Supporting Information

Lewis Acid-Mediated Asymmetric [2,3]-Sigmatropic Rearrangement of Allylic Amines. Scope and Mechanistic Investigation

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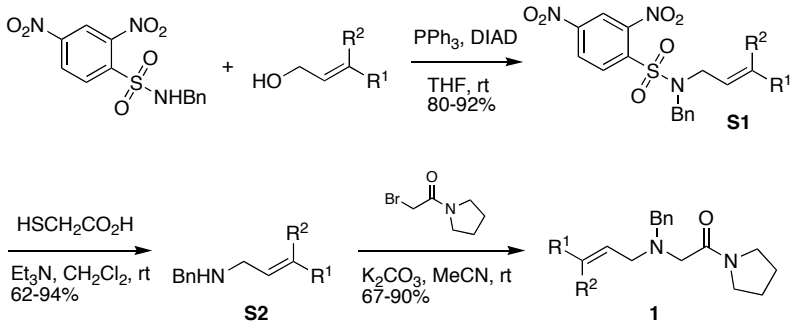
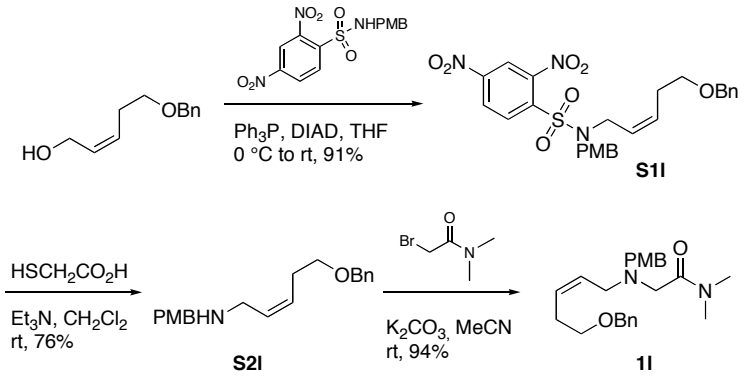
Syntheses of allylamines **1e-i**

Table S1



Entry	Substrate	R^1	R^2	Yields (%)		
				S1	**S2**	**1**
1	**e**	H	Ph	89	78	81
2	**f**	CH_2OBn	H	80	94	76
3	**g**	H	CH_2OBn	90	74	-
4	**h**	$SiMe_2Ph$	H	92	84	90
5	**i**	H	$SiMe_2Ph$	92	62	67

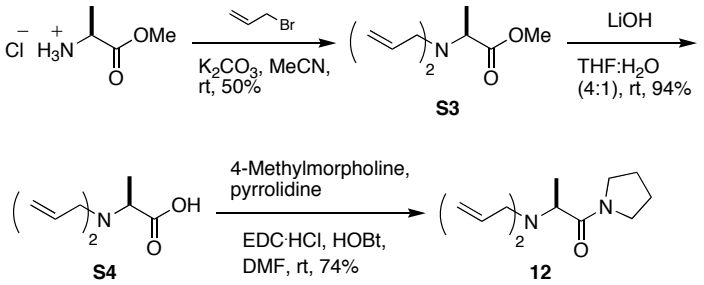
Synthesis of allylamine **1l**



Synthesis of diallylamine **12**

Synthesis of racemic **12** was prepared analogously starting from DL-alanine methyl ester hydrochloride.

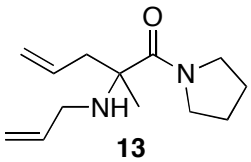
Scheme S1



Experimental section

General Methods.

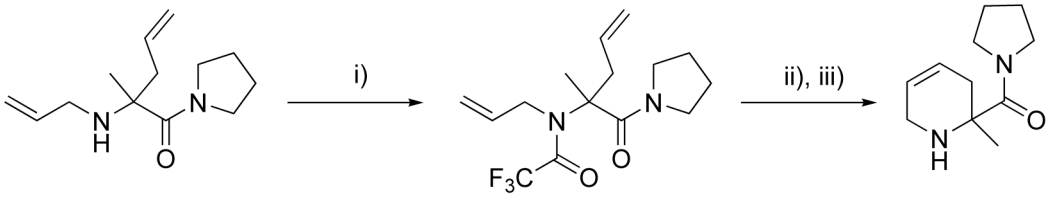
^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz or a 500 MHz spectrometer in $CDCl_3$ using the residual peak of $CHCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.0) or added TMS (δ 0.00) as internal standard. ^{11}B spectrum was recorded on a 500 MHz spectrometer using $BF_3{\cdot}OEt_2$ as an external standard. Chemical shifts are reported in the δ-scale with multiplicity (b=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constants (Hz) and integration. Analytical thin layer chromatography was performed on Merck silica gel 60 F_{254} plates; the plates were visualized with UV light and phosphomolybdic acid/cerium sulfate staining reagent (purchased from Aldrich as a 20 wt% solution in ethanol but diluted to ca 5 wt% before use) or I_2/MeOH. Chromatography employed Millipore Matrex™ 60A/35-70 μm silica gel. Air and moisture sensitive reactions were carried out in flame-dried, septum-capped flasks under an atmospheric pressure of nitrogen. All liquid reagents were transferred via oven-dried syringes. THF, Et_2O and toluene were distilled from sodium-benzophenone ketyl before use and CH_2Cl_2 and Et_3N from CaH_2.



13

2-(allylamino)-2-methyl-1-(pyrrolidin-1-yl)pent-4-en-1-one (13).

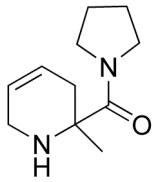
^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 5.82 (m, 2H), 5.10 (m, 4H), 3.87 (bs, 2H), 3.50 (bs, 2H), 3.07 (d, *J*=5.7 Hz, 2H), 2.51 (d, *J*=7.4 Hz, 2H), 1.83 (m, 4H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 173.0, 136.8, 133.6, 118.8, 115.2, 62.1, 47.8, 47.7, 46.2, 41.7, 27.2, 23.1, 22.8; IR (neat) 2974, 1622, 1404 cm^{-1}; HRMS (FAB+) calcd for $C_{13}H_{23}N_2O$ $[M+H]^+$: 223.1810, found: 223.1819. Enantioselectivity was determined by HPLC analysis of **14**, using a Chiracel OD-H column (^{i}PrOH:hexane 1:99 → 10:90 within 40 min; 0.8 ml/min; λ 254 nm); retention times: 36.5, 37.7 min.



rac-**13**
13

rac-**14**
14

Reaction conditions:
i) TFA, CH_2Cl_2, RT, (70%); ii) 2nd Grubbs, CH_2Cl_2, RT, (quant.); iii) K_2CO_3, MeOH/H_2O, (quant.)

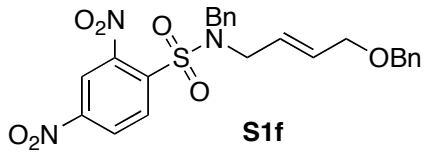


14

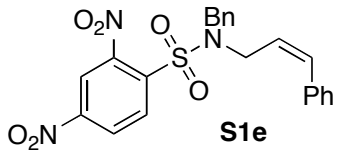
(1,2,3,6-tetrahydro-2-methylpyridin-2-yl)(pyrrolidin-1-yl)methanone (14).

^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 5.82-5.78 (m, 1H), 5.67-5.64 (m, 1H) 3.93-3.45 (m, 4H) 3.34-3.23 (m, 2H) 2.90-2.85 (m, 1H) 1.92-1.86 (m, 5H) 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 173.0, 125.7, 125.2, 58.1, 47.8, 42.4, 35.0, 30.9, 24.2;

Syntheses of allylamines **1**:



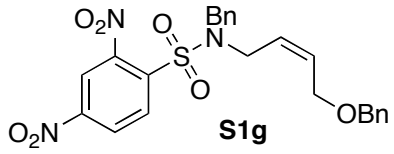
(*E*)-*N*-Benzyl-4-(benzyloxy)but-2-enyl-2,4-dinitro-benzenesulfonamide (S1f). To a solution of Ph_3P (0.67 g, 2.56 mmol) in THF (10 mL) at 0 °C was added DIAD (0.5 ml, 2.54 mmol) and the resultant mixture was stirred at 0 °C for 30 min. To the solution at rt was added *N*-benzyl-2,4-dinitro-benzenesulfonamide (0.62 g, 1.83 mmol) and a solution of (*E*)-4-(benzyloxy)but-2-en-1-ol[1] (0.37 g, 2.06 mmol) in THF (6 mL) and the resultant mixture was stirred for 1 h. Removal of the solvents and chromatography (pentane:EtOAc 19:1→2:1) gave **S1f** (0.73 g, 80%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.43 (d, *J*=2.2 Hz, 1H), 8.34 (dd, *J*=8.7, 2.2 Hz, 1H), 8.12 (d, *J*=8.7 Hz, 1H), 7.37-7.22 (m, 10H), 5.68 (m, 1H), 5.53 (m, 1H), 4.54 (s, 2H), 4.44 (s, 2H), 3.93 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 149.4, 147.7, 139.5, 137.8, 134.7, 132.7, 132.6, 128.7, 128.4, 128.3, 128.2, 127.7, 127.5, 125.9, 125.3, 119.6, 72.4, 69.3, 51.0, 48.9; IR (neat) 3101, 3033, 2858, 1549, 1360, 1163, 1107, 739 cm^{-1}; HRMS (FAB+) calcd for $C_{24}H_{24}N_3O_7S$ $[M+H]^+$: 498.1335, found: 498.1347.



(*Z*)-*N*-Benzyl-3-phenylprop-2-enyl-2,4-dinitro-benzenesulfonamide (S1e). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.47 (d, *J*=2.2 Hz, 1H), 8.30 (dd, *J*=8.6, 2.2 Hz, 1H), 8.00 (d, *J*=8.8 Hz, 1H), 7.32-7.15 (m, 6H), 7.09-6.99 (m, 4H), 6.58 (d, *J*=11.7 Hz,

[1] Löfstedt, J.; Pettersson-Fasth, H.; Bäckvall, J.-E. *Tetrahedron* **2000**, *56*, 2225-2230.

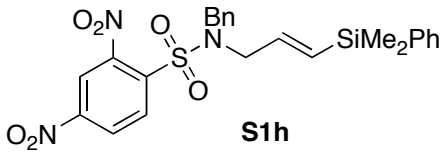
1H), 5.50 (dt, *J*=11.7, 6.6 Hz, 1H), 4.50 (s, 2H), 4.18 (dd, *J*=6.6, 1.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 149.5, 139.5, 135.5, 134.6, 133.9, 132.9, 128.7, 128.5, 128.44, 128.37, 128.28, 128.1, 127.7, 125.9, 125.1, 119.7, 51.3, 44.5; IR (neat) 3101, 2927, 1549, 1352, 1161, 1107, 739 cm^{-1}; HRMS (FAB+) calcd for $C_{22}H_{20}N_3O_6S$ $[M+H]^+$: 454.1073, found: 454.1076.



S1g

(*Z*)-*N*-Benzyl-4-(benzyloxy)but-2-enyl-2,4-dinitro-benzenesulfonamide (S1g).

^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.46 (t, *J*=2.2 Hz, 1H), 8.32 (dt, *J*=8.7, 2.2 Hz, 1H), 8.12 (d, *J*=8.7 Hz, 1H), 7.35-7.20 (m, 10H), 5.74 (m, 1H), 5.38 (m, 1H), 4.52 (s, 2H), 4.39 (s, 2H), 3.98 (d, *J*=7.0 Hz, 2H), 3.82 (d, 2H, J=6.3Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 149.5, 147.8, 139.4, 137.7, 134.7, 132.8, 131.6, 128.8, 128.5, 128.3, 128.2, 127.8, 127.7, 126.0, 125.8, 119.6, 72.8, 65.4, 51.2, 44.4; IR (neat) 3101, 2927, 1552, 1350, 1165, 1107 cm^{-1}; HRMS (FAB+) calcd for $C_{24}H_{24}N_3O_7S$ $[M+H]^+$: 498.1335, found: 498.1343.

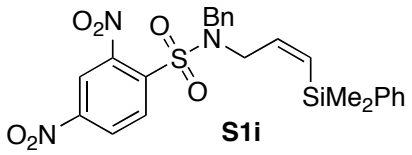


S1h

(*E*)-*N*-Benzyl-3-(dimethyl(phenyl)silyl)prop-2-enyl-2,4-dinitro-benzenesulfonamide (S1h).

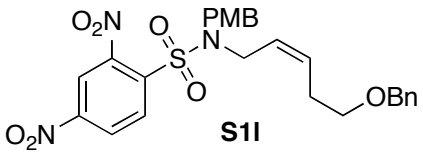
^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.36 (s, 1H), 8.24 (d, *J*=8.3 Hz, 1H), 8.08 (d, *J*=8.3 Hz, 1H), 7.35-7.23 (m, 10H), 5.84 (d, *J*=18.5 Hz, 1H), 5.73 (dd, *J*=18.5, 3.3 Hz, 1H), 4.53 (s, 2H), 3.97 (s, 2H), 0.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 149.4, 147.7, 139.7, 139.5, 137.4, 134.8, 134.0, 133.6, 132.7, 129.3, 128.8, 128.4, 128.2, 127.8,

125.8, 119.5, 51.8, 51.4, -3.0; IR (neat) 3101, 2956, 1552, 1365, 1165, 741 cm^{-1}; HRMS (FAB+) calcd for $C_{24}H_{26}N_3O_6SSi$ $[M+H]^+$: 512.1312, found: 512.1312.



(*Z*)-*N*-Benzyl-3-(dimethyl(phenyl)silyl)prop-2-enyl-2,4-dinitro-benzenesulfonamide (S1i).

^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.42 (d, *J*=2.3 Hz, 1H), 8.23 (dd, *J*=8.5, 2.3 Hz, 1H), 7.89 (d, *J*=8.5 Hz, 1H), 7.44-7.21 (m, 8H), 7.14-7.11 (m, 2H), 6.16 (dt, *J*=14.4, 6.4 Hz, 1H), 5.85 (dt, *J*=14.4, 1.4 Hz, 1H), 4.43 (s, 2H), 3.93 (dd, *J*=6.4, 1.4 Hz, 2H), 0.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 149.5, 147.9, 142.7, 139.5, 138.1, 135.0, 133.7, 133.1, 132.9, 129.5, 128.9, 128.3, 128.2, 128.2, 126.0, 119.7, 51.5, 49.6, -1.4; IR (neat) 3101, 2956, 1552, 1352, 1165, 739 cm^{-1}; HRMS (FAB+) calcd for $C_{24}H_{26}N_3O_6SSi$ $[M+H]^+$: 512.1312, found: 512.1310.



(*Z*)-*N*-(5-Benzyloxy-pent-2-enyl)-*N*-(4-methoxy-benzyl)-2,4-dinitro-benzenesulfonamide (S1l).

As described for **S1f** from (*Z*)-5-benzyloxy-pent-2-en-1-ol[2] and *N*-(4-methoxy-benzyl)-2,4-dinitro-benzenesulfonamide[3] ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.44 (d,

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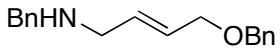
[2] Schmidt, J; Eschgfäller, S. A. *Helv. Chim. Acta* **2003**, *86*, 2937-2958.

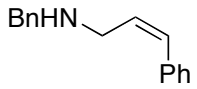
[3] (a) Fukuyama, T.; Jow, C.-K.; Cheung, M. *Tetrahedron Lett.* **1995**, *36*, 6373-6374; (b) Fukuyama, T.; Cheung, M.; Jow, C.-K.; Hidai, Y.; Kan, T. *Tetrahedron Lett.* **1997**, *38*, 5831-5834.

J=2.1 Hz, 1H), 8.31 (dd, *J*=8.7, 2.3 Hz, 1H), 8.10 (d, *J*=8.5 Hz, 1H), 7.36-7.25 (m, 5H), 7.17-7.14 (m, 2H), 6.81-6.78 (m, 2H), 5.64-5.58 (m, 1H), 5.30-5.25 (m, 1H), 4.46 (s, 2H), 4.44 (s, 2H), 3.95 (m_c, 2H) 3.77 (s, 3H), 3.42 (t, *J*=6.4 Hz, 2H), 2.18 (m_c, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 159.7, 149.5, 148.0, 139.8, 138.3, 132.9, 132.2, 130.0, 128.5, 127.8, 127.7, 126.9, 126.0, 124.8, 119.7, 114.2, 73.2, 69.3, 55.4, 50.7, 44.3, 28.1; IR (neat) 3101, 3032, 2866, 1539, 1516, 1362, 1107, 741 cm^{-1}; HRMS (FAB+) calcd for $C_{26}H_{28}N_3O_8S$ $[M+H]^+$: 542.1597, found: 542.1596.



S2f

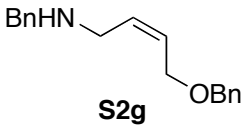
(*E*)-*N*-Benzyl-4-(benzyloxy)but-2-en-1-amine (S2f). To a stirred solution of **S1f** (0.70 g, 1.4 mmol) and Et_3N (0.39 mL, 2.8 mmol) in CH_2Cl_2 (5 mL) was added mercaptoacetic acid (166 mg, 1.8 mmol). The resultant solution was stirred at rt for 2 h and then diluted with Et_2O (10 mL). The organic phase was washed with saturated $NaHCO_3$ (3×10 mL) and the aqueous phase was extracted with Et_2O (5 mL). The combined organic phases were dried (K_2CO_3) and the concentrated residue was purified by chromatography (CH_2Cl_2:MeOH 49:1→1:1) to provide **S2f** (0.35 g, 94%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.35-7.23 (m, 10H), 5.86 (dt, *J*=15.6, 5.5 Hz, 1H), 5.78 (dt, *J*=15.6, 5.5 Hz, 1H), 4.52 (s, 2H), 4.03 (d, *J*=5.5 Hz, 2H), 3.80 (s, 2H), 3.30 (d, *J*=5.5 Hz, 2H), 1.5 (bs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 140.1, 138.2, 131.9, 128.3, 128.3, 128.1, 128.1, 127.7, 127.5, 126.9, 72.1, 70.4, 53.3, 50.5; IR (neat) 3315, 3028, 2852, 1115 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1701, found: 268.1699.



S2e

(*Z*)-*N*-Benzyl-3-phenylprop-2-en-1-amine (S2e).

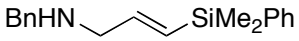
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.35-7.18 (m, 10H), 6.52 (d, *J*=12.1 Hz, 1H), 5.79 (m, 1H), 3.77 (s, 2H), 3.54 (d, *J*=6.6 Hz, 2H), 1.63 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 140.0, 137.1, 130.9, 130.8, 128.8, 128.5, 128.4, 128.2, 127.0, 126.9, 53.6, 47.0; IR (neat) 3311, 3026, 2833, 1452 cm^{-1}; HRMS (FAB+) calcd for $C_{16}H_{18}N$ $[M+H]^+$: 224.1439, found: 224.1434.



S2g

(*Z*)-*N*-Benzyl-4-(benzyloxy)but-2-en-1-amine (S2g).

^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.29-7.17 (m, 10H), 5.67 (m, 2H), 4.42 (s, 2H), 3.98 (m, 2H), 3.69 (s, 2H), 3.21 (m, 2H), 1.54 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 140.0, 138.2, 131.6, 128.39, 128.38, 128.3, 128.1, 127.7, 127.6, 127.0, 72.3, 65.7, 53.3, 45.7; IR (neat) 3311, 3028, 2854, 1454, 1092 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1701, found: 268.1696.

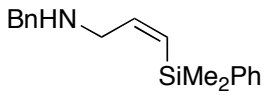


S2h

(*E*)-*N*-Benzyl-3-(dimethyl(phenyl)silyl)prop-2-en-1-amine (S2h).

^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.46 (m, 2H), 7.28 (m, 8H), 6.15 (dt, *J*=18.7, 5.3 Hz, 1H), 5.92 (dt, *J*=18.7, 1.5 Hz, 1H), 3.74 (s, 2H), 3.30 (dd, *J*=5.3, 1.5 Hz, 2H), 1.32 (bs, 1H), 0.29 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 146.4, 140.3, 138.7, 133.8,

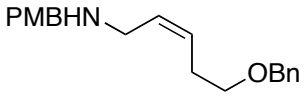
128.9, 128.7, 128.4, 128.2, 127.7, 126.9, 54.0, 53.5, -2.6; IR (neat) 3313, 3066, 2956, 1603, 1250, 1115 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{24}NSi$ $[M+H]^+$: 282.1678, found: 282.1683.



S2i

(*Z*)-*N*-Benzyl-3-(dimethyl(phenyl)silyl)prop-2-en-1-amine (S2i).

