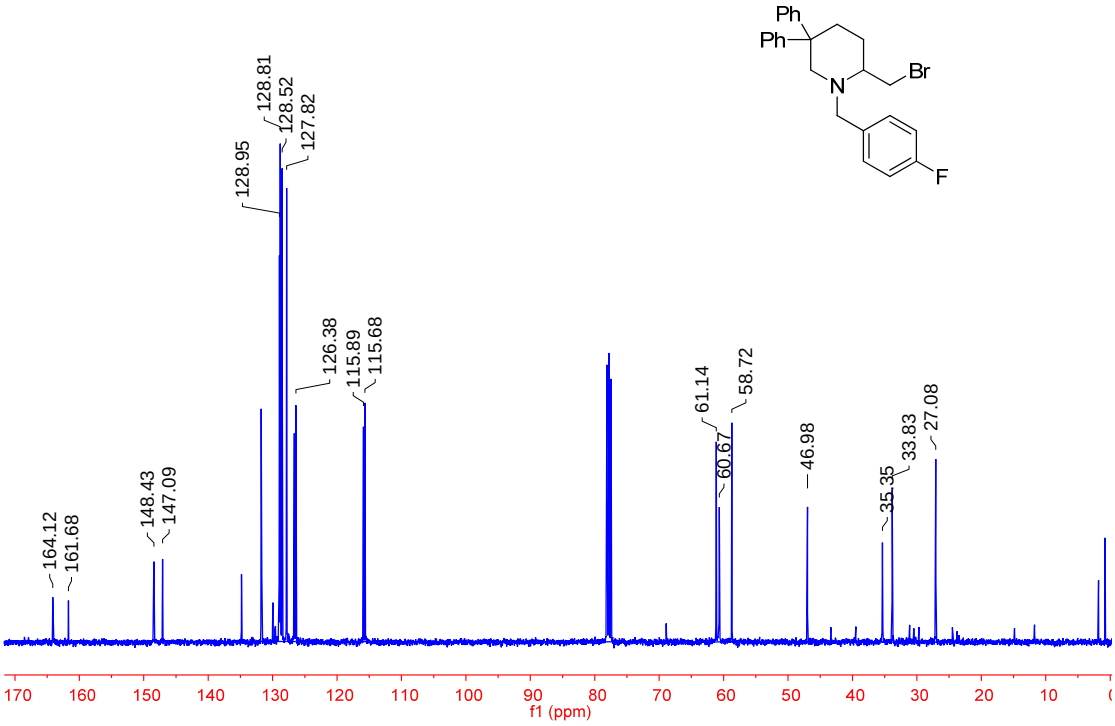
0.95
1.00
0.96
1.02
0.90
1.03
1.03
2.02
f1 (ppm)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Ph
N
Br
F
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128.52
127.82
126.38
115.89
115.68
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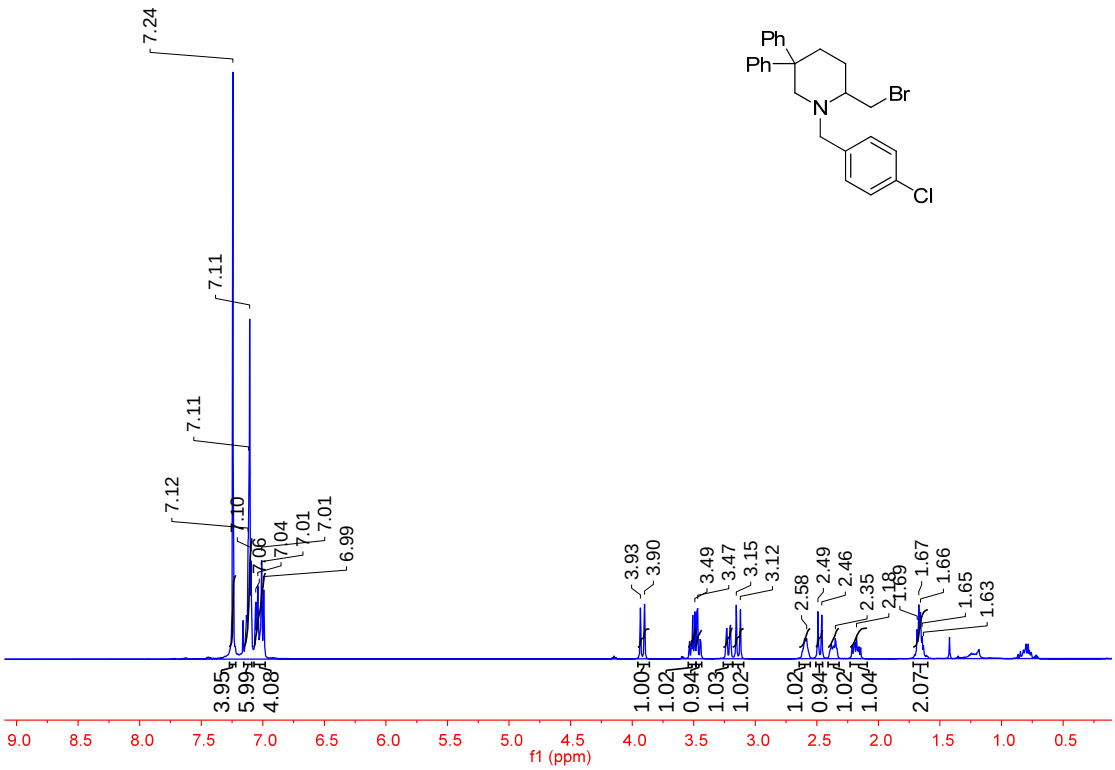
147.09
61.14
60.67
58.72
46.98
35.35
33.83
27.08
f1 (ppm)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Ph
Br
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Cl
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7.11
7.12
7.10
7.06
7.04
7.01
7.01
6.99
3.93
3.90
3.49
3.47
3.15
3.12
2.58
2.49
2.46
2.35
2.18
1.69
1.67
1.66
1.65
1.63
3.95
5.99
4.08
1.00
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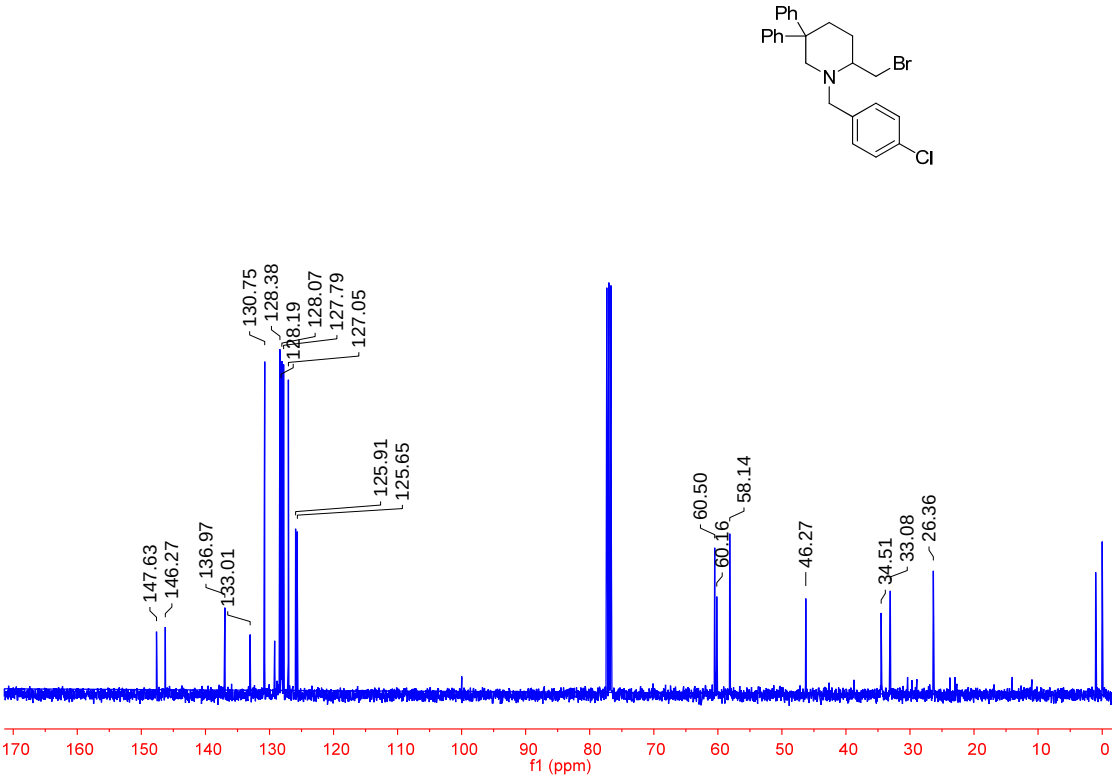
0.94
1.03
1.02
1.02
0.94
1.02
1.04
2.07
f1 (ppm)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Ph
Br
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Cl
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128.07
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127.05
125.91
125.65
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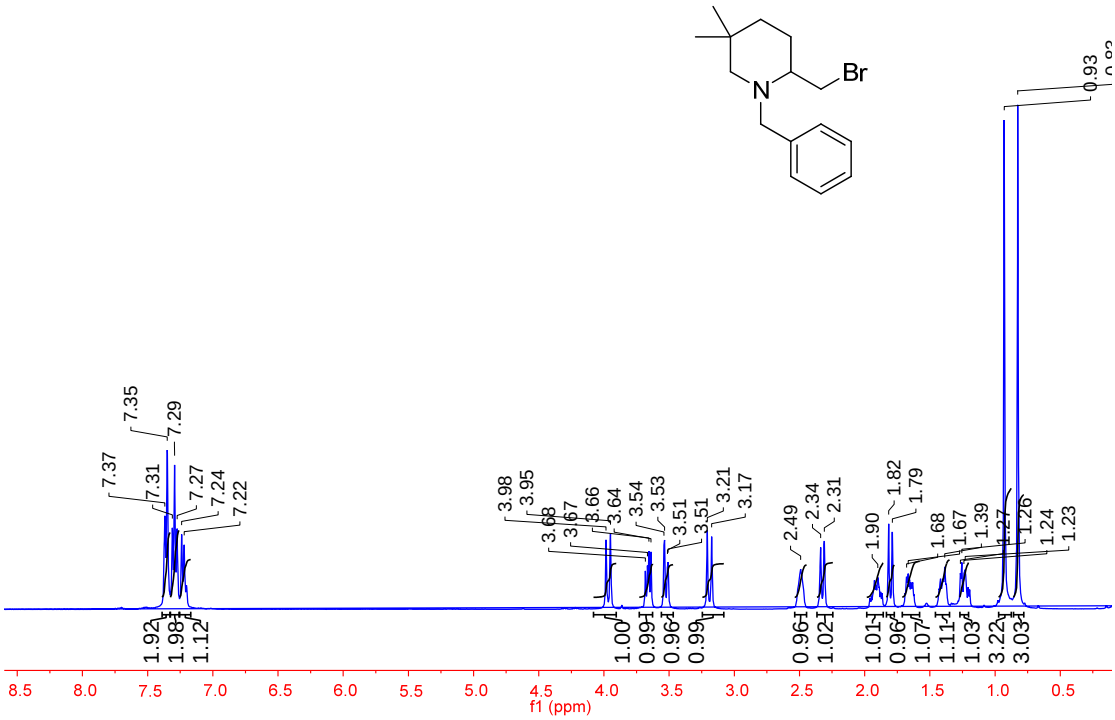
133.01
60.50
60.16
58.14
46.27
34.51
33.08
26.36
f1 (ppm)


Br
N
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7.27
7.24
7.22
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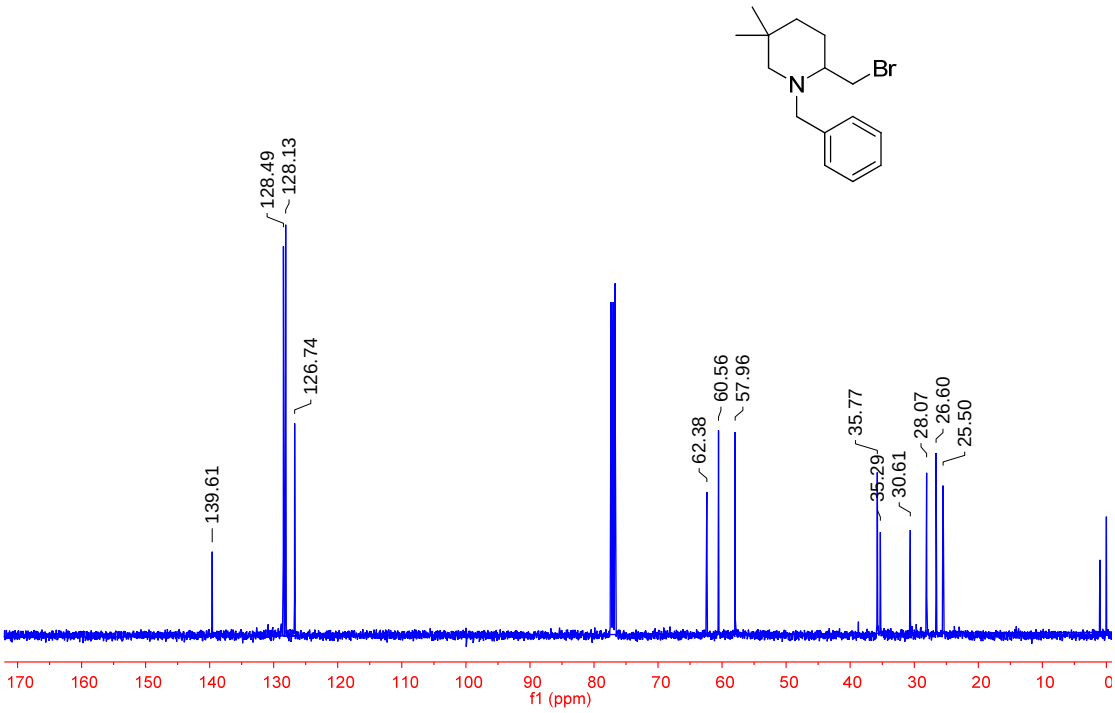
3.95
3.68
3.67
3.66
3.64
3.54
3.53
3.51
3.51
3.21
3.17
2.49
2.34
2.31
1.90
1.82
1.79
1.68
1.67
1.39
1.27
1.26
1.24
1.23
0.93
1.92
1.98
1.12
1.00
0.99
0.96
0.99
0.96
1.02
1.01
0.96
1.07
1.11
1.03
3.22
3.03
f1 (ppm)


Br
N
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128.13
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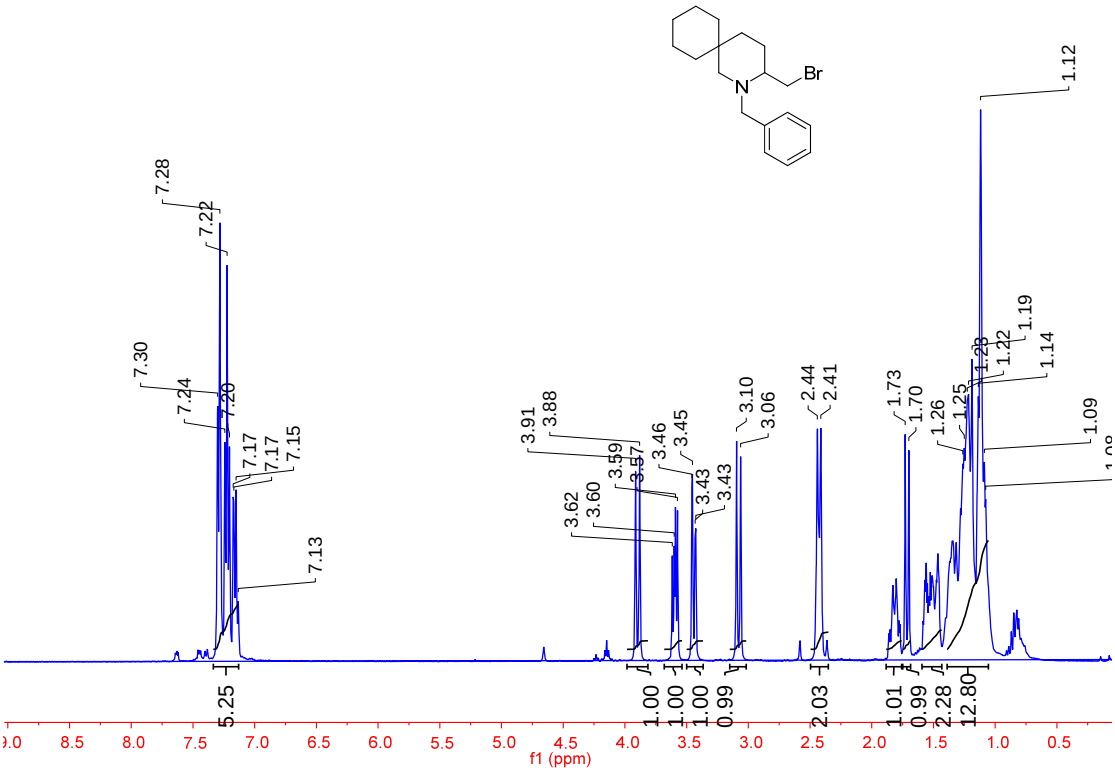
35.29
30.61
28.07
26.60
25.50
f1 (ppm)


