Supporting Information

A Facile Access to *N*-Sulfonylimidates and their Synthetic Utility for the transformation to amidines and amides

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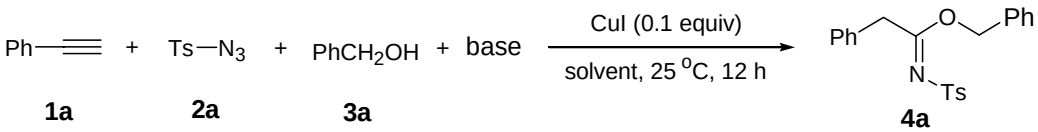
General Methods. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. Visualization on TLC was achieved by use of UV light (254 nm) and treatment with phosphomolybdic acid and anisaldehyde stain followed by heating. Flash column chromatography was undertaken on silica gel (Merck Kieselgel 60 F_{254} 400-630 mesh). ^{1}H NMR was recorded on Bruker FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Brucker FT AM 400 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell on Bruker EQUINOX 55. Frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were recorded on a Jeol JMS-

HX110/110A by using FAB method.

Experimental Procedure for the Optimization Studies (Table S1). To a stirred mixture of phenylacetylene (**1a**, 51.1 mg, 0.5 mmol), *p*-toluenesulfonyl azide (**2a**, 118.3 mg, 0.6 mmol), CuI (9.5 mg, 0.05 mmol) and benzyl alcohol (**3a**, 0.062 mL, 0.6 mmol) in a solvent (1.0 mL) was slowly added base (0.6 mmol) at room temperature under an N_2 atmosphere. After 12 h, the reaction mixture was diluted by adding CH_2Cl_2 (2 mL) and saturated NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 min and two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The NMR yield of desired product **4a**, benzyl *N*-(4-methylbenzensulfonyl)phenylacetimidate, was determined by integration using an internal standard (*p*-anisole).

Table S1. Optimization of the Cu-Catalyzed Three-Component Coupling



1a **2a** **3a** **4a**

Entry	Base	Solvent	Yield (%)[a]	Entry	Base	Solvent	Yield
1	–	THF	No conversion	10	Et_3N	$ClCH_2CH_2Cl$	64
2	K_2CO_3	THF	No conversion	11		1,4-dioxane	80
3	MgO	THF	No conversion	12		CH_2Cl_2	75
---4---	TMEDA[b]	THF	No conversion	13		CH_3CN	19
5	DBU[c]	THF	No conversion	14		DME	27
6	2.6-Lutidine	THF	67	15		DMF	<5
7		$CHCl_3$	59	16		DMA	<5
8	Pyridine	$CHCl_3$	41	17	Et_3N (1.0 eq)	$CHCl_3$	83
9	Et_3N	$CHCl_3$	87	18	Et_3N (0.4 eq)	$CHCl_3$	55

[a] NMR yield based on an internal standard (*p*-anisole).

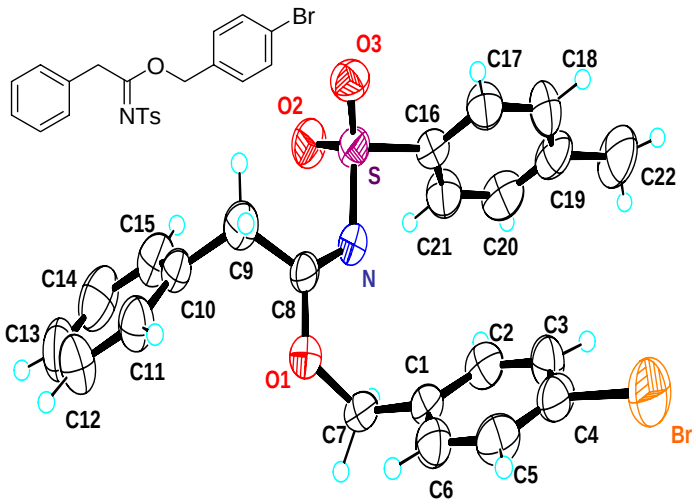
[b] TMEDA: *N,N,N',N'*-tetramethylethylenediamine. [c] DBU: 1,8-diazobicyclo[5.4.0]-undec-7-ene.

Representative Procedure for the Preparation of Imidates (Table 1). To a stirred mixture of phenylacetylene (**1a**, 51.1 mg, 0.5 mmol), *p*-toluenesulfonyl azide (**2a**, 118.3 mg, 0.6 mmol), benzyl alcohol (**3a**, 0.062 mL, 0.6 mmol, except a diol being 0.25 mmol, entry11) and CuI (9.5 mg, 0.05 mmol) in $CHCl_3$ (1.0 mL) was slowly added Et_3N (0.084 mL, 0.6 mmol) at room temperature under an N_2 atmosphere. After stirring the reaction mixture for 12 h at room temperature, it was diluted with CH_2Cl_2 (2 mL) and then with aqueous NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 min at room temperature and two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 mL x 3) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude residue was purified by flash column chromatograph with EtOAc/n-hexane = 1:5 to give the desired product **4a**, benzyl *N*-(4-methylbenzensulfonyl)-phenylacetimidate (331 mg, 87%), as a brownish liquid.

Benzyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4a): brownish liquid (87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.6, 1.7 Hz, 2H), 7.37-7.26 (m, 10H), 7.12 (dd, *J* = 7.0, 1.6 Hz, 2H), 5.08 (s, 2H), 4.28 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 143.2, 138.8, 134.5, 133.4, 129.6, 129.3, 128.5, 128.4, 128.3, 127.9, 127.2, 126.6, 70.1, 39.5, 21.5; IR (KBr) ν 1615, 1456, 1303, 1155, 1094, 979, 688 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{22}H_{22}NO_3S$ $[M+H]^+$: 380.1320, found: 380.1326.

4-Bromobenzyl-*N*-(4-methylbenzensulfonyl)phenylacetimidate (4b): white solid (91%); m.p. 91-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.35-7.24 (m, 9H), 6.92 (d, *J* = 8.4 Hz, 2H), 5.00 (s, 2H), 4.25 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 143.4, 138.7, 133.7, 133.4, 131.6, 129.6, 129.6, 129.4, 128.6, 127.4, 126.7, 122.4, 69.3, 39.5, 21.5; IR (KBr) ν 1613, 1303, 1156, 1092, 734, 688, 595 cm^{-1}. An ORTEP plot of **4b** is shown below.

Figure S1. ORTEP plot of **4-bromo-*N*-(4-methylbenzensulfonyl)phenylacetimidate (4b)**



Methyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4c): white solid (93%); m.p. 72-75 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.35-7.25 (m, 7H), 4.25 (s, 2H), 3.68 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 143.2, 138.9, 133.4, 129.5, 129.3, 128.5, 127.2, 126.6, 55.6, 39.4, 21.4; IR (KBr) ν 1614, 1303, 1153, 1092, 687, 598 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{16}H_{18}NO_3S$ $[M+H]^+$: 304.1007, found: 304.1008.

Isopropyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4d): white solid (73%); m.p. 83-84 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34-7.22 (m, 7H), 5.00 (septet, *J* = 6.2, 1H), 4.19 (s, 2H), 2.38 (s, 3H), 1.14 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 143.0, 139.1, 133.7, 129.3, 129.2, 128.4, 127.0, 126.4, 72.3, 39.7, 21.4, 21.0; IR (KBr) ν 1597, 1303, 1157, 1094, 691 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{22}NO_3S$ $[M+H]^+$: 332.1320, found: 332.1319.

Phenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4e): white solid (61%); m.p. 95-97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.35-7.15 (m, 8H), 6.90 (dd, *J* = 8.8, 1.2 Hz, 2H), 4.43 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 172.4, 151.6, 143.2, 138.4, 133.3, 129.5, 129.2, 129.2, 128.7, 128.4, 127.4, 126.4, 126.1, 121.1, 39.5, 21.4; IR (KBr) ν 1633, 1586, 1488, 1305, 1156, 1094, 761, 686 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{21}H_{20}NO_3S$ $[M+H]^+$: 336.1164, found: 336.1167.

4-Methoxyphenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4f): white solid (65%); m.p. 93-96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.55-7.16 (m, 7H), 6.80-6.74 (m, 5H), 4.39 (s, 2H), 3.73 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 157.4, 145.1, 143.2, 133.4, 129.6, 129.2, 128.7, 127.4, 126.5, 121.9, 114.1, 55.5, 39.5, 21.4; IR (KBr) ν 1633, 1505, 1157, 1093, 834, 685 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{22}H_{23}NO_4S$ $[M+H]^+$: 396.1270, found: 396.1273.

***tert*-Butyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4g):** white solid (31%); m.p. 91-94 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32-7.25 (m, 7H), 4.14 (s, 2H), 2.39 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 142.8, 139.4, 134.2, 129.3, 129.2, 128.3, 126.9, 126.3, 85.2, 40.7, 27.5, 21.4; IR (KBr) ν 2980, 2932, 1595, 1313, 1145, 1093, 690 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{24}NO_3S$ $[M+H]^+$: 346.1477, found: 346.1472.

Methoxycarbonylmethyl *N*-(4-methylbenzenesulfonyl)phenylacetimidate (4h): white solid (62%); m.p. 70-71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.32-7.25 (m, 5H), 4.57 (s, 2H), 4.29 (s, 2H), 3.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 167.0, 143.5, 138.3, 133.0, 129.6, 129.5, 129.3, 129.3, 129.1, 128.6, 128.4, 127.3,

126.7, 63.9, 52.0, 38.9, 21.5; IR (KBr) ν 1765, 1621, 1318, 1158, 686, 606 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{20}NO_5S$ $[M+H]^+$: 362.1062, found: 362.1064.

3-Bromopropyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4i): brownish liquid (92%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.33-7.24 (m, 7H), 4.24 (s, 2H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.19 (t, *J* = 6.5 Hz, 2H), 2.40 (s, 3H), 2.08-2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 143.3, 138.7, 133.4, 129.4, 129.3, 128.5, 127.2, 126.6, 66.0, 39.5, 30.8, 28.8, 21.4; IR (KBr) ν 1730, 1455, 1345, 1166, 1088, 815, 665, 541 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{21}NO_3S$ Br $[M+H]^+$: 412.0426, found: 412.0406.

2-Butynyl *N*-(4-methylbenzenesulfonyl)phenylacetimidate (4j): brownish liquid (68%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.37-7.24 (m, 7H), 4.61 (q, *J* = 2.3 Hz, 2H), 4.24 (s, 2H), 2.40 (s, 3H), 1.77 (t, *J* = 2.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 143.3, 138.8, 133.2, 129.5, 129.3, 128.6, 127.3, 126.7, 84.2, 72.1, 56.9, 39.3, 21.5, 3.5; IR (KBr) ν 1614, 1303, 1156, 1094, 688, 599 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{20}NO_3S$ $[M+H]^+$: 342.1164, found: 342.1166.

Bisimidate (4k): white solid (86%); m.p. 87-88 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 4H), 7.28-7.21 (m, 14H), 4.18 (s, 4H), 3.92 (s, 4H), 2.39 (s, 6H), 1.43 (t, *J* = 2.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 143.3, 138.8, 133.5, 129.5, 129.4, 128.5, 127.2, 126.6, 67.8, 39.5, 24.3, 21.5; IR (KBr) ν 1598, 1303, 1155, 1093, 689, 603 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{34}H_{37}N_2O_6S_2$ $[M+H]^+$: 633.2093, found: 633.2090.

Benzyl *N*-(methanesulfonyl)phenylacetimidate (4l): brownish liquid (84%); ^1H NMR (400 MHz,

$CDCl_3$) δ 7.35-7.19 (m, 10H), 5.14(s, 2H), 4.20 (s, 2H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 134.5, 133.2, 129.6, 128.5, 128.5, 128.4, 127.8, 127.3, 70.1, 42.9, 39.7; IR (KBr) ν 1615, 1305, 1144, 970, 793, 699, 625, 565 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{16}H_{18}NO_3S$ $[M+H]^+$: 304.1007, found: 304.1006.

Benzyl *N*-[2-(trimethylsilyl)ethanesulfonyl)phenylacetimidate (4m): white solid (84%); m.p. 51-54 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.0 Hz, 2H), 7.32-7.16 (m, 8H), 5.14 (s, 2H), 4.22 (s, 2H), 3.04-2.99 (m, 2H), 1.03-0.99 (m, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 134.8, 133.4, 129.6, 128.5, 128.4, 128.3, 127.5, 127.2, 69.8, 51.1, 39.7, 9.9, -2.1; IR (KBr) ν 2953, 2132, 1621, 1315, 1169, 1138, 838, 748, 698, 565 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{11}H_{16}NO_4S$ $[M+H]^+$: 258.0800, found: 258.0795.

Benzyl *N*-(butanesulfonyl)phenylacetimidate (4n): brownish liquid (77%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.36-7.25 (m, 6H), 7.19-7.17 (m, 2H) 5.13 (s, 2H), 4.21 (s, 2H), 3.11-3.07 (m, 2H), 1.82-1.75 (m, 2H), 1.47-1.41 (m, 2H), 0.95-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 134.7, 133.3, 129.6, 128.5, 128.4, 128.3, 127.6, 127.2, 69.8, 54.6, 39.8, 25.3, 21.4, 13.5; IR (KBr) ν 2961, 1619, 1308, 1137, 730, 698 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{24}NO_3S$ $[M+H]^+$: 346.1477, found: 346.1480.

Benzyl *N*-(4-nitrobenzensulfonyl)phenylacetimidate (4o): white solid (37%); m.p. 101-103 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (m, 2H), 7.98 (m, 2H), 7.33-7.25 (m, 8H), 7.10-7.08 (m, 2H), 5.10 (s, 2H), 4.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 149.9, 147.1, 134.2, 132.9, 129.6, 128.7, 128.6, 128.6, 128.0, 127.8, 127.6, 124.0, 70.8, 40.2; IR (KBr) ν 1610, 1530, 1349, 1306, 1158, 1093, 744 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{21}H_{19}N_2O_5S$ $[M+H]^+$: 411.1015, found:

411.1017.

Benzyl *N*-(4-methylbenzensulfonyl)-(4-trifluoromethylphenyl)acetimidate (4p): white solid (88%); m.p. 84-86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.29-7.24 (m, 5H), 7.10 (dd, *J* = 6.2 Hz, 1.7 Hz, 2H), 5.09 (s, 2H), 4.33 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 143.5, 138.6, 137.5, 134.3, 130.0, 129.4, 129.4, 128.5, 128.5, 128.1, 126.7, 125.5, 125.5, 125.4, 125.4; IR (KBr) ν 1603, 1330, 1294, 1154, 1119, 723 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{23}H_{21}NO_3SF_3$ $[M+H]^+$: 448.1194, found: 448.1197.

Benzyl *N*-(4-methylbenzensulfonyl)-(4-methylphenyl)acetimidate (4q): white solid (89%); m.p. 56-57 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.29-7.25 (m, 7H), 7.16-7.11 (m, 4H), 5.01 (s, 2H), 4.25 (s, 2H), 2.43 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 143.2, 138.9, 136.8, 134.6, 130.3, 129.4, 129.2, 129.2, 128.3, 128.2, 127.9, 126.6, 70.1, 39.1, 21.4, 21.0; IR (KBr) ν 3035, 2926, 2960, 1605, 1304, 1156, 1095, 687 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{23}H_{24}NO_3S$ $[M+H]^+$: 394.1477, found: 394.1476.

Benzyl *N*-(4-methylbenzensulfonyl)-(4-methoxylphenyl)acetimidate (4r): yellowish liquid (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.29-7.26 (m, 7H), 7.14-7.12 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 2H), 4.21 (s, 2H), 3.77 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 158.7, 143.2, 138.9, 134.6, 130.6, 129.3, 128.3, 128.3, 127.9, 126.6, 125.3, 113.9, 70.1, 55.1, 38.7, 21.4; IR (KBr) ν 2960, 2839, 1614, 1514, 1303, 1250, 1154, 1094, 687 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{23}H_{24}NO_4S$ $[M+H]^+$: 410.5126, found: 410.1431.