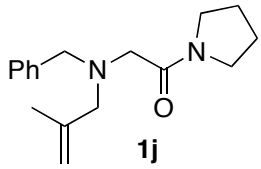
^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.54-7.50 (m, 2H), 7.37-7.19 (m, 8H), 6.54 (dt, *J*=14.1, 6.8 Hz, 1H), 5.82 (dt, *J*=14.1, 1.3 Hz, 1H), 3.60 (s, 2H), 3.22 (dd, *J*=6.8, 1.3 Hz, 2H), 1.47 (bs, 1H), 0.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 147.7, 139.6, 139.4, 133.8, 130.3, 129.1, 128.5, 128.4, 128.0, 127.2, 53.4, 51.2, -0.89; IR (neat) 3313, 3066, 2956, 1606, 1250, 1113 cm^{-1}; HRMS (FAB+) calcd for $C_{18}H_{24}NSi$ $[M+H]^+$: 282.1678, found: 282.1678.



S2l

(*Z*)-*N*-(5-Benzyloxy-pent-2-enyl)-(4-methoxy-benzyl)-amine (S2l).

^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.36-7.26 (m, 5H), 7.23-7.20 (m, 2H), 6.87-6.84 (m, 2H), 5.65-5.60 (m, 1H), 5.58-5.52 (m, 1H), 4.50 (s, 2H), 3.79 (s, 3H), 3.70 (s, 2H), 3.48 (t, *J*=6.7 Hz, 2H), 3.28 (dd, *J*=6.6, 1.0 Hz, 2H), 2.37 (m_c, 2H), 1.32 (bs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 158.7, 138.5, 132.6, 130.2, 129.5, 128.5, 128.2, 127.7, 127.7, 113.9, 73.1, 69.8, 55.4, 53.0, 45.8, 28.3; IR (neat) 3313, 3012, 2854, 1612, 1512, 1454, 1246, 1099, 741 cm^{-1}; HRMS (FAB+) calcd for $C_{20}H_{26}NO_2$ $[M+H]^+$: 312.1964, found: 312.1966.

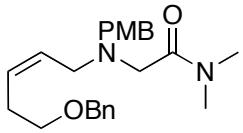


1j

2-(*N*-Benzyl-(2-methylallyl)amino)-1-(pyrrolidin-1-yl)ethanone (1j). To a suspension of *N*-benzyl-2-methylprop-2-en-1-amine[4] (225 mg, 1.4 mmol) and K_2CO_3 (587 mg, 4.25 mmol) in MeCN (5 mL) was added bromoacetyl pyrrolidide[5] (312 mg, 1.62 mmol) in MeCN (5 mL) and the resultant mixture was stirred for 3.5 h. The suspension was poured into saturated $NaHCO_3$ (15 mL) and extracted with CH_2Cl_2 (3×10 mL). The dried (K_2CO_3) and concentrated organic phases were purified by chromatography (MeOH:CH_2Cl_2 1:82→1:9) to provide the title compound (345 mg, 91%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.31 (m, 4H), 7.22 (t, *J*=7.1 Hz, 1H), 4.95 (s, 1H), 4.87 (s, 1H), 3.70 (s, 2H), 3.41 (t, *J*=6.9 Hz, 2H), 3.29 (t, *J*=6.6 Hz, 2H), 3.19 (s, 2H), 3.15 (s, 2H), 1.87-1.74 (m, 4H), 1.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 169.3, 143.5, 139.2, 129.1, 128.1, 126.9, 113.2, 61.2, 58.2, 56.2, 45.9, 45.5, 26.2, 24.0, 20.8; IR (neat) 2972, 2875, 1642, 1443 cm^{-1}; HRMS (FAB+) calcd for $C_{17}H_{25}N_2O$ $[M+H]^+$: 273.1967, found: 273.1959.

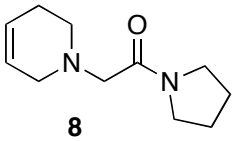
[4] Zhou, J.-Q.; Alper, H. *J. Org. Chem.* **1992**, *57*, 3328-3331.

[5] (a) Hama, T.; Liu, X.; Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 11176-11177; (b) Hand, E. S.; Johnson, S. C.; Baker, D. C. *J. Org. Chem.* **1997**, *62*, 1348-1355.



1l

(*Z*)-2-[*N*-(5-Benzyloxy-pent-2-enyl)-(4-methoxy-benzyl)-amino]-*N*,*N*-dimethyl-acetamide (1l). As described for **1j** from **S2l** and α-bromo-dimethylacetamide[6]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.35-7.25 (m, 5H), 7.24-7.21 (m, 2H), 6.85-6.82 (m, 2H), 5.65-5.57 (m, 2H), 4.49 (s, 2H), 3.79 (s, 3H), 3.59 (s, 2H), 3.46 (t, *J*=6.7 Hz, 2H), 3.23 (s, 2H), 3.17 (d, *J*=5.5 Hz, 2H), 2.95 (s, 3H), 2.88 (s, 3H), 2.36 (m_c, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 170.9, 158.8, 138.6, 130.9, 130.5, 129.7, 128.5, 128.5, 127.7, 127.6, 113.7, 73.0, 69.8, 57.9, 56.4, 55.4, 50.8, 37.2, 35.6, 28.3; IR (neat) 3012, 2931, 2854, 1643, 1512, 1454, 1250, 1099, 741 cm^{-1}; HRMS (FAB+) calcd for $C_{24}H_{33}N_2O_3$ $[M+H]^+$: 397.2491, found: 397.2477.



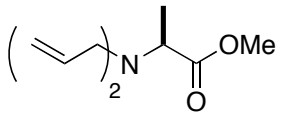
8

2-(5,6-Dihydropyridin-1(2*H*)-yl)-1-(pyrrolidin-1-yl)ethanone (8). To a solution of bromoacetyl pyrrolidide[5] (518 mg, 2.7 mmol) and K_2CO_3 (1.02 g, 7.4 mmol) in CH_3CN (15 ml) was added 1,2,5,6-tetrahydropyridine (0.20 ml, 2.2 mmol) and the resultant solution stirred at rt for 3.5 h. The reaction mixture was poured into sat. $NaHCO_3$ (30 ml) and extracted with CH_2Cl_2 (3×20 mL). The combined organic phases were dried (K_2CO_3) and concentrated. Purification by flash chromatography (MeOH:CH_2Cl_2 0:1→1:4) provided the title compound (426 mg, 85%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 5.71 (m, 1H), 5.62 (m, 1H), 3.49 (t, J=6.7,

[6] Cai, L.; Han, Y.; Ren, S.; Huang, L. *Tetrahedron* **2000**, *56*, 8253-8262.

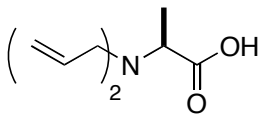
2H), 3.45 (t, J=6.9, 2H), 3.18 (s, 2H), 3.06 (m, 2H), 2.65 (t, J=5.7, 2H), 2.15 (m, 2H), 1.91 (m, 2H), 1.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 168.3, 125.1, 124.9, 61.3, 52.5, 49.9, 46.2, 45.7, 26.2, 26.0, 24.1; IR (neat) 2970, 2875, 1641, 1450 cm^{-1}; HRMS (FAB+) calcd for $C_{11}H_{19}N_2O$ $[M+H]^+$: 195.1497, found: 195.1513.

Synthesis of allylamine **12**:



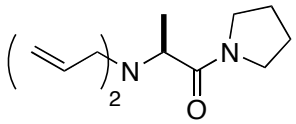
S3

(*S*)-Methyl 2-(diallylamino)propanoate) (S3). To a suspension of L-alanine methyl ester hydrochloride (476 mg, 3.4 mmol) and K_2CO_3 (2.95 g, 21.3 mmol) in MeCN (20 mL) was added allylbromide (0.77 mL, 8.9 mmol) and the resultant mixture was stirred for 24 h. The suspension was poured into saturated $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (2×10 mL). The dried (K_2CO_3) and concentrated organic phases were purified by chromatograpy (pentane:EtOAc 1:0→1:9) to provide the title compound (310 mg, 50%) as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.74 (m, 2H), 5.12 (ddd, *J*=17.1, 3.2, 1.5 Hz, 2H), 5.04 (d, *J*=10.1 Hz, 2H), 3.63 (s, 3H), 3.54 (q, *J*=7.1 Hz, 1H), 3.19 (dd, *J*=14.4, 5.7 Hz, 2H), 3.07 (dd, *J*=14.4, 6.9 Hz, 2H), 1.20 (d, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 174.4, 136.4, 117.1, 57.3, 53.6, 51.3, 14.6; IR (neat) 2922, 1739, 1410 cm^{-1}; HRMS (FAB+) calcd for $C_{10}H_{18}NO_2$ $[M+H]^+$: 184.1338, found: 184.1342; $[\alpha]_D^{20}$ -0.7 (c = 1.00, CH_2Cl_2).



S4

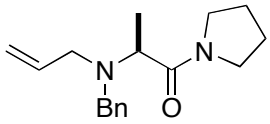
(*S*)-2-(Diallylamino)propanoic acid (S4). To a stirred solution of **S3** (265 mg, 1.44 mmol) in THF (12 mL) was added LiOH·H_2O (307 mg, 7.32 mmol) in H_2O (3 mL) and the resultant mixture was stirred for 3 days. The concentrated residue was dissolved in H_2O and treated with Dowex H^+ resin until pH 7 was reached. The resin was filtered off and rinsed with H_2O and MeOH. Removal of the solvent provided **S4** as a white solid (248 mg, 94%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 9.18 (bs, 1H), 5.96 (m, 2H), 5.35 (m, 4H), 3.67 (m, 3H), 3.40 (m, 2H), 1.42 (d, *J*=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 172.4, 129.9, 122.6, 60.7, 53.4, 12.0; IR (neat) 3454, 2983, 1628 cm^{-1}; HRMS (FAB+) calcd for $C_9H_{16}NO_2$ $[M+H]^+$: 170.1181, found: 170.1183; $[\alpha]_D^{20}$ +3.9 (c = 0.84, CH_2Cl_2).



12

(*S*)-2-(Diallylamino)-1-(pyrrolidin-1-yl)propan-1-one (12). To a stirred solution of **S4** (78.4 mg, 0.48 mmol) in DMF (15 mL) was added sequentially at 0°C 4-methylmorpholine (60 μL, 0.55 mmol), pyrrolidine (45 μL, 0.54 mmol), 1-hydroxybenzotriazole hydrate (80 mg, 0.59 mmol) and EDC·HCl (115.3 mg, 0.60 mmol). The reaction mixture was allowed to reach rt and stirred for 18 h. The concentrated residue was dissolved in CH_2Cl_2 (50 mL) and washed with saturated $NaHCO_3$ (30 mL), H_2O (30 mL) and brine (30 mL). The combined water phases were extracted with CH_2Cl_2 (20 mL) and the organic phases dried (K_2CO_3) and concentrated. Purification by chromatography provided the title compound (80 mg, 74%) as colourless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 5.79 (dd, *J*=17.2, 10.1 Hz,

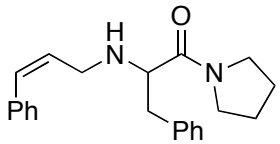
2H), 5.14 (ddd, *J*=17.2, 3.2, 1.5 Hz, 2H), 5.07 (d, *J*=10.1 Hz, 2H), 3.82 (dt, *J*=10.4, 6.8 Hz, 1H), 3.65 (q, *J*=6.7 Hz, 1H), 3.44 (m, 2H), 3.32 (m, 1H), 3.27 (m, 2H), 3.04 (dd, *J*=14.3, 7.3 Hz, 2H), 1.90 (m, 2H), 1.80 (m, 2H), 1.14 (d, *J*=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 171.9, 136.8, 116.8, 56.3, 53.3, 46.2, 45.8, 26.2, 24.1, 9.9; IR (neat) 2974, 1641, 1435 cm^{-1}; HRMS (FAB+) calcd for $C_{13}H_{23}N_2O$ $[M+H]^+$: 223.1810, found: 223.1814; $[\alpha]_D^{20}$ +9.4 (c = 1.51, CH_2Cl_2).



10

(*S*)-2-(*N*-Allyl-*N*-benzylamino)-1-(pyrrolidin-1-yl)propan-1-one (10).

^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.30-7.18 (m, 5H), 5.81 (dddd, *J*=17.2, 10.1, 7.4, 5.7 Hz, 1H), 5.17 (ddd, *J*=17.2, 3.1, 1.6 Hz, 1H), 5.08 (dd, *J*=10.1, 0.8 Hz, 1H), 3.79 (d, *J*=13.9 Hz, 1H), 3.65 (m, 2H), 3.54 (d, *J*=13.9 Hz, 1H), 3.42 (m, 2H), 3.25 (dd, *J*=14.1, 5.7 Hz, 1H), 3.11 (m, 2H), 1.83 (m, 4H), 1.21 (d, *J*=6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 172.0, 140.1, 136.8, 128.8, 128.1, 126.7, 117.1, 55.9, 54.0, 53.8, 46.0, 45.8, 26.2, 24.1, 9.9; IR (neat) 2923, 1637, 1435 cm^{-1}; HRMS (FAB+) calcd for $C_{17}H_{25}N_2O$ $[M+H]^+$: 273.1961, found: 273.1970; $[\alpha]_D^{20}$ +21.2 (c = 1.02, CH_2Cl_2).

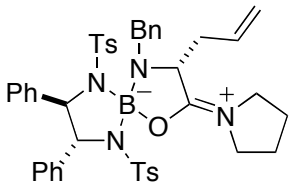


7e

(*Z*)-2-(Cinnamylamino)-3-phenyl-1-(pyrrolidin-1-yl)propan-1-one (7e).

^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.32-7.15 (m, 10H), 6.53 (bd, *J*=11.8 Hz, 1H), 5.73 (dt, *J*=11.8, 6.9 Hz, 1H), 3.46-3.51 (m, 3H), 3.19-3.25 (m, 2H), 2.93 (dd, *J*=12.9, 5.6 Hz, 1H), 2.88 (dd, *J*=9.9, 6.9 Hz, 1H), 2.81 (dd, *J*=12.6, 9.3 Hz, 1H), 2.29-2.35 (m,

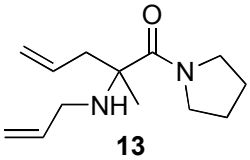
1H), 1.82 (bs, 1H), 1.23-1.50 (m, 3H), 0.83-0.90 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 172.7, 138.0, 136.9, 131.3, 131.1, 129.4, 129.0, 128.3, 128.3, 127.1, 126.7, 61.0, 45.8, 45.5, 45.4, 40.7, 25.8, 24.0; IR (neat) 3303, 3026, 2926, 1633, 1446 cm^{-1}; HRMS (FAB+) calcd for $C_{22}H_{27}N_2O$ $[M+H]^+$: 335.2123, found: 335.2123.



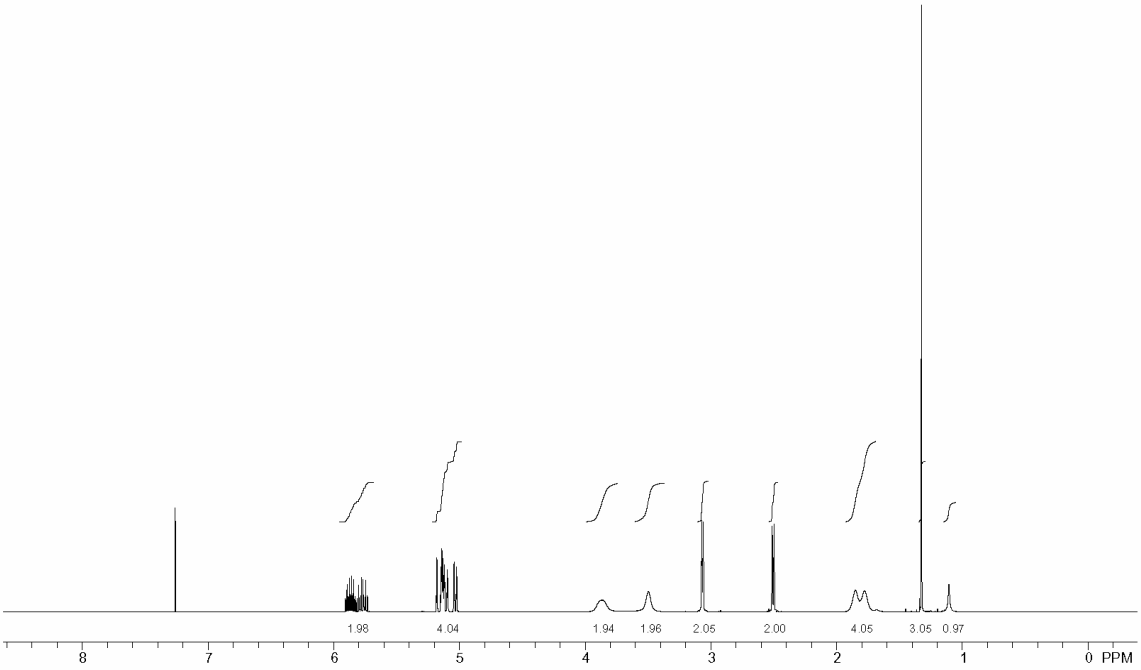
6

Complex 6.

^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.57 (d, *J*=7.4 Hz, 2H), 7.44 (d, *J*=8.2 Hz, 2H), 7.32 (dd, *J*=14.1, 7.4 Hz, 4H), 7.20 (t, *J*=7.3 Hz, 1H), 7.09 (m, 5H), 7.01 (t, *J*=7.3 Hz, 1H), 6.95 (t, *J*=7.7 Hz, 2H), 6.90 (m, 4H), 6.81 (d, *J*=8.0 Hz, 2H), 6.29 (m, 1H), 4.99 (d, *J*=10.0 Hz, 1H), 4.91 (d, *J*=17.1 Hz, 1H), 4.79 (d, *J*=2.5 Hz, 1H), 4.64 (d, *J*=2.5 Hz, 1H), 4.32 (s, 1H), 4.23 (d, *J*=16.6 Hz, 1H), 3.82 (m, 2H), 3.68 (m, 1H), 3.60 (m, 1H), 3.54 (d, *J*=16.6 Hz, 1H), 2.50 (m, 2H), 2.32 (s, 3H), 2.25 (s, 3H), 2.17 (m, 2H), 2.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 180.2, 143.3, 142.1, 141.7, 141.4, 141.3, 140.6, 139.1, 135.4, 128.5, 128.3, 128.0, 127.8, 127.7, 127.41, 127.39, 127.3, 127.2, 126.9, 126.4, 126.2, 126.0, 116.1, 69.1, 68.1, 66.2, 51.8, 49.0, 48.8, 35.7, 25.8, 23.9, 21.3, 21.2; ^{11}B NMR ($CDCl_3$, 160 MHz) δ_B 9.3 (s).