Br
N
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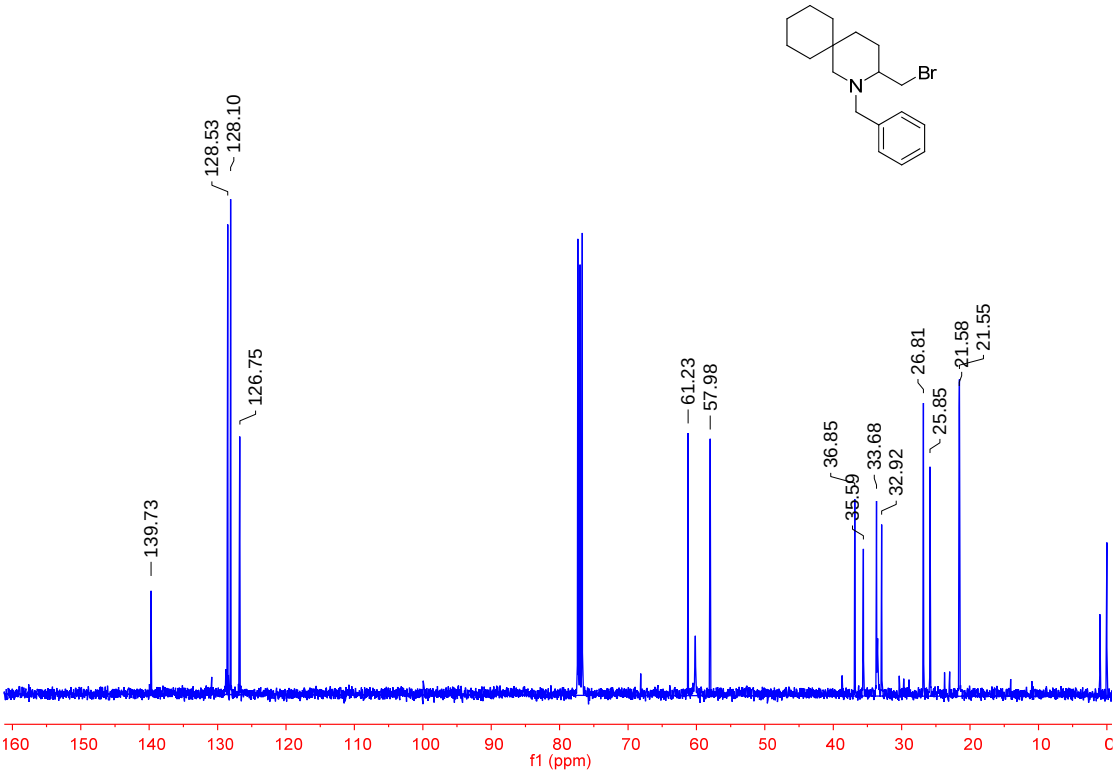
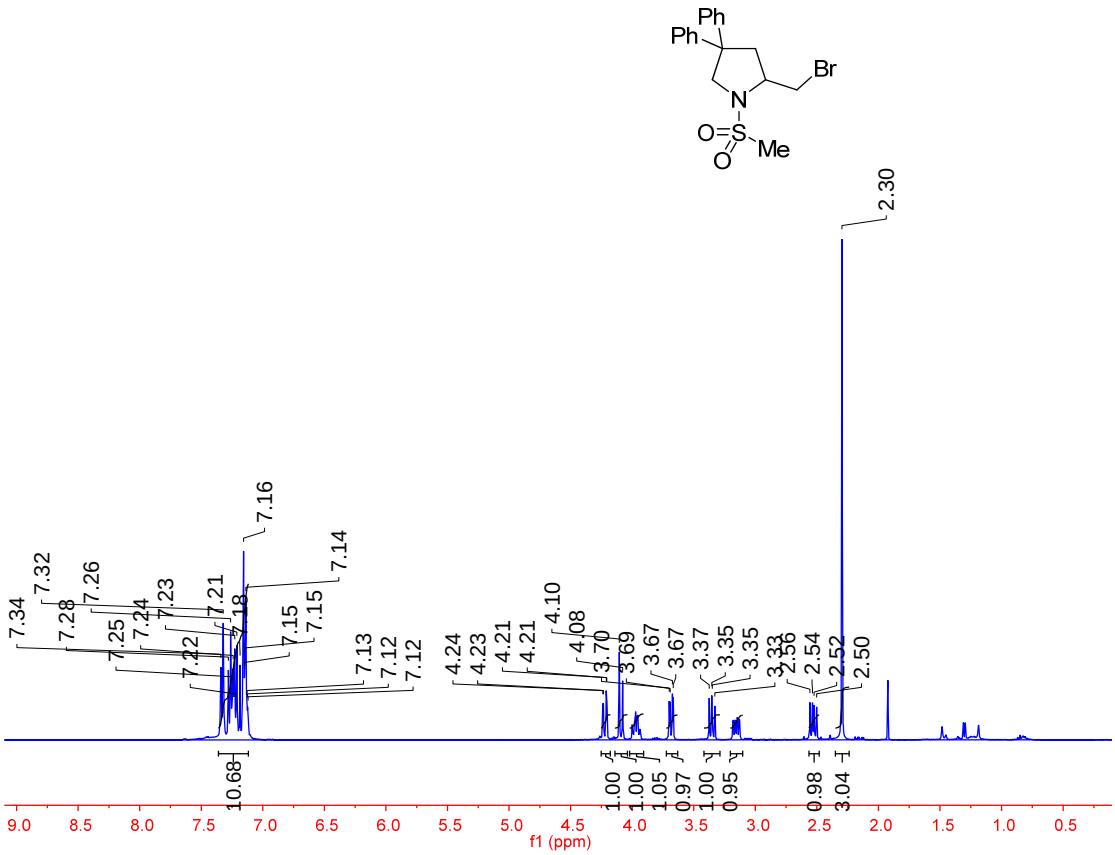
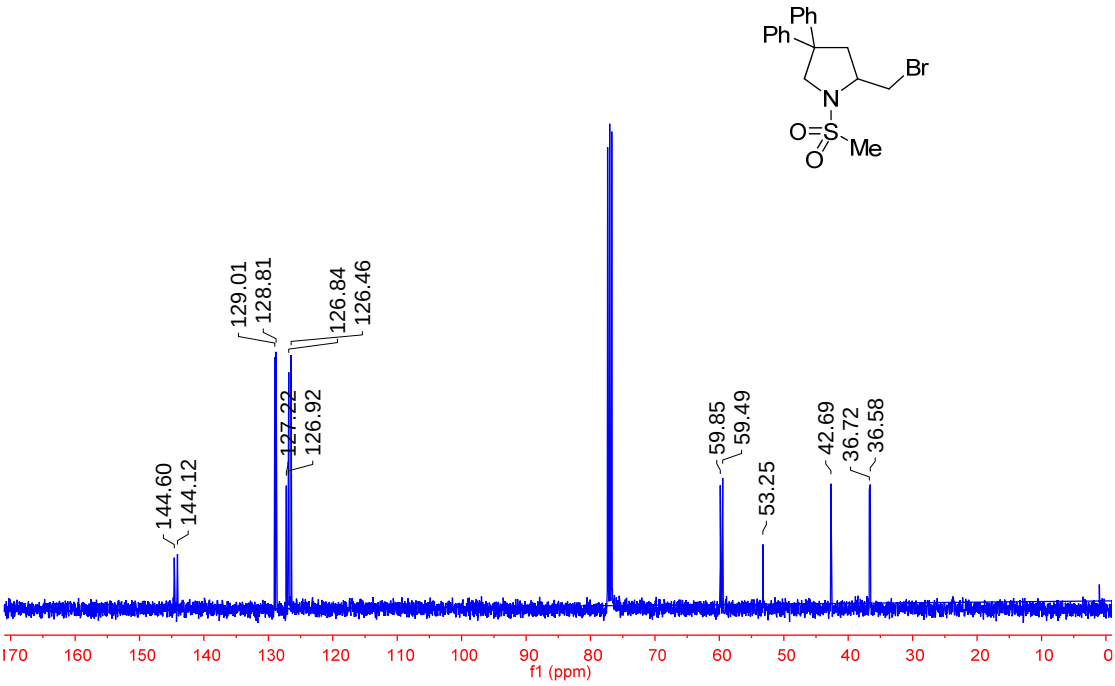
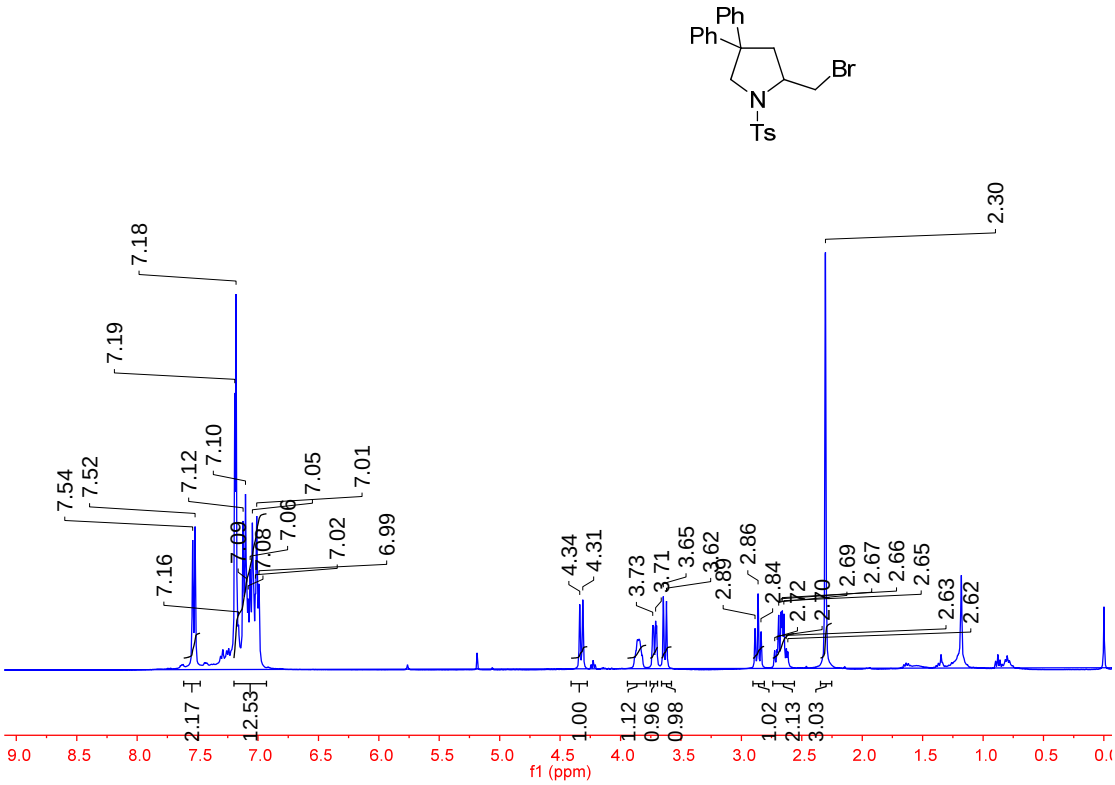
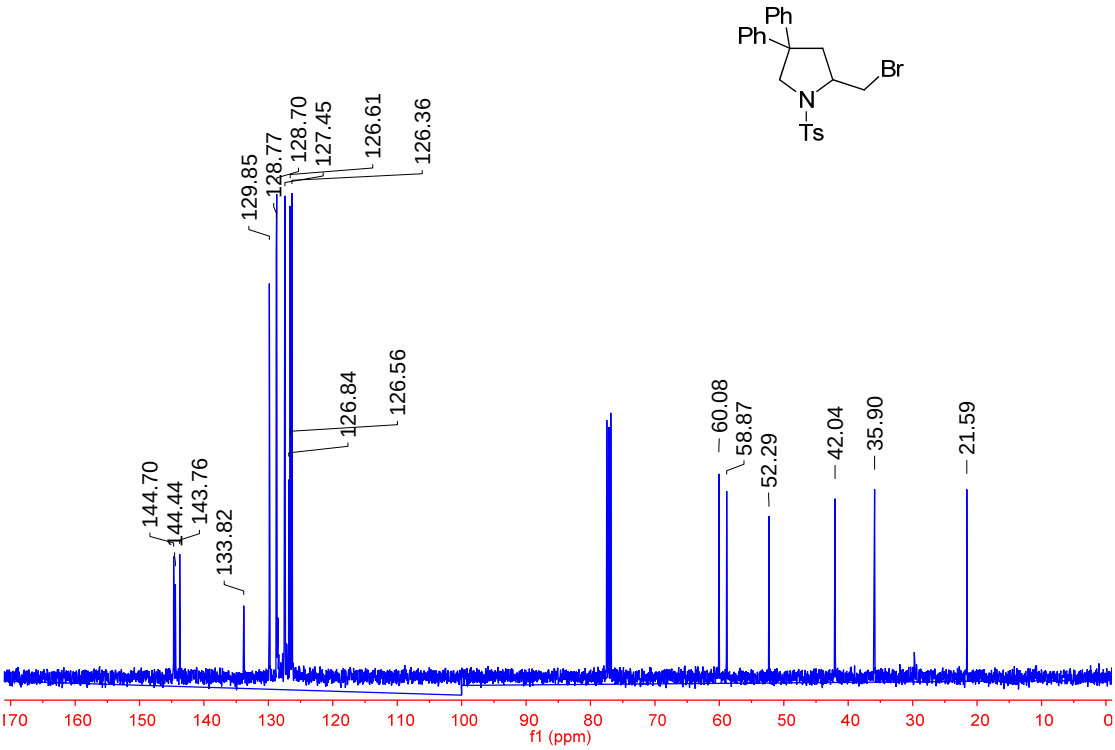
7.22
7.30
7.24
7.20
7.17
7.15
7.13
3.91
3.88
3.59
3.57
3.46
3.45
3.62
3.60
3.43
3.43
3.10
3.06
2.44
2.41
1.73
1.70
1.26
1.25
1.12
1.19
1.22
1.14
1.09
5.25
1.00
1.00
1.00
0.99
2.03
1.01
0.99
2.28
12.80
f1 (ppm)


Br
N
128.53
128.10
126.75
139.73
61.23
57.98
36.85
35.59
33.68
32.92
26.81
25.85
21.58
21.55
f1 (ppm)


Ph
Ph
Br
N
O=S
Me
O
2.30
7.34
7.32
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.18
7.16
7.15
7.14
7.13
7.12
7.12
4.24
4.23
4.21
4.21
4.10
4.08
3.70
3.69
3.67
3.67
3.37
3.35
3.35
3.33
2.56
2.54
2.52
2.50
10.68
1.00
1.00
1.05
0.97
1.00
0.95
0.98
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph
Ph
Br
N
O=S
Me
O
129.01
128.81
126.84
126.46
127.22
126.92
144.60
144.12
59.85
59.49
53.25
42.69
36.72
36.58
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ph
Ph
Br
N
Ts
7.18
7.19
7.54
7.52
7.12
7.10
7.05
7.01
7.16
7.09
7.08
7.06
7.02
6.99
4.34
4.31
3.73
3.71
3.65
3.62
2.89
2.86
2.84
2.72
2.70
2.69
2.67
2.66
2.65
2.63
2.62
2.30
2.17
12.53
1.00
1.12
0.96
0.98
1.02
2.13
3.03
f1 (ppm)


Ph
Ph
Br
N
Ts
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126.36
126.84
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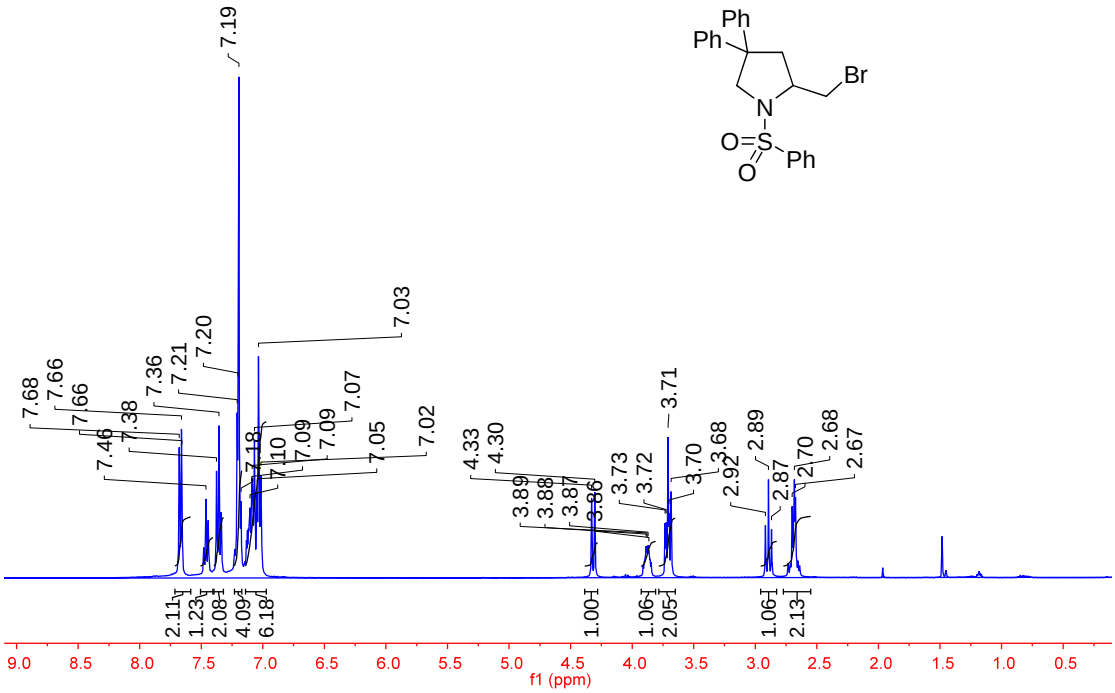
143.76
133.82
60.08
58.87
52.29
42.04
35.90
21.59
f1 (ppm)