Benzyl *N*-(4-methylbenzensulfonyl)-(thien-3-yl)acetimidate (4s): white solid (72%); m.p. 56-58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.29-7.22 (m, 7H), 7.16-7.14 (m, 2H), 7.07-7.06 (m, 1H), 5.01 (s, 2H), 4.29 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 143.3, 138.7, 134.5, 132.5, 129.3, 128.6, 128.4, 128.4, 128.0, 126.6, 125.5, 123.8, 70.2, 34.3, 21.4; IR (KBr) ν 1614, 1317, 1158, 1094, 764, 685 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{20}H_{20}NO_3S_2$ $[M+H]^+$: 386.0885, found: 386.0881.

Benzyl *N*-(4-methylbenzensulfonyl)heximidate (4t): yellowish liquid (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.32-7.24 (m, 7H), 5.08 (s, 2H), 2.89 (t, *J* = 7.8, 2H), 2.41 (s, 3H), 1.71-1.67 (m, 2H), 1.32-1.29 (m, 4H), 0.87-0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 143.1, 139.1, 134.7, 129.3, 128.5, 128.5, 128.3, 126.6, 70.0, 33.8, 31.3, 25.6, 22.1, 21.5, 13.8; IR (KBr) ν 3068, 3037, 2964, 2935, 2874, 1614, 1303, 1160, 1096, 689 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{20}H_{26}NO_3S$ $[M+H]^+$: 360.1633, found: 360.1631.

Benzyl *N*-(4-methylbenzenesulfonyl)-(3,3-dimethyl)butyrimidate (4u): yellowish liquid (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.29-7.26 (m, 7H), 5.09 (s, 2H), 2.90 (s, 2H), 2.40 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 143.0, 139.3, 134.6, 129.2, 128.5, 128.4, 128.4, 126.6, 69.9, 45.5, 32.0, 30.2, 21.4; IR (KBr) ν 2961, 1614, 1313, 1160, 1095, 686 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{20}H_{26}NO_3S$ $[M+H]^+$: 360.1633, found: 360.1637.

Benzyl *N*-(4-methylbenzensulfonyl)-(5-chloro)valerimidate (4v): yellowish liquid (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.6, 1.7 Hz, 2H), 7.32-7.23 (m, 7H), 5.09 (s, 2H), 3.50 (t, *J* = 6.3 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 1.89-1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 143.2, 138.8, 134.4, 129.3, 128.5, 128.3, 126.6, 70.1, 44.1, 32.9, 31.8, 23.1, 21.4;

IR (KBr) ν 3036, 2960, 1605, 1314, 1158, 1096, 689 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{23}ClNO_3S$ $[M+H]^+$: 380.1087, found: 380.1090.

Benzyl *N*-(4-methylbenzenesulfonyl)-(3-methoxy)propionimidate (4w): yellowish liquid (82%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.32-7.23 (m, 7H), 5.11 (s, 2H), 3.73-3.70 (m, 2H), 3.32-3.29 (m, 3H), 3.22-3.19 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 143.1, 138.8, 134.5, 129.2, 128.4, 128.4, 128.1, 126.6, 70.1, 78.0, 58.4, 34.1, 21.4; IR (KBr) ν 1614, 1455, 1393, 1304, 1161, 1119, 1096, 816, 690 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{22}NO_4S$ $[M+H]^+$: 348.1270, found: 348.1267.

Benzyl *N*-(4-methylbenzenesulfonyl)-(1-cyclohexenyl)acetimidate (4x): yellowish liquid (79%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 6.6, 1.7 Hz, 2H), 7.30-7.22 (m, 7H), 5.52 (d, *J* = 1.3 Hz, 1H), 5.11 (s, 2H), 3.56 (s, 2H), 2.40 (s, 3H), 1.97-1.94 (m, 4H), 1.58-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 73.5, 143.0, 138.9, 134.7, 130.3, 129.2, 128.3, 128.2, 128.0, 126.6, 126.1, 69.8, 41.5, 28.6, 25.2, 22.6, 21.7, 21.4; IR (KBr) ν 1729, 1600, 1497, 1455, 1304, 1157, 1094, 815, 739, 685 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{22}H_{26}NO_3S$ $[M+H]^+$: 384.1633, found: 384.1631.

Benzyl *N*-(4-methylbenzenesulfonyl)-[4,4-bis(ethoxycarbonyl)]-6-heptimidate (4y): yellowish liquid (80%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.30-7.21 (m, 7H), 5.67-5.63 (m, 1H), 5.13 (d, *J* = 1.5 Hz, 1H), 5.09 (s, 1H), 5.06 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 2.91-2.87 (m, 2H), 2.65 (d, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 2.29-2.24 (m, 2H), 1.24-1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 170.4, 143.2, 138.8, 134.5, 131.8, 129.3, 128.4, 128.4, 128.2, 126.6, 119.4, 70.1, 61.4, 56.7, 36.9, 29.0, 28.3, 21.4, 13.9; IR (KBr) ν 3247, 2987, 1731, 1446, 1089, 861, 663, 548 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{24}H_{34}NO_7S$ $[M+H]^+$: 516.2056, found: 516.2060.

Benzyl *N*-(4-methylsulfonylbenzen)acetimidate (4z): yellowish liquid (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.32-7.28 (m, 7H), 5.09 (s, 2H), 2.51 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 143.2, 138.7, 134.4, 129.3, 128.5, 128.5, 128.5, 126.6, 70.2, 21.4, 20.4; IR (KBr) ν 1614, 1302, 1160, 1097, 689 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{16}H_{18}NO_3S$ $[M+H]^+$: 304.1007, found: 304.1005.

2-Propenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (8a): yellowish liquid (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.37-7.23 (m, 7H), 5.82-5.75 (m, 1H), 5.16 (d, *J* = 1.2 Hz, 1H), 5.12 (quintet, *J* = 1.5 Hz, 1H), 4.6 (dt, *J* = 5.6, 1.3 Hz, 2H), 4.26 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 143.2, 138.9,133.4, 130.6, 129.6, 129.3, 128.5, 127.2, 126.6, 119.0, 68.9, 39.5, 21.4; IR (KBr) ν 3036, 1615, 1497, 1456, 1303, 1158, 1095, 984, 815, 734, 691, 599 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{20}NO_3S$ $[M+H]^+$: 330.1164, found: 380.1166.

2-(3-Butenyl) *N*-(4-methylbenzensulfonyl)phenylacetimidate (8b): yellowish liquid (51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 6.7 Hz, 2H), 7.77-7.23 (m, 7H), 5.67-5.63 (m, 1H), 5.34-5.32 (m, 1H), 5.04-4.97 (m, 2H), 4.21 (d, *J* = 3.6 Hz, 2H), 2.40 (s, 3H), 1.22 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 143.1, 139.1, 136.2, 133.7, 129.5, 129.3, 128.5, 127.2, 126.6, 116.7, 75.3, 39.9, 21.5, 19.3; IR (KBr) ν 2987, 1598, 1316, 1158, 1094, 732, 692, 601, 556 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1320, found: 344.1315.

2-Methyl-2-propenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (8c): yellowish liquid (79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.36-7.24 (m, 7H), 4.83 (s, 1H), 4.78 (s, 1H), 4.44 (s, 2H), 4.26 (s, 2H), 2.41 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

172.7, 143.3, 139.0, 138.6, 133.5, 129.7, 129.3, 128.5, 127.3, 126.7, 113.9, 71.8, 39.7, 21.5, 19.3; IR (KBr) ν 2979, 1599, 1316, 1156, 1095, 689, 601 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1320, found: 344.1318.

(*E*)-2-Butenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (8d): yellowish liquid (86%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.35-7.24 (m, 7H), 5.68-5.62 (m, 1H), 5.48-5.44 (m, 1H), 4.49-4.48 (d, *J* = 6.5 Hz, 2H), 4.22 (s, 2H), 2.40 (s, 3H), 1.63 (dd, *J* = 6.6, 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 143.2, 139.1, 133.6, 132.6, 129.6, 129.3, 128.5, 127.2, 126.7, 123.7, 69.4, 39.7, 21.5, 17.7; IR (KBr) ν 1598, 1316, 1288, 1157, 1094, 968, 689, 603 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1320, found: 344.1316.

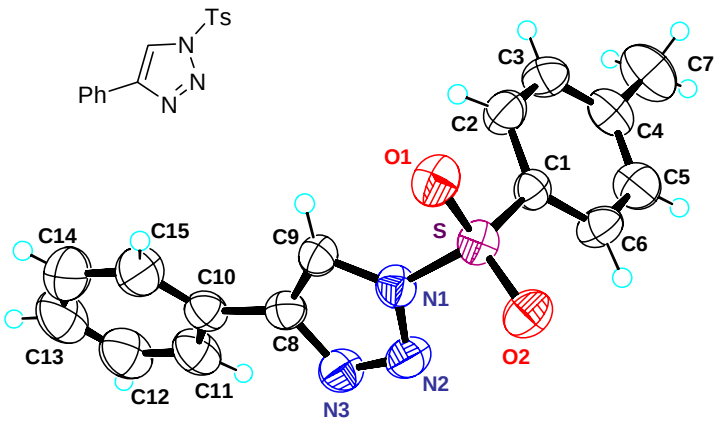
Representative Experimental Procedure of the Scale-up Reactions. To a stirred mixture of phenylacetylene (**1a**, 1.1 mL, 10.0 mmol), *p*-toluenesulfonyl azide (**2a**, 1.7 mL, 1.2 mmol), methanol (0.5 mL, 1.2 mmol), and CuI (95.2 mg, 0.5 mmol) in chloroform (20 mL) was slowly added triethylamine (1.7 mL, 12.0 mmol) under N_2 at room temperature. After stirring the reaction mixture for 12 h at room temperature, it was diluted by adding CH_2Cl_2 (20 mL) and aqueous NH_4Cl solution (50 mL). The mixture was stirred for an additional 30 min and two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (50 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude residue was recrystallized with CH_2Cl_2/n-hexane = 1:5 to give the desired product **4c** (2.89 g, 95%).

Experimental Procedure of the Product Ratio Observation Studies (Scheme 3). To a stirred mixture of *p*-toluenesulfonyl azide (**2a**, 592 mg, 3.0 mmol), phenylacetylene (**1a**, 258 mg, 2.5 mmol), benzyl alcohol (**3a**, 0.31 mL, 3.0 mmol), and CuI (47.5 mg, 0.25 mmol) in $CHCl_3$ (5.0 mL)

was slowly added 2,6-lutidine (0.35 mL, 3.0 mmol) under an N_2 atmosphere. The reaction mixture was allowed to stir at 25°C. The ratio of benzyl *N*-(4-methylbenzensulfonyl)-phenylacetimidate (**4a**) versus 1-(4-methylbenzensulfonyl)-4-phenyl-1,2,3-triazole (**5a**) was determined by ^{1}H NMR (300 MHz) using an internal standard (1,4-dimethoxybenzene).

1-(4-Methylbenzensulfonyl)-4-phenyl-1,2,3-triazole (5a): white solid; m.p. 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H,), 7.82-7.79 (m, 2H), 7.43-7.35 (m, 5H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 130.4, 129.1, 129.0, 128.7, 126.1, 118.9, 21.8; IR (KBr) ν 3142, 1594, 1393, 1196, 1176, 987, 670, 587, 543, 447 cm^{-1}.

Figure S2. ORTEP plot of **1-(4-Methylbenzensulfonyl)-4-phenyl-1,2,3-triazole (5a)**



Representative Procedure for the Transformation of Imidates to Amidines (Scheme 4). To a stirred solution of methyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (**4c**, 60.7 mg, 0.2 mmol) and NaCN (2.0 mg, 0.04 mmol) in pyrrolidine (0.31 mL, 3.7 mmol) was added MeOH (0.1 mL) under an N_2 atmosphere. After stirring the reaction mixture at 50 ^oC for 12 h, an aqueous KOH solution (1.0 M, 2.0 ml) was added, and then the mixture was extracted with CH_2Cl_2 (3 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude residue was purified by flash column chromatograph with EtOAc/n-hexane = 1:1 to afford the desired product as a white solid, N^1-pyrrolidinyl-N^2-(4-methylbenzensulfonyl)-2-phenylacetamidine (**5a**, 54.1 mg, 79%).

***N*^{1}-Pyrrolidinyl-*N*^{2}-(4-methylbenzensulfonyl)-2-phenylacetamidine (6a):** white solid (79%); m.p. 133-134 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 6.7, 1.6 Hz, 2H), 7.25-7.12 (m, 7H), 4.33 (s, 2H), 3.57 (t, *J* = 6.7 Hz, 2H), 3.23 (t, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 1.83-1.78 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 141.7, 141.4, 133.6, 129.0, 128.8, 128.2, 126.7, 126.4, 48.9, 47.6, 38.3, 25.7, 24.0, 21.4; IR (KBr) ν 2975, 2878, 1547, 1272, 1141, 1089, 814, 732, 695, 555 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{23}N_2O_2S$ $[M+H]^+$: 343.1480, found: 343.1479.

***N*^{1}-Piperidinyl-*N*^{2}-(4-methylbenzensulfonyl)-2-phenylacetamidine (6b):** yellowish liquid (74%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.25-7.11 (m, 7H), 4.38 (s, 2H), 3.71 (s, 2H), 3.25 (t, *J* = 5.5 Hz, 2H), 2.34 (s, 3H), 1.50 (d, *J* = 2.5 Hz, 4H), 1.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 141.7, 141.3, 134.4, 129.0, 128.7, 128.0, 126.6, 126.3, 47.8, 46.0, 36.9, 25.8, 25.2, 23.9, 21.3; IR (KBr) ν 3029, 2940, 2860, 1555, 1446, 1271, 1145, 1089, 722, 686, 556 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{20}H_{25}N_2O_2S$ $[M+H]^+$: 357.1637, found: 357.1639.

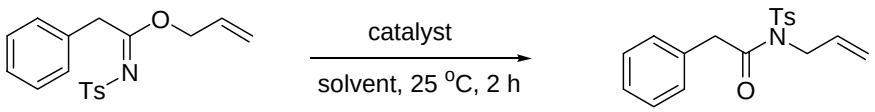
***N*^{1}-Morpholinyl-*N*^{2}-(4-methylbenzensulfonyl)-2-phenylacetamidine (6c):** white solid (77%); m.p. 148-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.27-7.13 (m, 7H), 4.41 (s, 2H), 3.76 (m, 2H), 3.60 (m, 2H), 3.30 (s, 4H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 142.1, 140.8, 134.0, 129.1, 129.0, 127.9, 127.0, 126.4, 66.2, 66.1, 46.9, 45.0, 36.7, 21.4; IR (KBr) ν 3251, 1633, 1548, 1272, 1143, 1089 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{23}N_2O_3S$ $[M+H]^+$: 359.1429, found: 359.1429.

Typical Procedure of *N*-Desulfonylation of *N*-Sulfonylamidines (Scheme 4). A solution of sodium naphthalenide in 1,2-dimethoxyethane (DME) was prepared by adding DME (6 mL) to a mixture of sodium (0.115 g, 20 mmol) and naphthalene (0.706 g, 22 mmol) followed by stirring the resulting mixture at room temperature for 2 h. The above prepared DME solution of sodium naphthalenide was added dropwsie to a solution of *N*^{1}-pyrrolidinyl-*N*^{2}-(4-methylbenzensulfonyl)-2-phenylacetamidine (**5a**, 85.5 mg, 0.25 mmol) in DME (1.5 mL) at -78 ^{o}C. The reaction mixture was stirred at the same temperature for 1 h, and it was quenched by adding water (1 mL). After addition of anhydrous K_2CO_3 (6 g), the mixture was stirred for additional 6 h at room temperature, filtered, and the precipitates were rinsed with ether (3 x 20 mL). The combined filtrate was concentrated under reduced pressure, and the residue was chromatographed. [CH_2Cl_2 (sat. NH_3)/MeOH, 10:1] to afford *N*-pyrrolidinyl-2-phenylacetamidine (**7a**, 42.3 mg, 90%) as a white solid; m.p. 123-124 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.16 (m, 5H), 4.93 (s, 1H), 3.59 (s, 2H), 3.36 (s, 4H), 1.86-1.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 135.3, 129.3, 128.6, 126.9, 46.8, 42.1; IR (KBr) ν 3445, 2971, 2872, 1673, 1631, 1589, 1454, 1349, 744, 705 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{12}H_{17}N_2$ $[M+H]^+$: 189.1392, found: 189.1396.