13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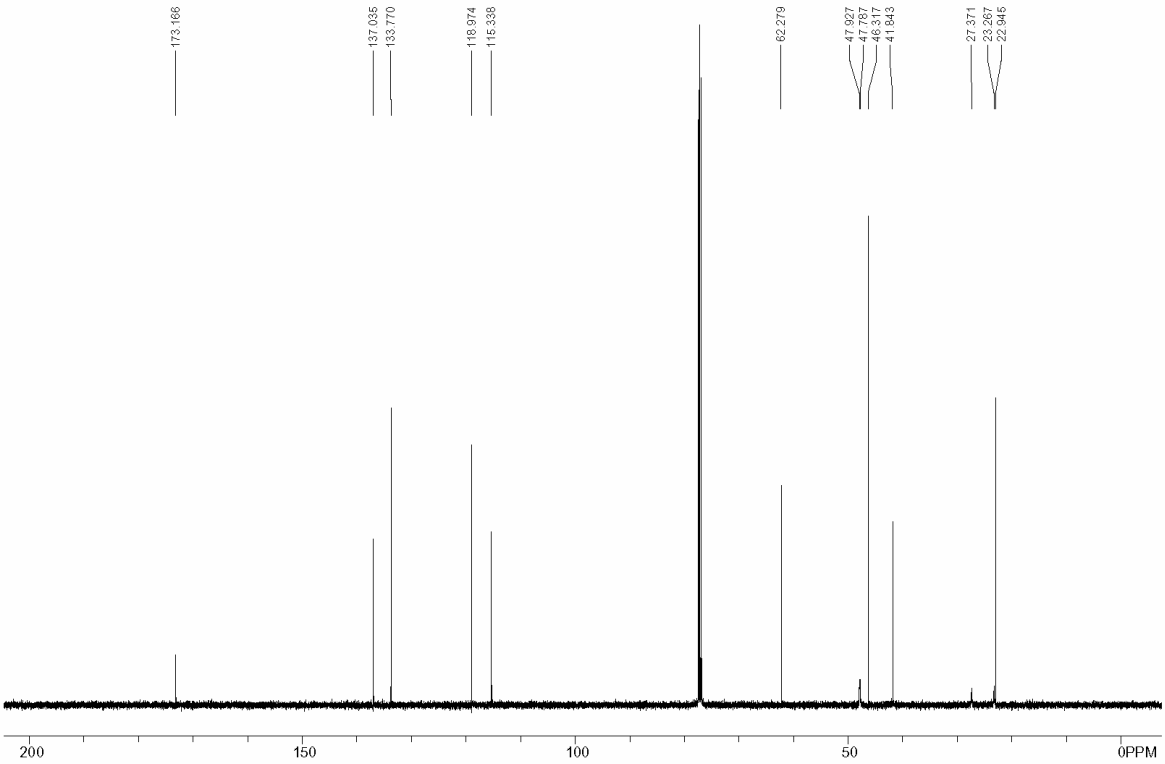
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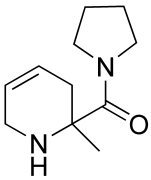
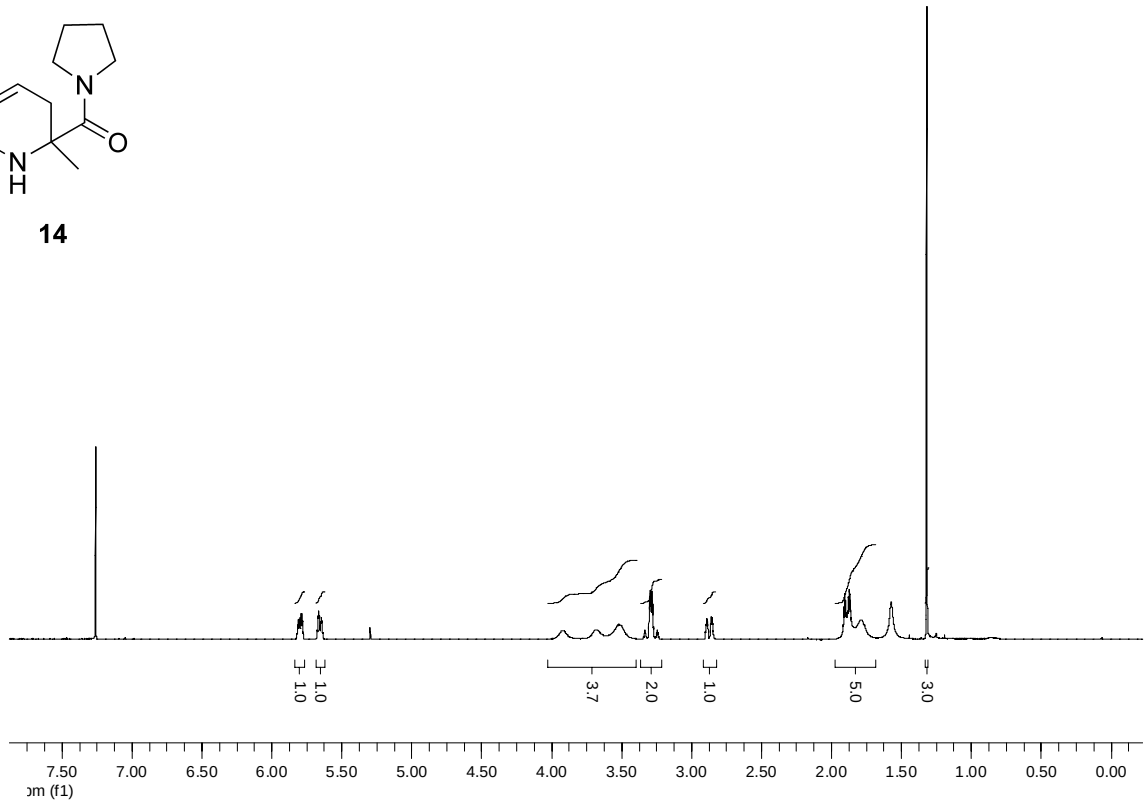


14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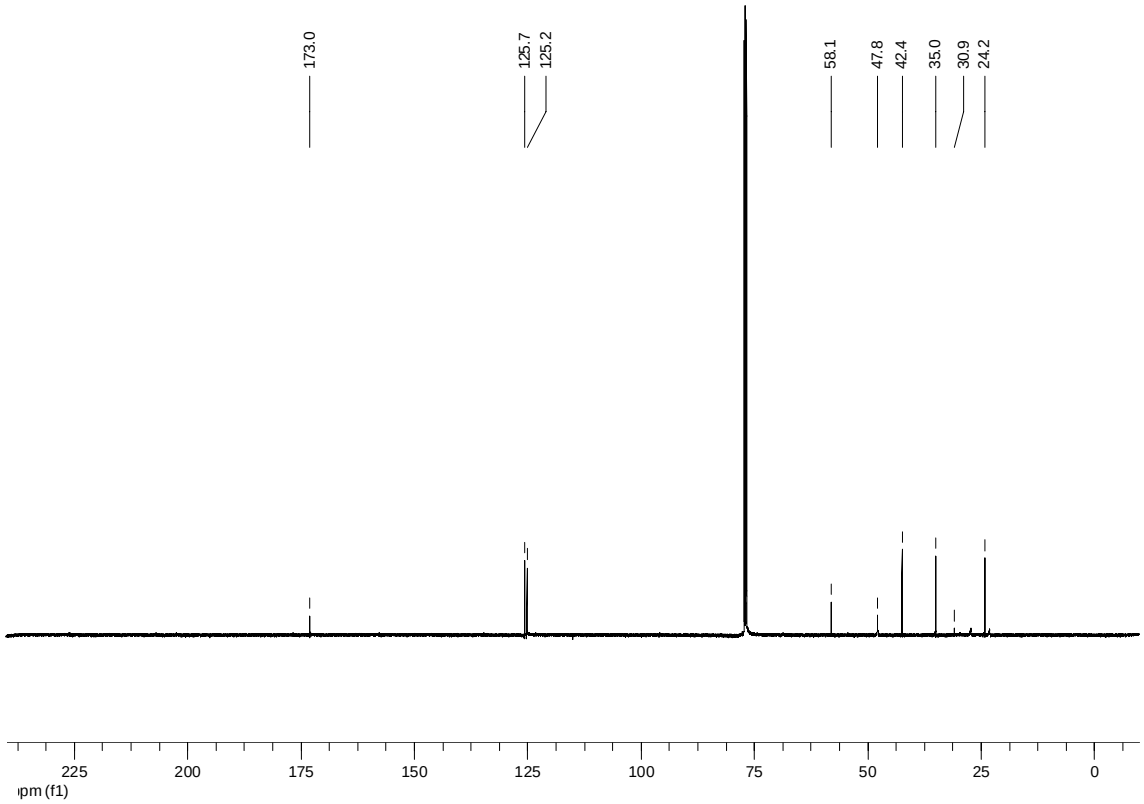
pm (f1)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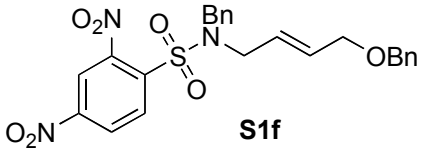
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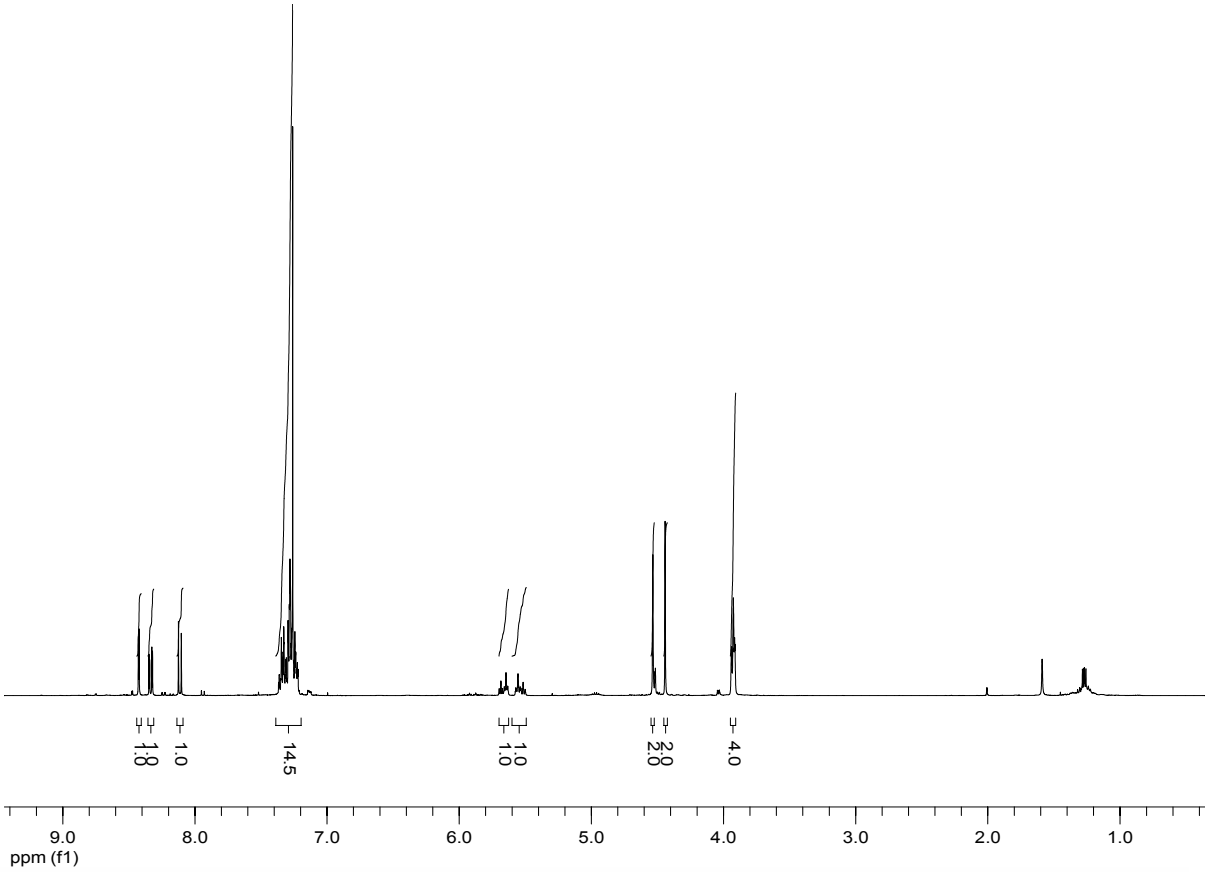
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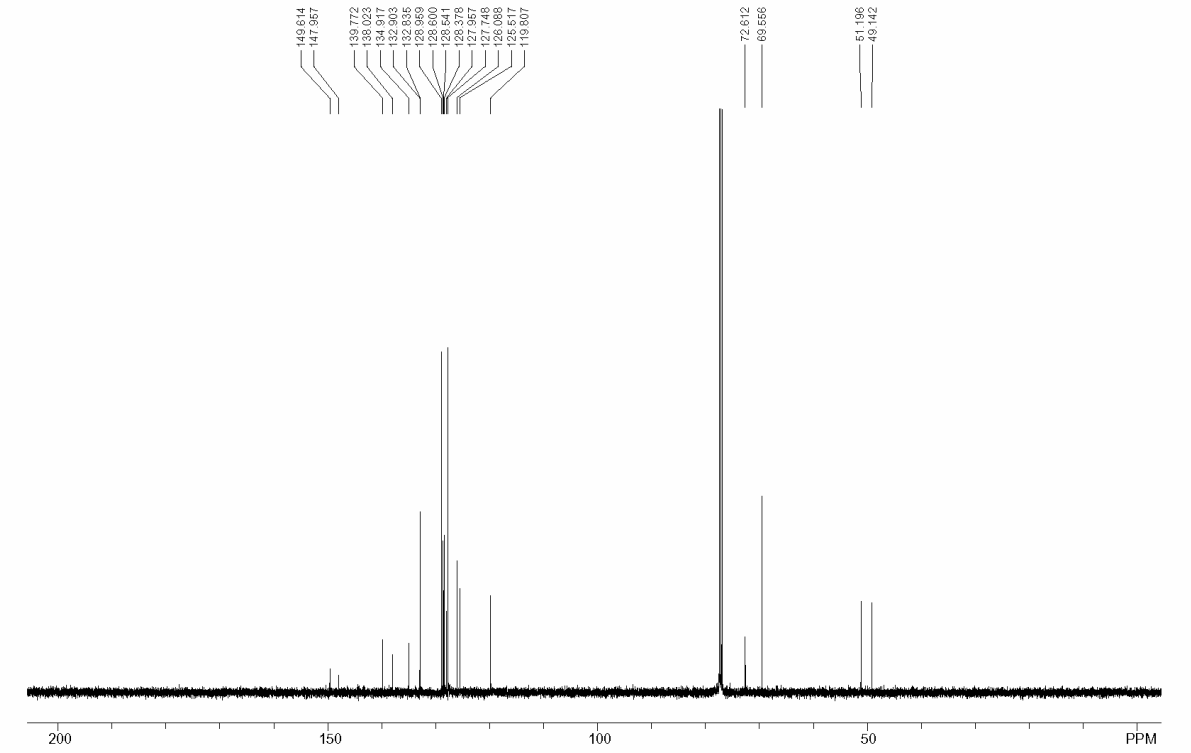
ppm (f1)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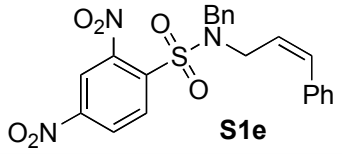
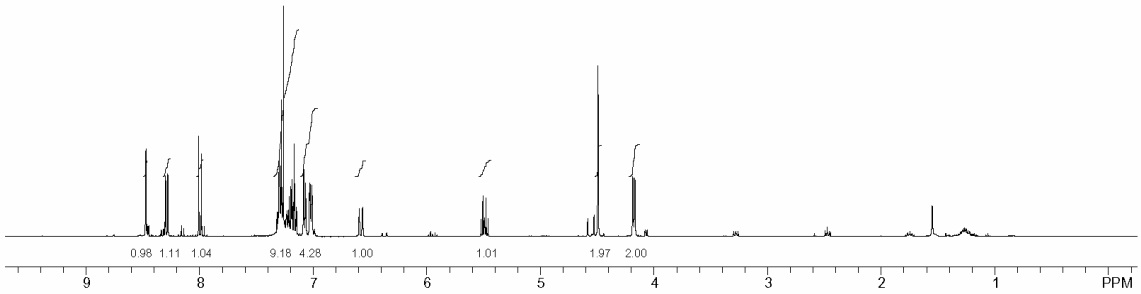
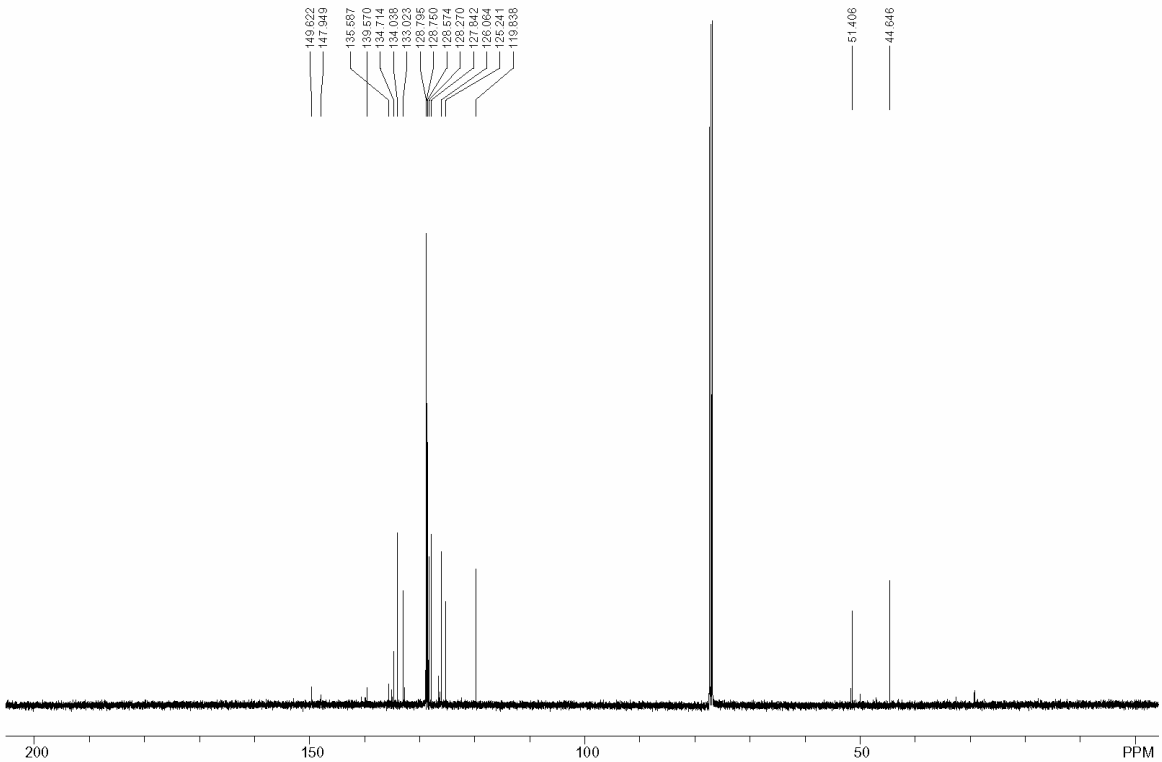
139.772
138.023
134.917
132.903
132.835
128.969
128.600
128.541
128.378
127.957
127.748
126.088
125.617
119.807
72.612
69.556
51.196
49.142
200
150
100
50
PPM


O2N
O
Bn
N
S
O
Ph
O2N

S1e


0.98 1.11 1.04 9.18 4.28 1.00 1.01 1.97 2.00
9
8
7
6
5
4
3
2
1
PPM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135.587
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134.714
134.038
133.023
128.796
128.760
128.574
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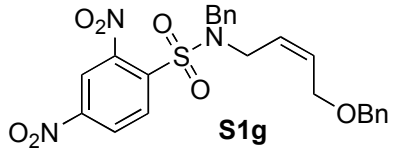
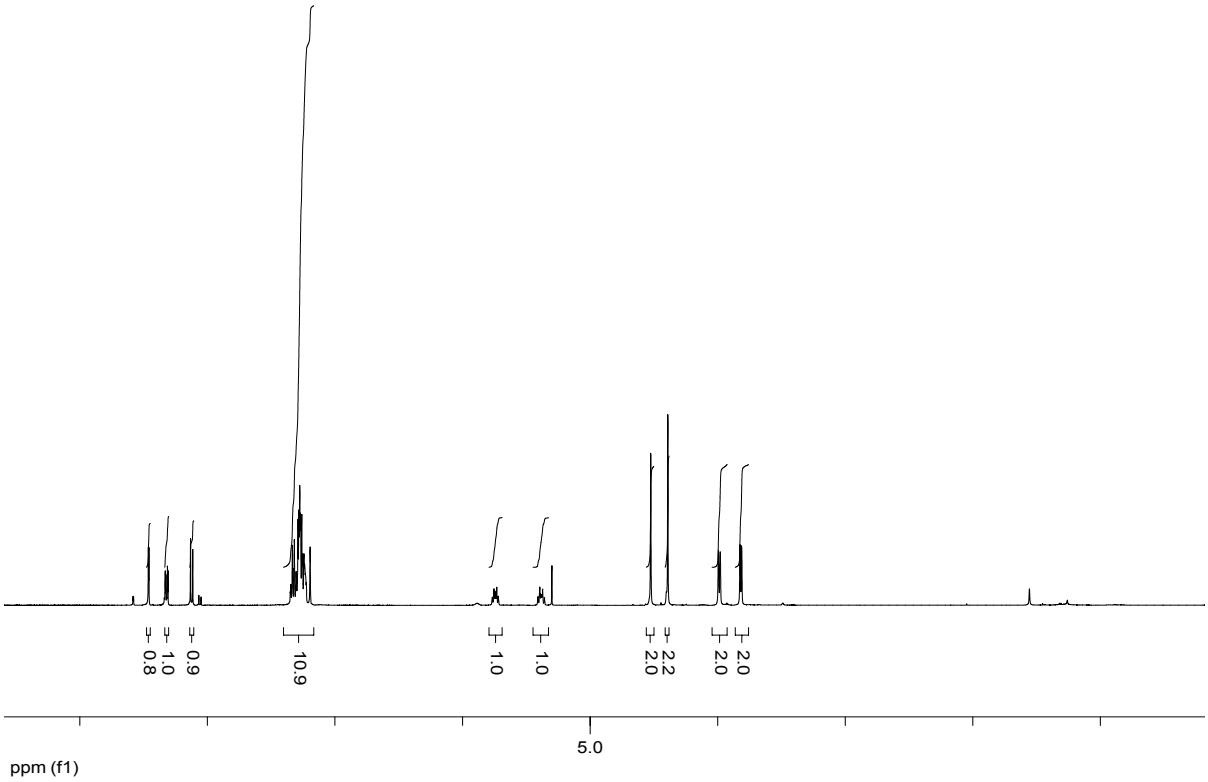
127.842
126.064
125.241
119.838
51.406
44.646
200
150
100
50
PPM