Ph
Ph
Br
N
O=S
Ph
O
7.19
7.03
7.68
7.66
7.66
7.36
7.21
7.20
7.38
7.46
7.07
7.09
7.09
7.05
7.02
7.18
7.10
4.33
4.30
3.89
3.88
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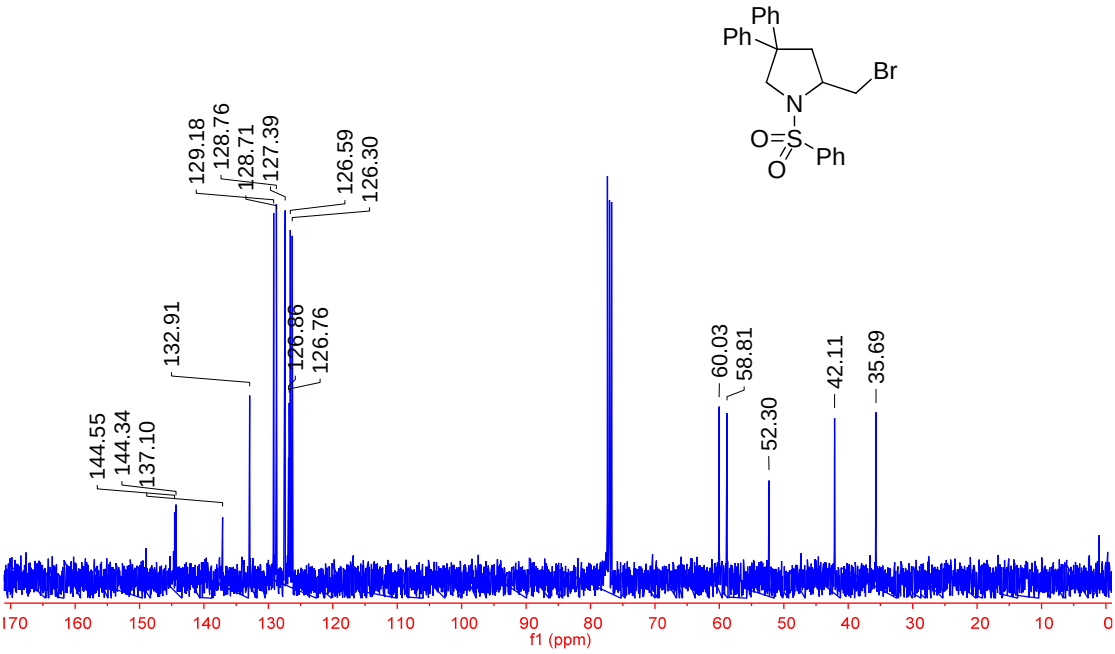
3.73
3.72
3.71
3.70
3.68
2.92
2.89
2.87
2.70
2.68
2.67
2.11
1.23
2.08
4.09
6.18
1.00
1.06
2.05
1.06
2.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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Ph
Br
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O=S
Ph
O
129.18
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128.71
127.39
126.59
126.30
132.91
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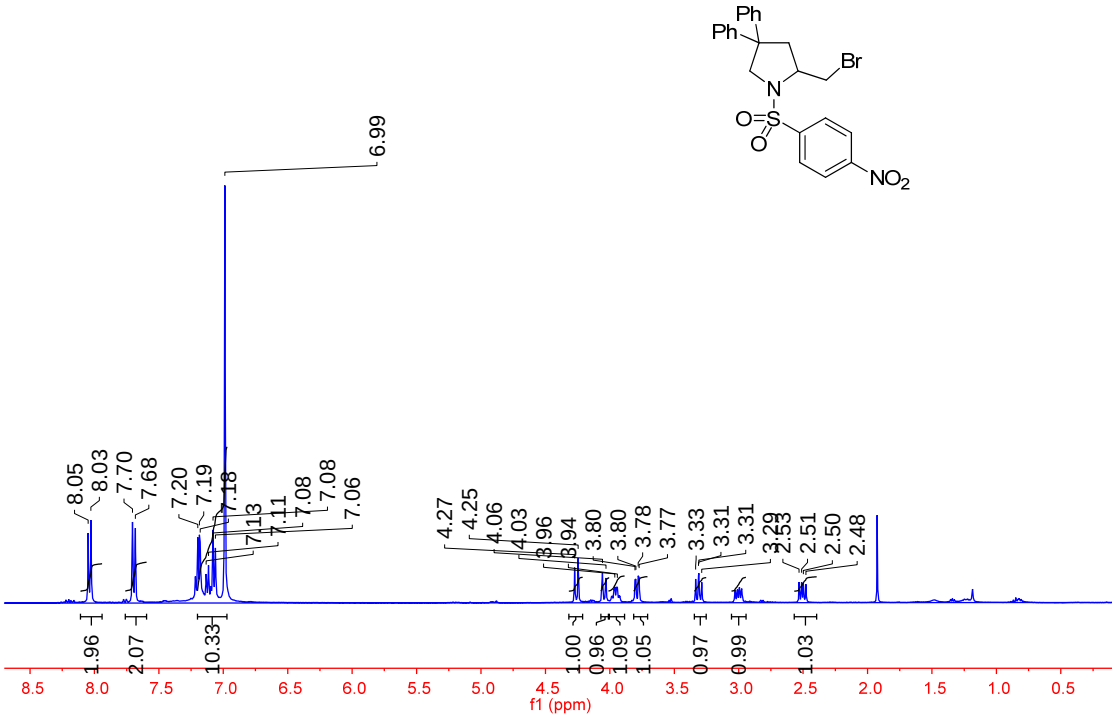
126.76
144.55
144.34
137.10
60.03
58.81
52.30
42.11
35.69
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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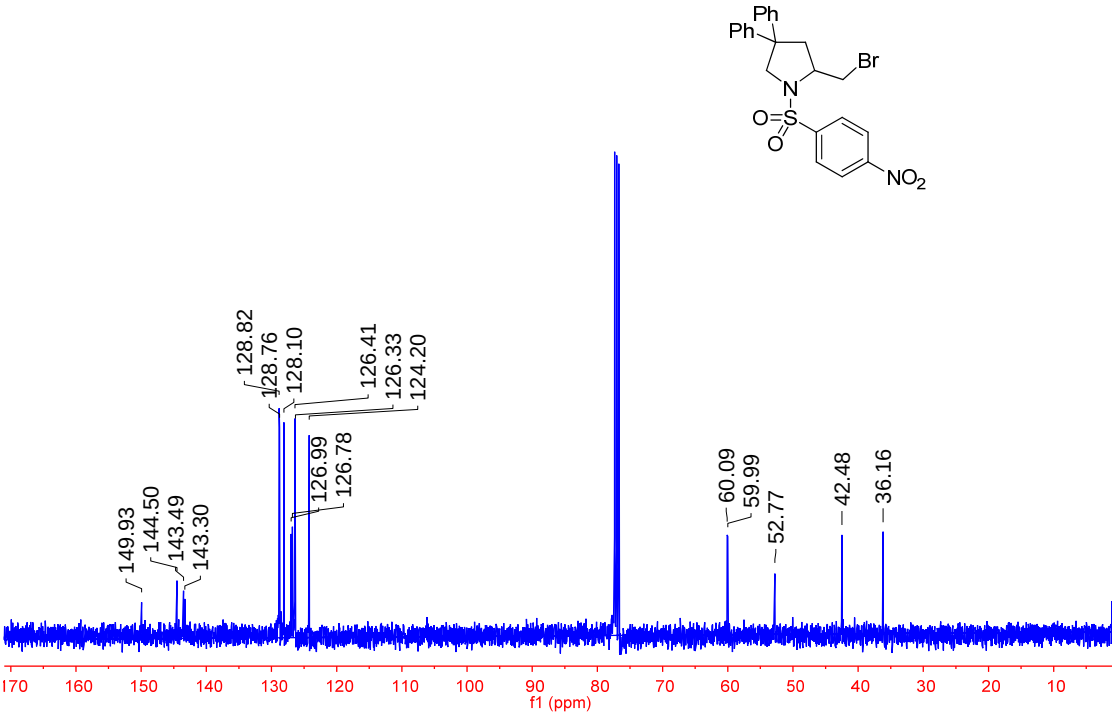
Ph
Br
N
O
S
O
NO2
6.99
8.05
8.03
7.70
7.68
7.20
7.19
7.18
7.13
7.11
7.08
7.08
7.06
4.27
4.25
4.06
4.03
3.96
3.94
3.80
3.80
3.78
3.77
3.33
3.31
3.31
3.29
2.53
2.51
2.50
2.48
1.96
2.07
10.33
1.00
0.96
1.09
1.05
0.97
0.99
1.03
f1 (ppm)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Ph
Br
N
O
S
O
NO2
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126.33
124.20
126.99
126.78
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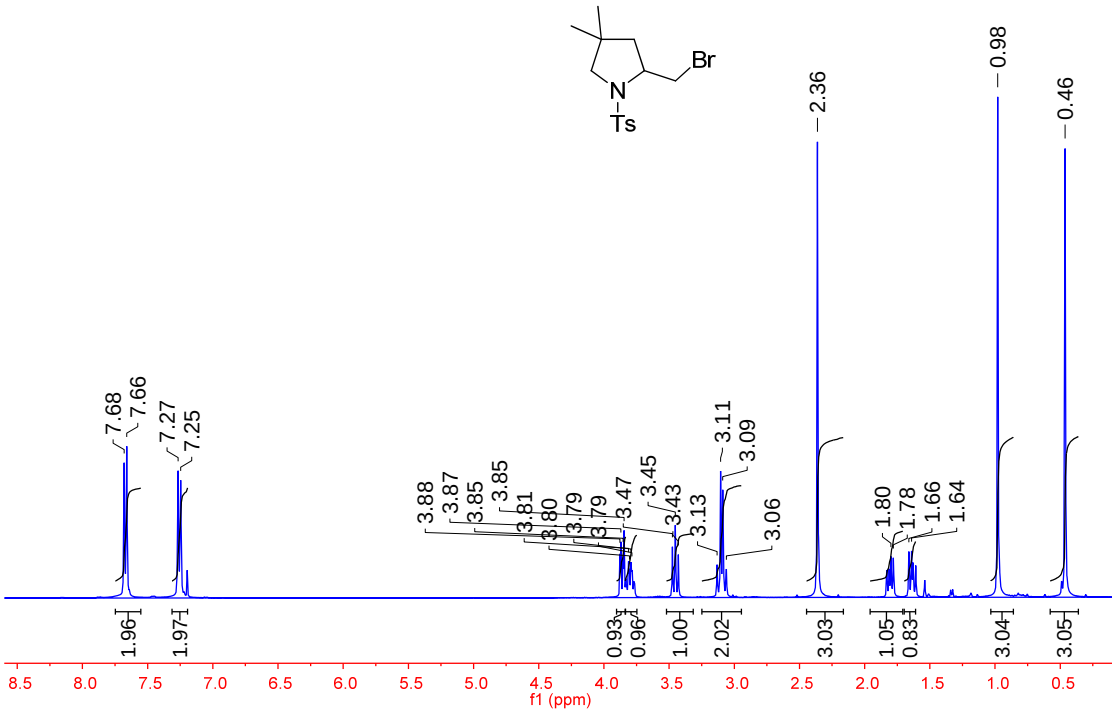
144.50
143.49
143.30
60.09
59.99
52.77
42.48
36.16
f1 (ppm)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Ts
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7.25
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3.87
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3.85
3.81
3.80
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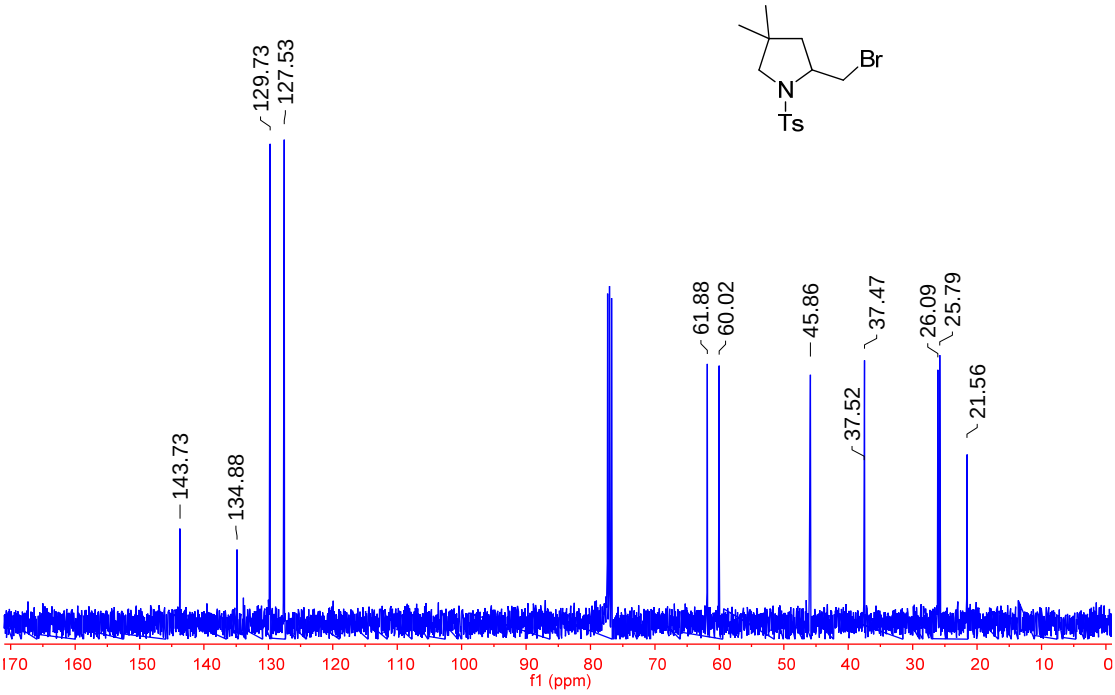
3.79
3.47
3.45
3.43
3.13
3.11
3.09
3.06
2.36
1.80
1.78
1.66
1.64
0.98
0.46
1.96
1.97
0.93
0.96
1.00
2.02
3.03
1.05
0.83
3.04
3.05
f1 (ppm)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Ts
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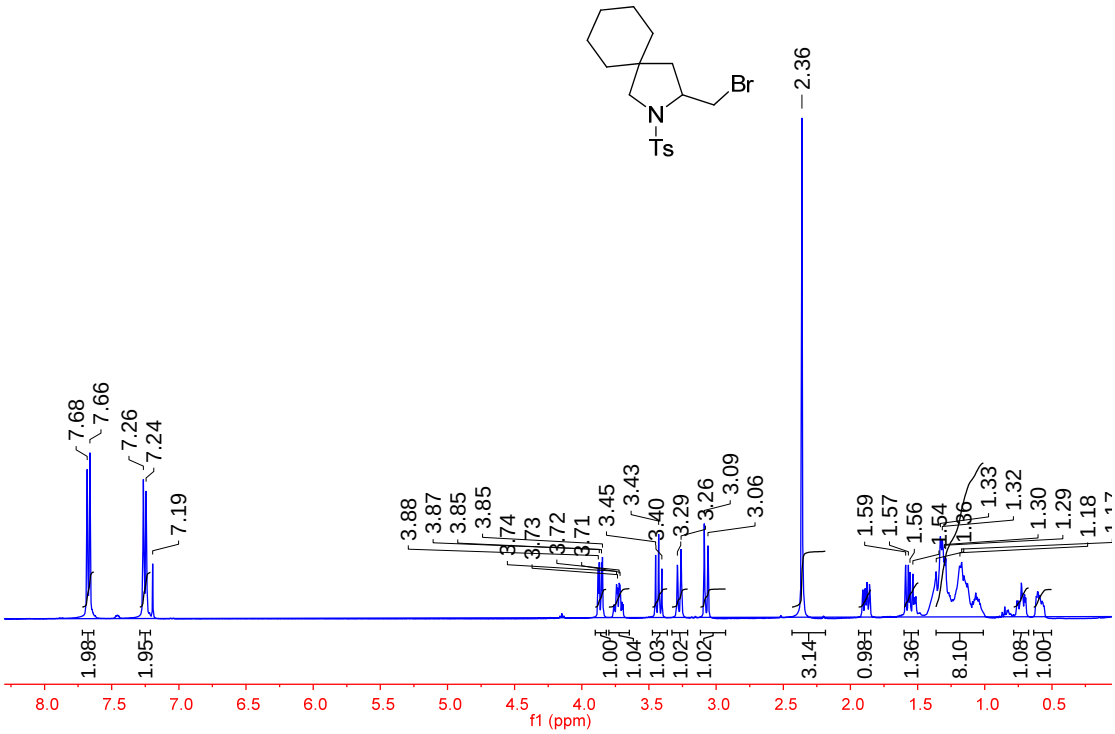
37.47
37.52
26.09
25.79
21.56
f1 (ppm)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Ts
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7.19
3.88
3.87
3.85
3.85
3.74
3.73
3.72
3.71
3.45
3.43
3.40
3.29
3.26
3.09
3.06
1.59
1.57
1.56
1.54
1.36
1.33
1.32
1.30
1.29
1.18
1.98
1.95
1.00
1.04
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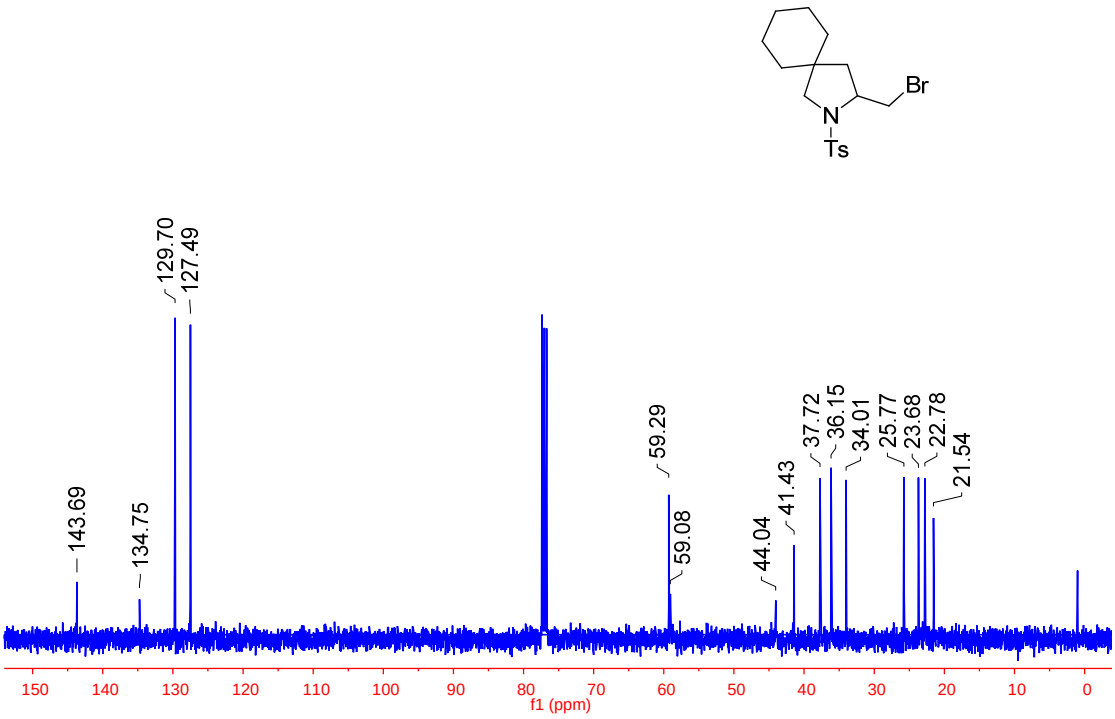
1.02
1.02
3.14
0.98
1.36
8.10
1.08
1.00
f1 (ppm)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Ts
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129.70
127.49
59.29
59.08
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41.43
37.72
36.15
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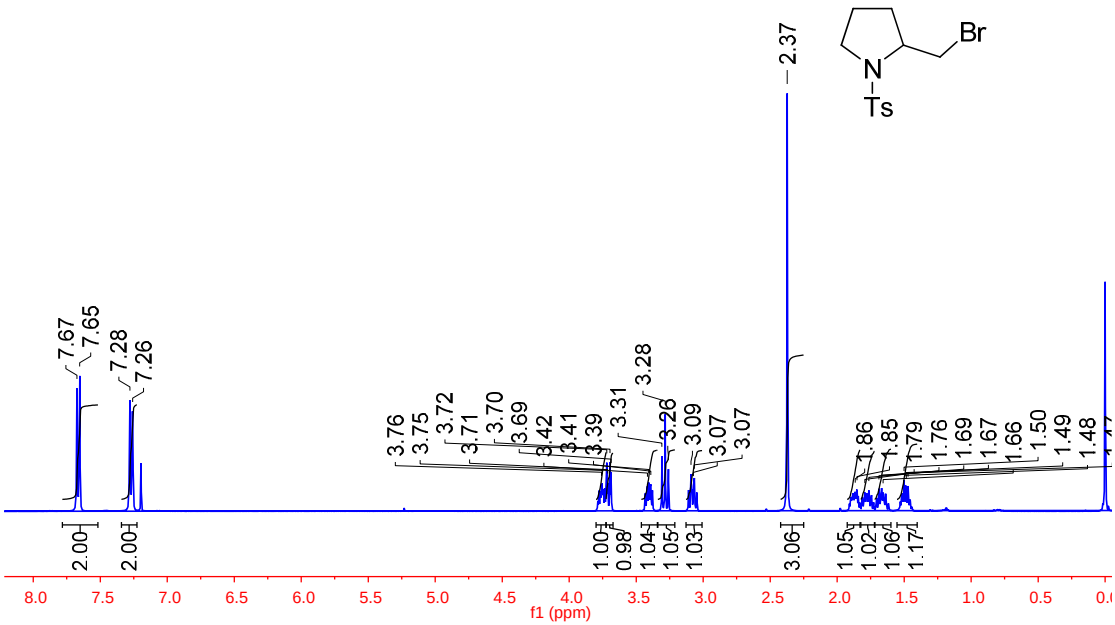
25.77
23.68
22.78
21.54
f1 (ppm)