Experimental Procedure for the Optimization of the Pd-Catalyzed Rearrangement of Allylic

imidates to Amides (Table S2). A solution of catalyst (0.01 mmol) and 2-propenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (**7a**, 66.0 mg, 0.2 mmol) in the indicated solvent (1 mL) was stirred for 2 h at room temperature. After removal of organic solvent under reduced pressure, crude NMR yield of 4-methyl-*N*-(phenylacetyl)-*N*-(2-propenyl)benzenesulfonamide (**8a**) was determined by integration using an internal standard (*p*-anisole).

Table S2. Optimization of the Pd-Catalyzed rearrangement of allylic imidate to amide



8a **9a**

Entry	Catalyst	Solvent	Yield (%)[a]
1	$Pd(OAc)_2$	THF	<1
2	$PdCl_2(PPh_3)_2$	THF	<1
3	$PdCl_2(DPPF)$[b]	THF	<1
4	$PdCl_2(PhCN)_2$	THF	88
5	$PdCl_2(PhCN)_2$	CH_2Cl_2	89
6	$PdCl_2(PhCN)_2$	$Cl_2CH_2CH_2Cl_2$	>99
7	$PdCl_2(PhCN)_2$	CH_3CN	95
8	$PdCl_2(PhCN)_2$	1,4-dioxane	93
9	$PdCl_2(PhCN)_2$ + BINAP	THF	<1
10	$CuCl_2$	CH_2Cl_2	<1

[a] NMR yield based on an internal standard (*p*-anisole).

[b] DPPF: 1,1'-Bis(diphenylphosphino) ferrocene.

Representative Procedure for the Pd-Catalyzed Rearrangement of Allylic imidates to Amides (Scheme 5). A mixture of 2-propenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (**8a**, 66 mg, 0.20 mmol) and $PdCl_2(PhCN)_2$ (4.0 mg, 5.0 mol%) in 1,2-dichloroethane (1 mL) was stirred for 4 h at room temperature. The organic solvent was evaporated under reduced pressure and the crude residue was purified by flash column chromatograph (EtOAc/hexane, 1:5) to give the desired

product **9a**, 4-methyl-*N*-(phenylacetyl)-*N*-(2-propenyl)benzenesulfonamide, (65.4 mg, 99%).

4-Methyl-*N*-(phenylacetyl)-*N*-(2-propenyl)benzenesulfonamide (9a): yellowish solid (99%); m.p. 64-66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.30-7.22 (m, 5H), 7.07-7.04 (m, 2H), 5.90-5.83 (m, 1H), 5.29-5.22 (m, 2H), 4.46-4.44 (m, 2H), 3.90 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 144.9, 136.5, 133.2, 132.7, 129.6, 128.6, 128.1, 127.2, 118.3, 48.7, 42.7, 21.6; IR (KBr) ν 2980, 1705, 1355, 1187, 1173, 1088, 735, 595 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{18}H_{20}NO_3S$ $[M+H]^+$: 330.1164, found: 330.1163.

4-Methyl-*N*-[(*E*)-2-butenyl]-*N*-(phenylacetyl)benzenesulfonamide (9b): white solid (94%); m.p. 88-90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30-7.05 (m, 7H), 5.74-5.69 (m, 1H), 5.53-5.49 (m, 1H), 4.37 (d, *J* = 5.7 Hz, 2H), 3.89 (s, 2H), 2.42 (s, 3H), 1.67 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 144.7, 136.7, 133.3, 130.3, 129.6, 129.3, 128.5, 128.0, 127.1, 125.5, 48.3, 42.8, 21.6, 17.6; IR (KBr) ν 2914, 1701, 1347, 1165, 1119, 664 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1320, found: 344.1324.

4-Methyl-*N*-(2-methyl-2-propenyl)-*N*-(phenylacetyl)benzenesulfonamide (9c): white solid (99%); m.p. 96-99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.30-7.22 (m, 5H), 7.03-7.01 (m, 2H), 4.97 (s, 1H), 4.88 (s, 1H), 4.38 (s, 2H), 3.82 (s, 2H), 2.42 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 144.8, 140.2, 136.6, 133.1, 129.5, 129.1, 128.6, 128.4, 127.2, 111.9, 51.4, 42.5, 21.6, 20.2; IR (KBr) ν 2955, 1707, 1341, 1163, 1124, 755, 701, 532 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1320, found: 344.1316.

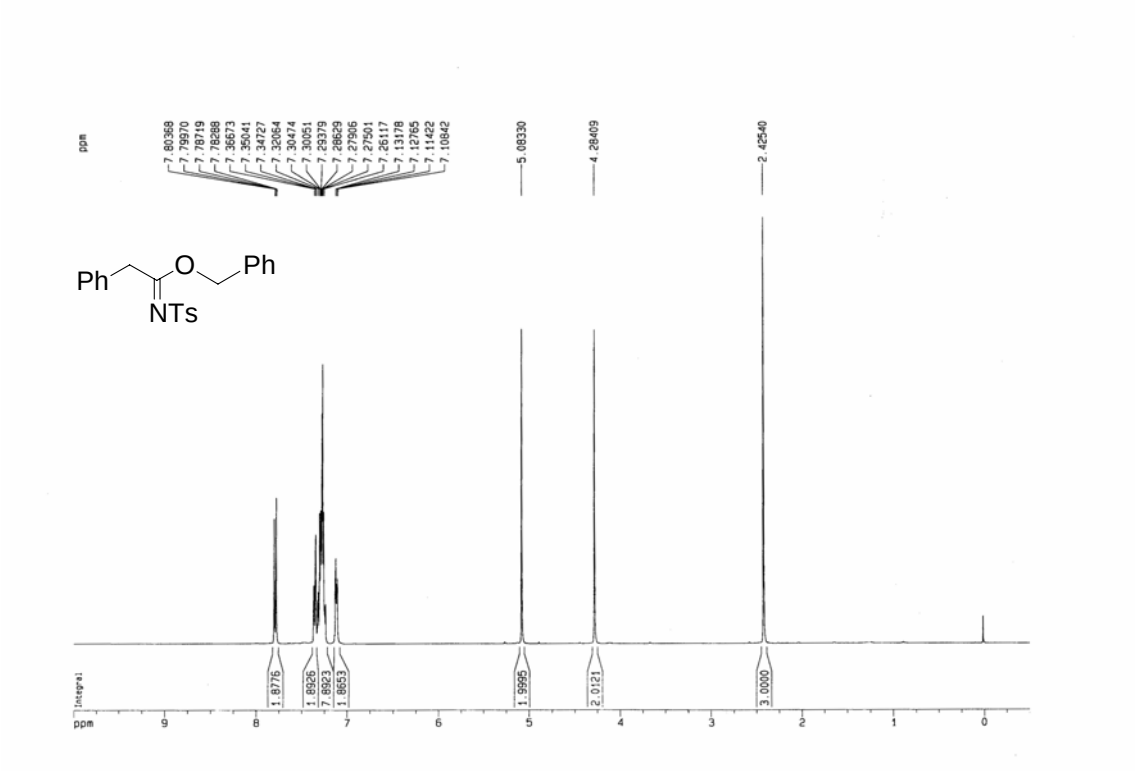
4-Methyl-*N*-[2-(3-butenyl)]-*N*-(phenylacetyl)benzenesulfonamide (9d): yellowish liquid (99%);

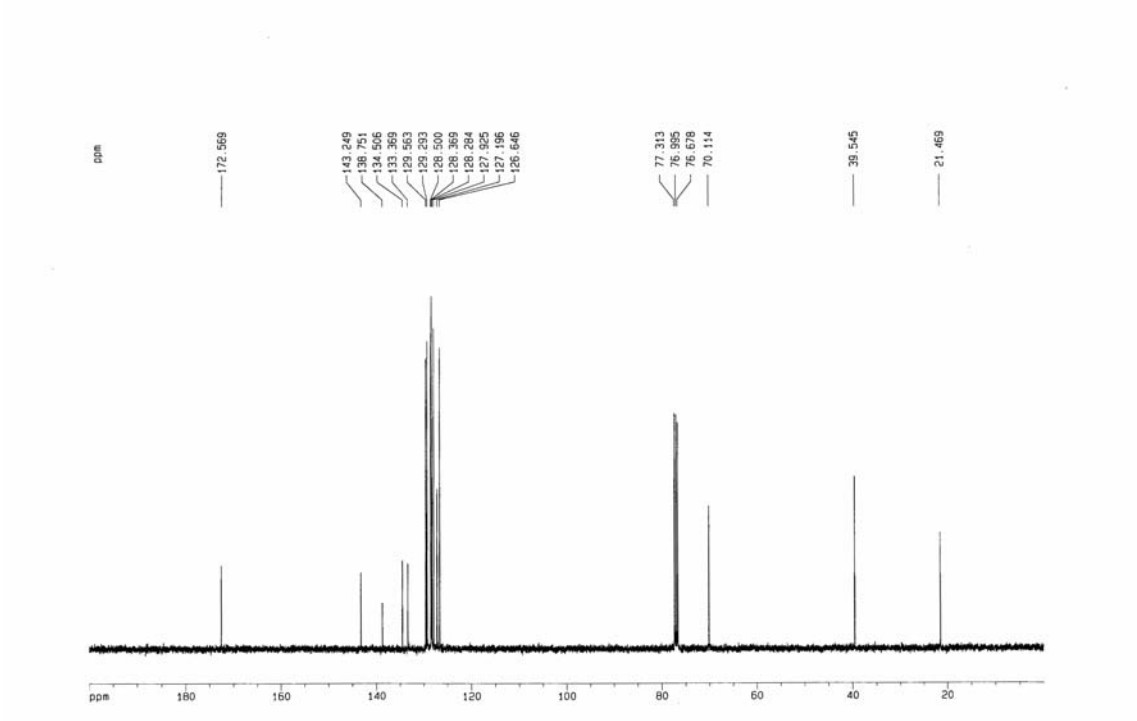
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.30-7.22 (m, 5H), 7.09-7.07 (m, 2H), 6.11-6.06 (m, 1H), 5.08-5.04 (m, 2H), 4.99-4.87 (m, 1H), 4.00 (q, *J* = 16.1 Hz, 2H), 2.43 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 144.8, 137.9, 137.0, 133.8, 129.8, 129.4, 128.4, 127.6, 127.0, 116.6, 58.0, 44.1, 21.6, 18.9; IR (KBr) ν 1694, 1355, 1170, 1087, 667, 586 cm^{-1}; HRMS (FAB) m/z calcd. for $C_{19}H_{22}NO_3S$ $[M+H]^+$: 344.1320, found: 344.1315.

Appendix Ⅰ

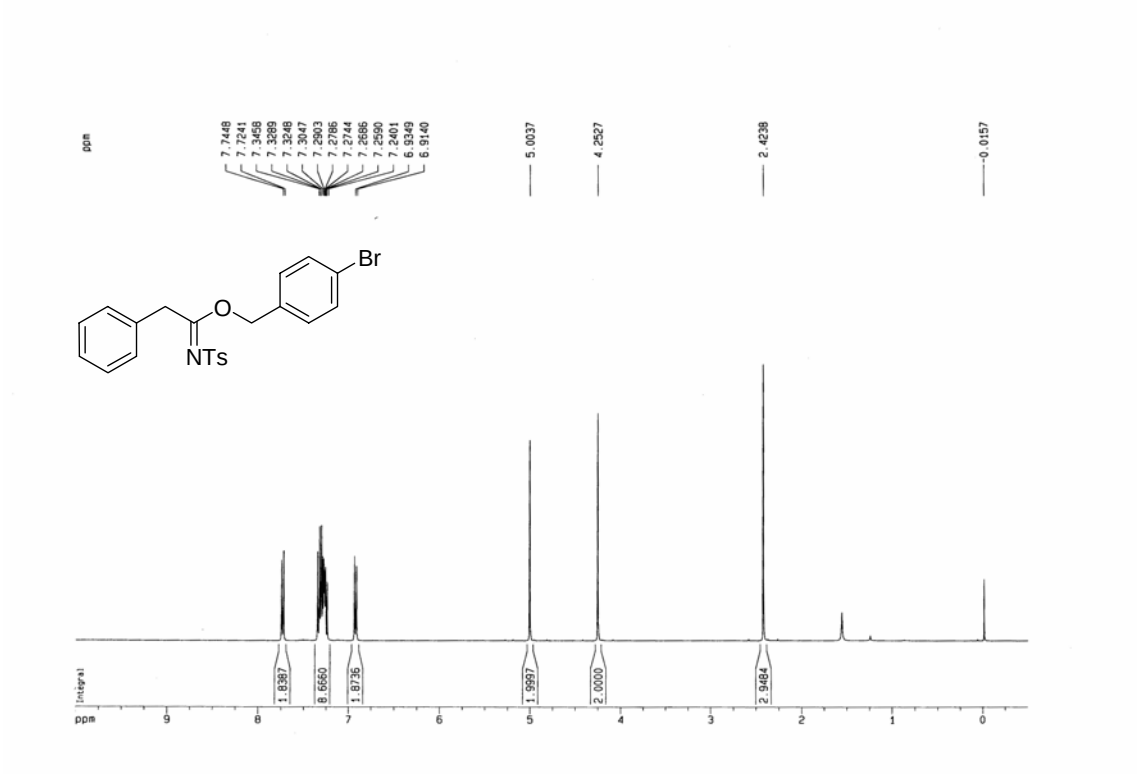
Spectral Copies of ^{1}H and ^{13}C NMR of New Compounds Obtained in this Study

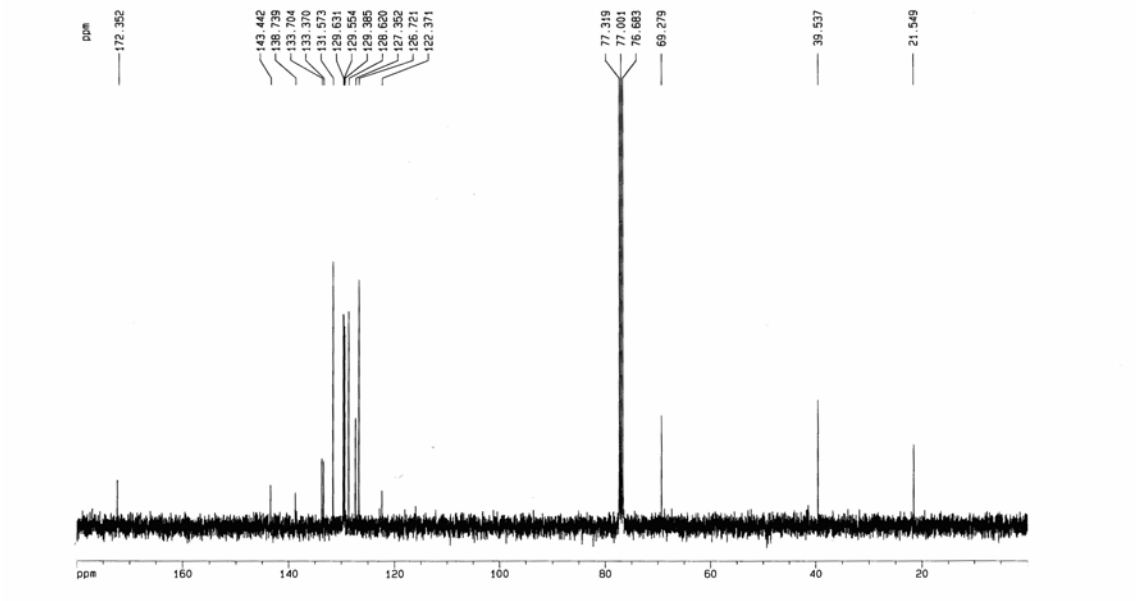
Benzyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4a)