O2N
O
Bn
N
S
O
O2N
OBn

S1g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1.0
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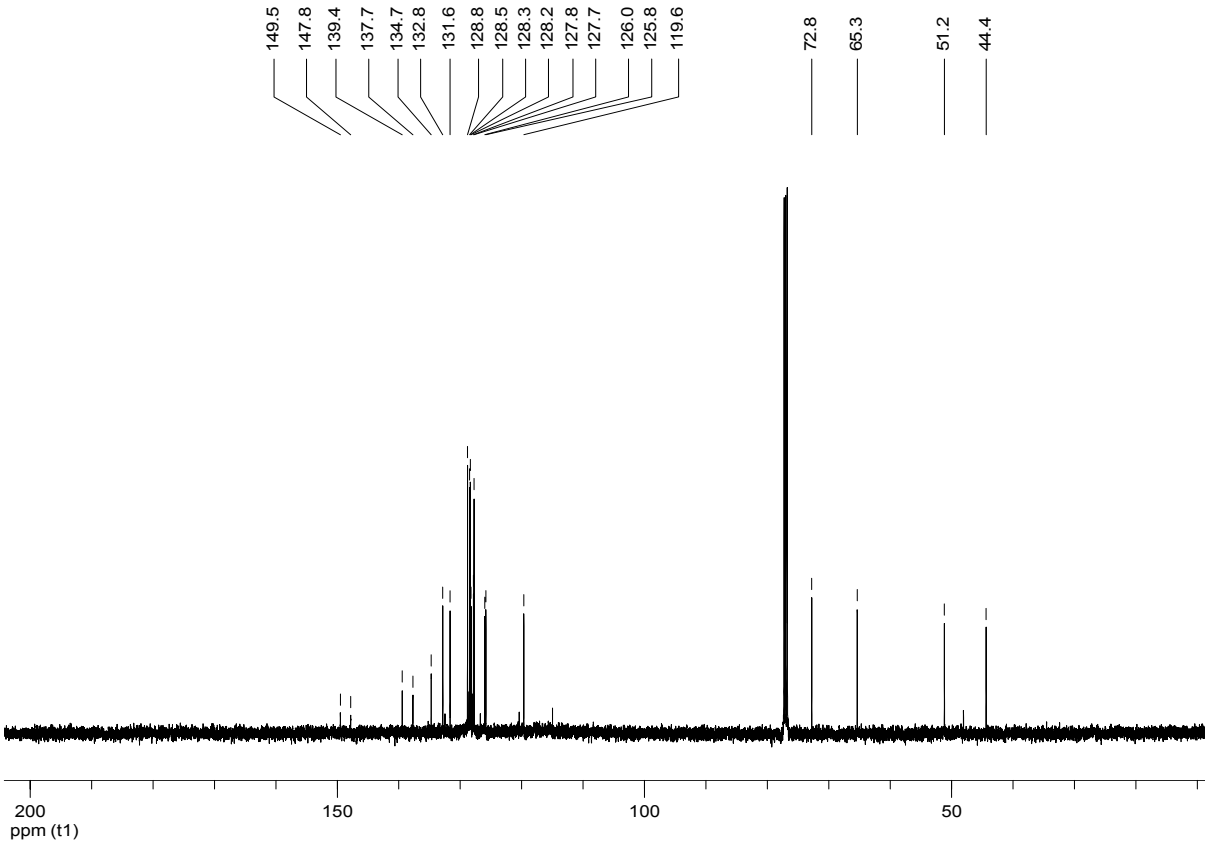
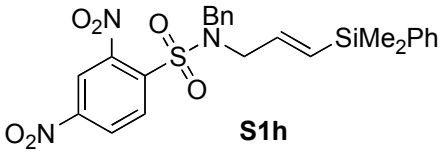
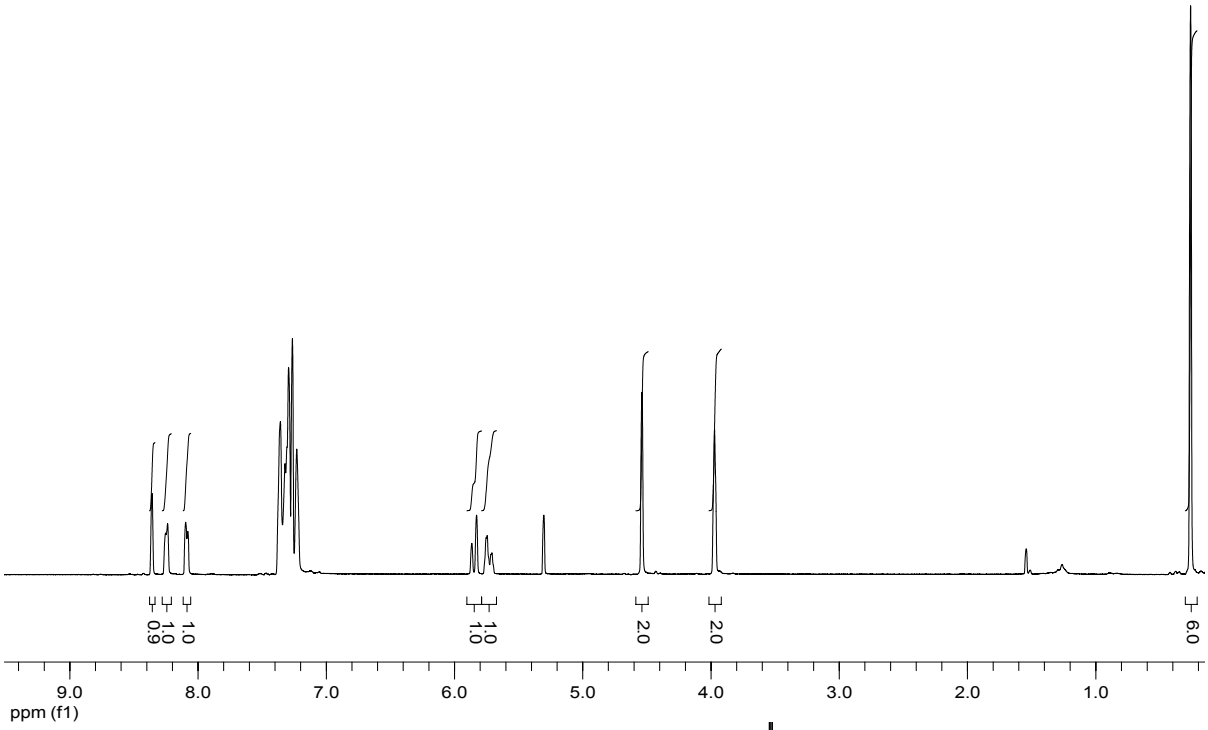
2.0
2.0
2.0
5.0
ppm (f1)


149.5
147.8
139.4
137.7
134.7
132.8
131.6
128.8
128.5
128.3
128.2
127.8
127.7
126.0
125.8
119.6
72.8
65.3
51.2
44.4
200
150
100
50
ppm (t1)


O2N
O
Bn
N
SiMe2Ph
S
O
O2N

S1h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1.0
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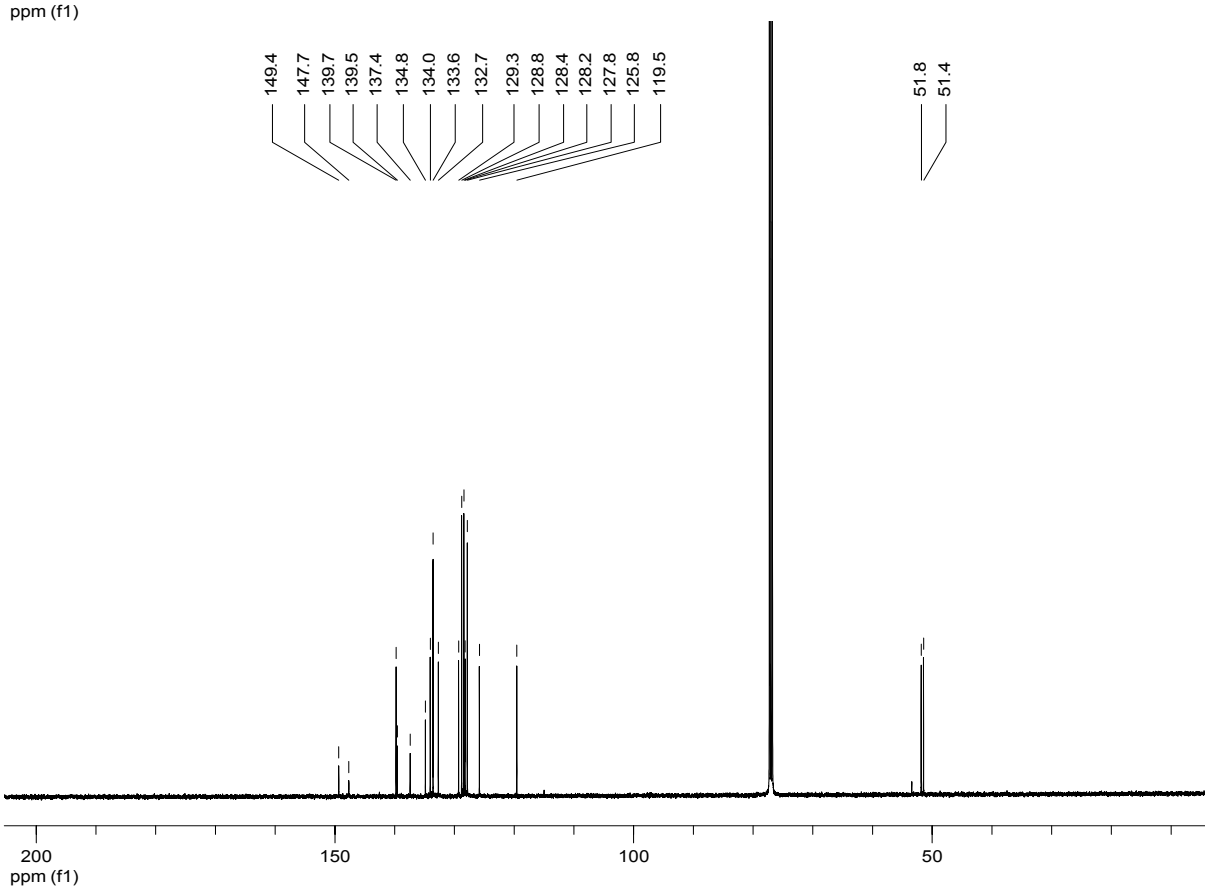
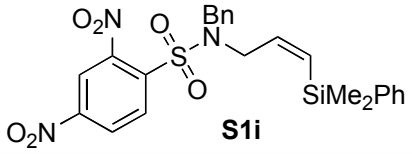
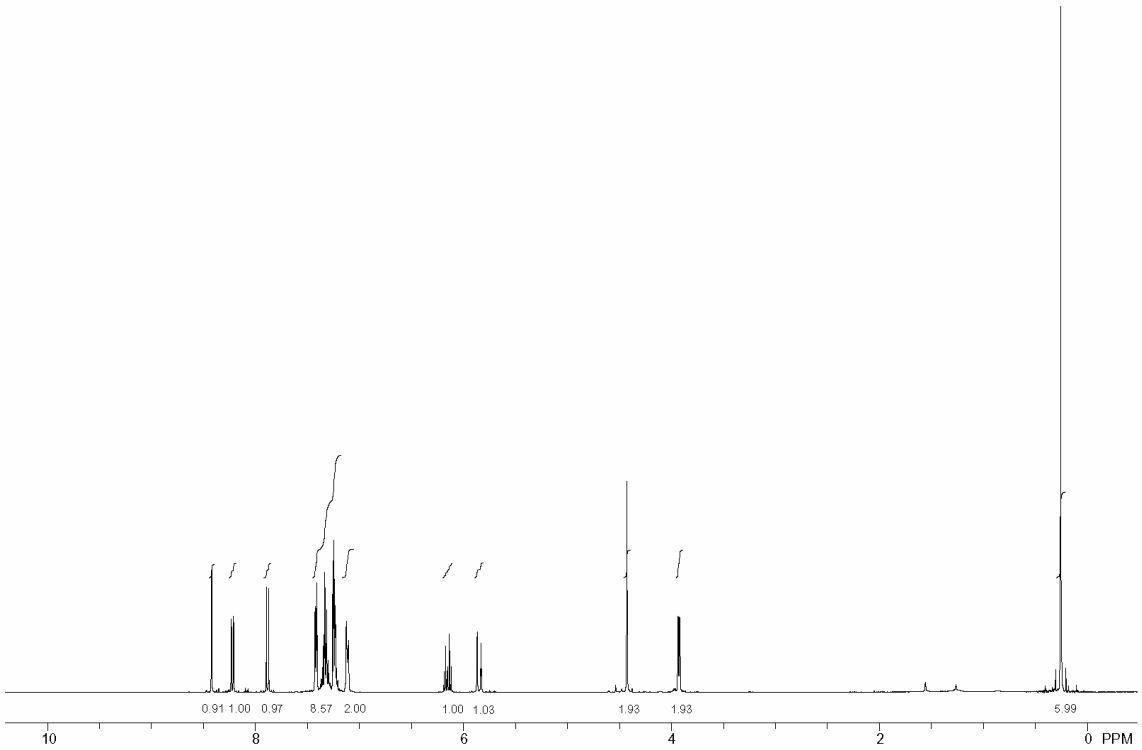
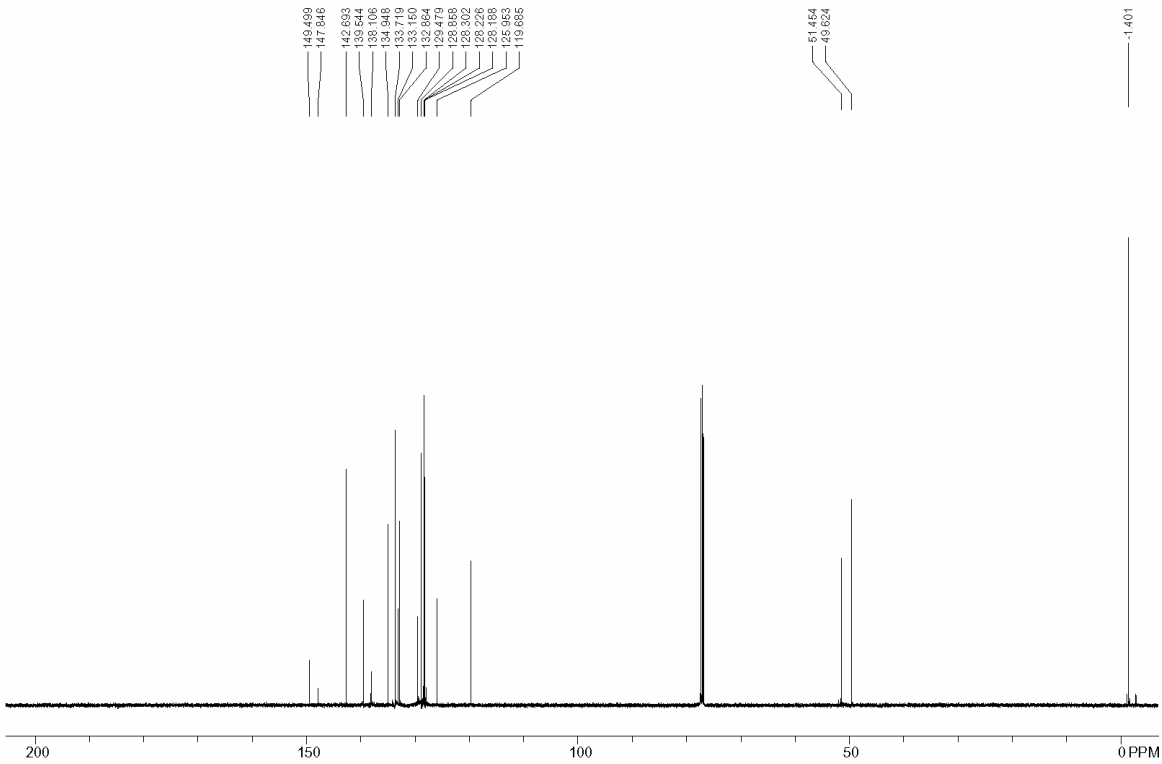
1.0
1.0
2.0
2.0
6.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

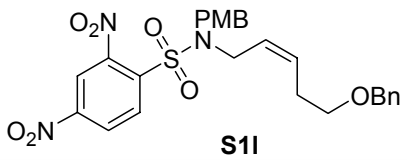

149.4
147.7
139.7
139.5
137.4
134.8
134.0
133.6
132.7
129.3
128.8
128.4
128.2
127.8
125.8
119.5
51.8
51.4
200
150
100
50
ppm (f1)


O2N
O
Bn
N
S
O
SiMe2Ph
O2N

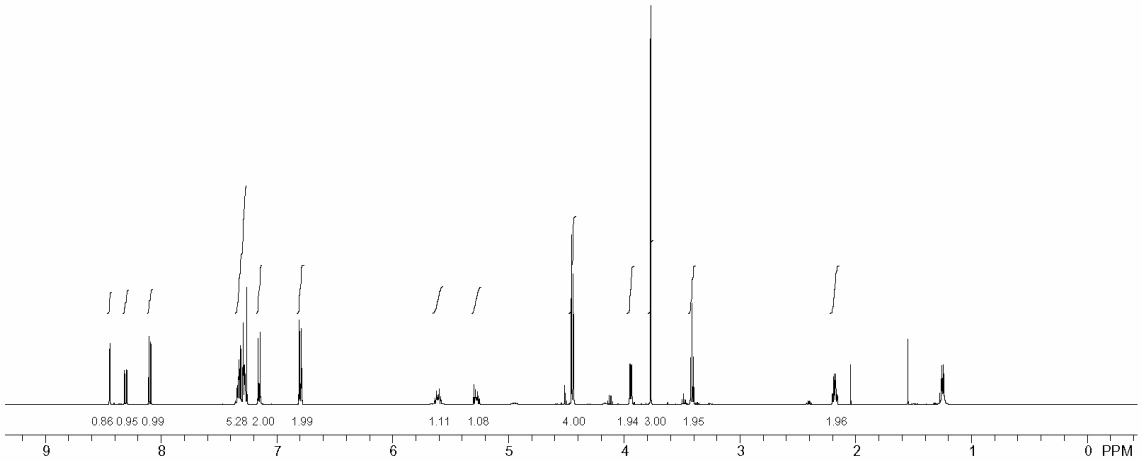
S1i

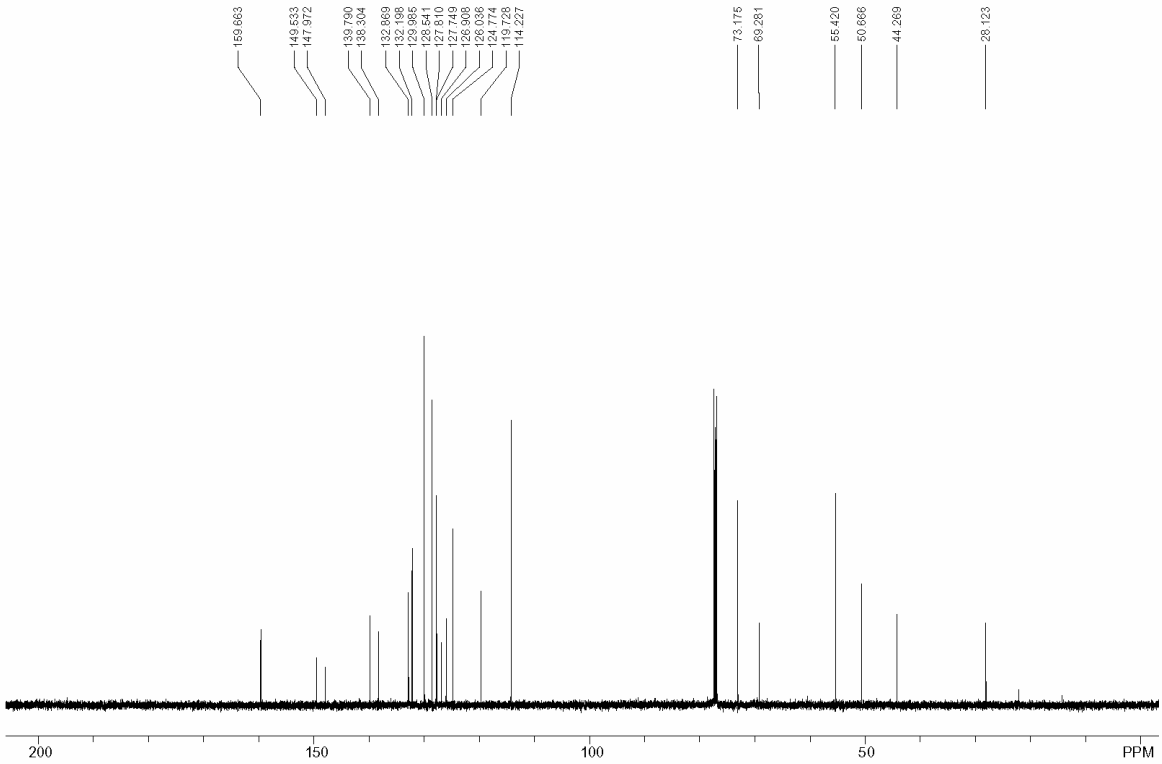

0.91 1.00 0.97 8.57 2.00 1.00 1.03 1.93 1.93 5.99
10
8
6
4
2
0 PPM

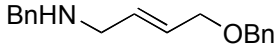

149.499
147.846
142.693
135.544
138.106
134.948
133.719
133.150
132.864
129.479
128.868
128.302
128.226
128.188
125.953
119.685
51.454
49.624
-1.401
200
150
100
50
0 PPM