Br
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Ts
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3.72
3.71
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3.69
3.42
3.41
3.39
3.31
3.28
3.26
3.09
3.07
3.07
1.86
1.85
1.79
1.76
1.69
1.67
1.66
1.50
1.49
1.48
2.00
2.00
1.00
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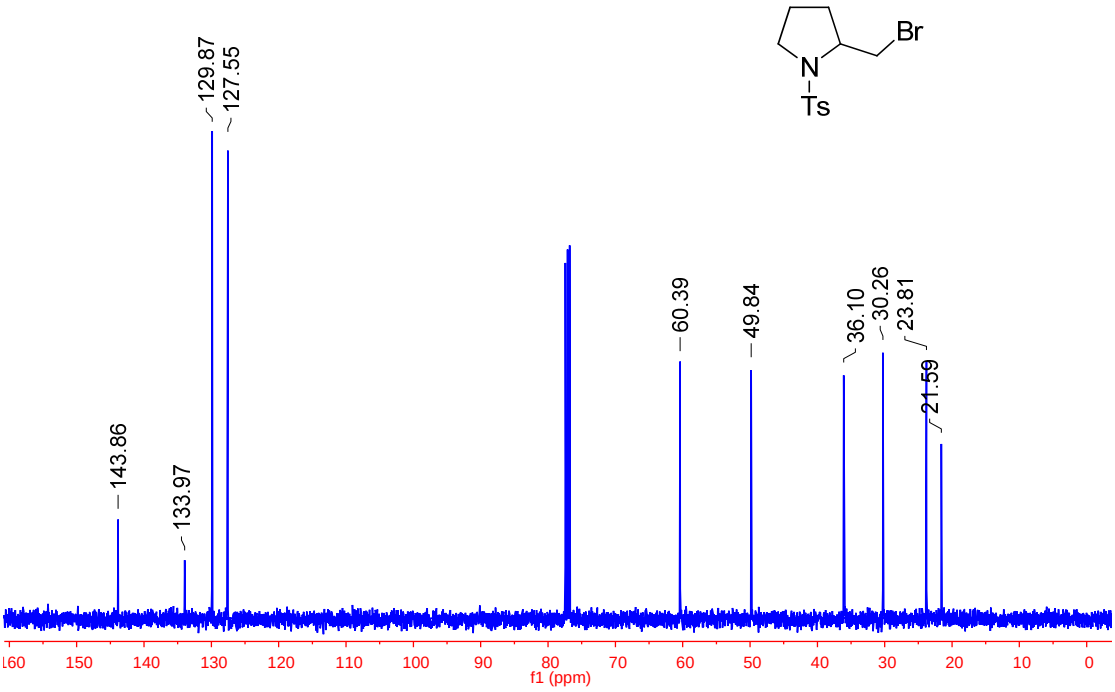
1.04
1.05
1.03
3.06
1.05
1.02
1.06
1.17
f1 (ppm)


Br
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Ts
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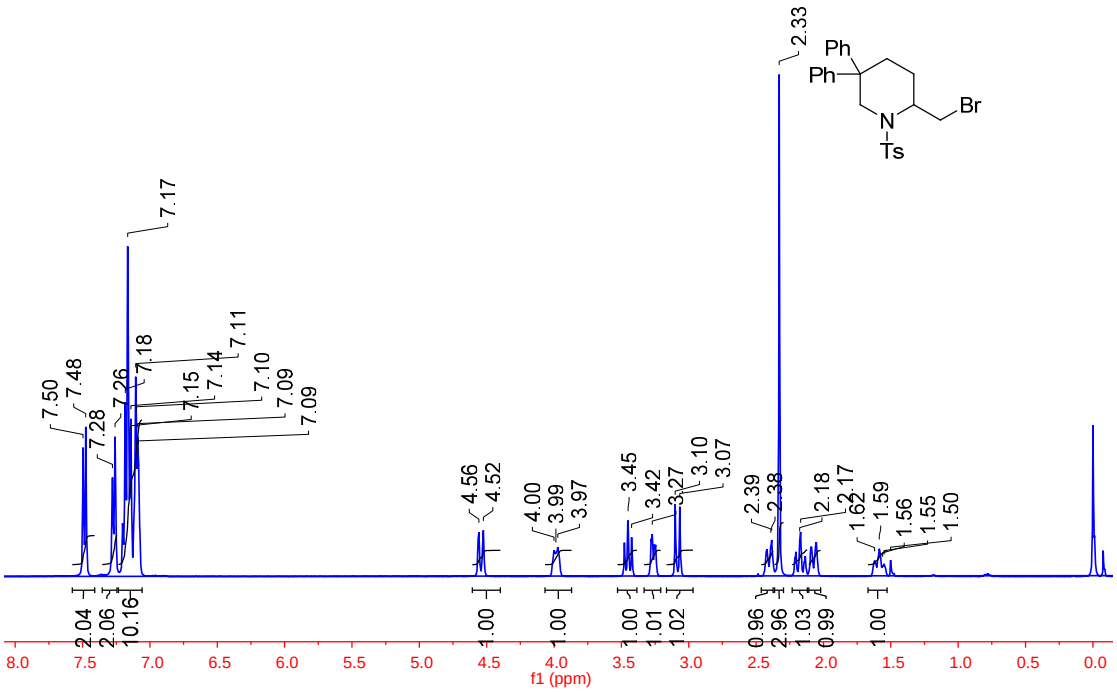
143.86
133.97
60.39
49.84
36.10
30.26
23.81
21.59
f1 (ppm)


Ph
Ph
N
Ts
Br
2.33
7.17
7.50
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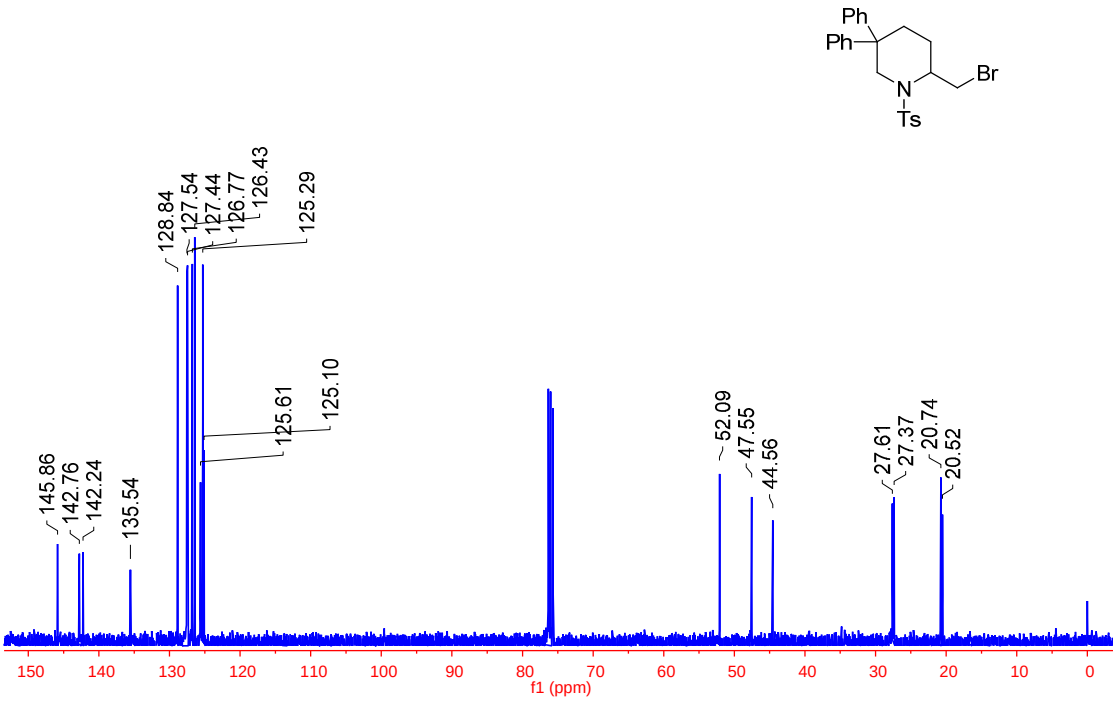
7.28
7.26
7.18
7.15
7.14
7.11
7.10
7.09
7.09
4.56
4.52
4.00
3.99
3.97
3.45
3.42
3.27
3.10
3.07
2.39
2.38
2.18
2.17
1.62
1.59
1.56
1.55
1.50
2.04
2.06
10.16
1.00
1.00
1.00
1.01
1.02
0.96
2.96
1.03
0.99
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
Ph
N
Ts
Br
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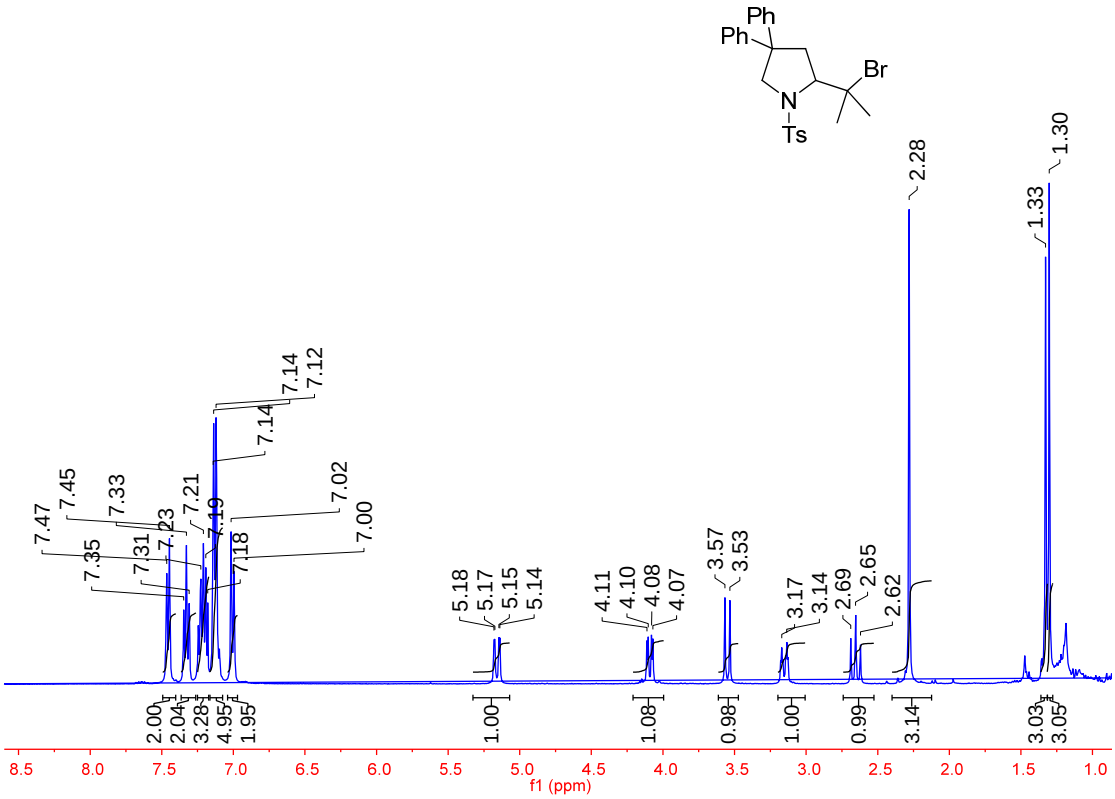
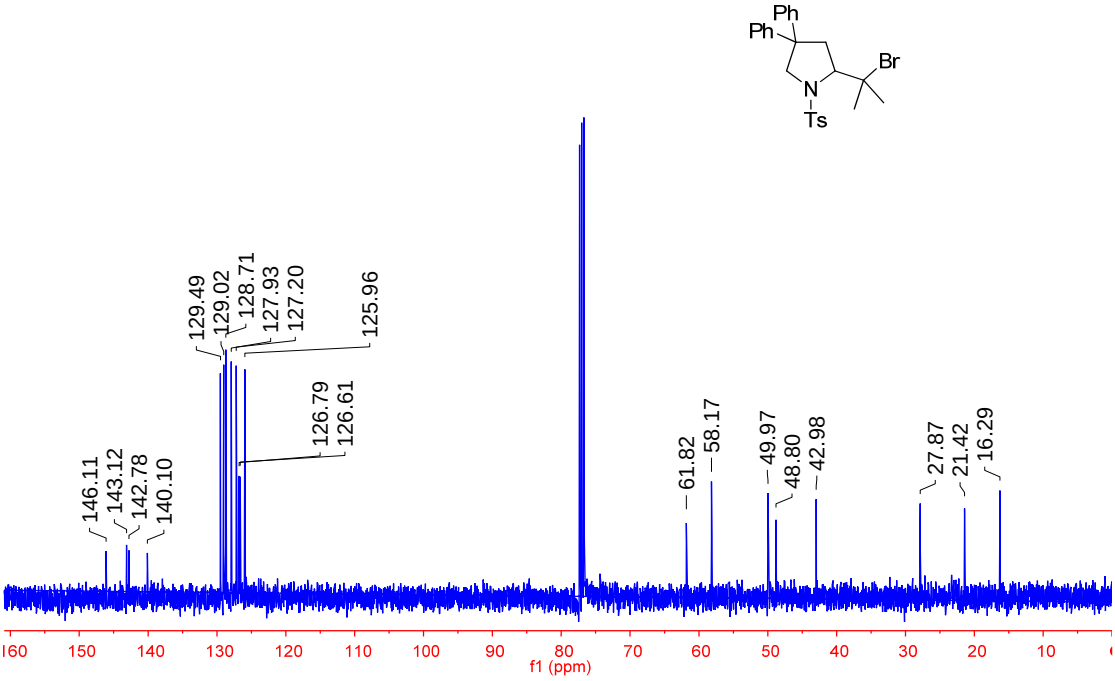
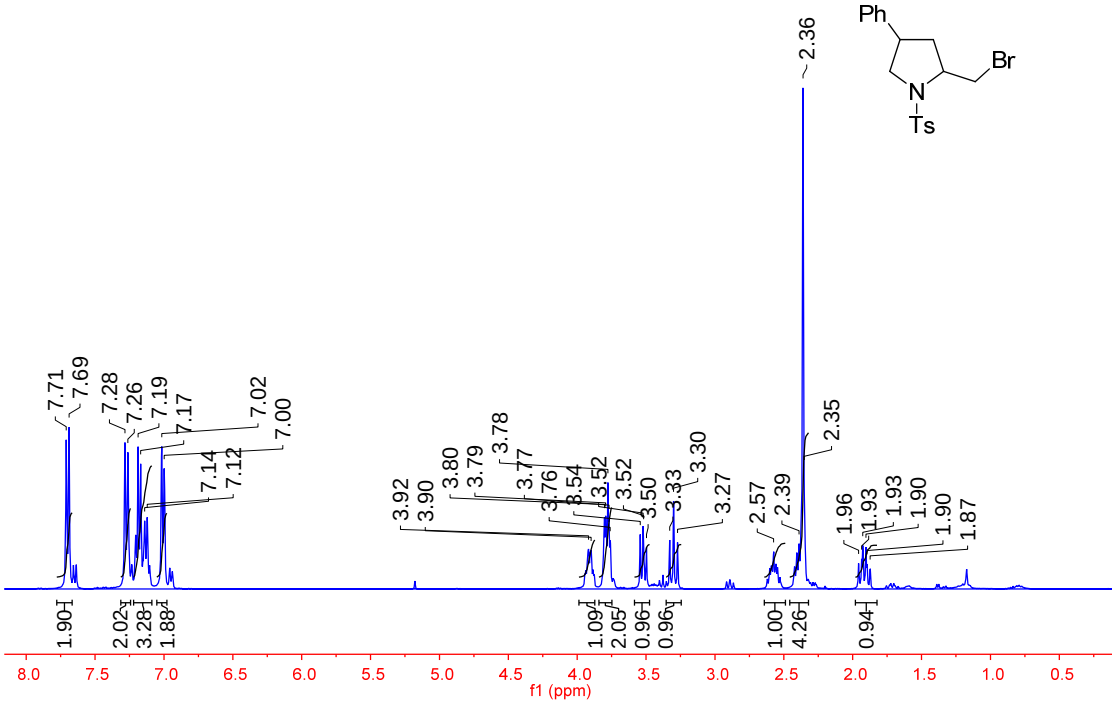
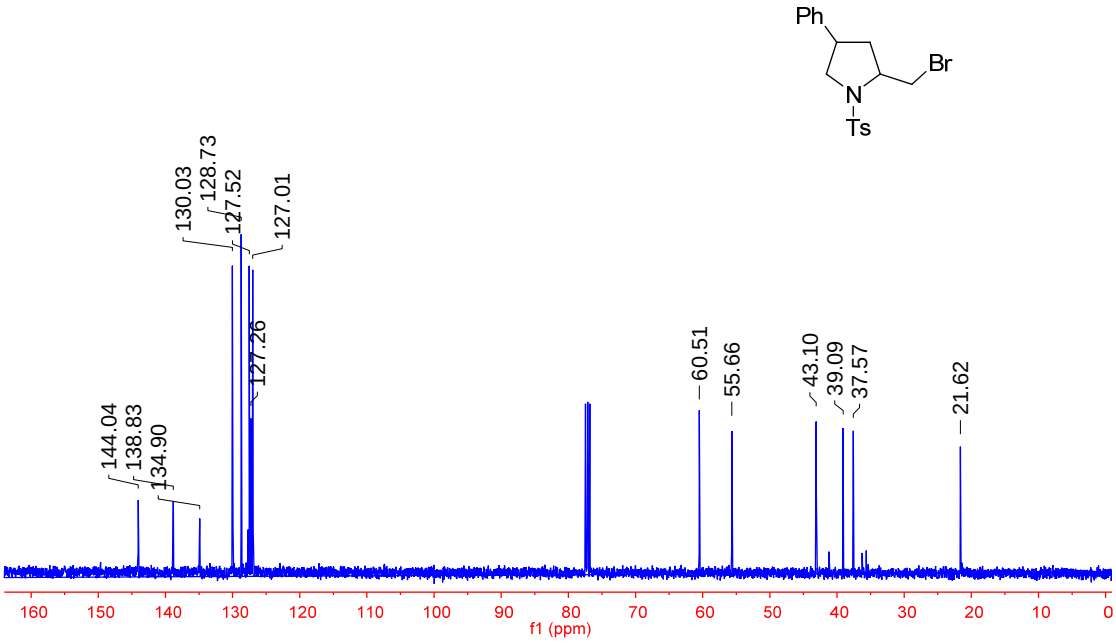
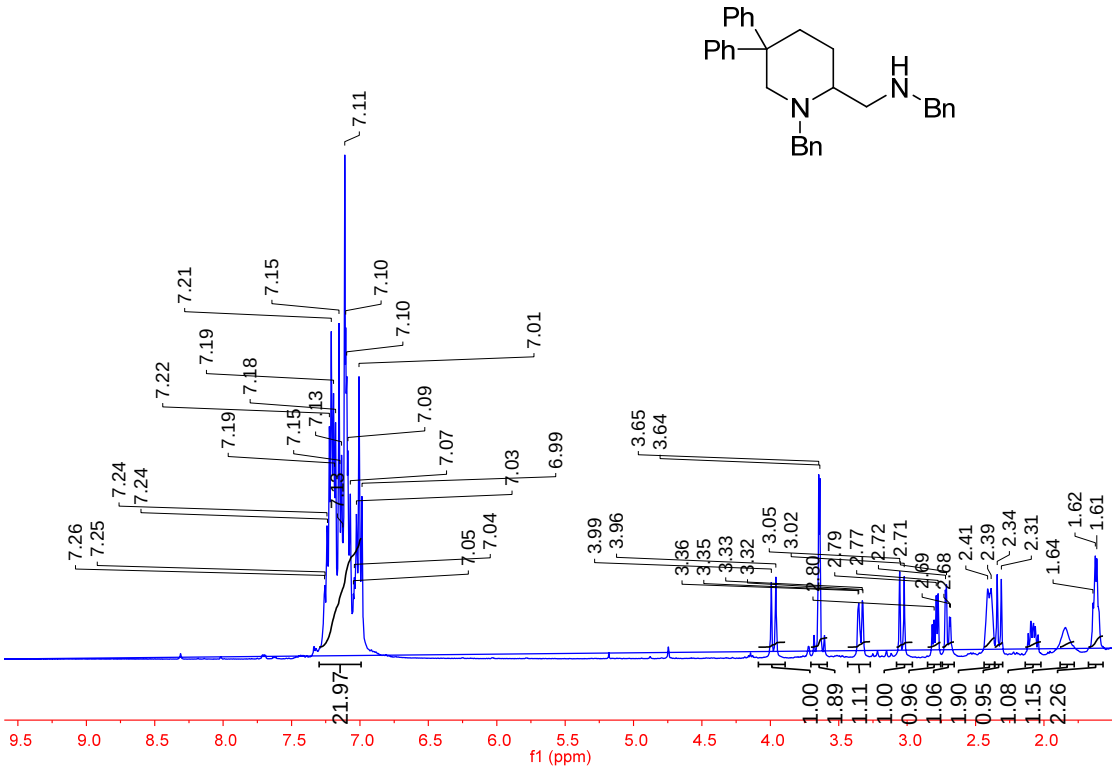
127.54
127.44
126.77
126.43
125.29
125.61
125.10
145.86
142.76
142.24
135.54
52.09
47.55
44.56
27.61
27.37
20.74
20.52
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