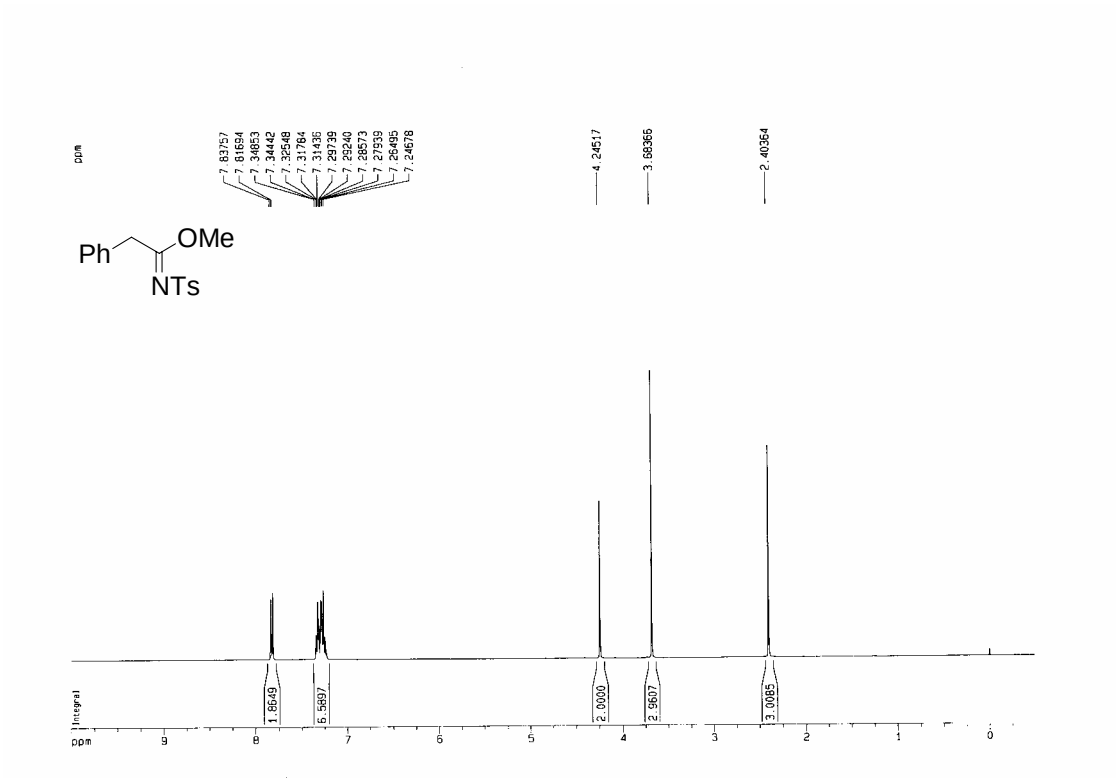


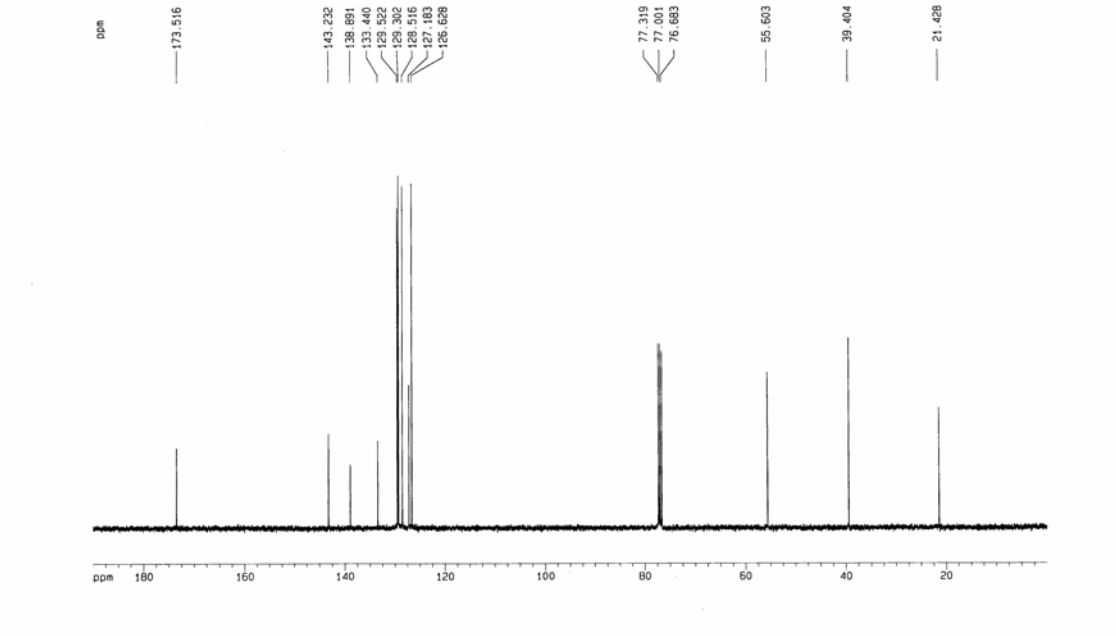
4-Bromobenzyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4b)



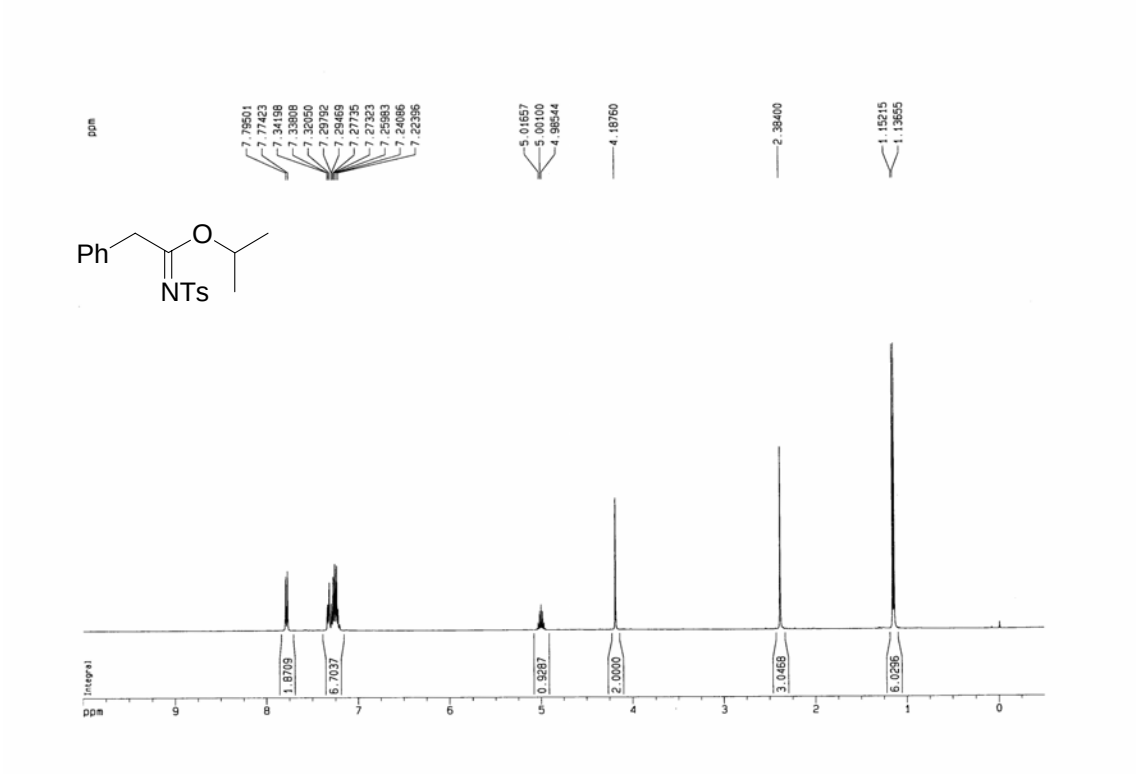


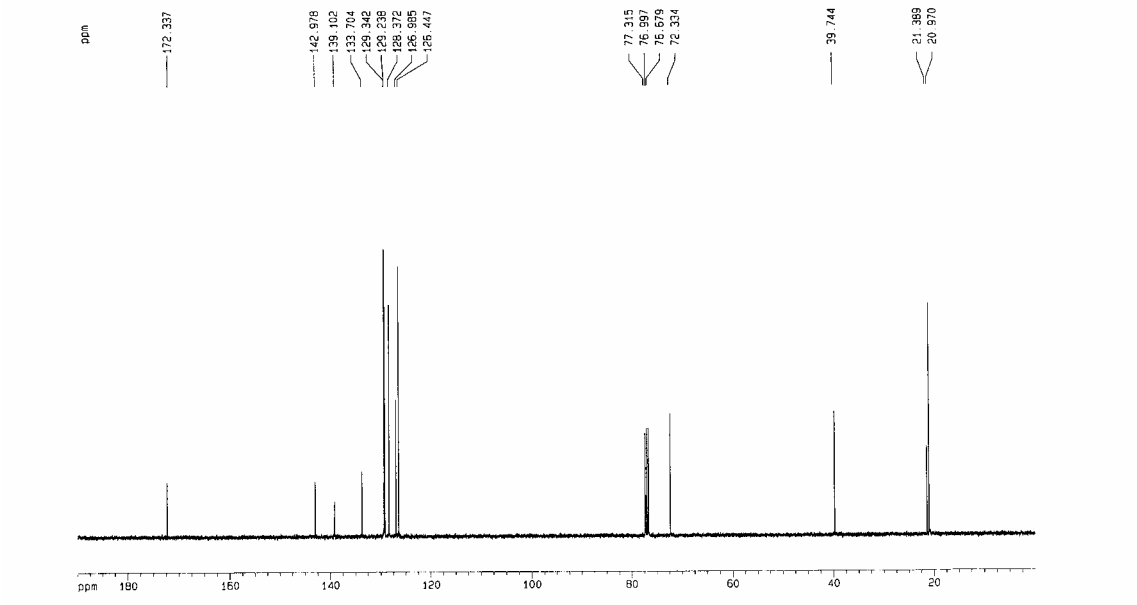
Methyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4c)



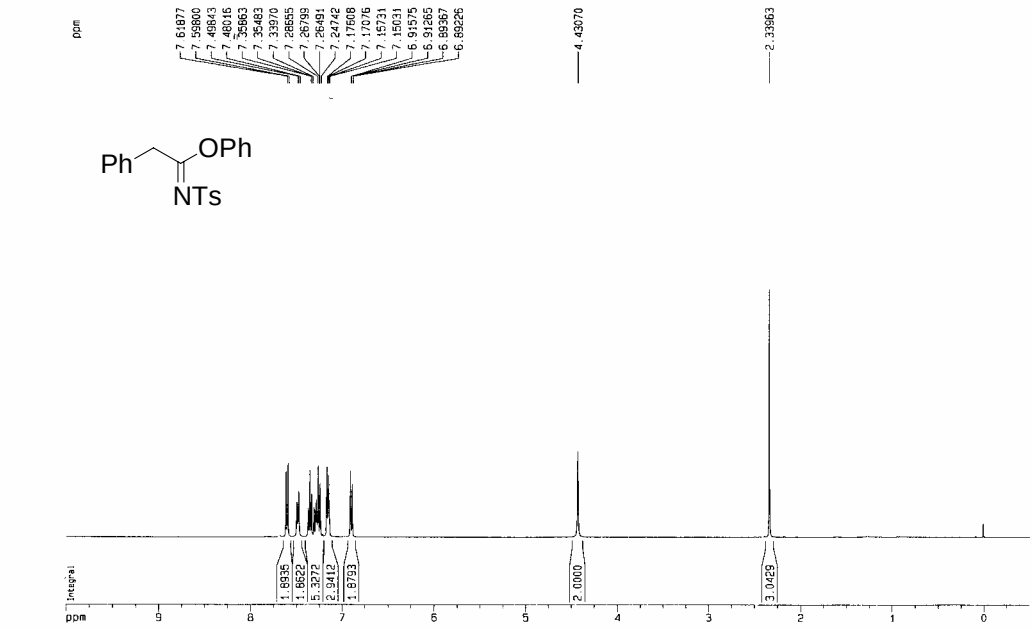


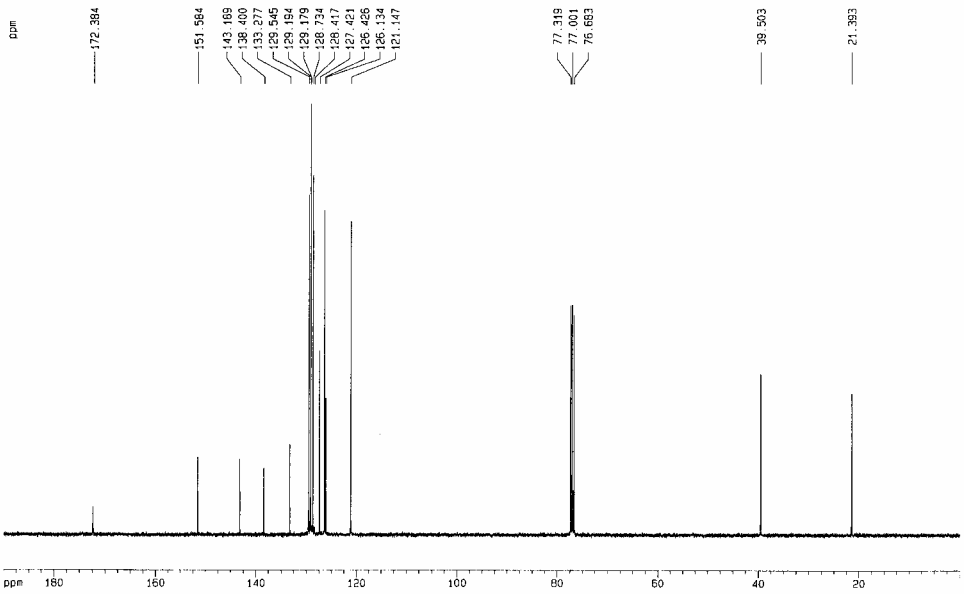
Isopropyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4d)