O2N
O
PMB
N
S
O
O2N
OBn

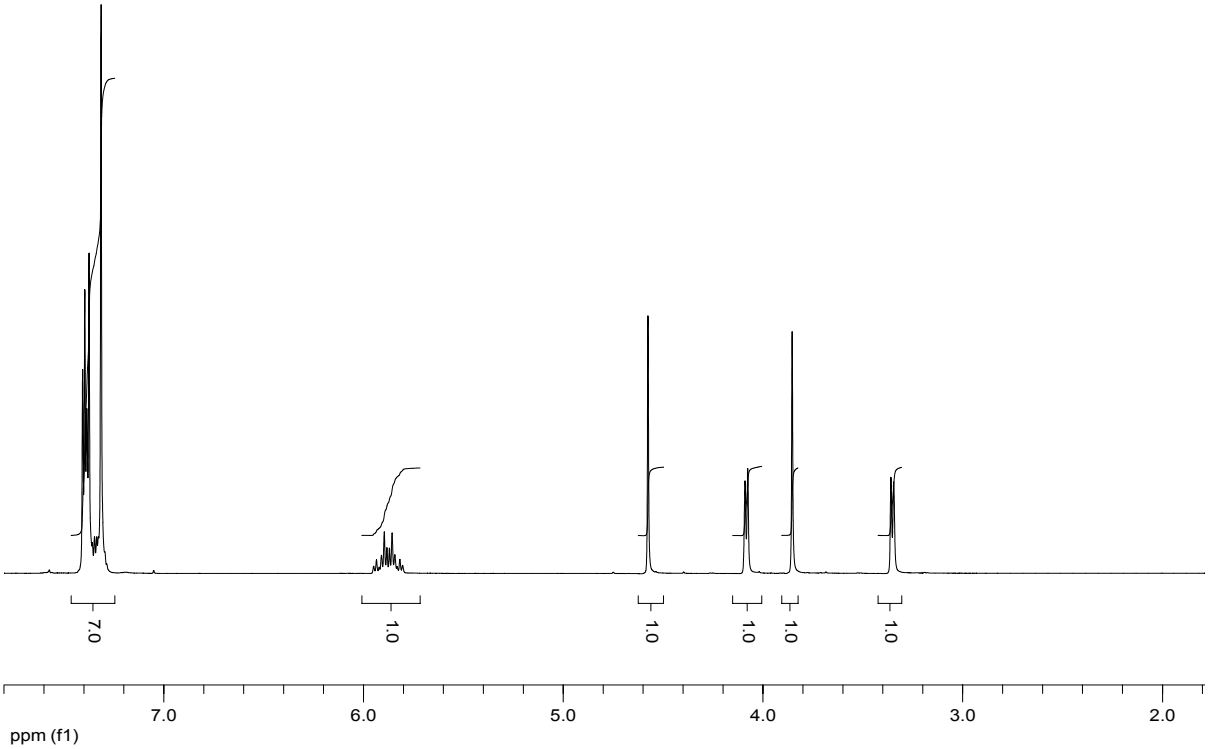
S1l

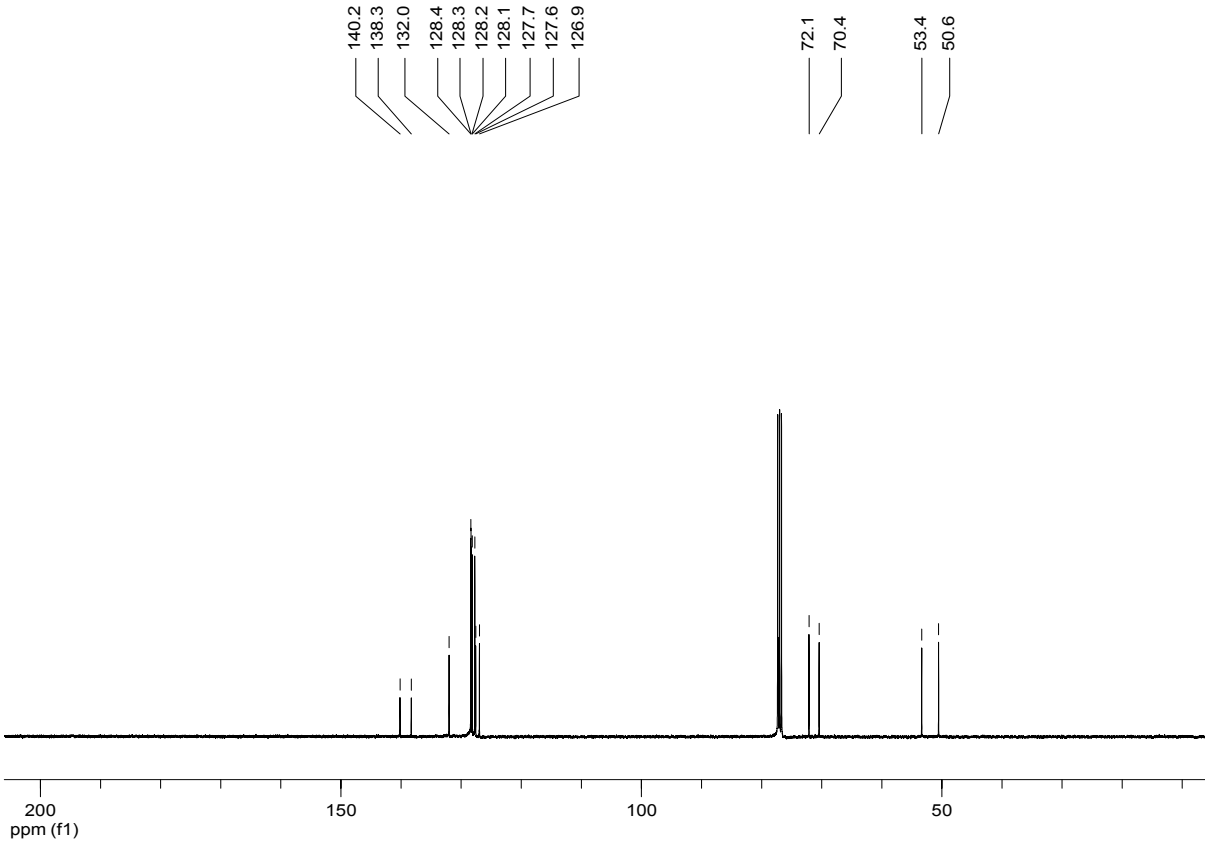

0.86 0.95 0.99
5.28 2.00
1.99
1.11
1.08
4.00
1.94 3.00
1.95
1.96
9
8
7
6
5
4
3
2
1
0 PPM

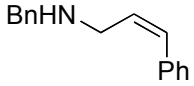

159.663
149.533
147.972
139.790
138.304
132.869
132.198
129.985
128.541
127.810
127.749
126.908
126.036
124.774
119.728
114.227
73.175
69.281
55.420
50.666
44.269
28.123
200
150
100
50
PPM


BnHN
OBn

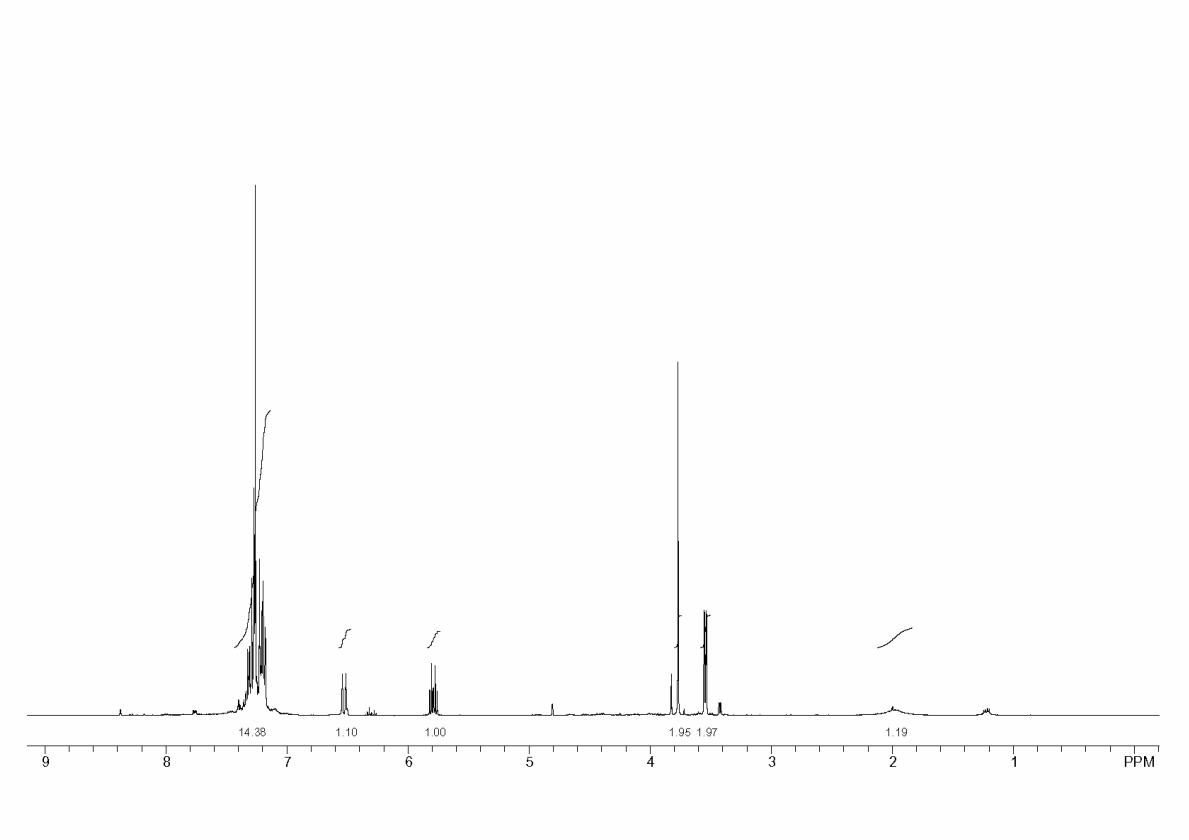
S2f

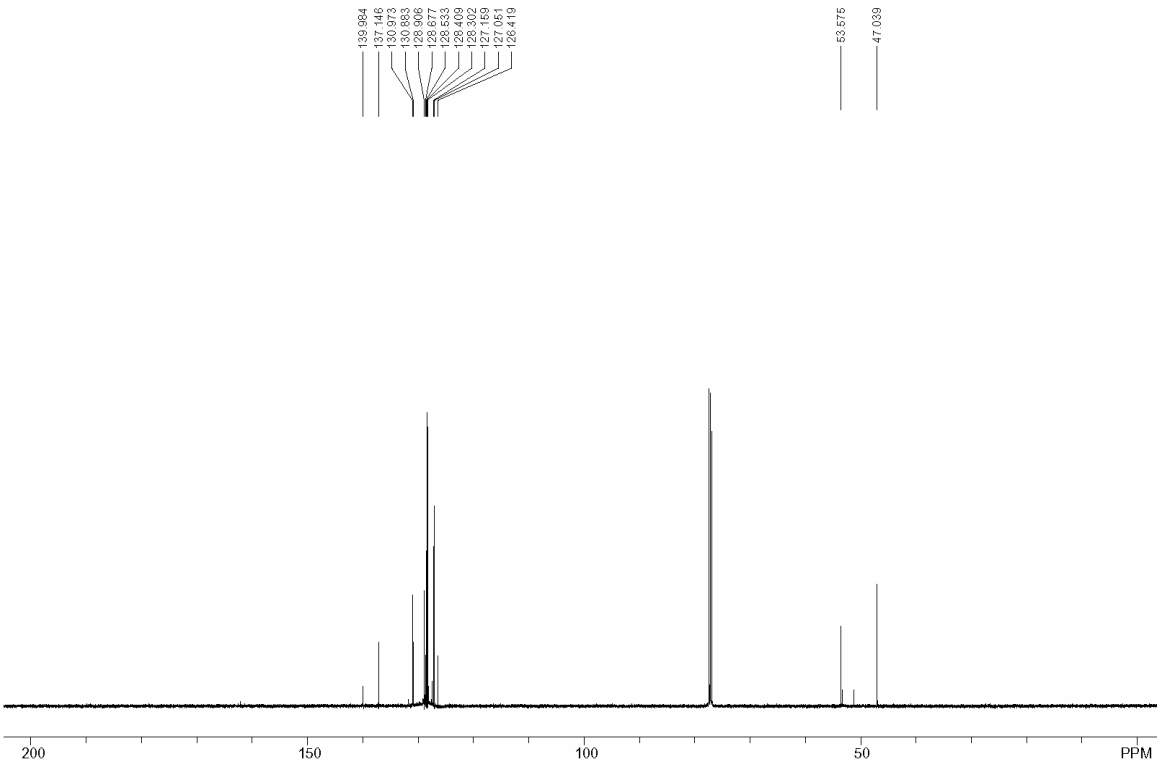

7.0
1.0
1.0
1.0
1.0
1.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (f1)

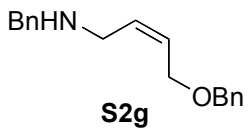

140.2
138.3
132.0
128.4
128.3
128.2
128.1
127.7
127.6
126.9
72.1
70.4
53.4
50.6
200
150
100
50
ppm (f1)


BnHN
Ph

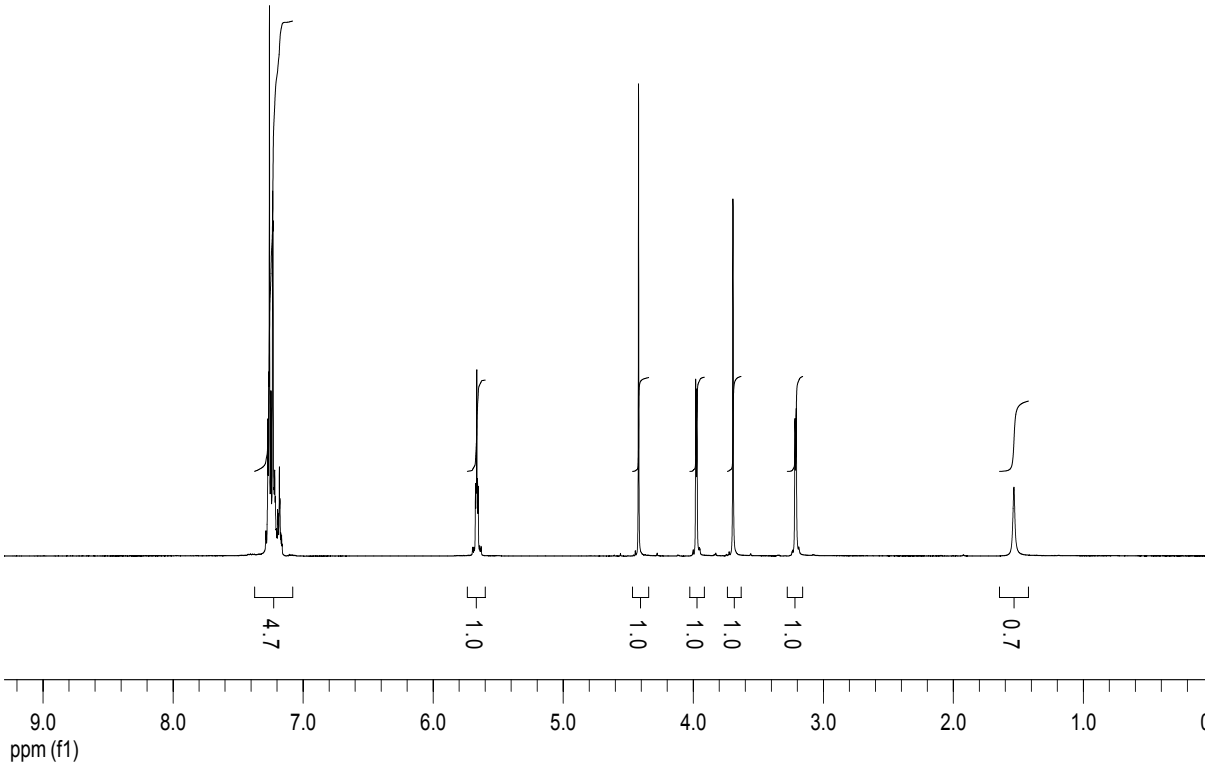
S2e


14.38
1.10
1.00
1.95 1.97
1.19
9
8
7
6
5
4
3
2
1
PPM


139.984
137.146
130.973
130.883
128.906
128.677
128.533
128.409
128.302
127.159
127.051
126.419
53.575
47.039
200
150
100
50
PPM


BnHN
OBn

S2g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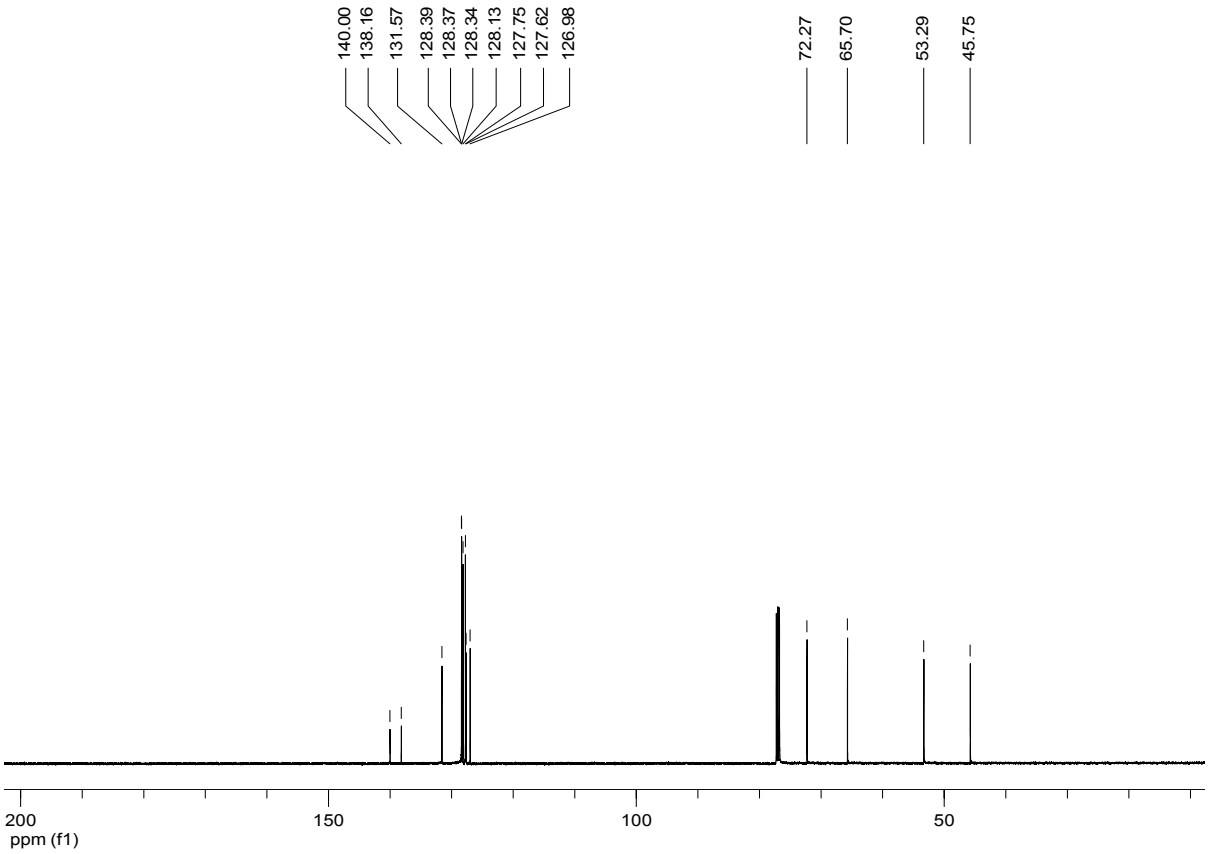
1.0
1.0
1.0
1.0
1.0
0.7
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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138.16
131.57
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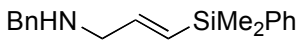
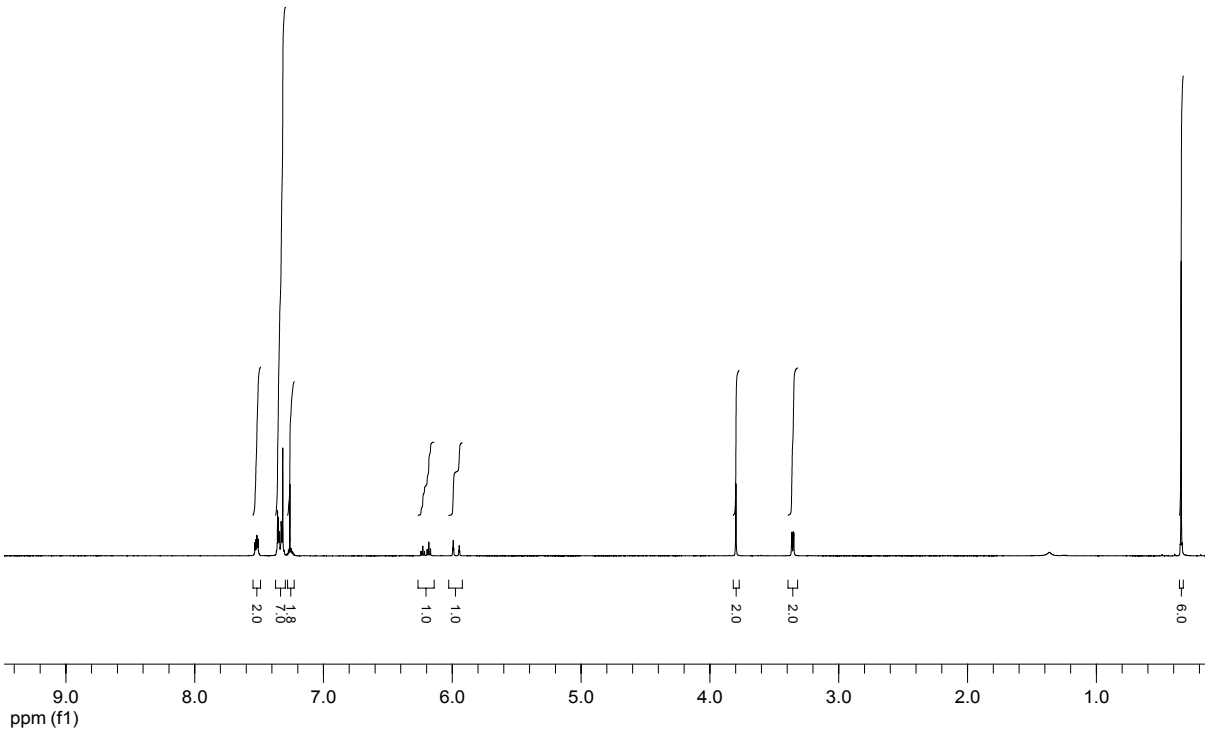
128.37
128.34
128.13
127.75
127.62
126.98
72.27
65.70
53.29
45.75
200
150
100
50
ppm (f1)