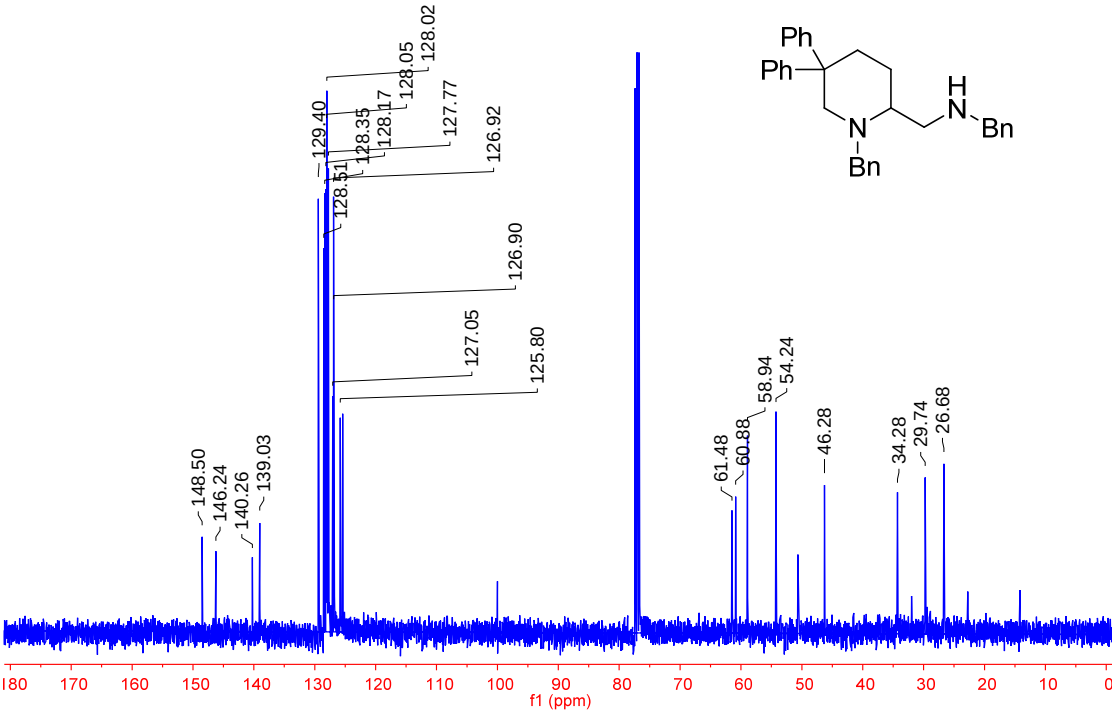

Ph
Ph
Br
N
Ts
7.47
7.45
7.35
7.33
7.31
7.23
7.21
7.19
7.18
7.14
7.14
7.12
7.02
7.00
5.18
5.17
5.15
5.14
4.11
4.10
4.08
4.07
3.57
3.53
3.17
3.14
2.69
2.65
2.62
2.28
1.33
1.30
2.00
2.04
3.28
4.95
1.95
1.00
1.08
0.98
1.00
0.99
3.14
3.03
3.05
f1 (ppm)

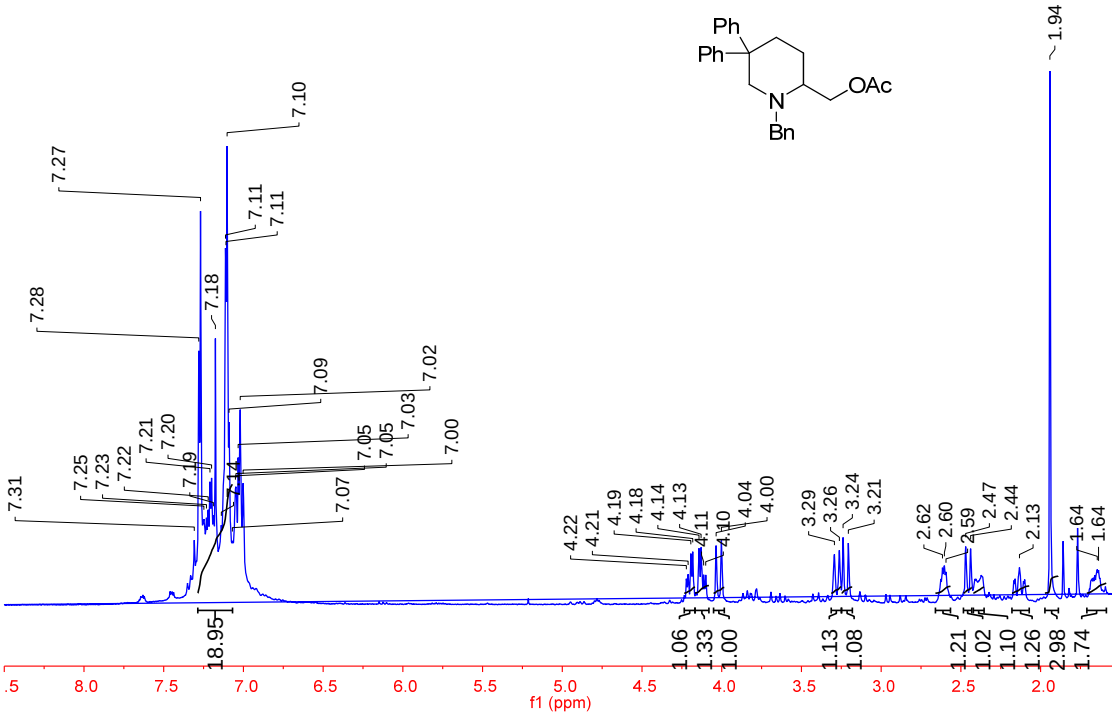

Ph
Ph
Br
N
Ts
146.11
143.12
142.78
140.10
129.49
129.02
128.71
127.93
127.20
125.96
126.79
126.61
61.82
58.17
49.97
48.80
42.98
27.87
21.42
16.29
f1 (ppm)


Ph
Br
N
Ts
2.36
7.71
7.69
7.28
7.26
7.19
7.17
7.02
7.00
7.14
7.12
3.92
3.90
3.80
3.79
3.78
3.77
3.76
3.54
3.52
3.52
3.50
3.33
3.30
3.27
2.57
2.39
2.35
1.96
1.93
1.93
1.90
1.90
1.87
1.90
2.02
3.28
1.88
1.09
2.05
0.96
0.96
1.00
4.26
0.94
f1 (ppm)


Ph
Br
N
Ts
130.03
128.73
127.52
127.01
127.26
144.04
138.83
134.90
60.51
55.66
43.10
39.09
37.57
21.62
f1 (ppm)


Ph
Ph
N
Bn
H
N
Bn
7.11
7.21
7.15
7.10
7.10
7.01
7.19
7.18
7.22
7.09
7.13
7.19
7.15
7.07
7.03
6.99
3.65
3.64
7.24
7.24
7.26
7.25
7.05
7.04
3.99
3.96
3.36
3.35
3.33
3.32
3.05
3.02
2.79
2.77
2.72
2.71
2.69
2.68
2.41
2.39
2.34
2.31
1.64
1.62
1.61
21.97
1.00
1.89
1.11
1.00
0.96
1.06
1.90
0.95
1.08
1.15
2.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


Ph
Ph
N
Bn
H
N
Bn
128.02
128.05
128.17
129.40
128.35
127.77
126.92
128.51
126.90
127.05
125.80
148.50
146.24
140.26
139.03
61.48
60.88
58.94
54.24
46.28
34.28
29.74
26.68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
Ph
N
Bn
OAc
1.94
7.10
7.27
7.11
7.11
7.28
7.18
7.09
7.02
7.03
7.21
7.20
7.05
7.05
7.00
7.25
7.23
7.22
7.19
7.14
7.31
7.07
4.22
4.21
4.19
4.18
4.14
4.13
4.11
4.10
4.04
4.00
3.29
3.26
3.24
3.21
2.62
2.60
2.59
2.47
2.44
2.13
1.64
1.64
18.95
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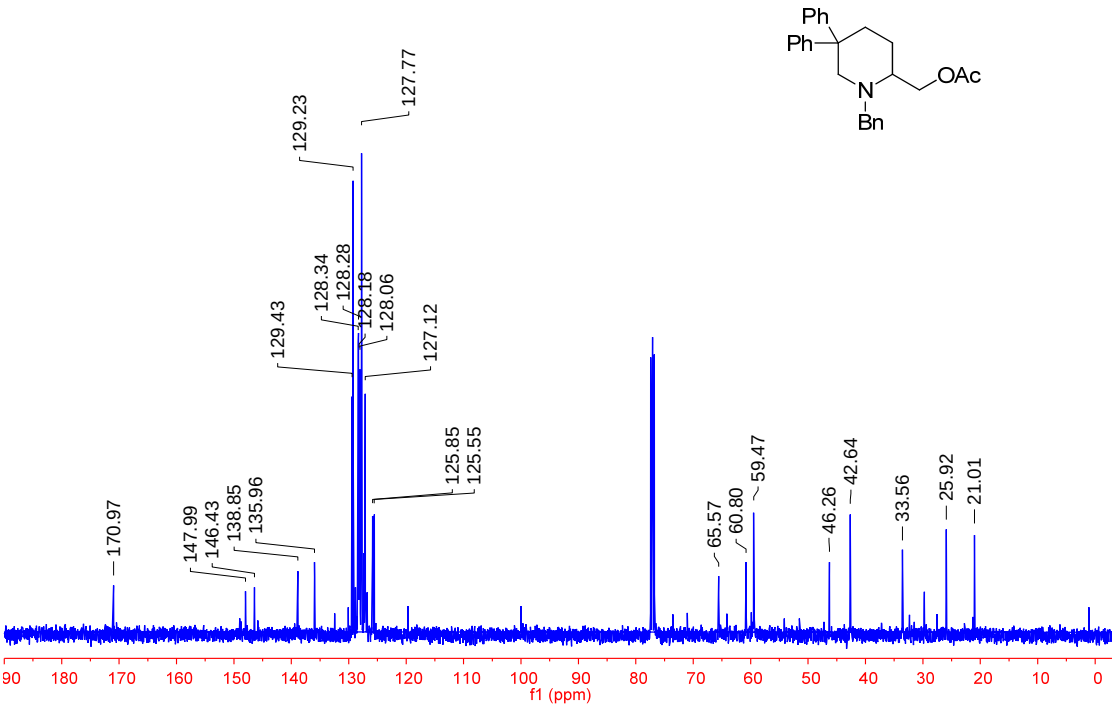
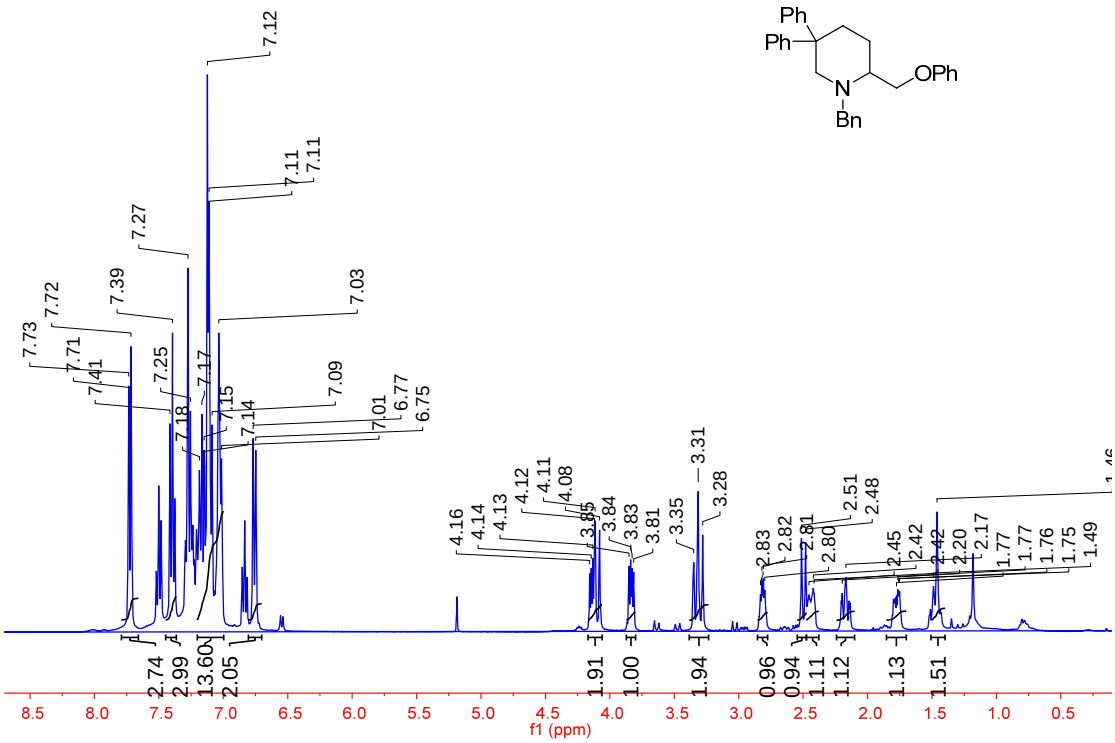
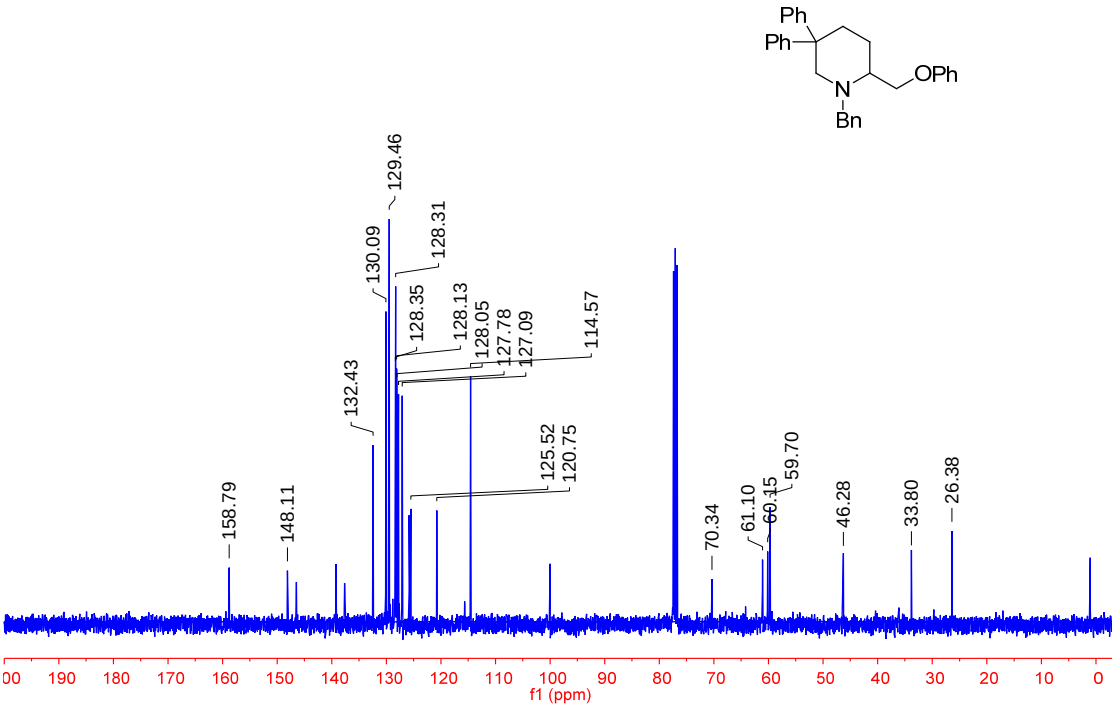
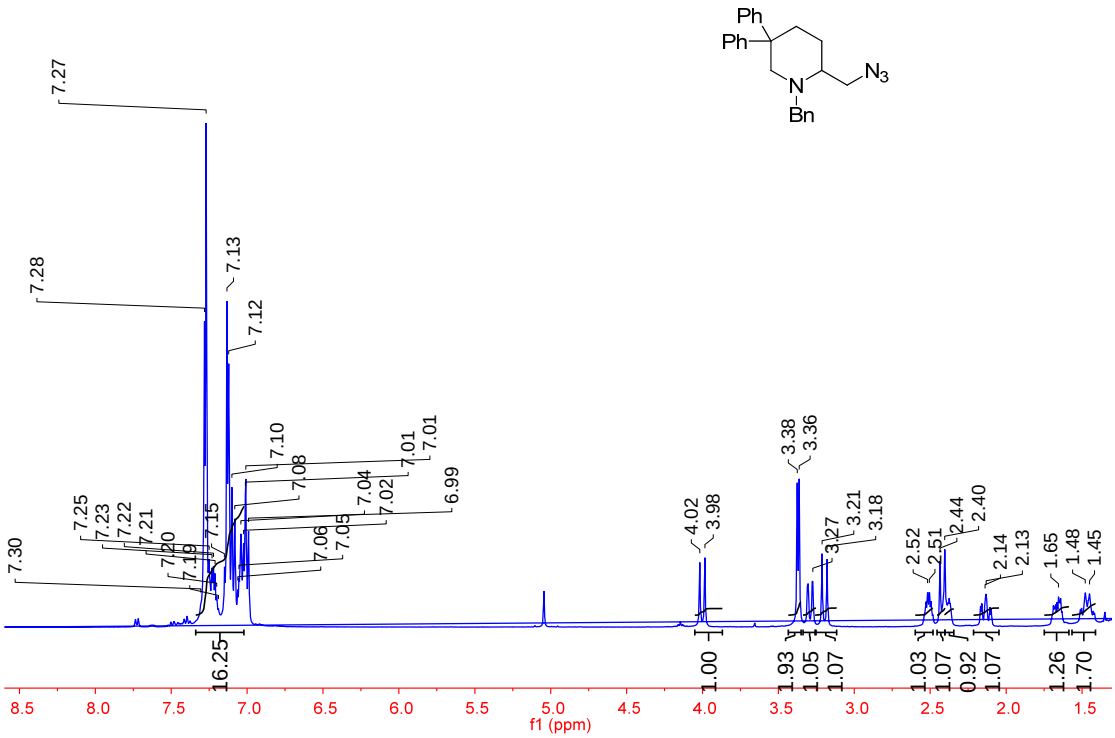
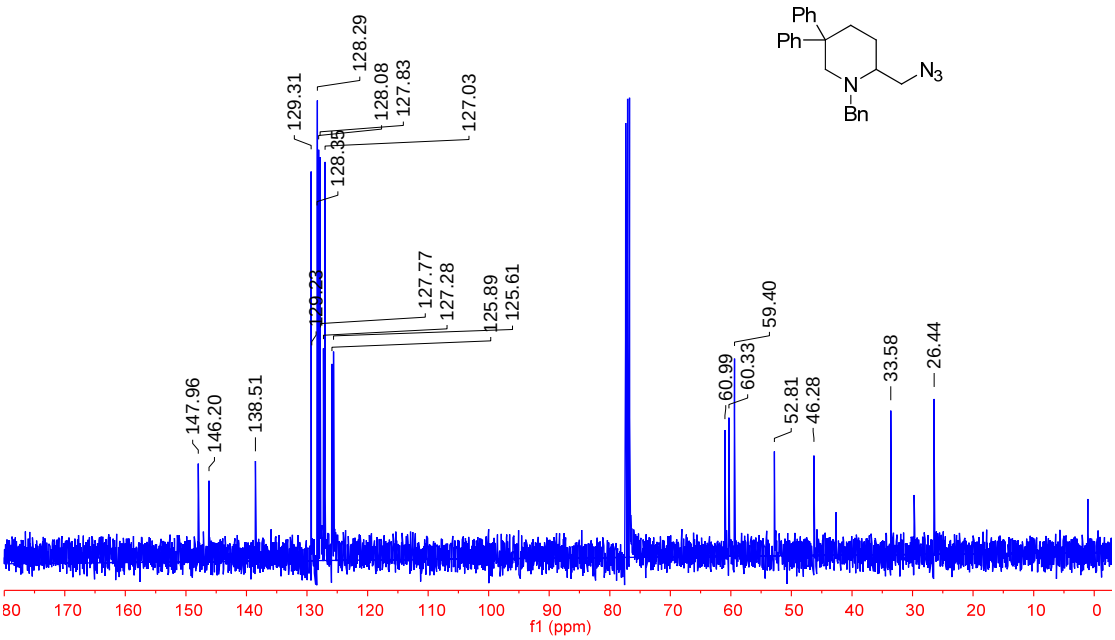
1.13
1.08
1.21
1.02
1.10
1.26
2.98
1.74
f1 (ppm)