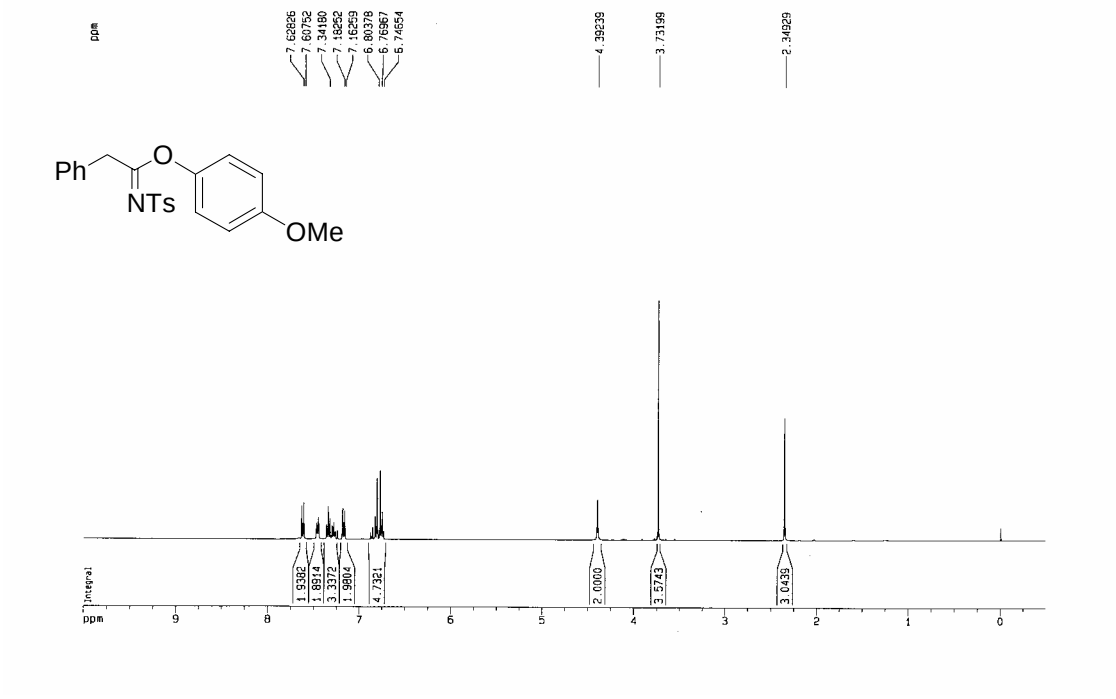


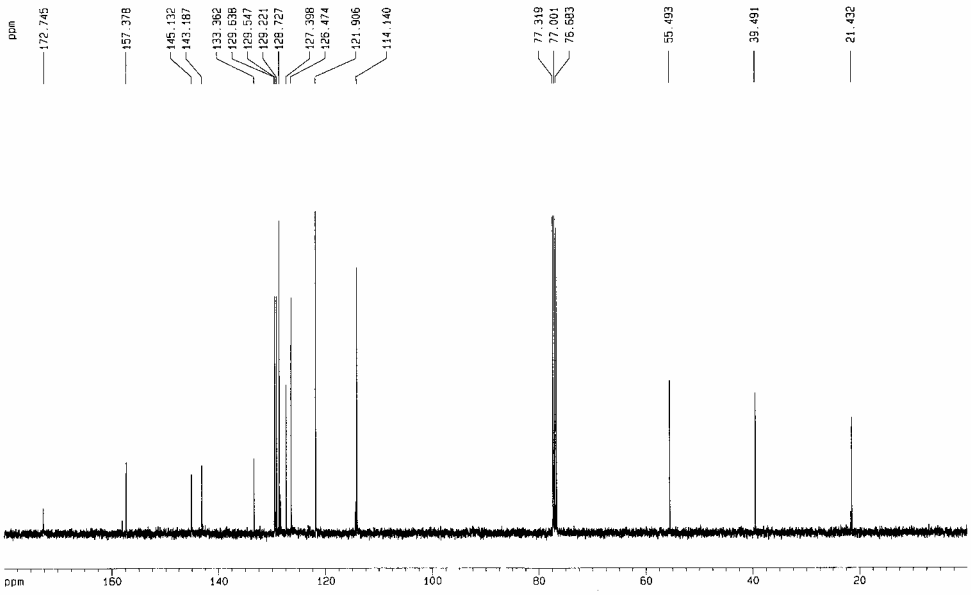
Phenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4e)



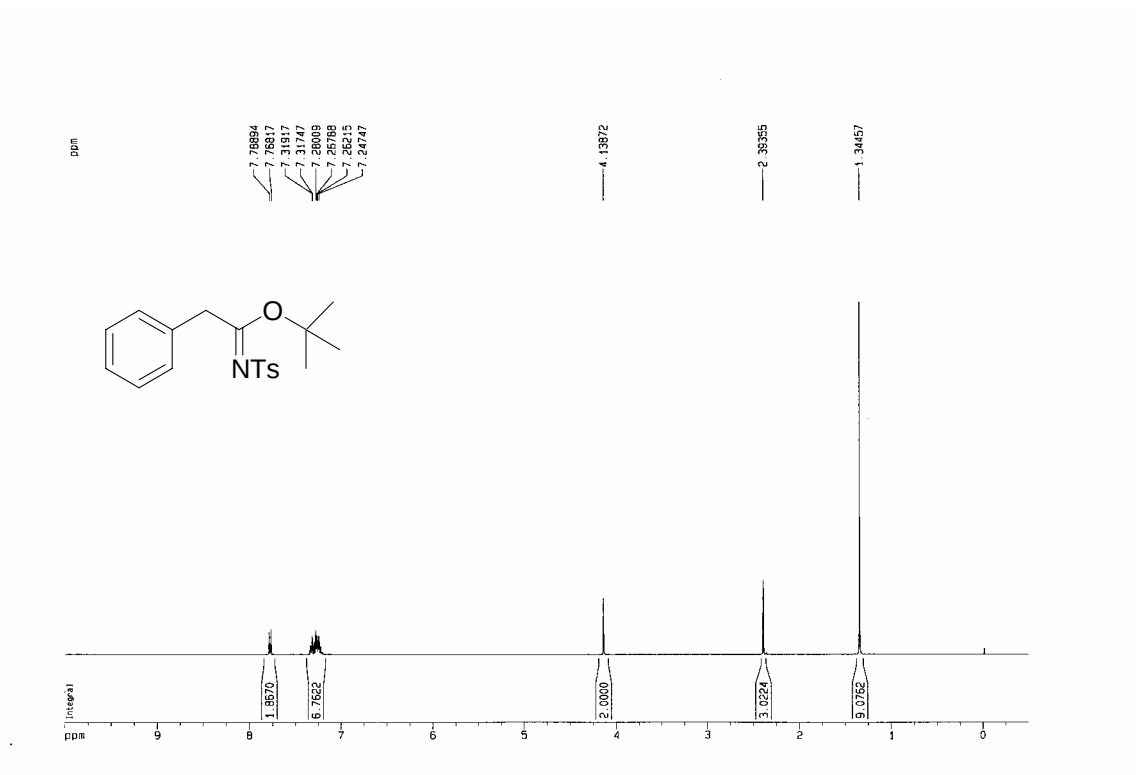


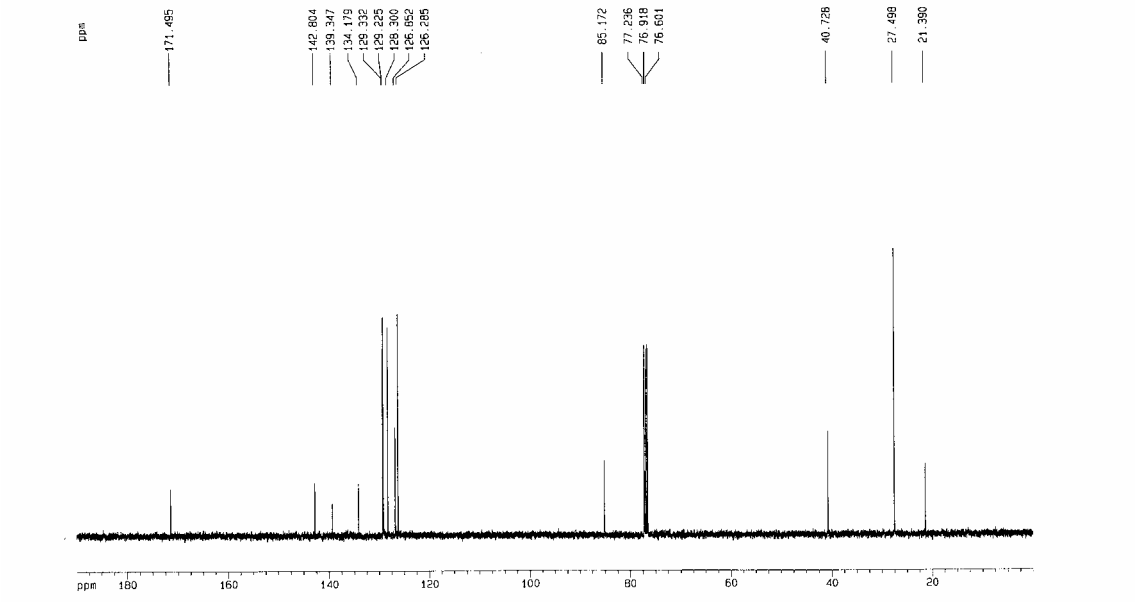
4-Methoxyphenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4f)



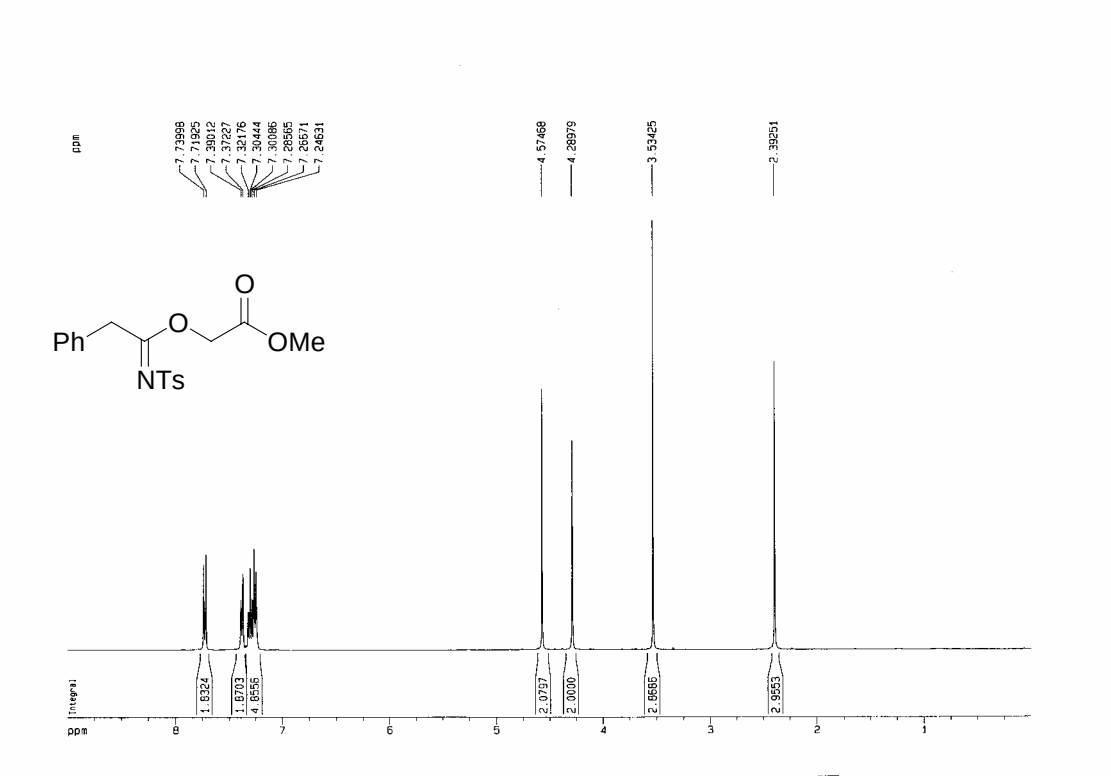


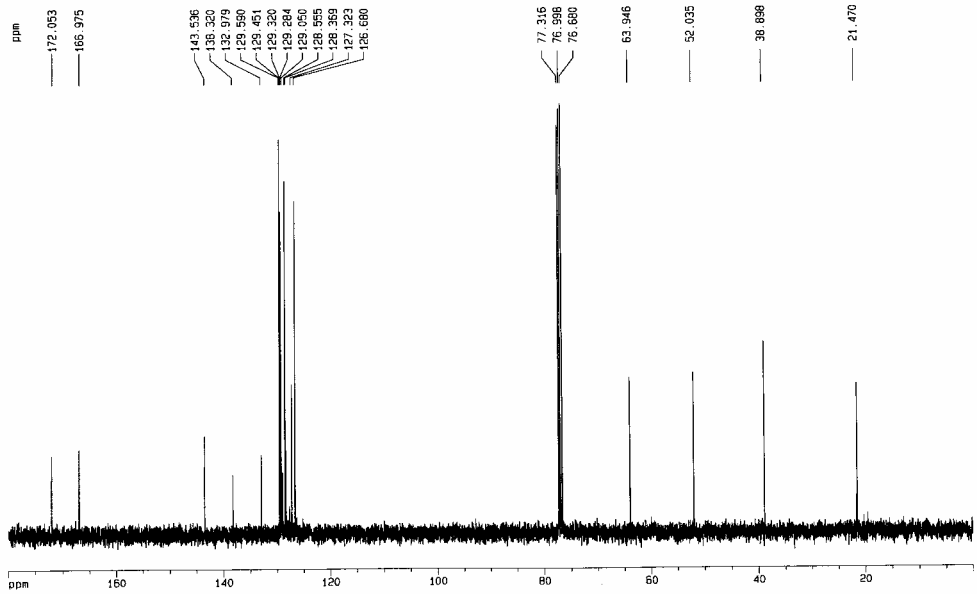
tert-Butyl _N_-(4-methylbenzensulfonyl)phenylacetimidate (4g)



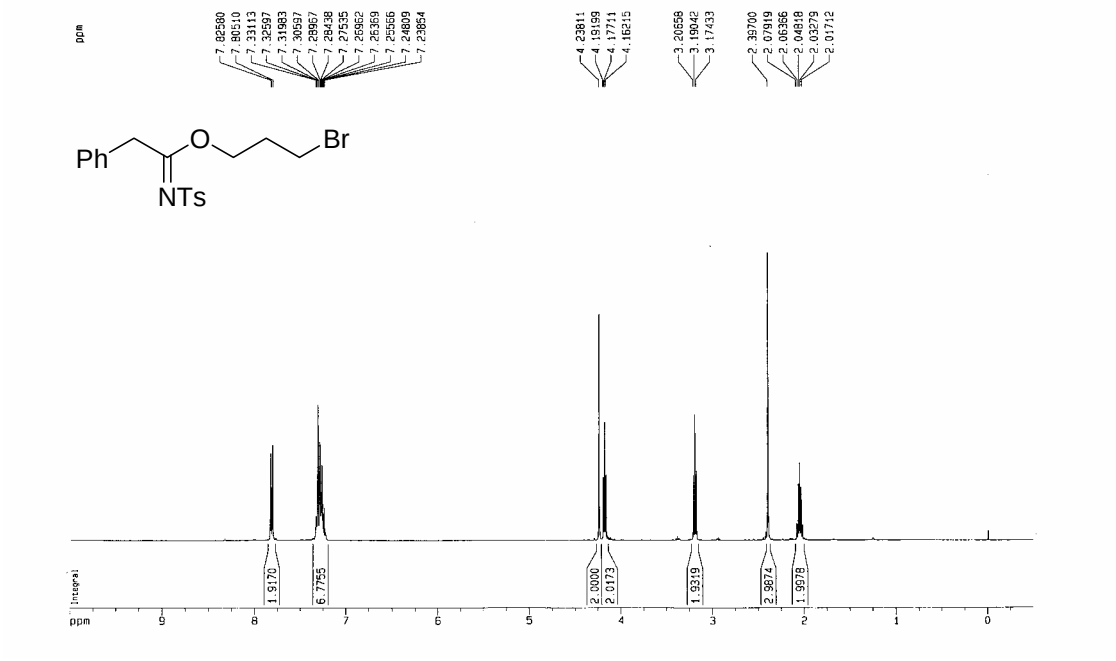


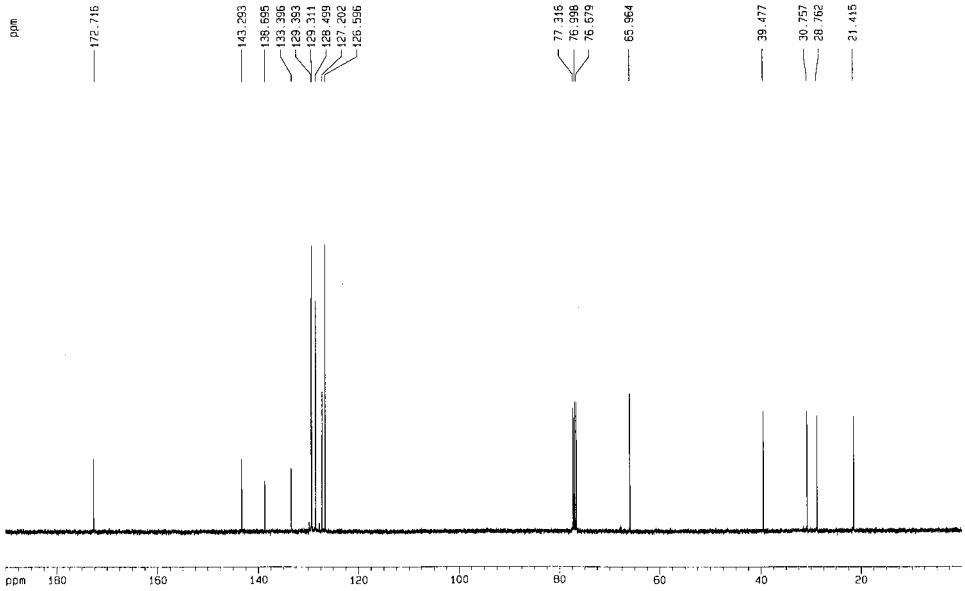
Methoxycarbonylmethyl *N*-(4-methylbenzenesulfonyl)phenylacetimidate (4h)