BnHN
SiMe2Ph

S2h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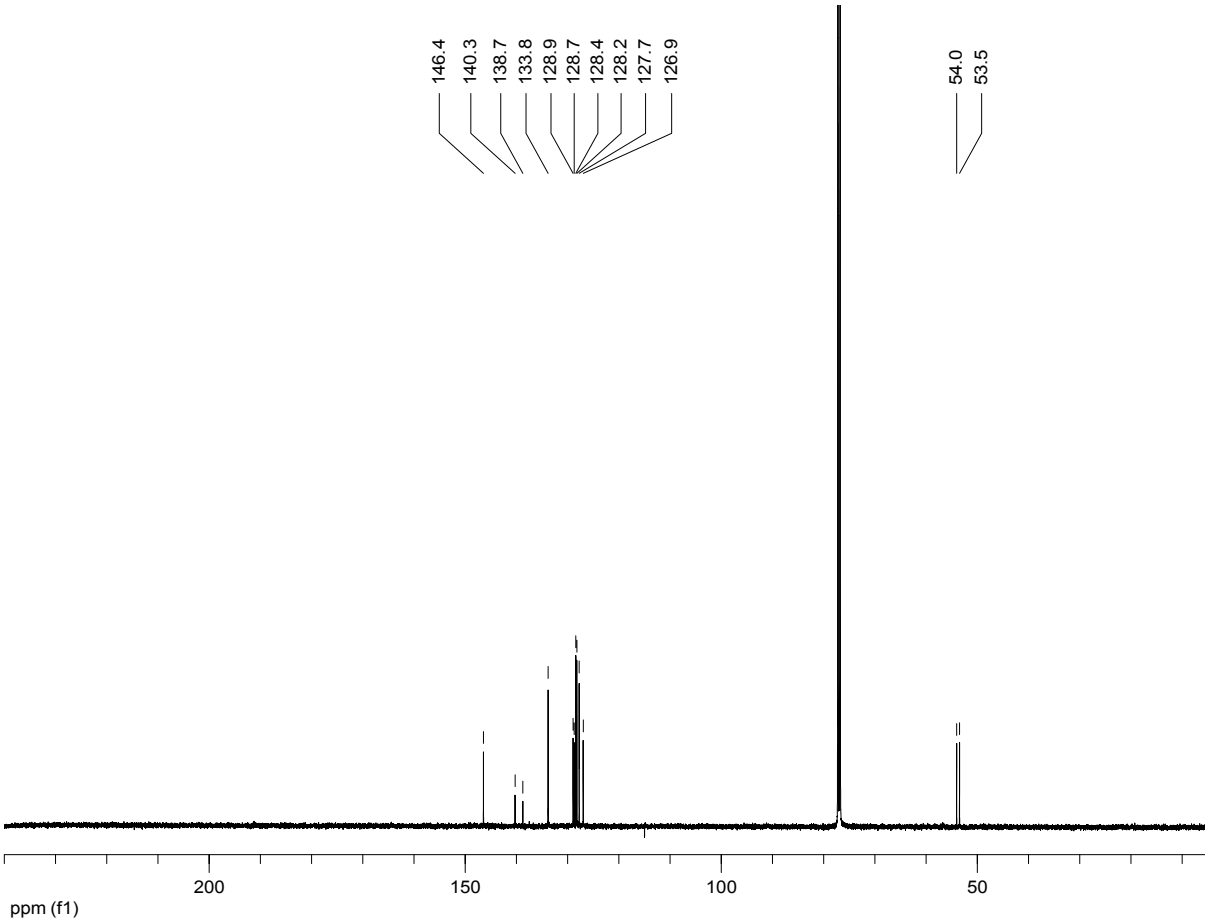
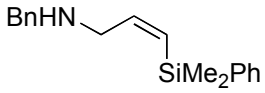
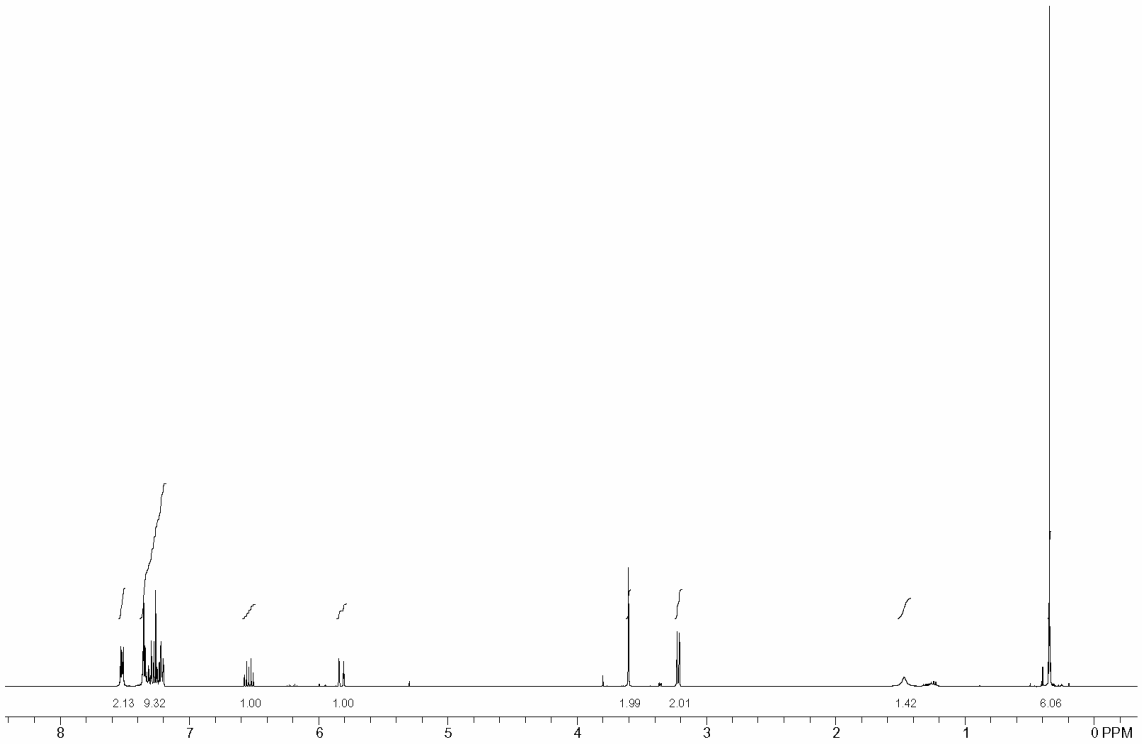
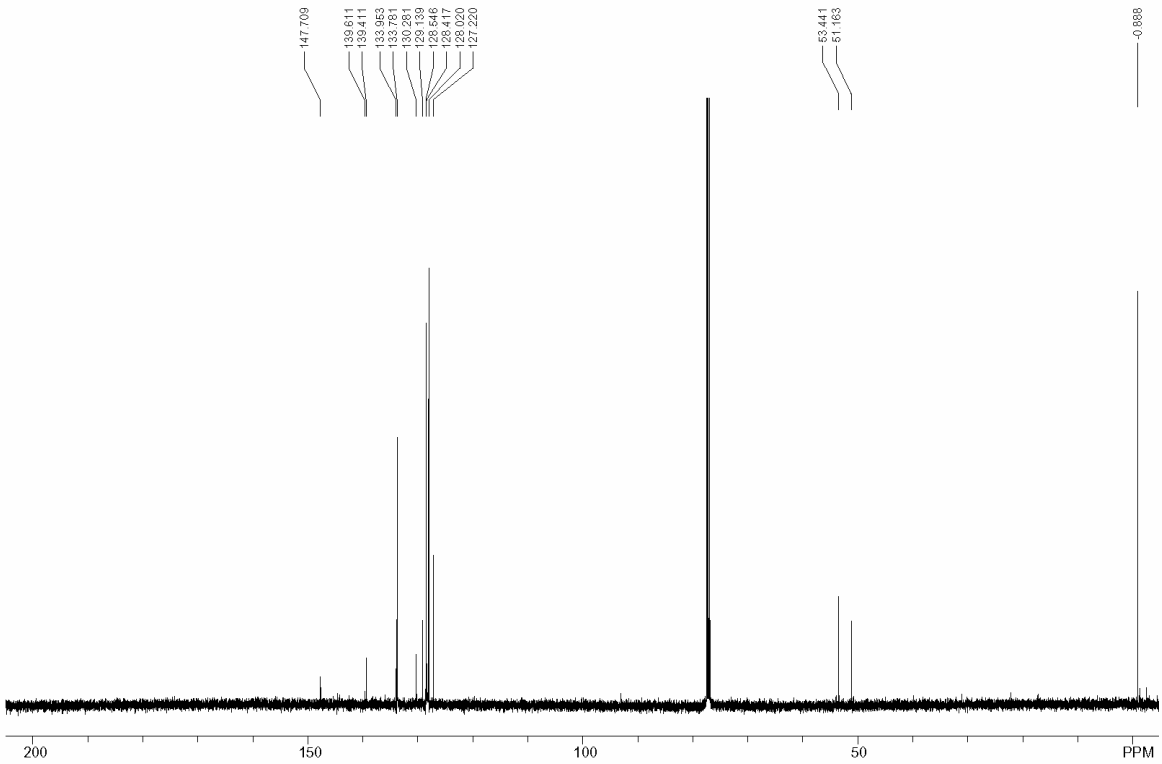
7.8
7.0
1.0
1.0
2.0
2.0
6.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


146.4
140.3
138.7
133.8
128.9
128.7
128.4
128.2
127.7
126.9
54.0
53.5
200
150
100
50
ppm (f1)


BnHN
SiMe2Ph

S2i


2.13
9.32
1.00
1.00
1.99
2.01
1.42
6.06
8
7
6
5
4
3
2
1
0 PPM


147.709
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139.411
133.953
133.781
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129.139
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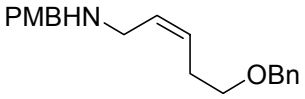
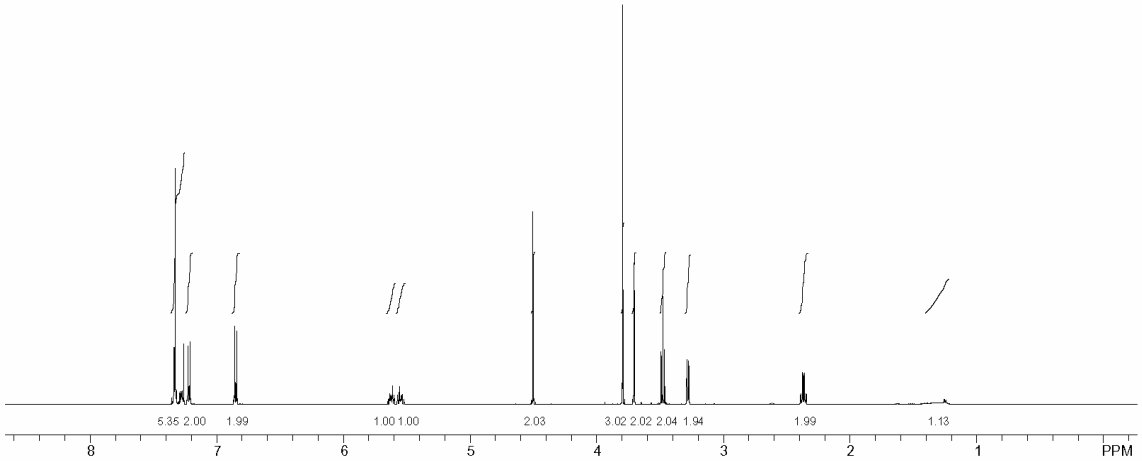
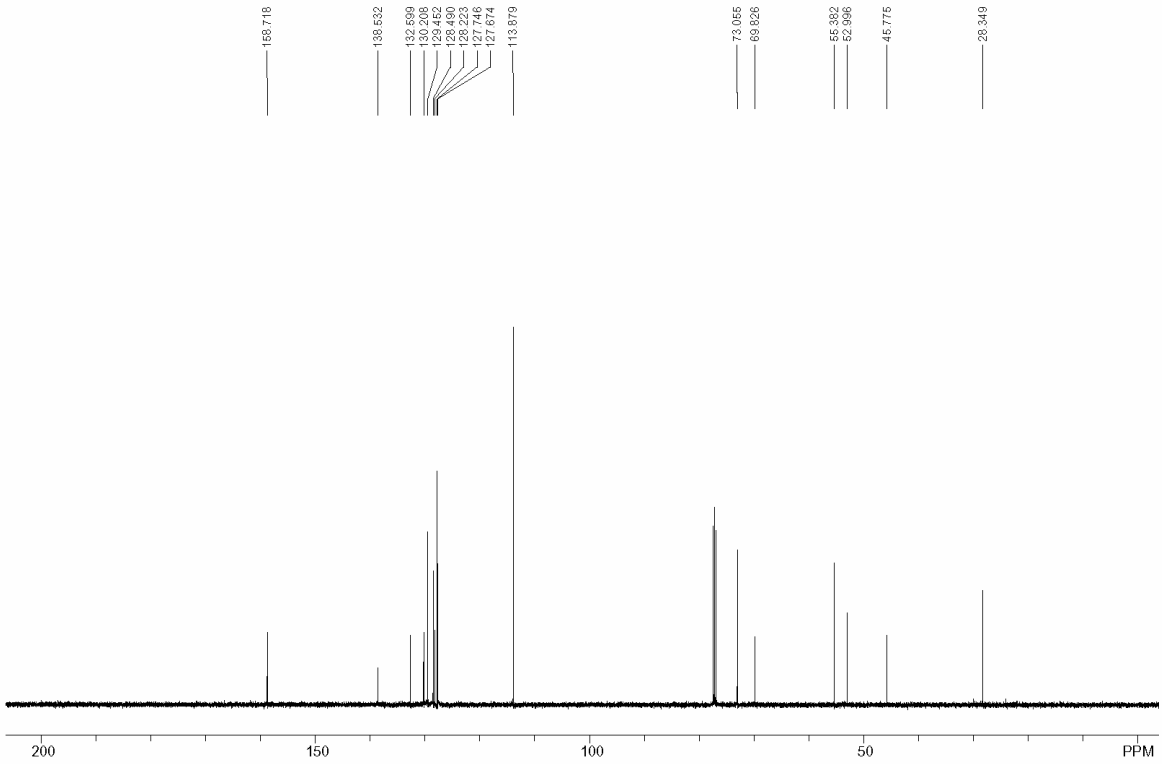
128.477
129.000
127.220
53.441
51.163
-0.888
200
150
100
50
PPM


PMBHN
OBn

S2l


5.35 2.00 1.99 1.00 1.00 2.03 3.02 2.02 2.04 1.94 1.99 1.13
8 7 6 5 4 3 2 1 PPM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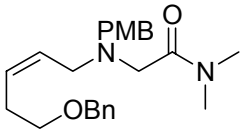
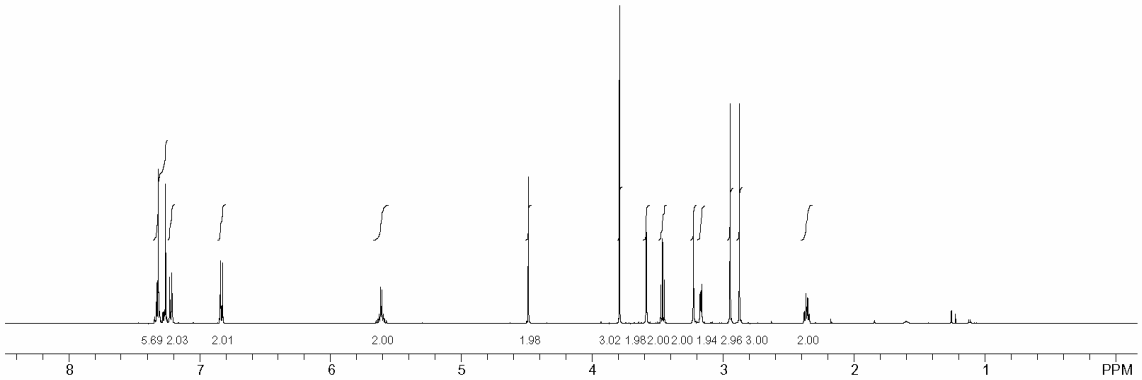
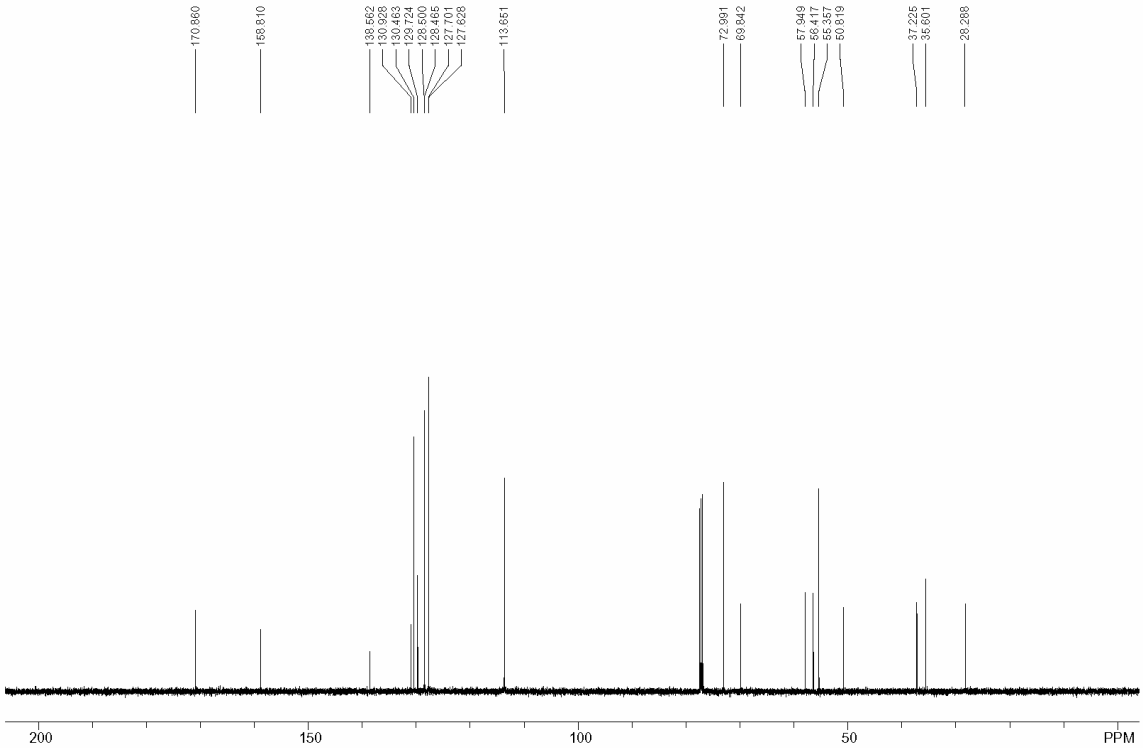
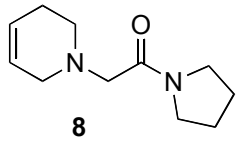
138.532
132.599
130.208
129.462
128.490
128.223
127.746
127.674
113.879
73.055
69.826
55.382
52.996
45.775
28.349
200 150 100 50 PPM