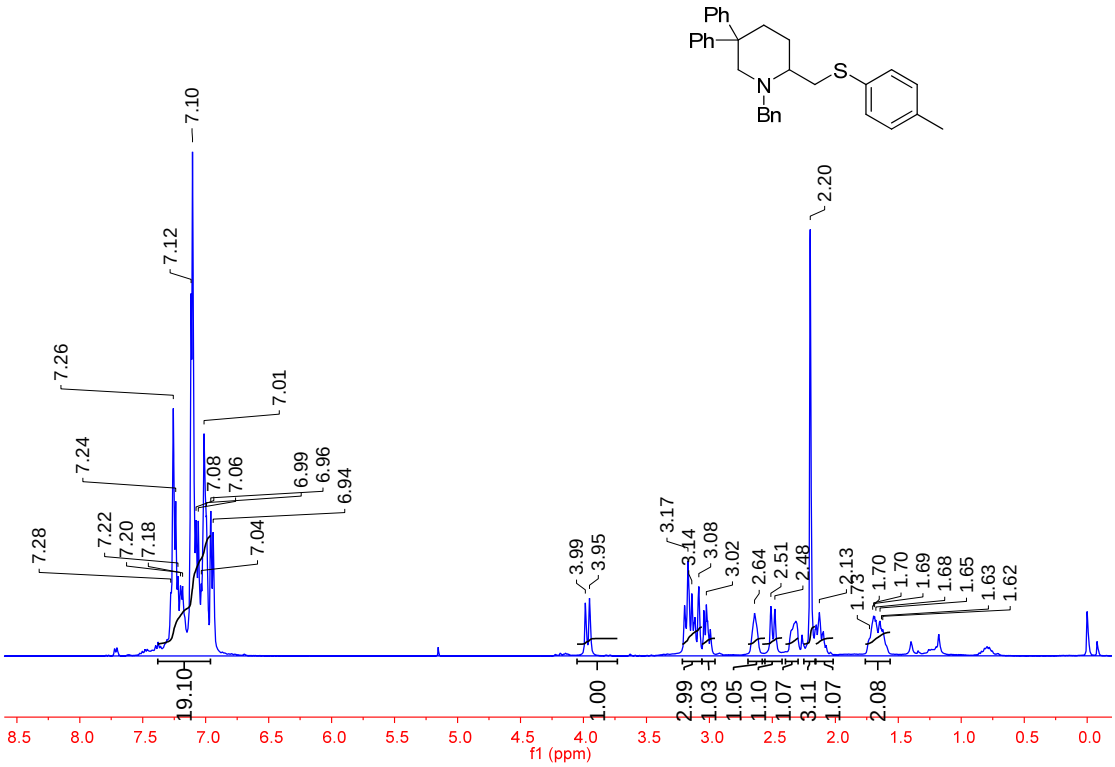

Ph
Ph
N
Bn
OAc
127.77
129.23
128.34
128.28
128.18
128.06
129.43
127.12
125.85
125.55
170.97
147.99
146.43
138.85
135.96
65.57
60.80
59.47
46.26
42.64
33.56
25.92
21.01
f1 (ppm)

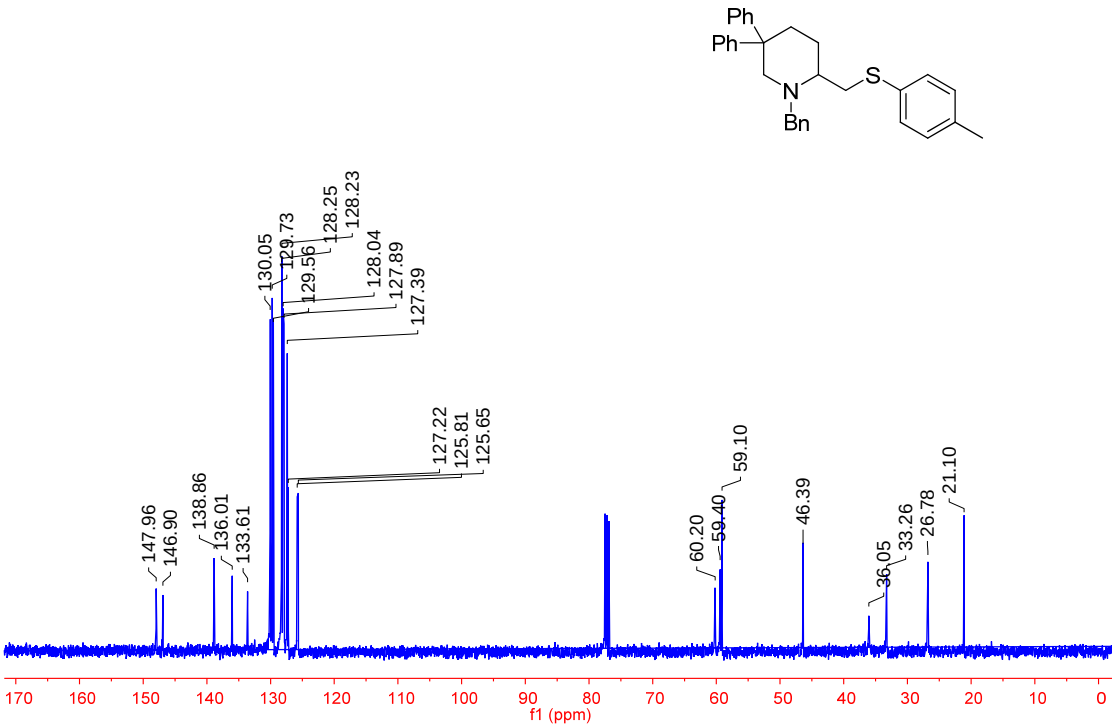

Ph
Ph
OPh
N
Bn
7.12
7.11
7.11
7.27
7.39
7.72
7.73
7.71
7.41
7.25
7.18
7.17
7.15
7.14
7.09
7.03
7.01
6.77
6.75
4.16
4.14
4.13
4.12
4.11
4.08
3.86
3.84
3.83
3.81
3.35
3.31
3.28
2.83
2.82
2.81
2.80
2.51
2.48
2.45
2.42
2.42
2.20
2.17
1.77
1.77
1.76
1.75
1.49
2.74
2.99
13.60
2.05
1.91
1.00
1.94
0.96
0.94
1.11
1.12
1.13
1.51
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

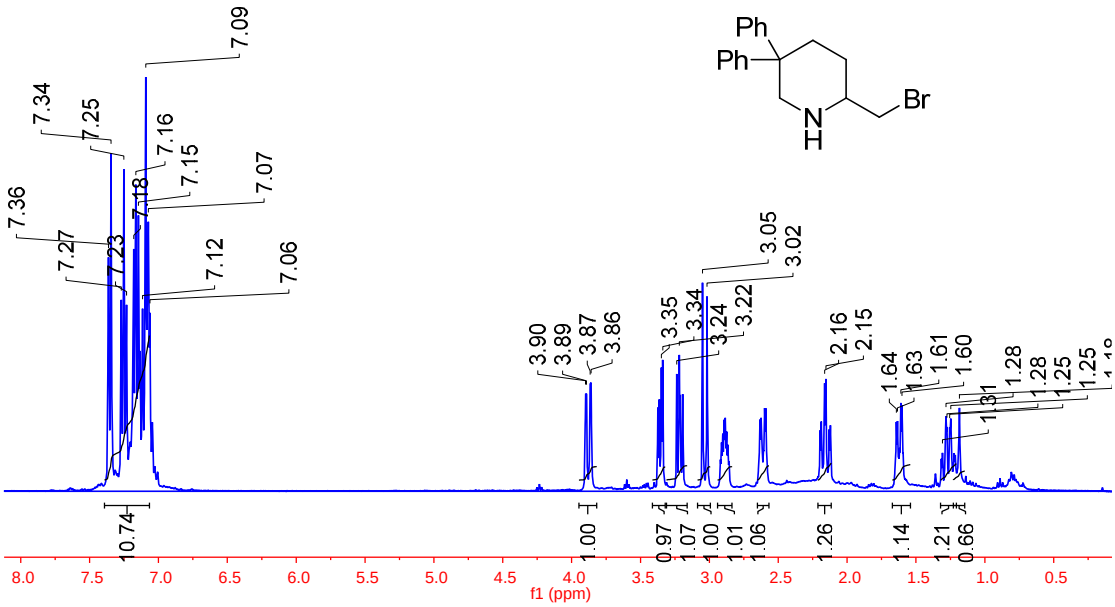

Ph
Ph
OPh
N
Bn
129.46
130.09
128.31
128.35
128.13
128.05
127.78
127.09
114.57
132.43
125.52
120.75
158.79
148.11
70.34
61.10
60.15
59.70
46.28
33.80
26.38
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

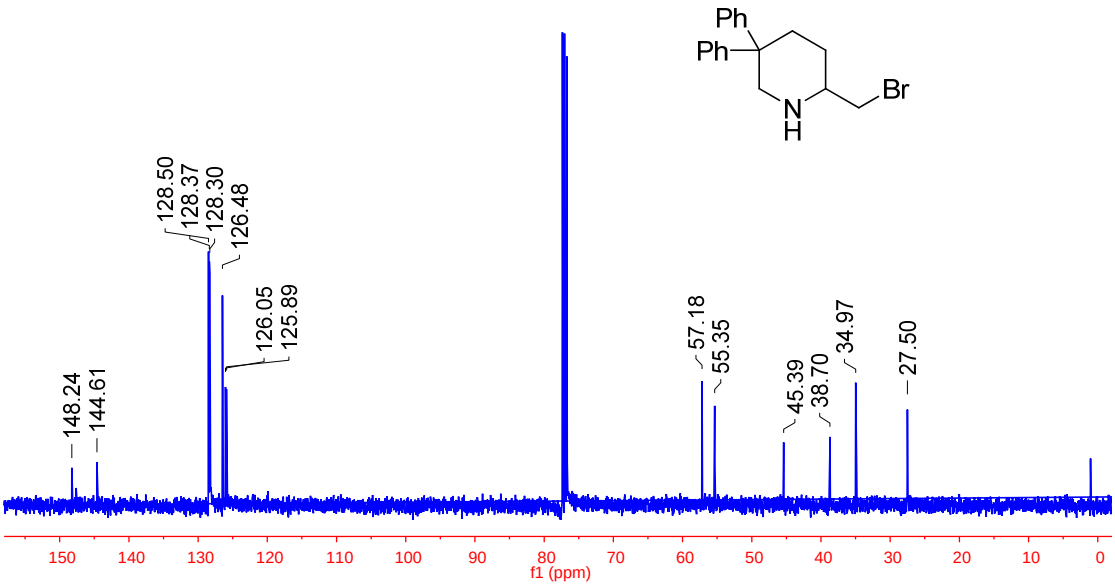

Ph
Ph
N
Bn
N3
7.27
7.28
7.13
7.12
7.10
7.08
7.01
7.01
7.04
7.02
6.99
7.25
7.23
7.22
7.21
7.20
7.19
7.15
7.06
7.05
7.30
4.02
3.98
3.38
3.36
3.27
3.21
3.18
2.52
2.51
2.44
2.40
2.14
2.13
1.65
1.48
1.45
16.25
1.00
1.93
1.05
1.07
1.03
1.07
0.92
1.07
1.26
1.70
f1 (ppm)

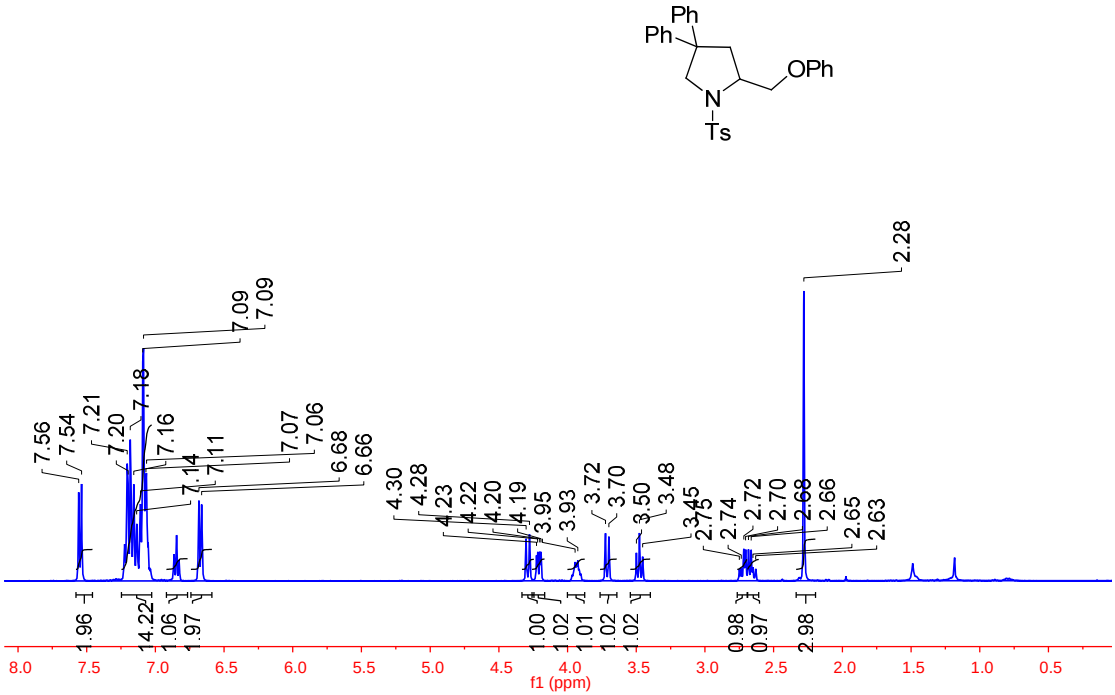

Ph
Ph
N
Bn
N3
128.29
129.31
128.08
127.83
127.03
128.35
127.77
127.28
125.89
125.61
120.23
147.96
146.20
138.51
59.40
60.99
60.33
52.81
46.28
33.58
26.44
f1 (ppm)