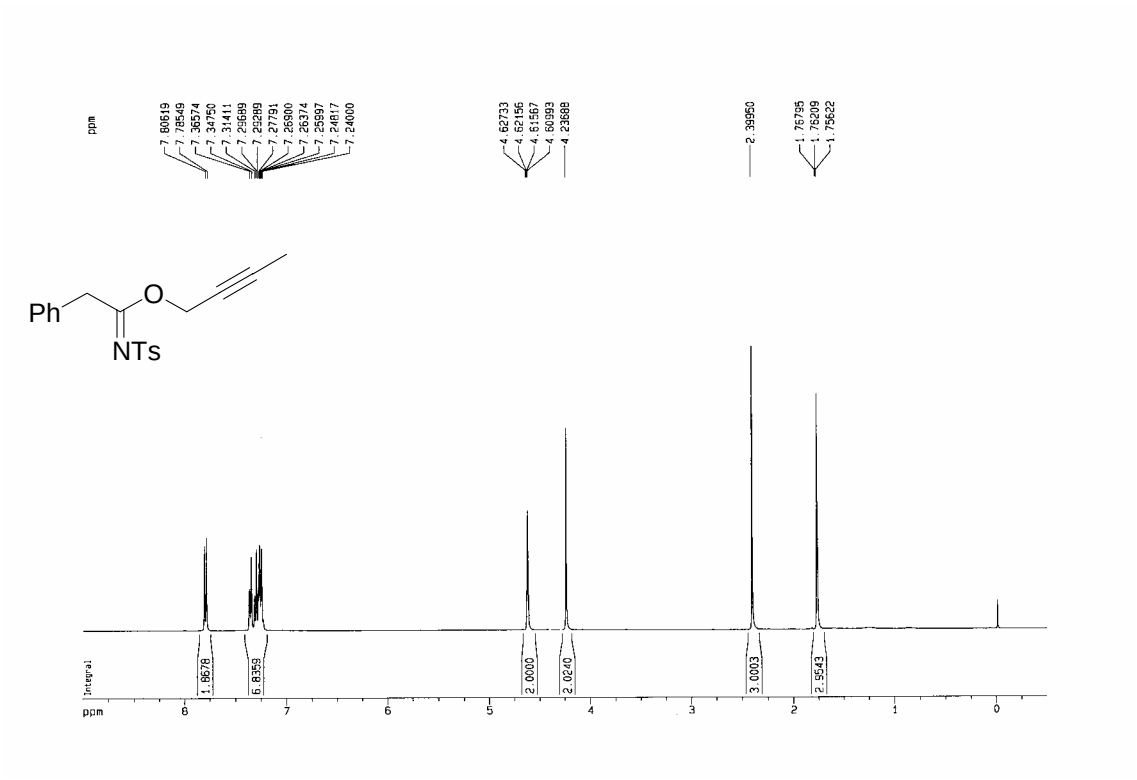


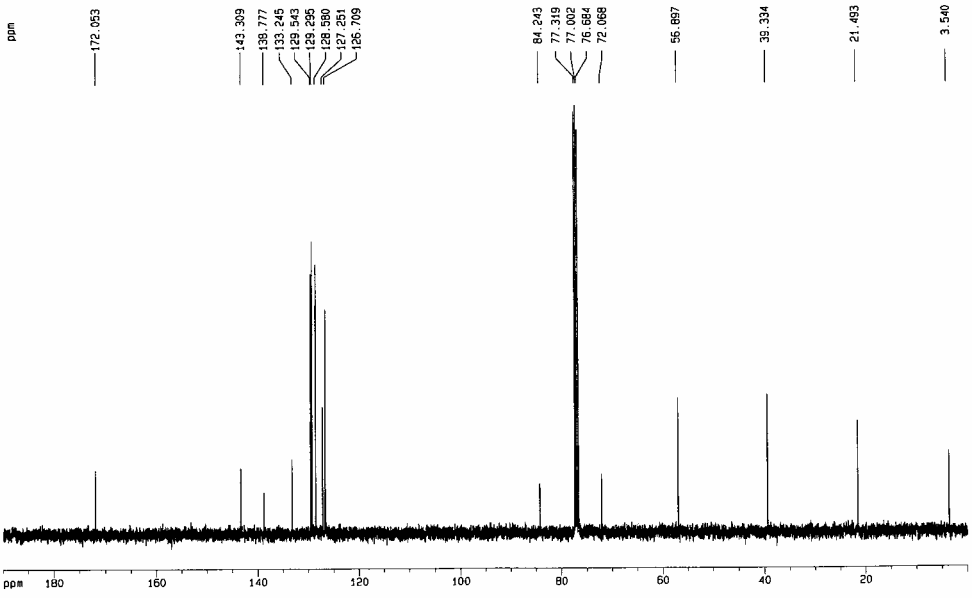
3-Bromopropyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (4i)



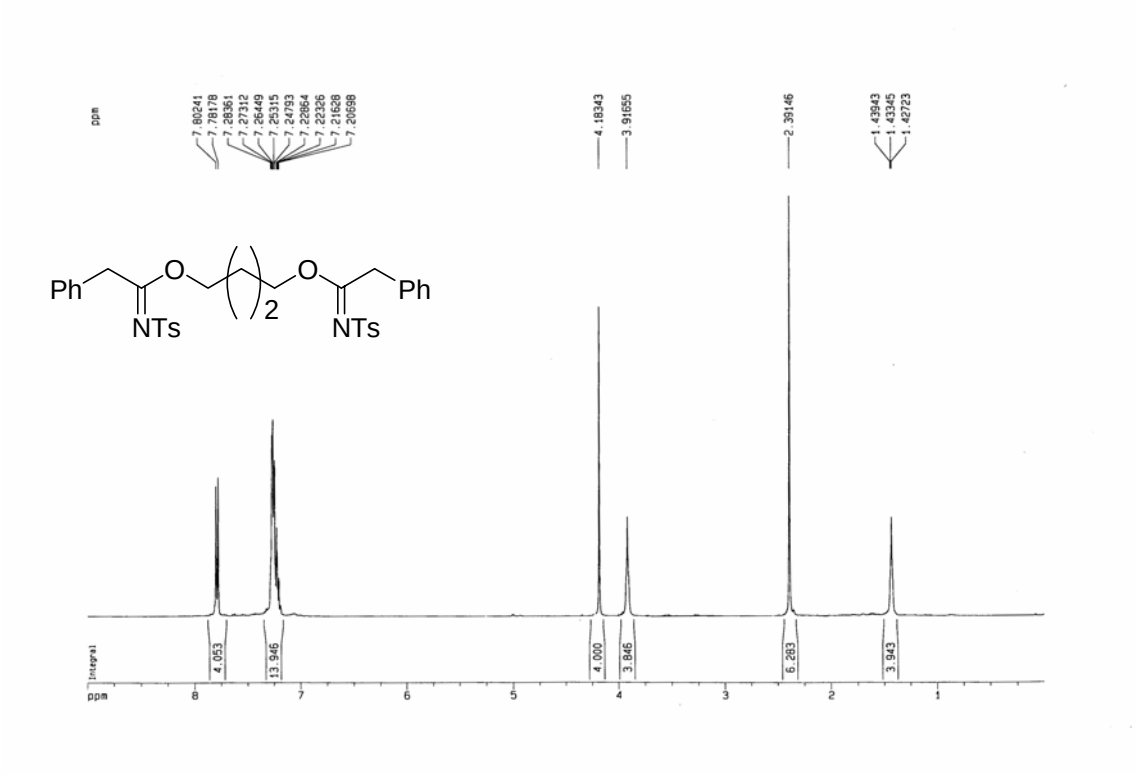


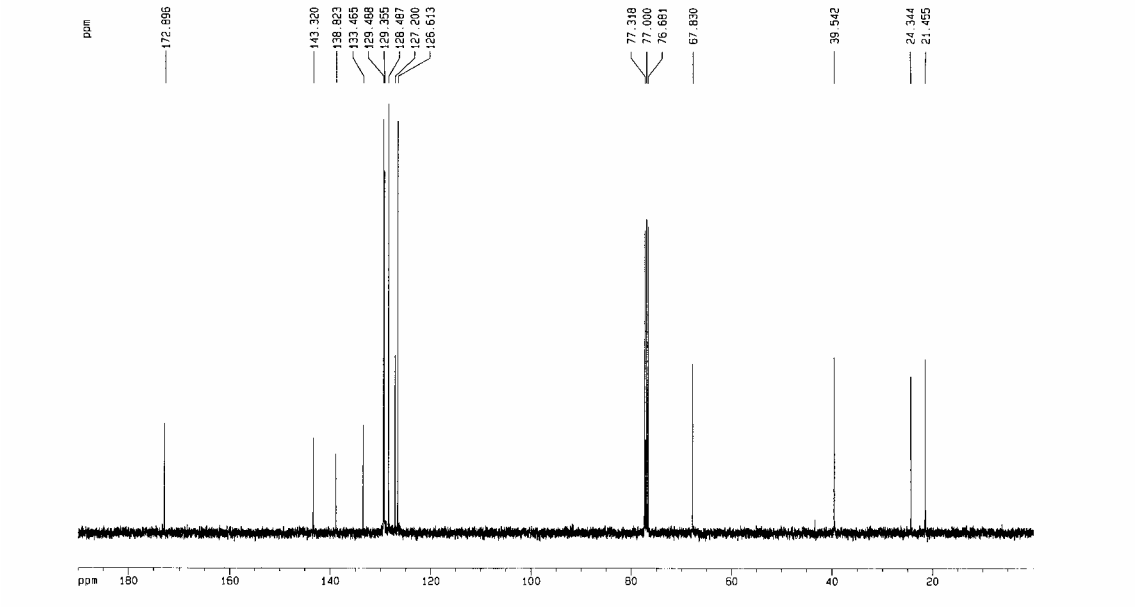
2-Butynyl *N*-(4-methylbenzenesulfonyl)phenylacetimidate (4j)



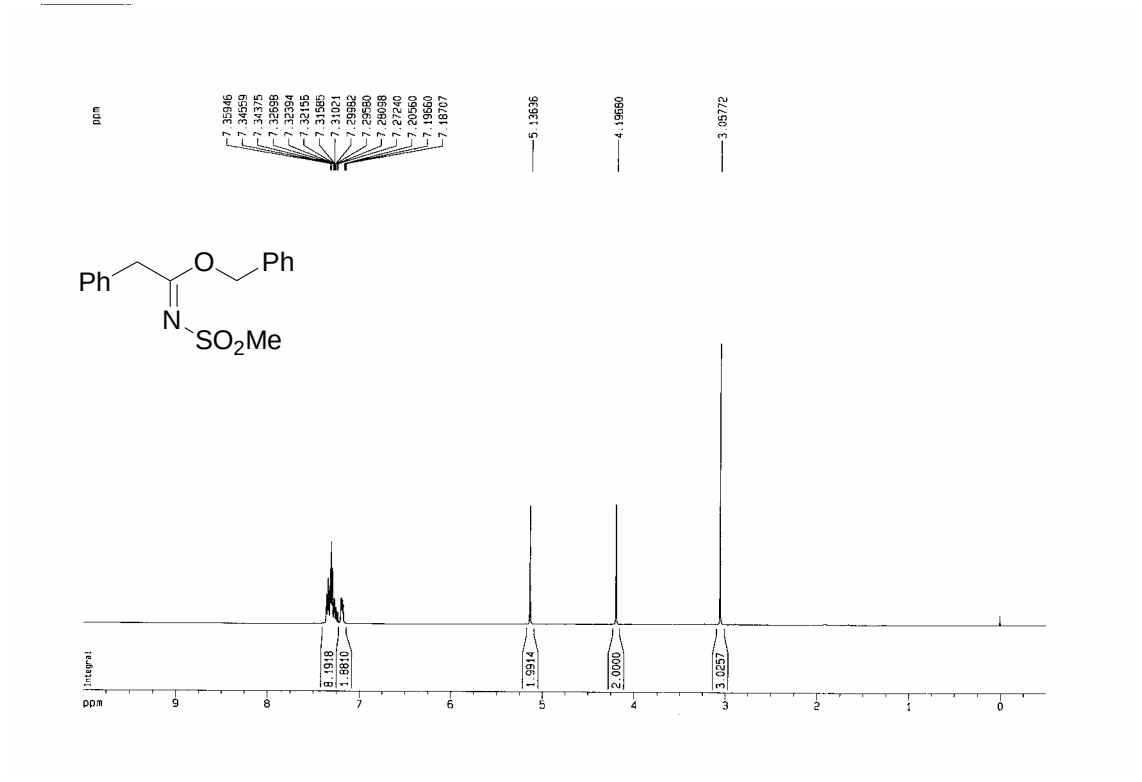


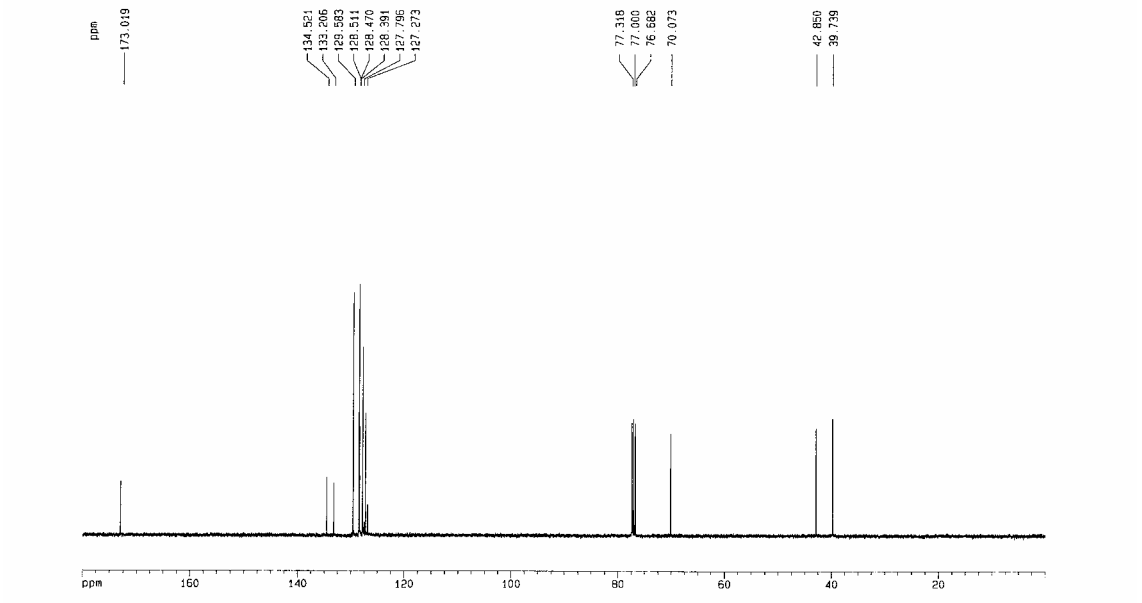
Bisimidate (4k)