PMB
O
N
N
OBn

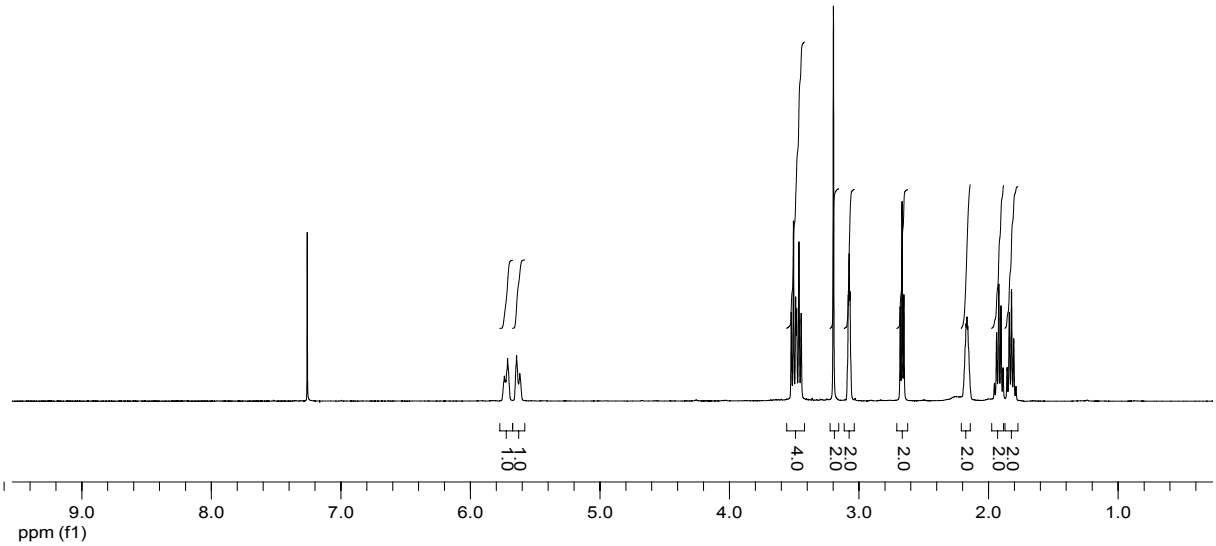
1l

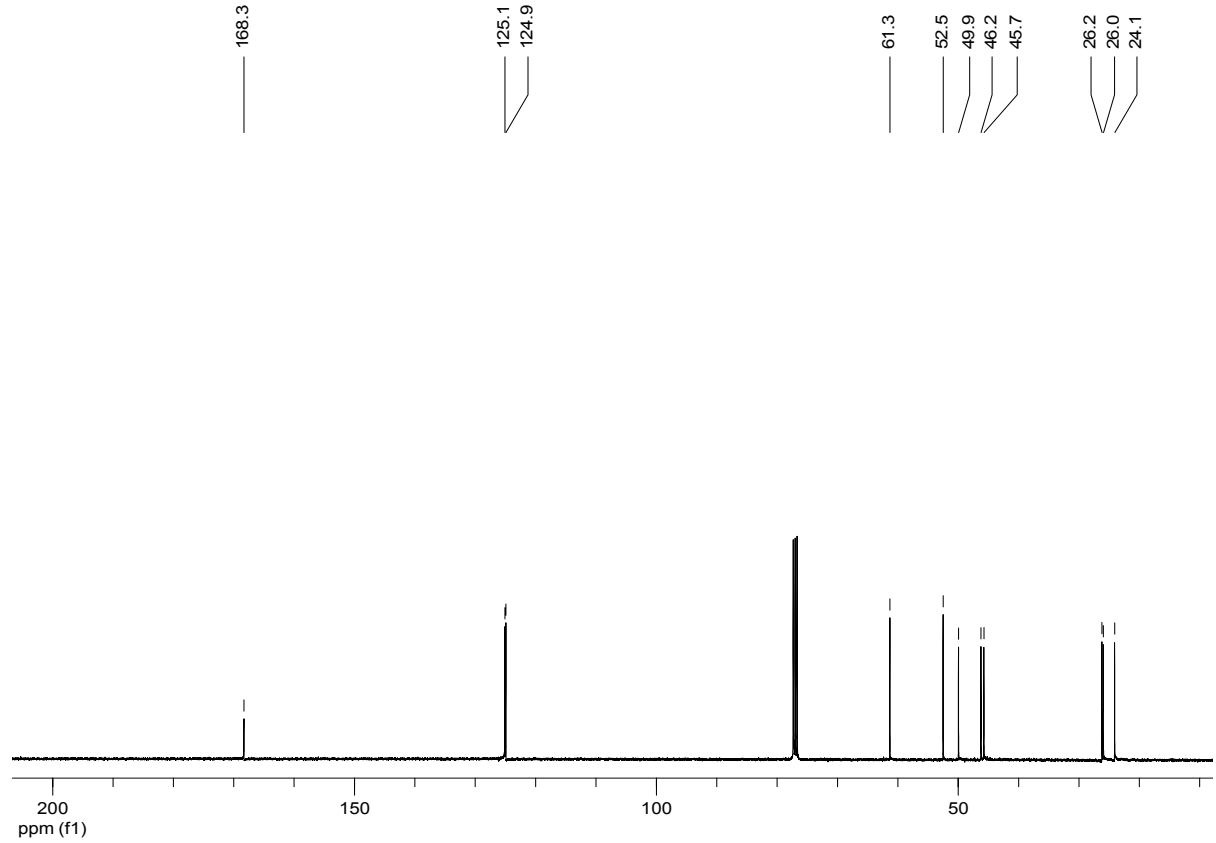

5.69 2.03
2.01
2.00
1.98
3.02 1.98 2.00 2.00 1.94 2.96 3.00
2.00
8
7
6
5
4
3
2
1
PPM

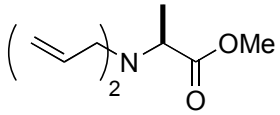

170.860
168.810
138.562
130.928
130.463
129.724
128.500
128.465
127.701
127.628
113.661
72.991
69.842
57.949
56.417
55.357
50.819
37.225
35.601
28.288
200
150
100
50
PPM



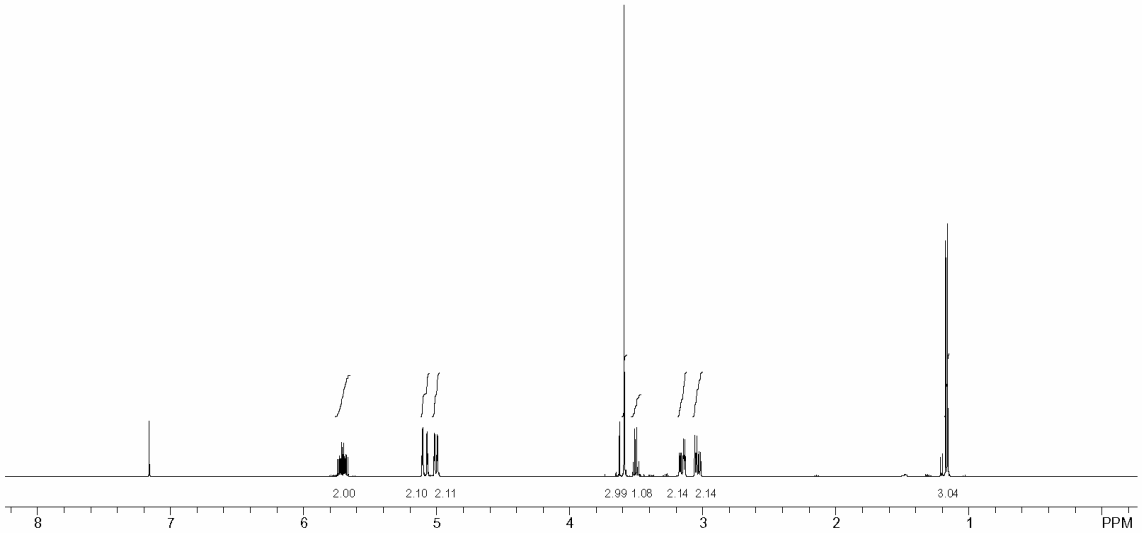
8

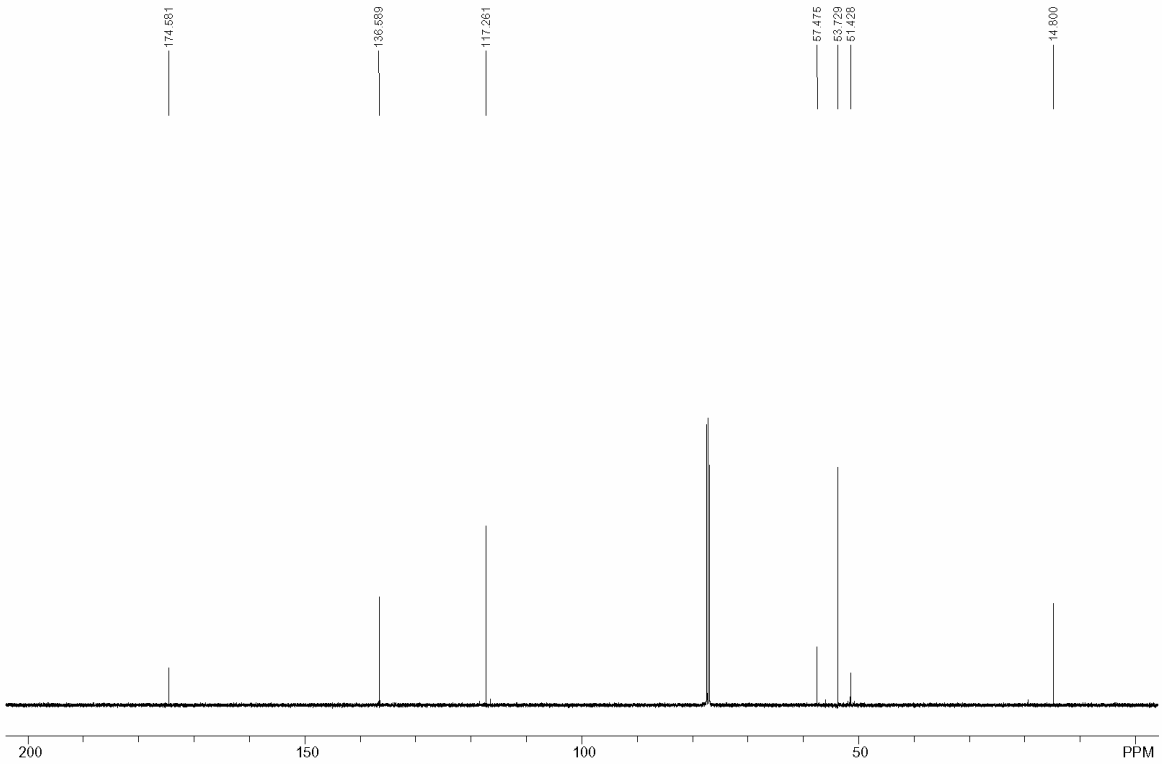

1.0
1.0
4.0
2.0
2.0
2.0
2.0
2.0
2.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

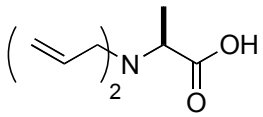

168.3
125.1
124.9
61.3
52.5
49.9
46.2
45.7
26.2
26.0
24.1
200
150
100
50
ppm (f1)