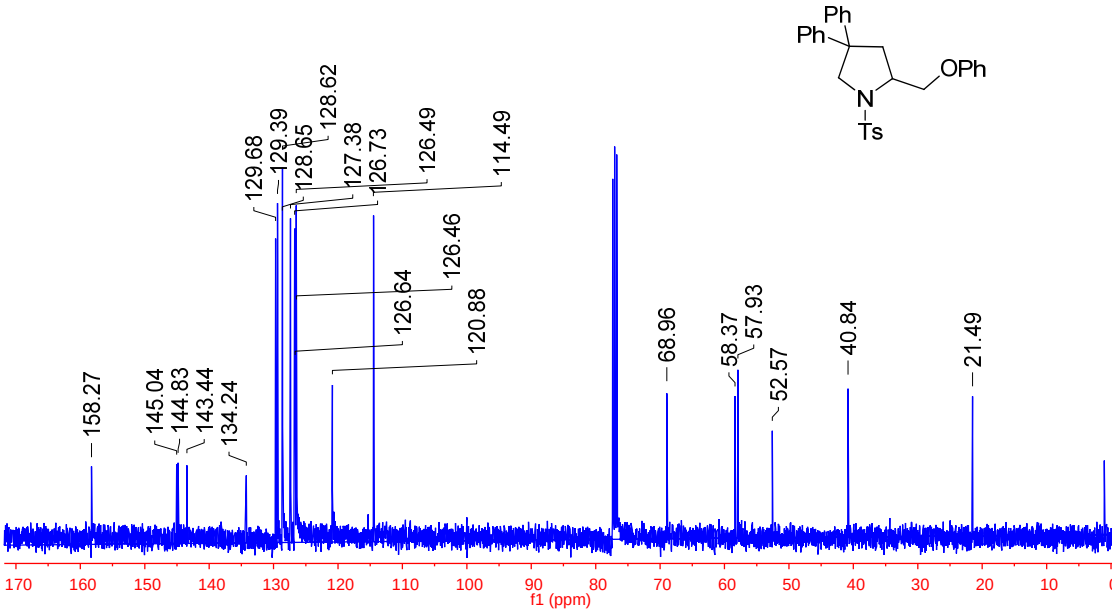

Ph
Ph
N
Bn
S
7.10
7.12
7.26
7.01
7.24
7.08
7.06
6.99
6.96
6.94
7.28
7.22
7.20
7.18
7.04
3.99
3.95
3.17
3.14
3.08
3.02
2.64
2.51
2.48
2.20
2.13
1.73
1.70
1.70
1.69
1.68
1.65
1.63
1.62
19.10
1.00
2.99
1.03
1.05
1.10
1.07
3.11
1.07
2.08
f1 (ppm)

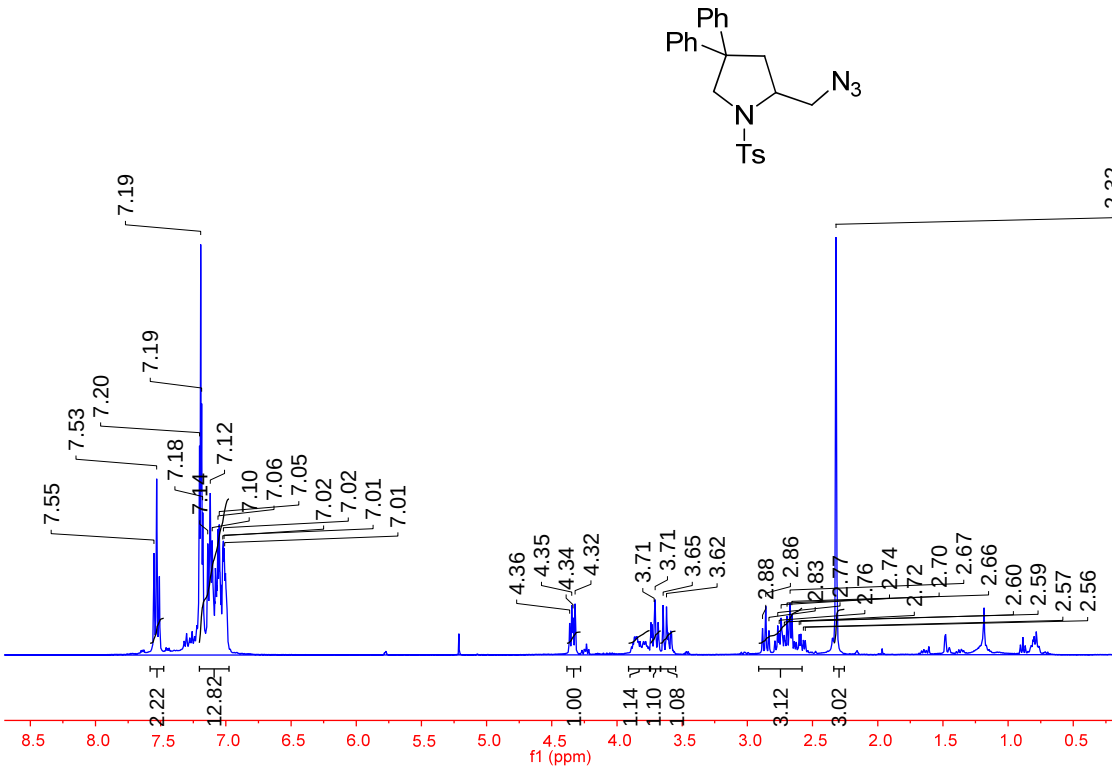

Ph
Ph
N
Bn
S
130.05
129.73
129.56
128.25
128.23
128.04
127.89
127.39
127.22
125.81
125.65
147.96
146.90
138.86
136.01
133.61
60.20
59.40
59.10
46.39
36.05
33.26
26.78
21.10
f1 (ppm)

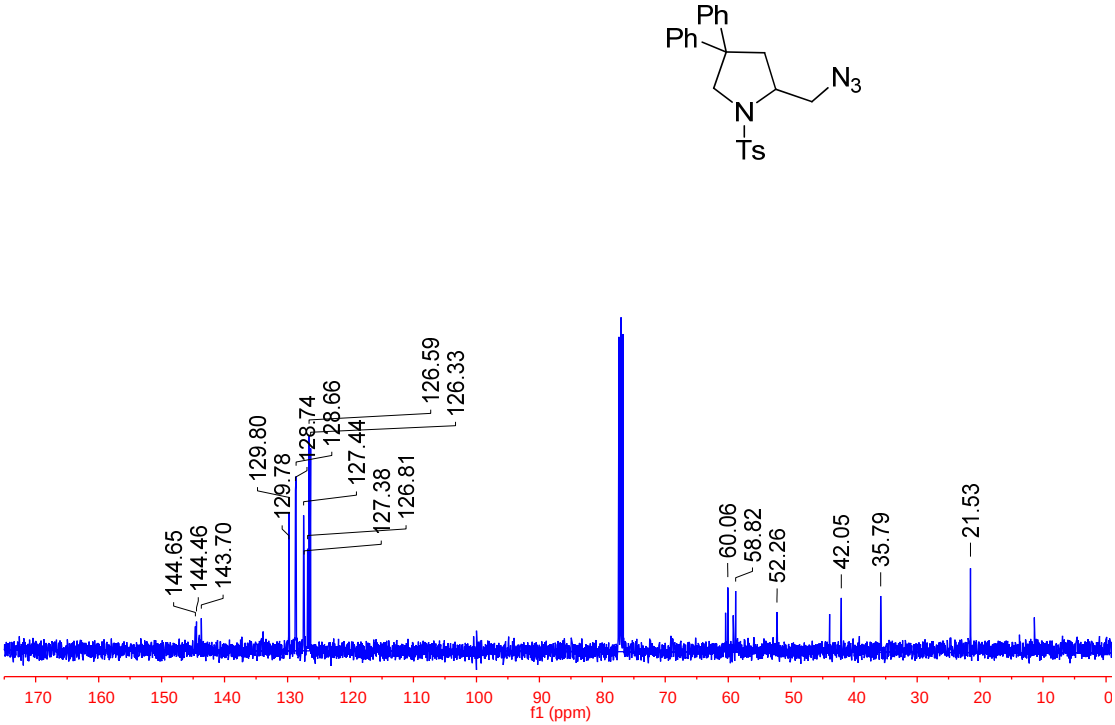

Ph
Ph
N
H
Br
7.09
7.34
7.25
7.16
7.15
7.07
7.36
7.27
7.23
7.18
7.12
7.06
3.90
3.89
3.87
3.86
3.35
3.34
3.24
3.22
3.05
3.02
2.16
2.15
1.64
1.63
1.61
1.60
1.28
1.25
10.74
1.00
0.97
1.07
1.00
1.01
1.06
1.26
1.14
1.21
0.66
f1 (ppm)

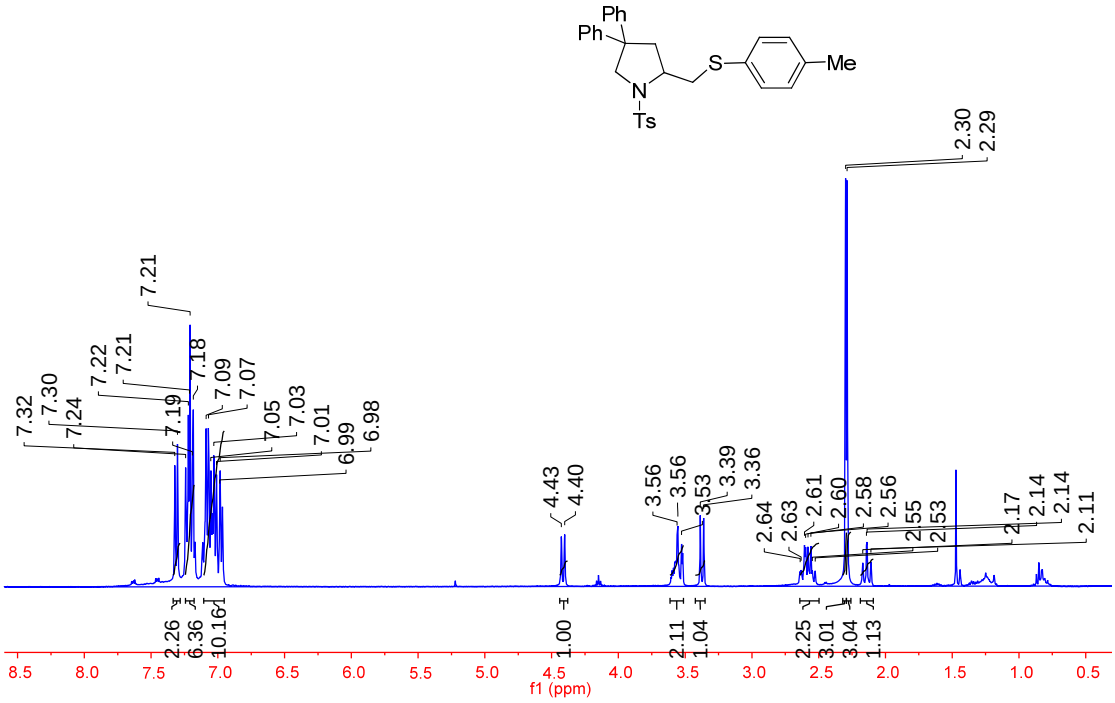

Ph
Ph
N
H
Br
128.50
128.37
128.30
126.48
126.05
125.89
148.24
144.61
57.18
55.35
45.39
38.70
34.97
27.50
f1 (ppm)

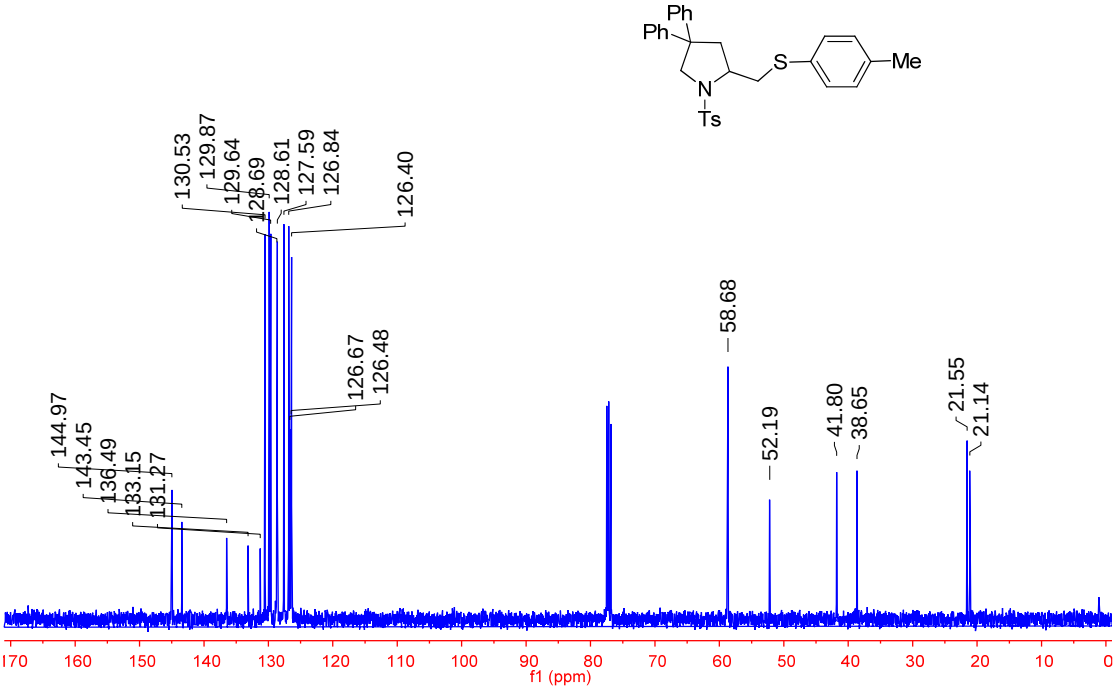

Ph
Ph
OPh
N
Ts
2.28
7.09
7.09
7.56
7.54
7.21
7.20
7.18
7.16
7.14
7.11
7.07
7.06
6.68
6.66
4.30
4.28
4.23
4.22
4.20
4.19
3.95
3.93
3.72
3.70
3.50
3.48
3.45
2.75
2.74
2.72
2.70
2.68
2.66
2.65
2.63
1.96
14.22
1.06
1.97
1.00
1.02
1.01
1.02
1.02
0.98
0.97
2.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

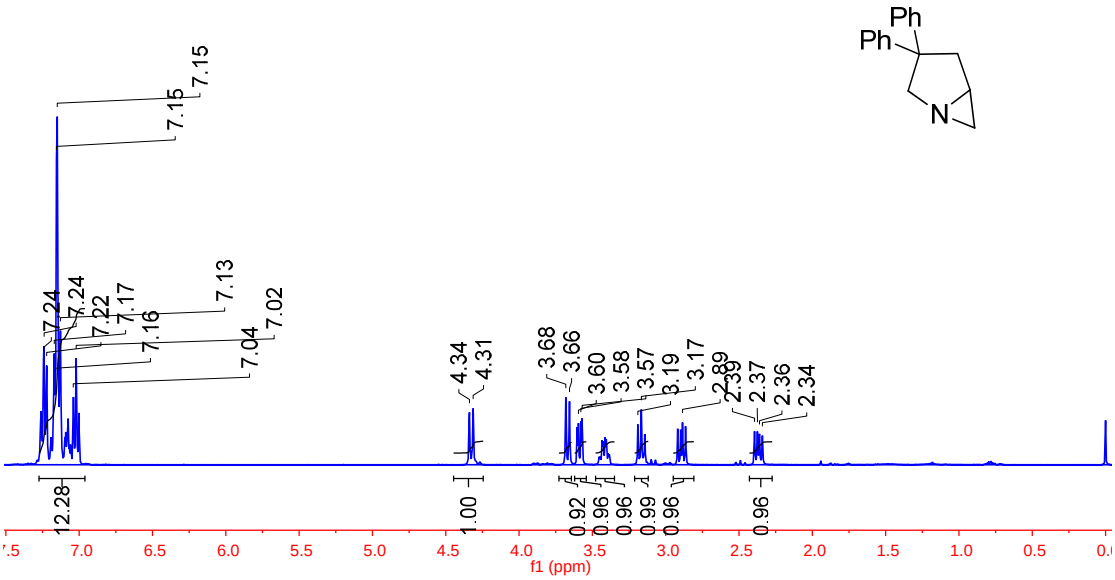

Ph
Ph
OPh
N
Ts
129.68
129.39
128.65
128.62
127.38
126.73
126.49
114.49
126.46
126.64
120.88
158.27
145.04
144.83
143.44
134.24
68.96
58.37
57.93
52.57
40.84
21.49
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

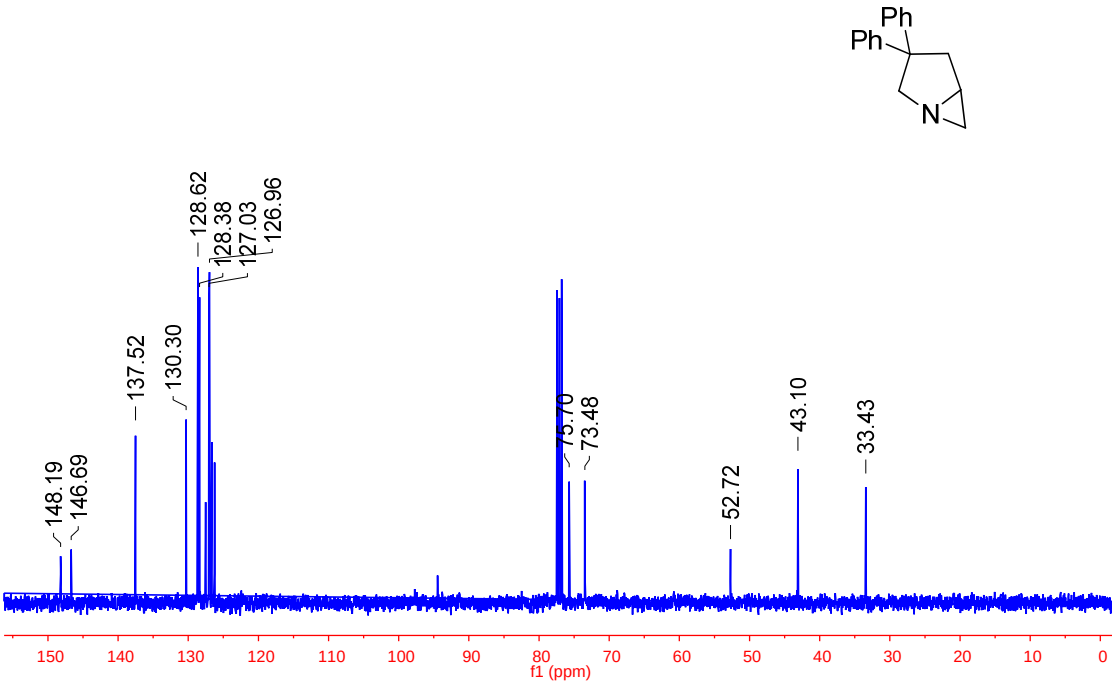

Ph
Ph
N3
N
Ts
7.19
7.19
7.20
7.53
7.18
7.12
7.10
7.06
7.05
7.02
7.02
7.01
7.01
7.55
4.36
4.35
4.34
4.32
3.71
3.71
3.65
3.62
2.88
2.86
2.83
2.77
2.76
2.74
2.72
2.70
2.67
2.66
2.60
2.59
2.57
2.56
2.22
12.82
1.00
1.14
1.10
1.08
3.12
3.02
f1 (ppm)