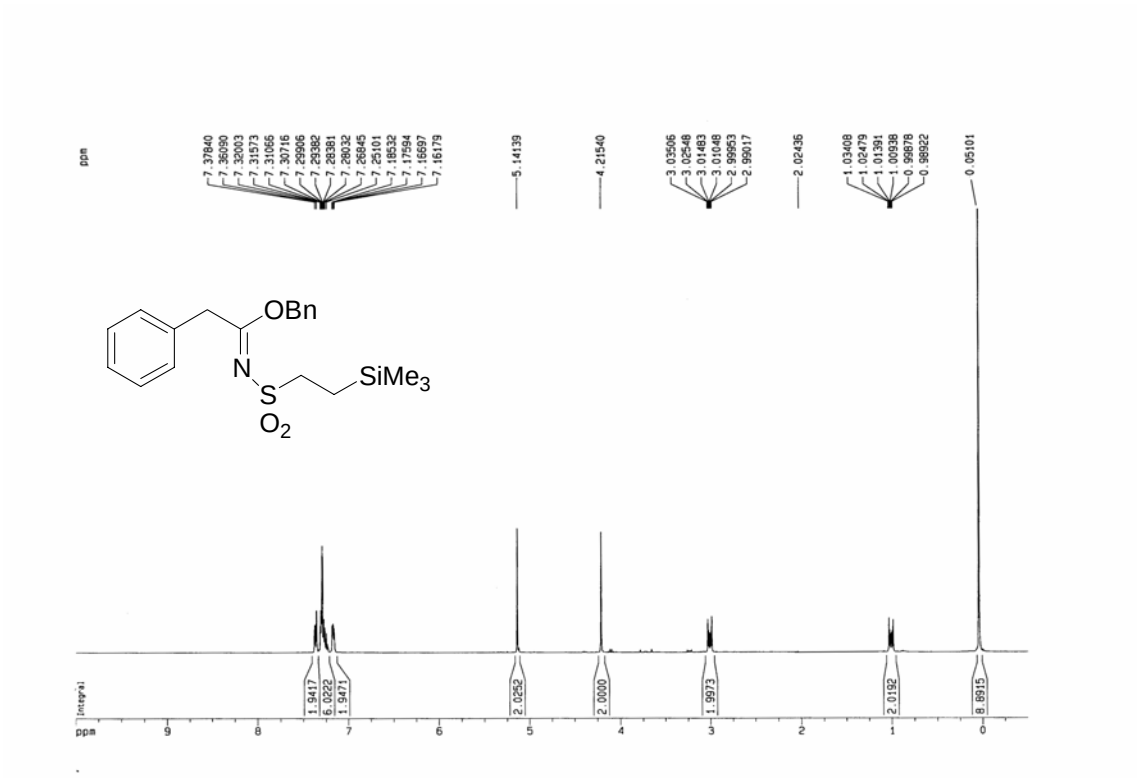


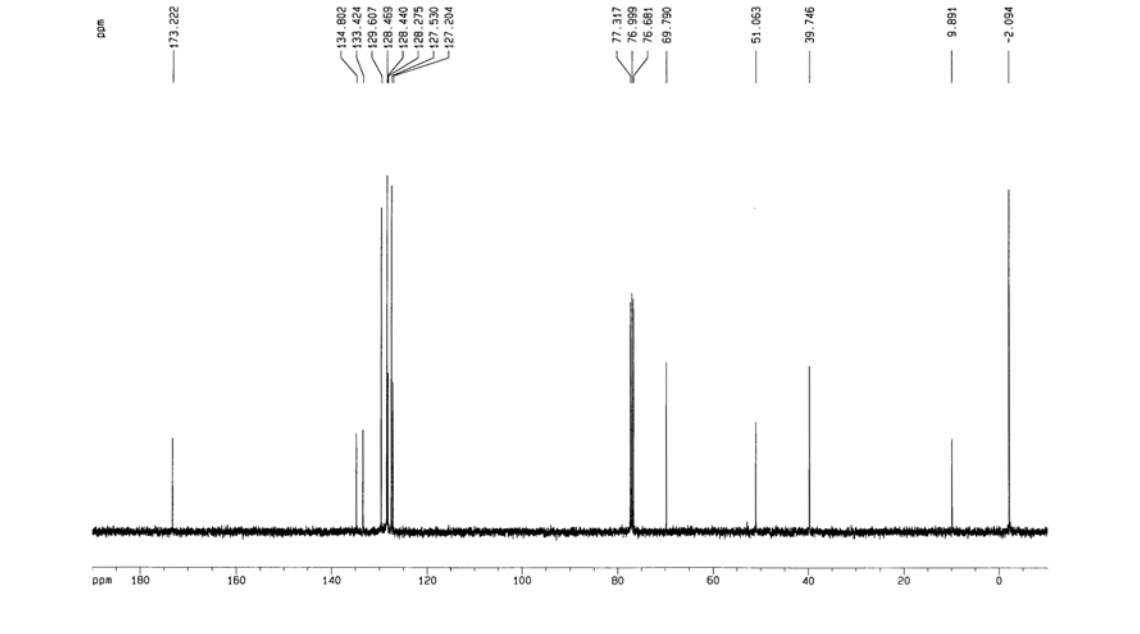
Benzyl *N*-(methanesulfonyl)phenylacetimidate (4l)



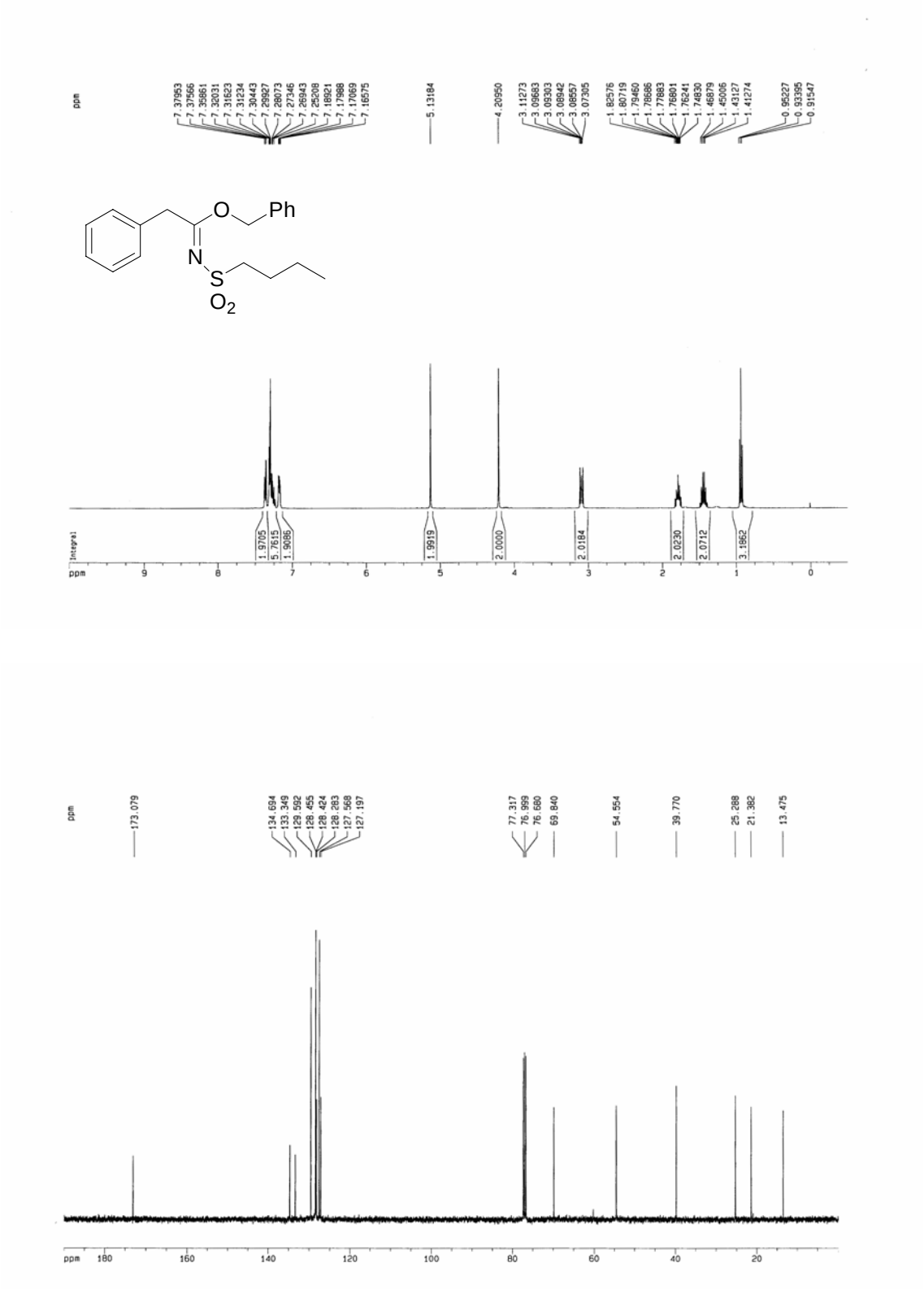


Benzyl *N*-[2-(trimethylsilyl)ethanesulfonyl)phenylacetimidate (4m)

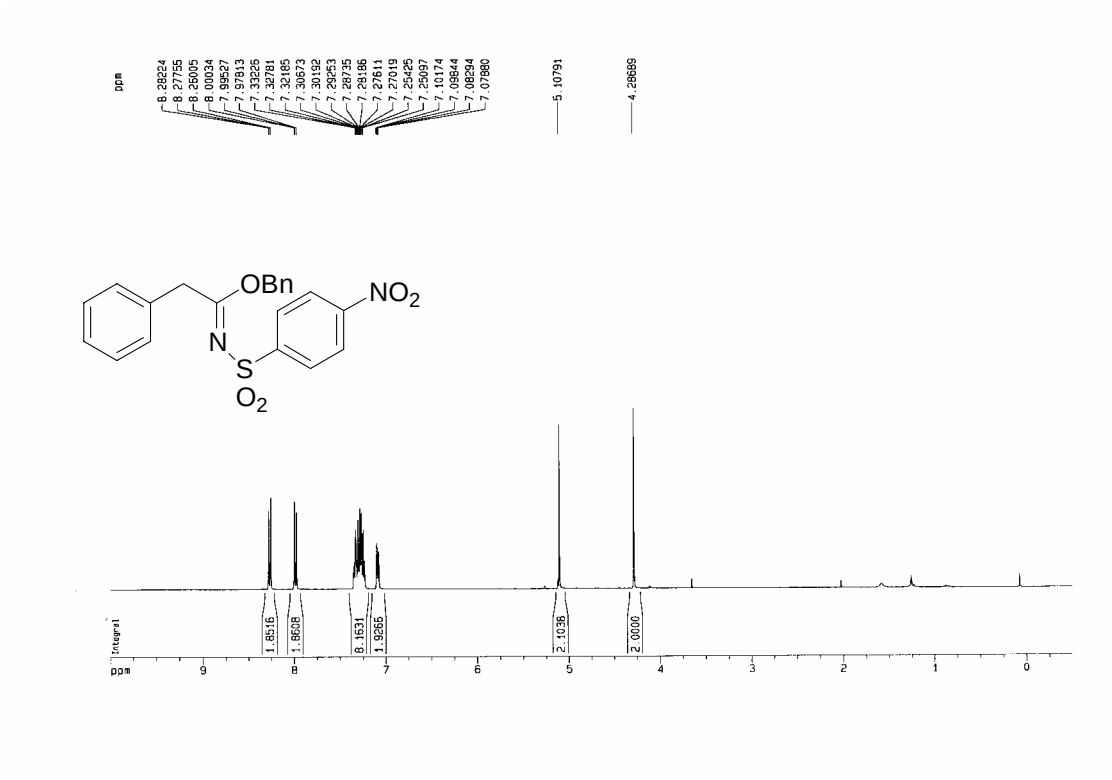


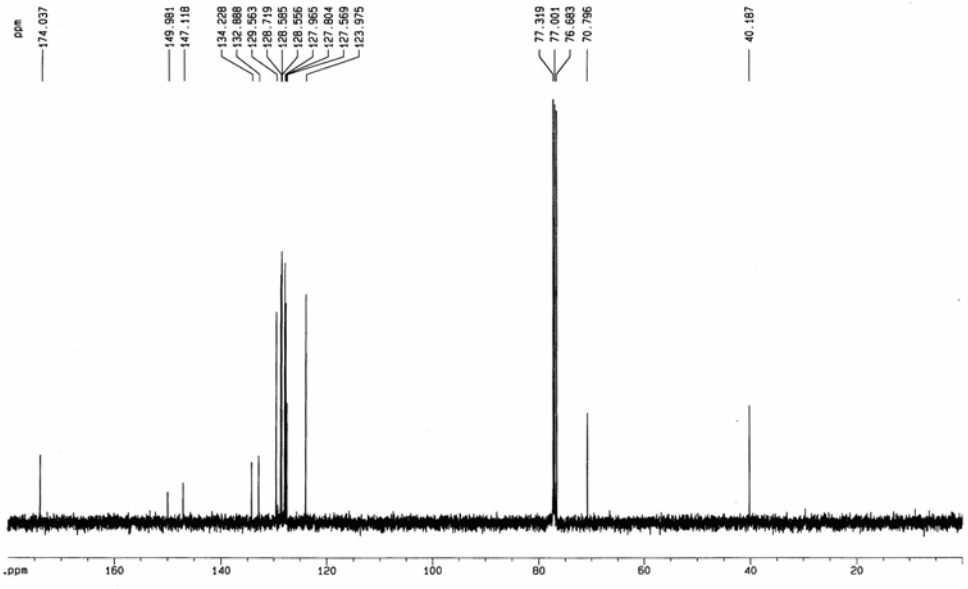


Benzyl *N*-(butanesulfonyl)phenylacetimidate (4n)