N
2
OMe
O

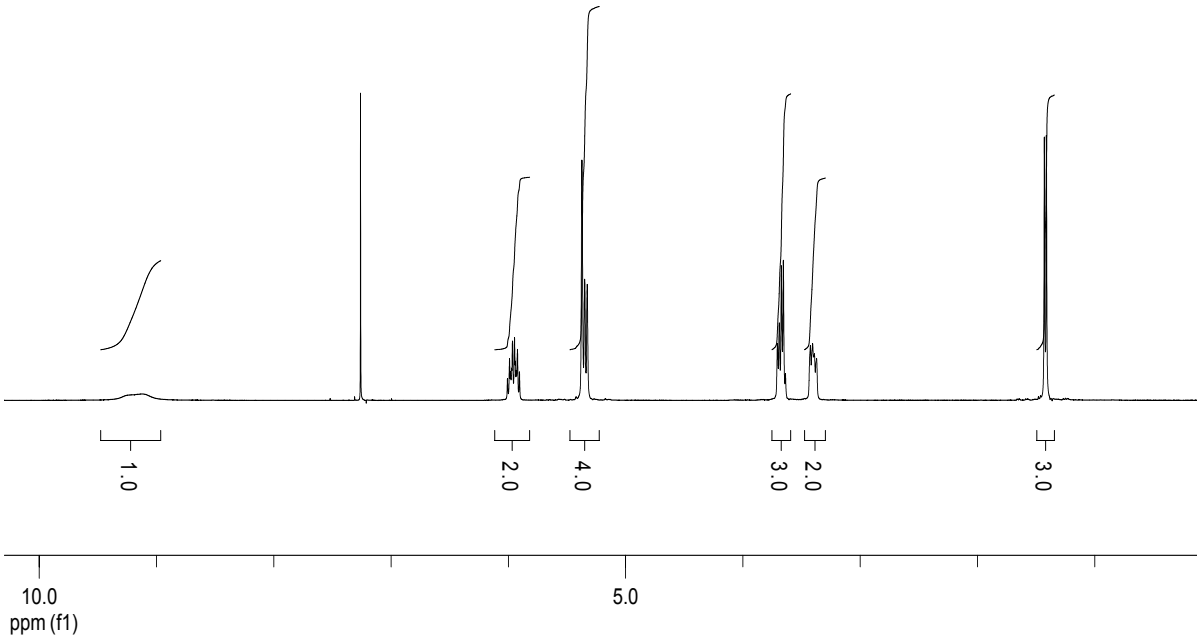
S3

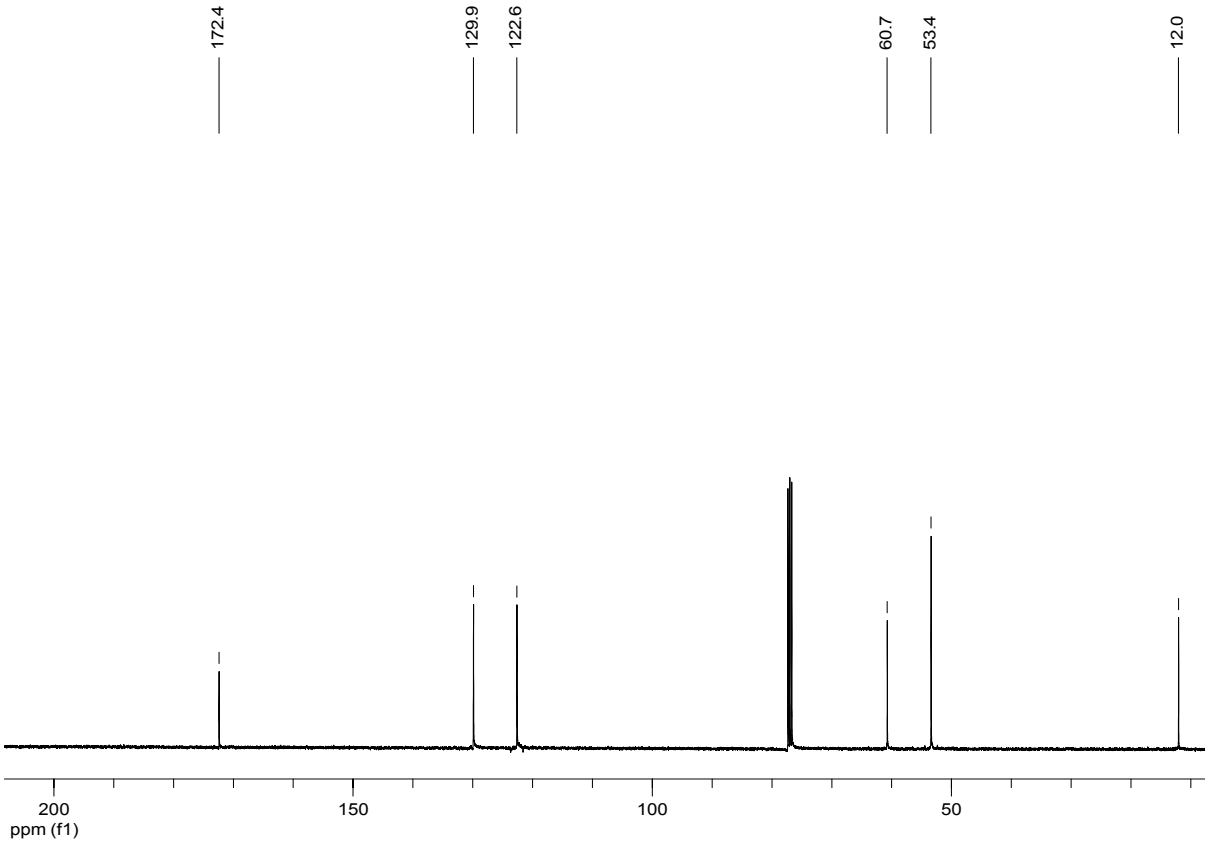

2.00
2.10
2.11
2.99
1.08
2.14
2.14
3.04
8
7
6
5
4
3
2
1
PPM

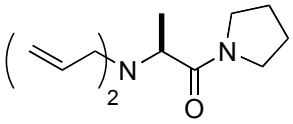

174.581
136.589
117.261
57.475
53.729
51.428
14.800
200
150
100
50
PPM


N
2
OH
O

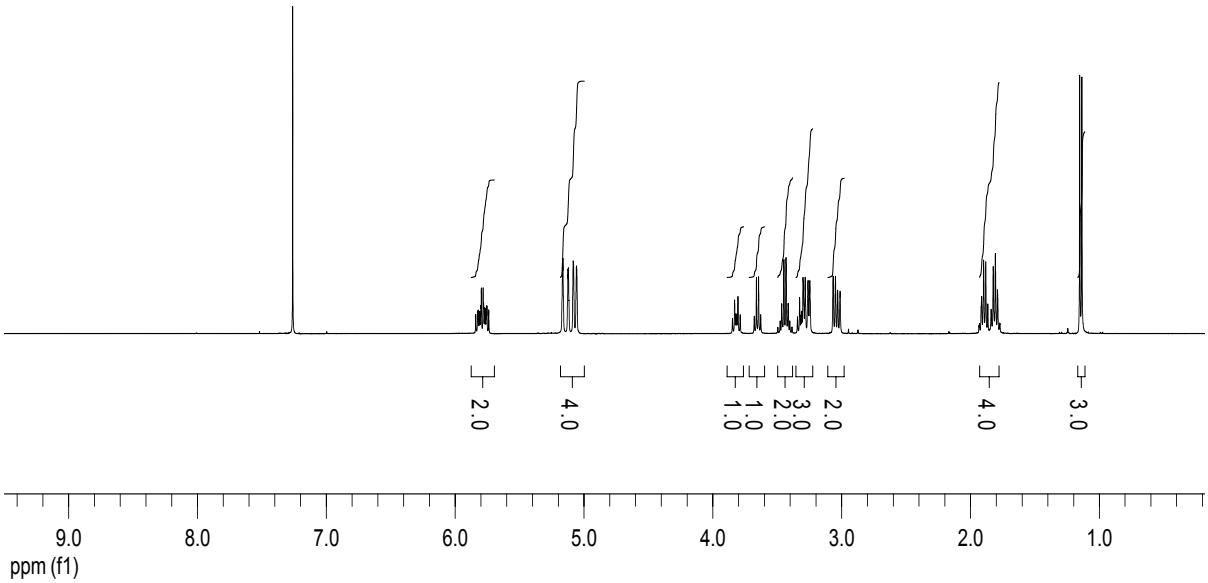
S4

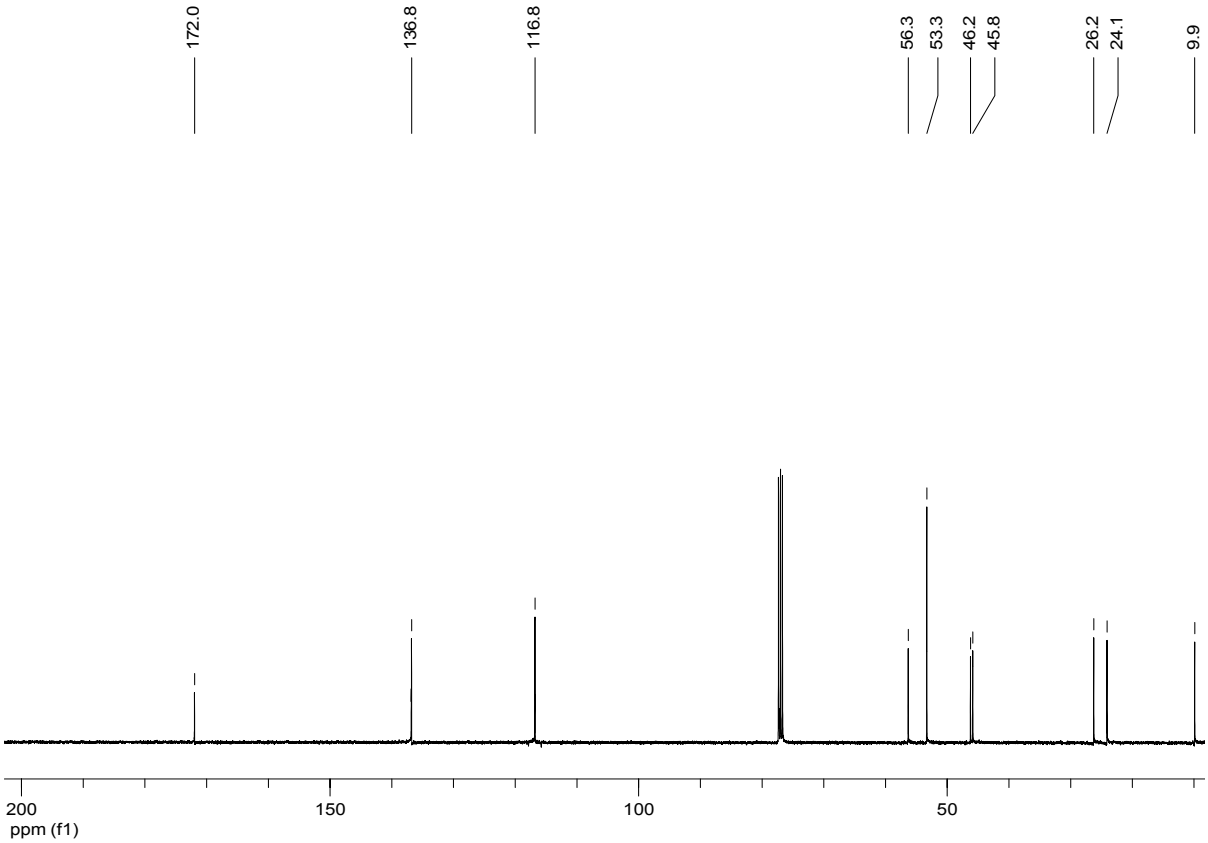

1.0
2.0
4.0
3.0
2.0
3.0
10.0
5.0
ppm (f1)

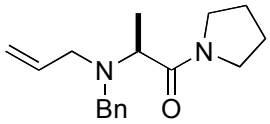

172.4
129.9
122.6
60.7
53.4
12.0
200
150
100
50
ppm (f1)



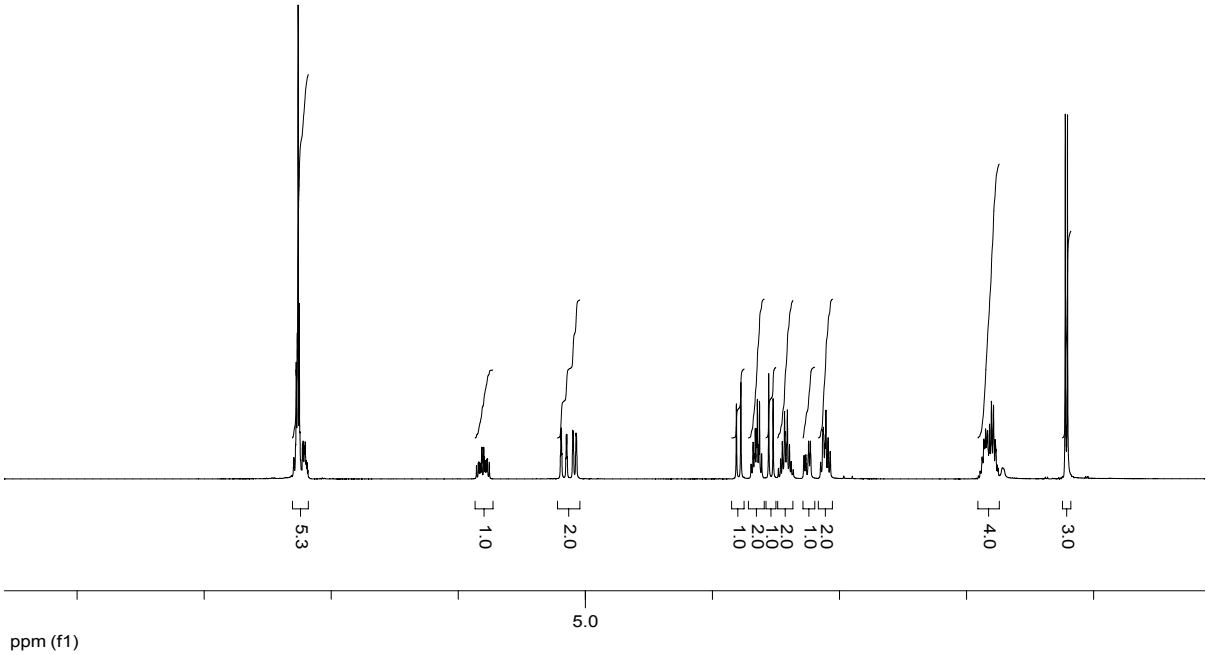
12

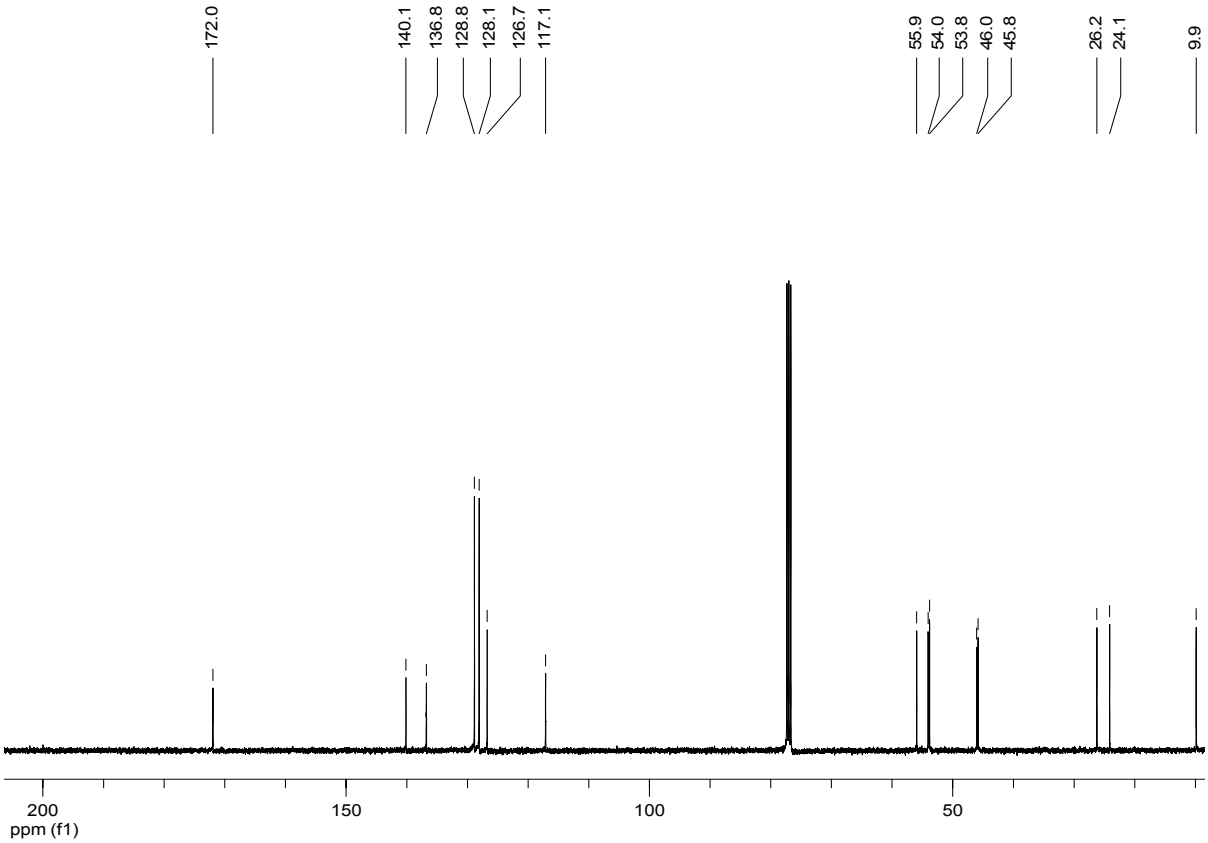

2.0
4.0
1.0
1.0
2.0
3.0
2.0
4.0
3.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

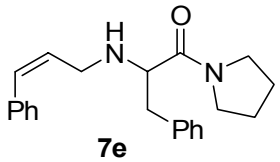

172.0
136.8
116.8
56.3
53.3
46.2
45.8
26.2
24.1
9.9
200
150
100
50
ppm (f1)


N
Bn
O
N

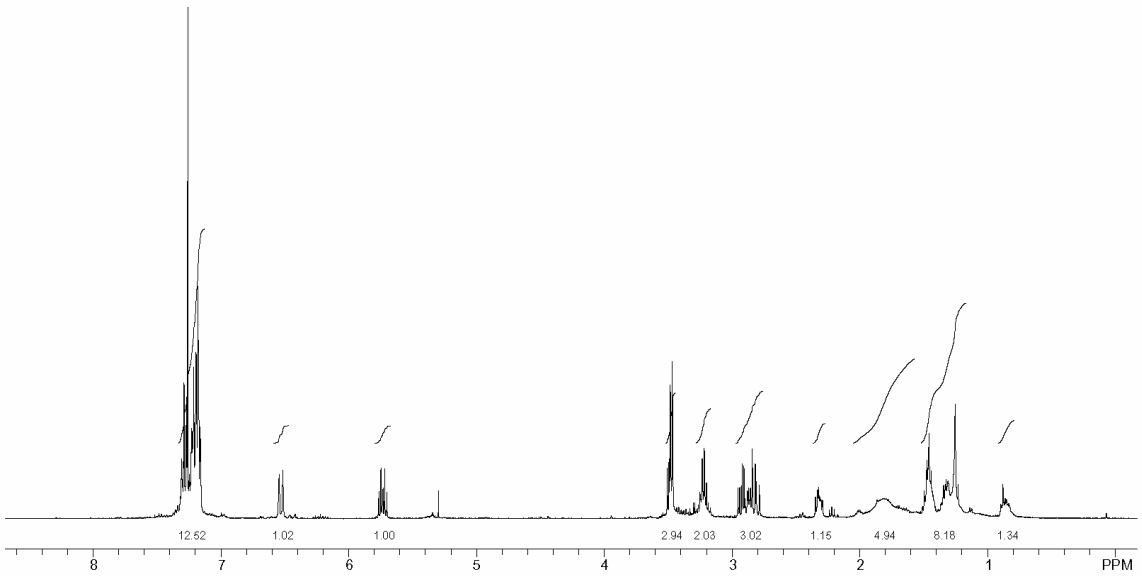
10

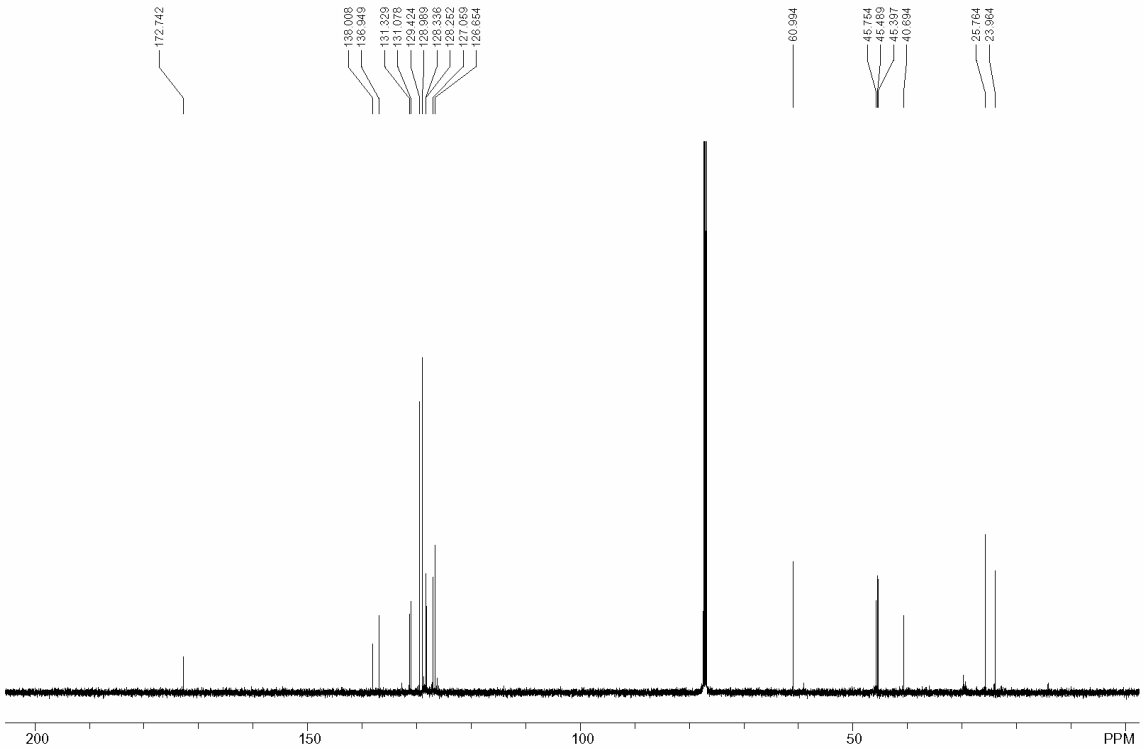

5.3
1.0
2.0
1.0
2.0
1.0
2.0
1.0
2.0
4.0
3.0
5.0
ppm (f1)

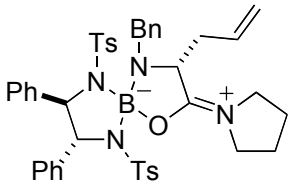

172.0
140.1
136.8
128.8
128.1
126.7
117.1
55.9
54.0
53.8
46.0
45.8
26.2
24.1
9.9
200
150
100
50
ppm (f1)



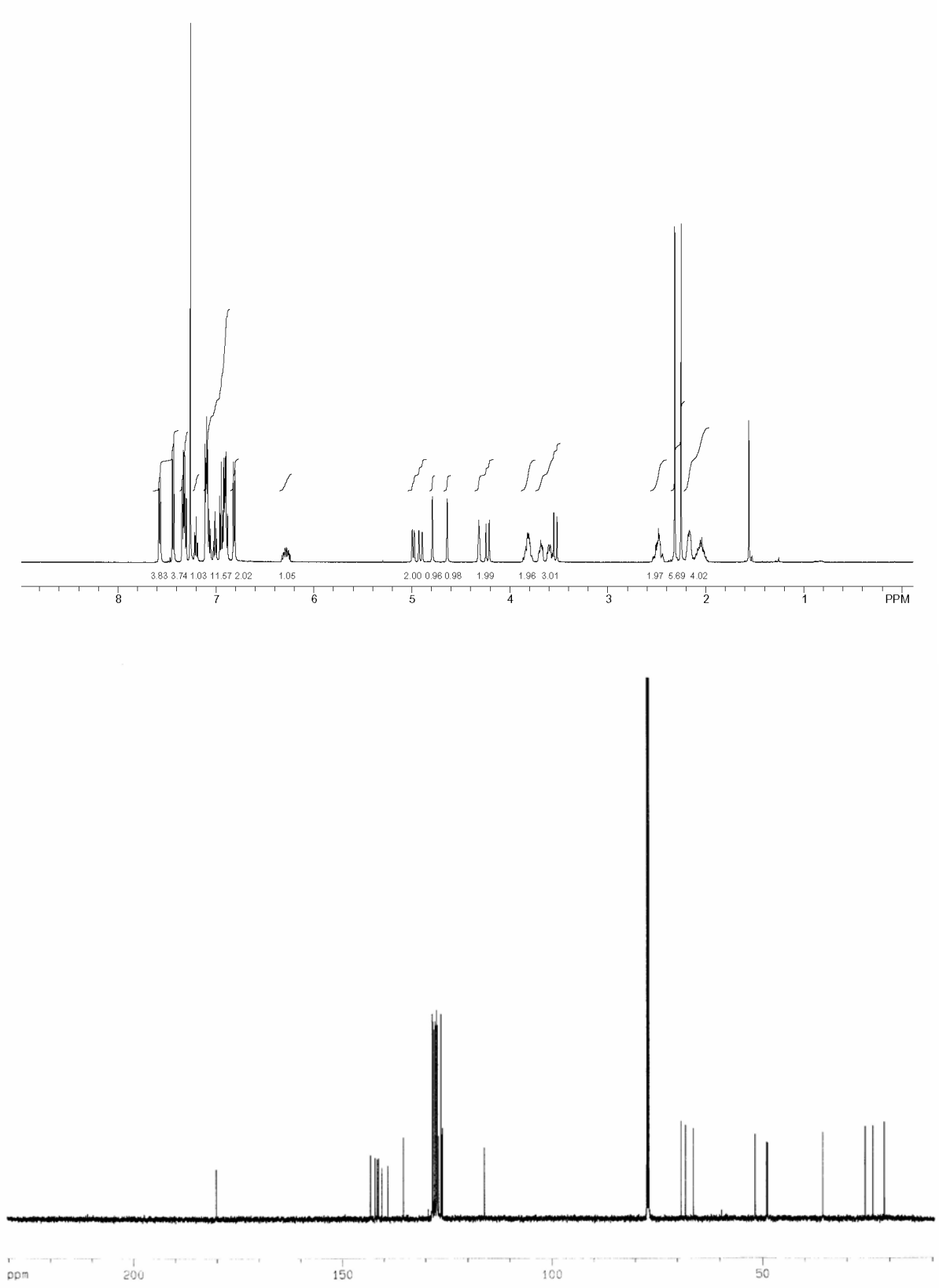
7e


12.52
1.02
1.00
2.94
2.03
3.02
1.15
4.94
8.18
1.34
8
7
6
5
4
3
2
1
PPM

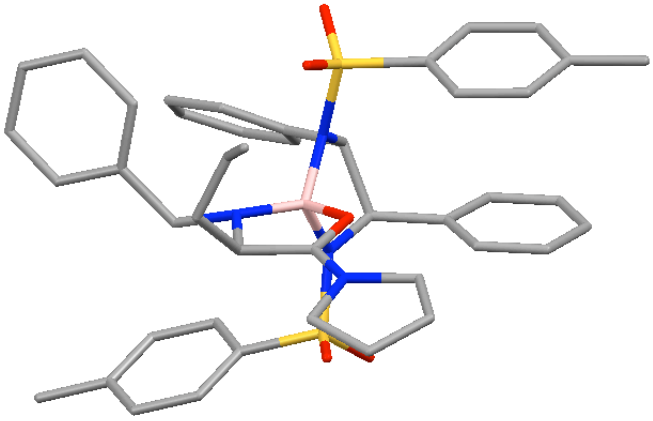

172.742
138.008
136.949
131.329
131.078
129.424
128.969
128.336
128.252
127.069
126.654
60.994
45.754
45.489
45.377
40.654
25.764
23.964
200
150
100
50
PPM


Ts
Bn
N
Ph
N
B
O
N
Ph
Ts

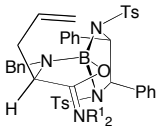
6


3.83 3.74 1.03 11.57 2.02
1.05
2.00 0.96 0.98
1.99
1.96 3.01
1.97 5.69 4.02
8
7
6
5
4
3
2
1
PPM
ppm
200
150
100
50

X-ray structure of **6**. Hydrogens ommited for clarity.



Blue=nitrogen
Red=oxygen
Yellow=sulphur
Pink=boron



6