Ph
Ph
N3
N
Ts
126.59
126.33
129.80
128.74
128.66
129.78
127.44
127.38
126.81
144.65
144.46
143.70
60.06
58.82
52.26
42.05
35.79
21.53
f1 (ppm)


Ph
Ph
S
Me
N
Ts
7.32
7.30
7.24
7.22
7.21
7.21
7.19
7.18
7.09
7.07
7.05
7.03
7.01
6.99
6.98
4.43
4.40
3.56
3.56
3.53
3.39
3.36
2.64
2.63
2.61
2.60
2.58
2.56
2.55
2.53
2.30
2.29
2.17
2.14
2.14
2.11
2.26
6.36
10.16
1.00
2.11
1.04
2.25
3.01
3.04
1.13
f1 (ppm)


Ph
Ph
S
Me
N
Ts
130.53
129.87
129.64
128.69
128.61
127.59
126.84
126.40
126.67
126.48
144.97
143.45
136.49
133.15
131.27
58.68
52.19
41.80
38.65
21.55
21.14
f1 (ppm)


Ph
Ph
N
7.15
7.15
7.24
7.24
7.22
7.17
7.16
7.13
7.04
7.02
4.34
4.31
3.68
3.66
3.60
3.58
3.57
3.19
3.17
2.39
2.37
2.36
2.34
12.28
1.00
0.92
0.96
0.96
0.99
0.96
0.96
f1 (ppm)


Ph
Ph
N
148.19
146.69
137.52
130.30
128.62
128.38
127.03
126.96
75.70
73.48
52.72
43.10
33.43
f1 (ppm)

8. X-ray Crystal Structure and Data of 5b

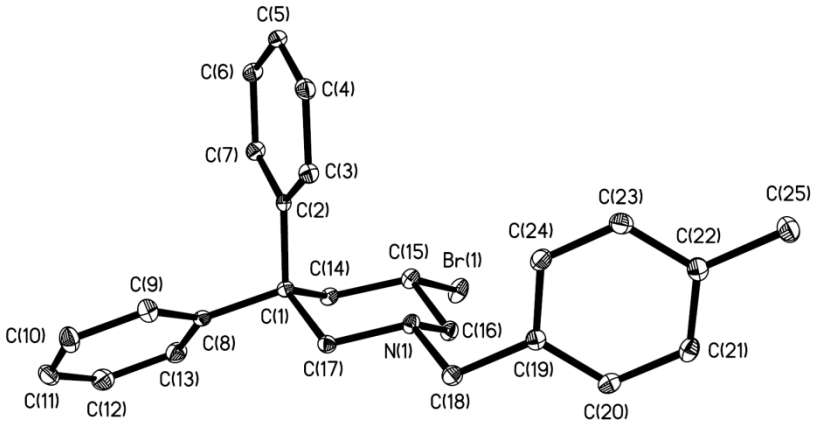


Figure 1. ORTEP drawing of **5b**

Table 6. Crystal data and structure refinement

Properties	Data
Empiritical	$C_{25}H_{26}BrN$
Formula weight	420.38
Temperature	113(2)
Wave length	0.71073A
Cell length a	12.021(3)A
Cell length b	10.387(3)A
Cell length c	16.401(4)A
Cell angle alpha	90.00
Cell angle beta	92.093(4)
Cell angle gamma	90.00
Cell volume	2046.5(9)
Cell formula units Z	4
Crystal Size	0.20 x 0.18 x 0.12

Table 7. Atomic coordination and equivalent isotropic displacement parameter

	X	Y	Z	U(eq)
Br(1)	221(1)	7543(1)	592(1)	27(1)
N(1)	2099(1)	5211(1)	2179(1)	16(1)
C(1)	2622(1)	7460(1)	2573(1)	14(1)
C(2)	3726(1)	7479(1)	2127(1)	14(1)
C(3)	4416(1)	6408(1)	2072(1)	18(1)

C(4)	5414(1)	6476(2)	1667(1)	20(1)
C(5)	5730(1)	7610(1)	1299(1)	20(1)
C(6)	5058(1)	8692(2)	1362(1)	21(1)
C(7)	4070(1)	8630(1)	1776(1)	19(1)
C(8)	2763(1)	8287(1)	3349(1)	16(1)
C(9)	3647(1)	8012(2)	3899(1)	21(1)
C(10)	3800(2)	8681(1)	4626(1)	26(1)
C(11)	3064(2)	9655(2)	4819(1)	26(1)
C(12)	2196(1)	9955(2)	4279(1)	29(1)
C(13)	2043(1)	9277(1)	3550(1)	24(1)
C(14)	1664(1)	7936(2)	1997(1)	17(1)
C(15)	1466(1)	6972(2)	1313(1)	18(1)
C(16)	1182(1)	5649(1)	1638(1)	19(1)
C(17)	2292(1)	6100(1)	2858(1)	16(1)
C(18)	1896(1)	3900(1)	2477(1)	19(1)
C(19)	2035(1)	2900(1)	1823(1)	17(1)
C(20)	1161(1)	2106(2)	1566(1)	20(1)
C(21)	1312(1)	1167(1)	971(1)	21(1)
C(22)	2330(1)	1012(1)	615(1)	20(1)
C(23)	3208(1)	1815(1)	877(1)	22(1)
C(24)	3066(1)	2736(1)	1476(1)	20(1)
C(25)	2486(2)	10(2)	-37(1)	29(1)

Table 8. Bond lengths

Br(1)-C(15)	1.9646(14)
N(1)-C(17)	1.4583(17)
N(1)-C(16)	1.4621(18)
N(1)-C(18)	1.4696(17)
C(1)-C(2)	1.539(2)
C(1)-C(8)	1.5393(19)
C(1)-C(17)	1.5444(18)
C(1)-C(14)	1.5445(19)
C(2)-C(3)	1.3928(19)
C(2)-C(7)	1.3965(19)
C(3)-C(4)	1.394(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.383(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(2)
C(5)-H(5)	0.9500

C(6)-C(7)	1.391(2)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(13)	1.392(2)
C(8)-C(9)	1.397(2)
C(9)-C(10)	1.386(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.388(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.379(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.394(2)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-C(15)	1.516(2)
C(14)-H(14A)	0.9900

C(14)-H(14B)	0.9900
C(15)-C(16)	1.517(2)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.507(2)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.389(2)
C(19)-C(24)	1.393(2)
C(20)-C(21)	1.396(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.385(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.400(2)
C(22)-C(25)	1.509(2)
C(23)-C(24)	1.387(2)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(17)-N(1)-C(16)	111.15(11)
C(17)-N(1)-C(18)	110.89(11)
C(16)-N(1)-C(18)	111.05(11)
C(2)-C(1)-C(8)	108.35(11)
C(2)-C(1)-C(17)	113.00(11)
C(8)-C(1)-C(17)	106.42(11)
C(2)-C(1)-C(14)	110.00(12)
C(8)-C(1)-C(14)	112.63(11)
C(17)-C(1)-C(14)	106.47(11)
C(3)-C(2)-C(7)	118.12(14)
C(3)-C(2)-C(1)	123.14(12)
C(7)-C(2)-C(1)	118.73(12)
C(2)-C(3)-C(4)	120.98(14)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	120.44(14)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8

C(4)-C(5)-C(6)	119.10(15)
C(4)-C(5)-H(5)	120.5
C(6)-C(5)-H(5)	120.5
C(5)-C(6)-C(7)	120.50(14)
C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7
C(6)-C(7)-C(2)	120.82(14)
C(6)-C(7)-H(7)	119.6
C(2)-C(7)-H(7)	119.6
C(13)-C(8)-C(9)	117.59(14)
C(13)-C(8)-C(1)	123.85(13)
C(9)-C(8)-C(1)	118.54(13)
C(10)-C(9)-C(8)	121.77(15)
C(10)-C(9)-H(9)	119.1
C(8)-C(9)-H(9)	119.1
C(9)-C(10)-C(11)	119.77(16)
C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	120.1
C(12)-C(11)-C(10)	119.37(15)
C(12)-C(11)-H(11)	120.3
C(10)-C(11)-H(11)	120.3
C(11)-C(12)-C(13)	120.71(15)
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-H(12)	119.6
C(8)-C(13)-C(12)	120.78(15)
C(8)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(15)-C(14)-C(1)	109.55(12)
C(15)-C(14)-H(14A)	109.8
C(1)-C(14)-H(14A)	109.8
C(15)-C(14)-H(14B)	109.8
C(1)-C(14)-H(14B)	109.8
H(14A)-C(14)-H(14B)	108.2
C(14)-C(15)-C(16)	111.70(12)
C(14)-C(15)-Br(1)	109.95(10)
C(16)-C(15)-Br(1)	108.02(10)
C(14)-C(15)-H(15)	109.0
C(16)-C(15)-H(15)	109.0
Br(1)-C(15)-H(15)	109.0
N(1)-C(16)-C(15)	108.73(11)
N(1)-C(16)-H(16A)	109.9
C(15)-C(16)-H(16A)	109.9
N(1)-C(16)-H(16B)	109.9

C(15)-C(16)-H(16B)	109.9
H(16A)-C(16)-H(16B)	108.3
N(1)-C(17)-C(1)	112.61(11)
N(1)-C(17)-H(17A)	109.1
C(1)-C(17)-H(17A)	109.1
N(1)-C(17)-H(17B)	109.1
C(1)-C(17)-H(17B)	109.1
H(17A)-C(17)-H(17B)	107.8
N(1)-C(18)-C(19)	112.19(12)
N(1)-C(18)-H(18A)	109.2
C(19)-C(18)-H(18A)	109.2
N(1)-C(18)-H(18B)	109.2
C(19)-C(18)-H(18B)	109.2
H(18A)-C(18)-H(18B)	107.9
C(20)-C(19)-C(24)	118.56(14)
C(20)-C(19)-C(18)	121.54(14)
C(24)-C(19)-C(18)	119.88(14)
C(19)-C(20)-C(21)	120.69(15)
C(19)-C(20)-H(20)	119.7

C(21)-C(20)-H(20)	119.7
C(22)-C(21)-C(20)	121.04(14)
C(22)-C(21)-H(21)	119.5
C(20)-C(21)-H(21)	119.5
C(21)-C(22)-C(23)	118.01(13)
C(21)-C(22)-C(25)	120.90(14)
C(23)-C(22)-C(25)	121.09(14)
C(24)-C(23)-C(22)	121.12(14)
C(24)-C(23)-H(23)	119.4
C(22)-C(23)-H(23)	119.4
C(23)-C(24)-C(19)	120.57(14)
C(23)-C(24)-H(24)	119.7
C(19)-C(24)-H(24)	119.7
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Table 9. Anisotropic displacement parameters

	U11	U22	U33	U23	U13	U12
Br(1)	24(1)	24(1)	30(1)	6(1)	-13(1)	-2(1)
N(1)	18(1)	12(1)	17(1)	2(1)	-2(1)	-2(1)
C(1)	12(1)	14(1)	15(1)	1(1)	0(1)	1(1)
C(2)	14(1)	16(1)	12(1)	-1(1)	-1(1)	-1(1)
C(3)	18(1)	18(1)	19(1)	0(1)	0(1)	1(1)
C(4)	17(1)	24(1)	20(1)	-4(1)	0(1)	3(1)
C(5)	14(1)	29(1)	18(1)	-5(1)	2(1)	-4(1)
C(6)	23(1)	21(1)	21(1)	2(1)	3(1)	-6(1)
C(7)	17(1)	17(1)	22(1)	0(1)	1(1)	0(1)
C(8)	17(1)	14(1)	16(1)	1(1)	3(1)	-3(1)
C(9)	26(1)	17(1)	19(1)	1(1)	-1(1)	3(1)
C(10)	37(1)	23(1)	19(1)	1(1)	-4(1)	-3(1)
C(11)	39(1)	23(1)	18(1)	-3(1)	8(1)	-8(1)
C(12)	27(1)	25(1)	35(1)	-11(1)	11(1)	0(1)
C(13)	19(1)	22(1)	30(1)	-3(1)	3(1)	0(1)
C(14)	14(1)	16(1)	19(1)	2(1)	-1(1)	0(1)
C(15)	15(1)	19(1)	19(1)	3(1)	-5(1)	1(1)
C(16)	17(1)	20(1)	19(1)	0(1)	-2(1)	-2(1)
C(17)	16(1)	16(1)	15(1)	1(1)	1(1)	0(1)
C(18)	24(1)	14(1)	19(1)	2(1)	3(1)	-2(1)

C(19)	21(1)	13(1)	16(1)	3(1)	0(1)	1(1)
C(20)	19(1)	19(1)	23(1)	3(1)	2(1)	-2(1)
C(21)	23(1)	16(1)	22(1)	2(1)	-4(1)	-3(1)
C(22)	27(1)	16(1)	16(1)	3(1)	0(1)	0(1)
C(23)	22(1)	21(1)	22(1)	1(1)	5(1)	1(1)
C(24)	20(1)	20(1)	21(1)	1(1)	0(1)	-4(1)
C(25)	39(1)	26(1)	22(1)	-5(1)	6(1)	-5(1)

Table 10. Hydrogen coordinates and isotropic displacement parameters

	X	Y	Z	U(eq)
H(3)	4203	5618	2314	21
H(4)	5879	5739	1643	24
H(5)	6398	7648	1007	24
H(6)	5276	9480	1122	26
H(7)	3623	9379	1819	22
H(9)	4156	7350	3771	25
H(10)	4406	8473	4990	32
H(11)	3158	10112	5319	32
H(12)	1698	10629	4406	35
H(13)	1439	9495	3185	29
H(14A)	977	8038	2306	20
H(14B)	1858	8784	1766	20
H(15)	2153	6907	990	21
H(16A)	486	5692	1942	22
H(16B)	1068	5037	1180	22
H(17A)	2891	5754	3225	19
H(17B)	1607	6161	3172	19
H(18A)	1131	3849	2678	23
H(18B)	2421	3713	2941	23
H(20)	453	2203	1797	24
H(21)	707	626	808	25
H(23)	3914	1727	640	26
H(24)	3677	3259	1651	24
H(25A)	2030	-747	77	43
H(25B)	3272	-242	-41	43
H(25C)	2257	366	-571	43

Table 11. Torsion angles

C(8)-C(1)-C(2)-C(3)	110.58(15)
C(17)-C(1)-C(2)-C(3)	-7.1(2)
C(14)-C(1)-C(2)-C(3)	-125.91(14)

C(8)-C(1)-C(2)-C(7)	-67.92(16)
C(17)-C(1)-C(2)-C(7)	174.42(12)
C(14)-C(1)-C(2)-C(7)	55.59(17)

C(7)-C(2)-C(3)-C(4)	-0.9(2)
C(1)-C(2)-C(3)-C(4)	-179.43(14)
C(2)-C(3)-C(4)-C(5)	-1.0(2)
C(3)-C(4)-C(5)-C(6)	2.2(2)
C(4)-C(5)-C(6)-C(7)	-1.3(2)
C(5)-C(6)-C(7)-C(2)	-0.7(2)
C(3)-C(2)-C(7)-C(6)	1.8(2)
C(1)-C(2)-C(7)-C(6)	-179.65(13)
C(2)-C(1)-C(8)-C(13)	127.76(14)
C(17)-C(1)-C(8)-C(13)	-110.44(15)
C(14)-C(1)-C(8)-C(13)	5.85(19)
C(2)-C(1)-C(8)-C(9)	-54.04(16)
C(17)-C(1)-C(8)-C(9)	67.75(16)
C(14)-C(1)-C(8)-C(9)	-175.95(12)
C(13)-C(8)-C(9)-C(10)	1.0(2)
C(1)-C(8)-C(9)-C(10)	-177.33(14)
C(8)-C(9)-C(10)-C(11)	-0.2(2)
C(9)-C(10)-C(11)-C(12)	-0.7(2)
C(10)-C(11)-C(12)-C(13)	0.9(2)
C(9)-C(8)-C(13)-C(12)	-0.8(2)
C(1)-C(8)-C(13)-C(12)	177.44(14)
C(11)-C(12)-C(13)-C(8)	-0.2(2)
C(2)-C(1)-C(14)-C(15)	67.22(14)
C(8)-C(1)-C(14)-C(15)	-171.80(12)
C(17)-C(1)-C(14)-C(15)	-55.54(15)

C(1)-C(14)-C(15)-C(16)	58.56(15)
C(1)-C(14)-C(15)-Br(1)	178.47(9)
C(17)-N(1)-C(16)-C(15)	59.17(15)
C(18)-N(1)-C(16)-C(15)	-176.87(11)
C(14)-C(15)-C(16)-N(1)	-58.78(16)
Br(1)-C(15)-C(16)-N(1)	-179.82(9)
C(16)-N(1)-C(17)-C(1)	-61.54(15)
C(18)-N(1)-C(17)-C(1)	174.42(11)
C(2)-C(1)-C(17)-N(1)	-62.72(16)
C(8)-C(1)-C(17)-N(1)	178.48(11)
C(14)-C(1)-C(17)-N(1)	58.13(15)
C(17)-N(1)-C(18)-C(19)	-162.87(12)
C(16)-N(1)-C(18)-C(19)	73.03(15)
N(1)-C(18)-C(19)-C(20)	-119.17(15)
N(1)-C(18)-C(19)-C(24)	62.41(18)
C(24)-C(19)-C(20)-C(21)	-0.2(2)
C(18)-C(19)-C(20)-C(21)	-178.66(13)
C(19)-C(20)-C(21)-C(22)	-0.8(2)
C(20)-C(21)-C(22)-C(23)	0.8(2)
C(20)-C(21)-C(22)-C(25)	-179.10(14)
C(21)-C(22)-C(23)-C(24)	0.1(2)
C(25)-C(22)-C(23)-C(24)	-179.94(14)
C(22)-C(23)-C(24)-C(19)	-1.1(2)
C(20)-C(19)-C(24)-C(23)	1.2(2)
C(18)-C(19)-C(24)-C(23)	179.64(14)

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