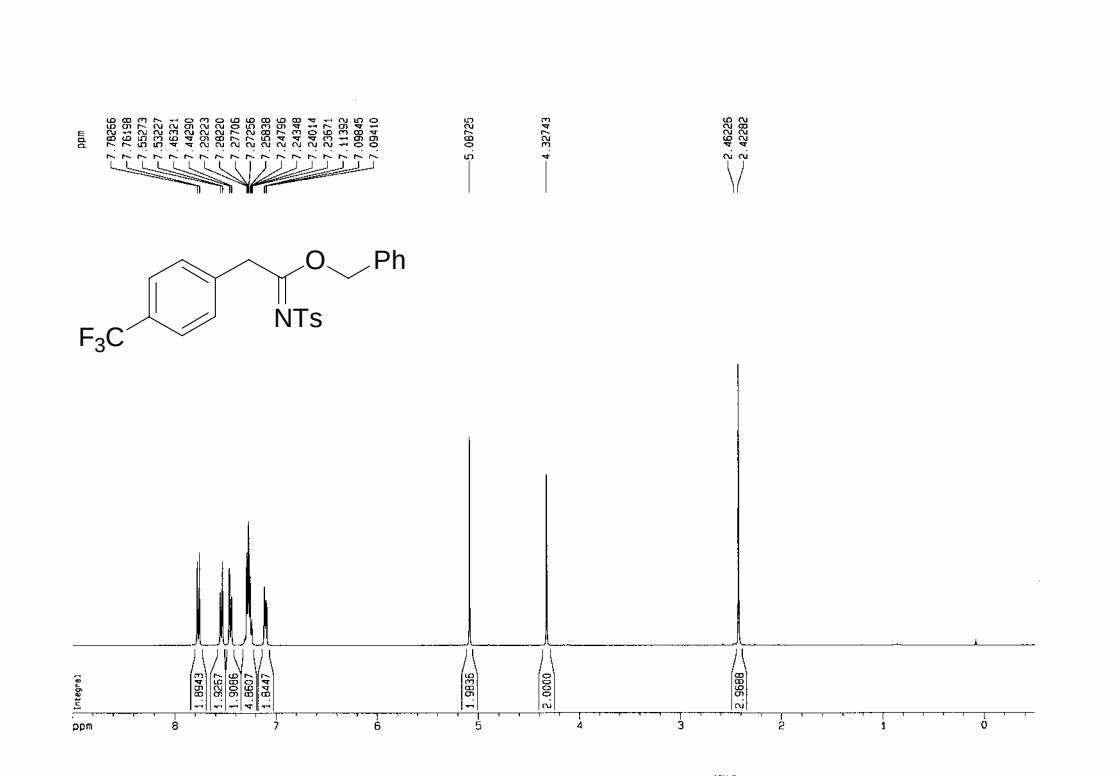


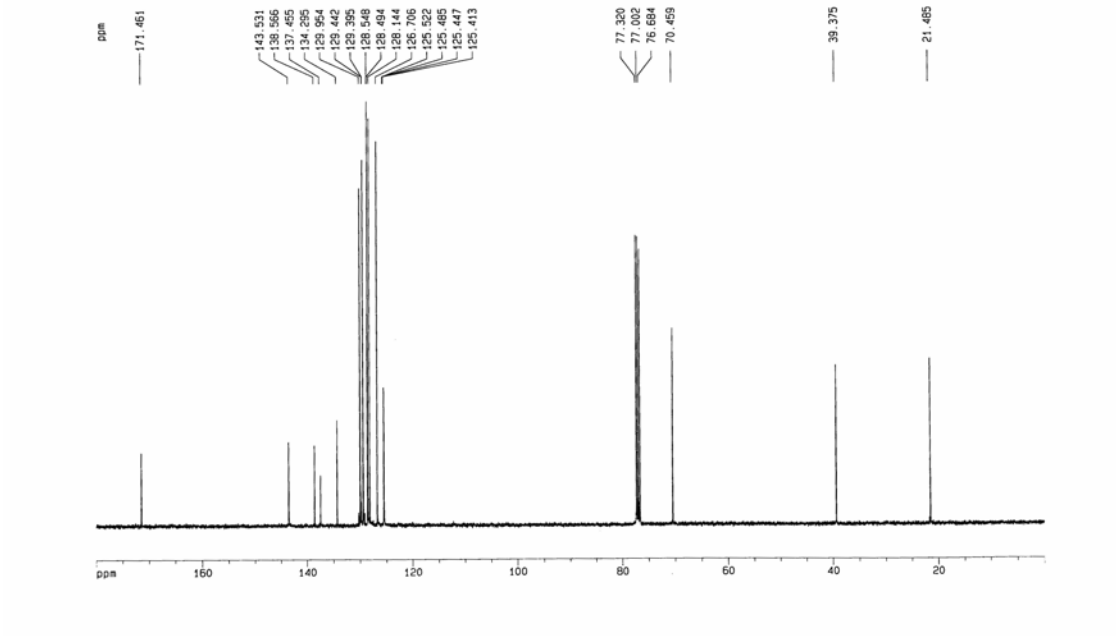
Benzyl *N*-(4-nitrobenzensulfonyl)phenylacetimidate (4o)



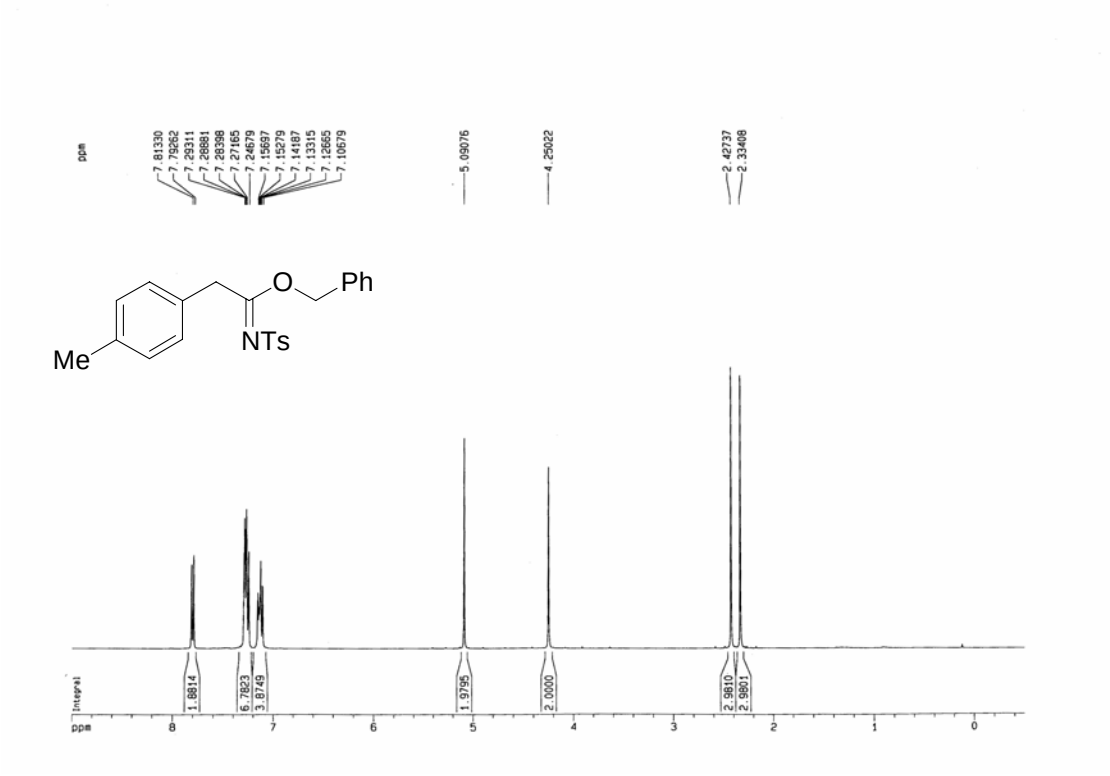


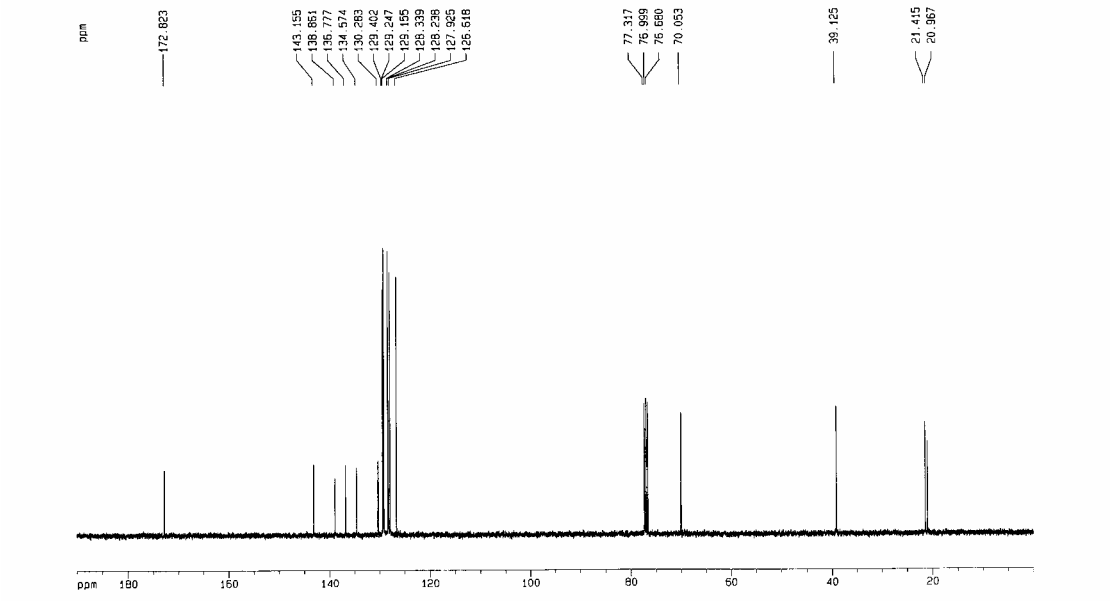
Benzyl *N*-(4-methylbenzensulfonyl)-(4-trifluoromethylphenyl)acetimidate (4p)



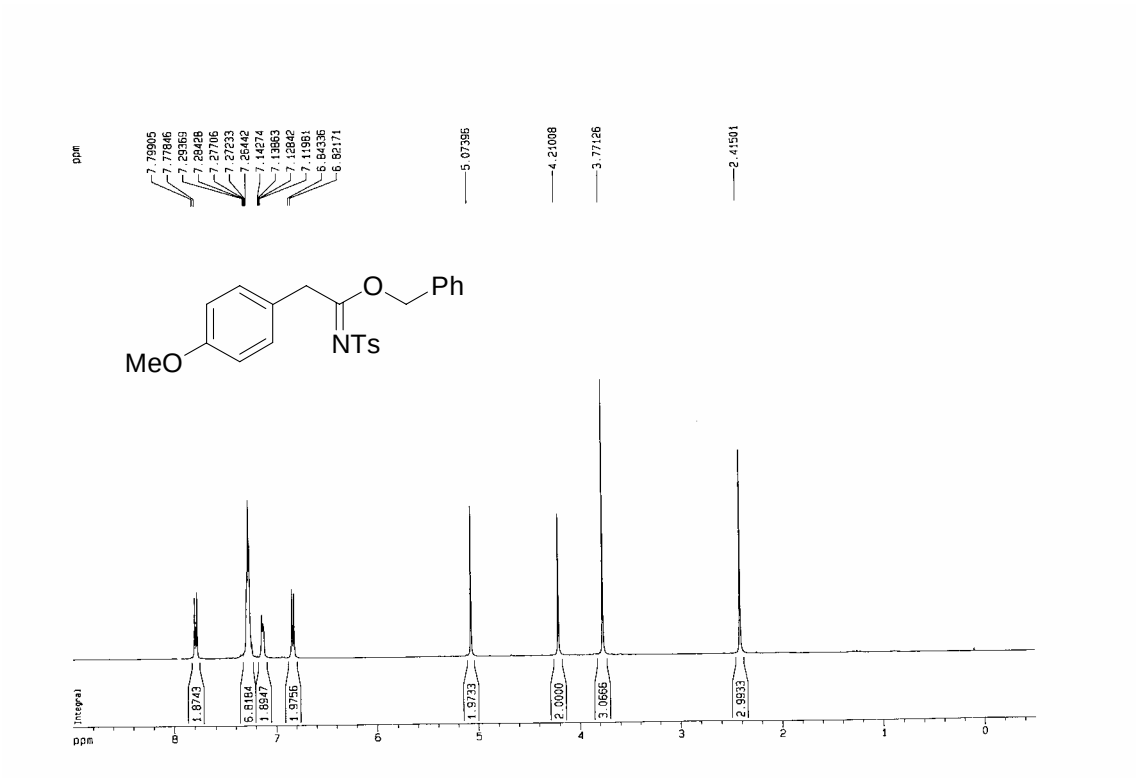


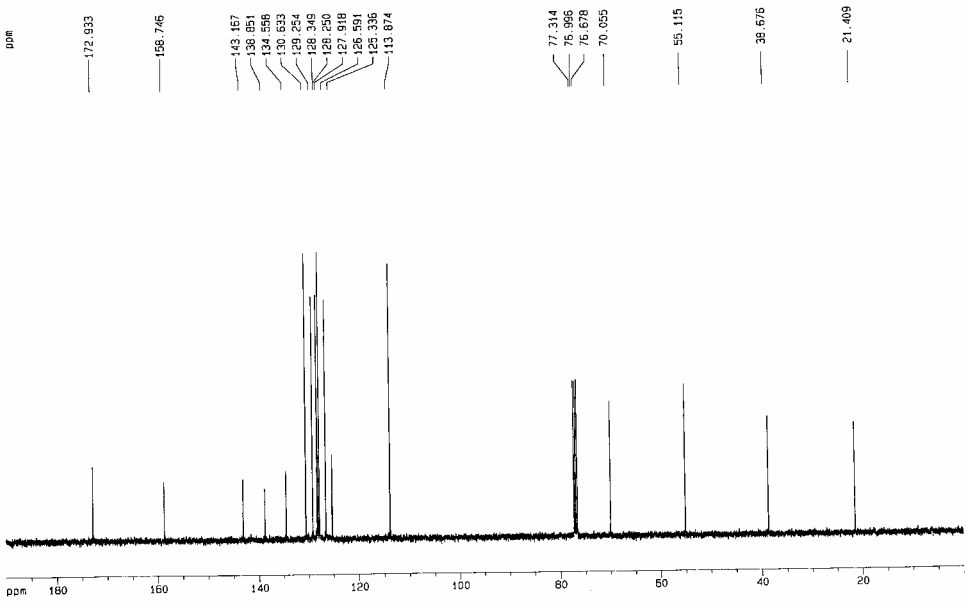
Benzyl *N*-(4-methylbenzensulfonyl)-(4-methylphenyl)acetimidate (4q)



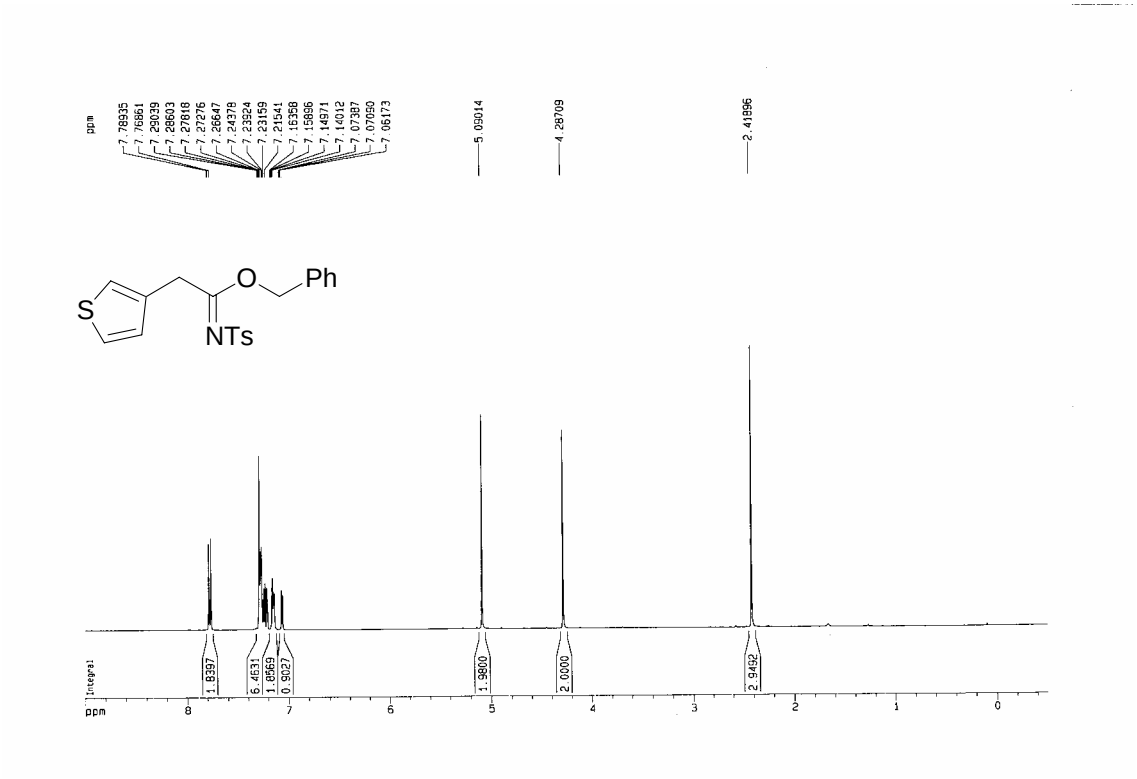


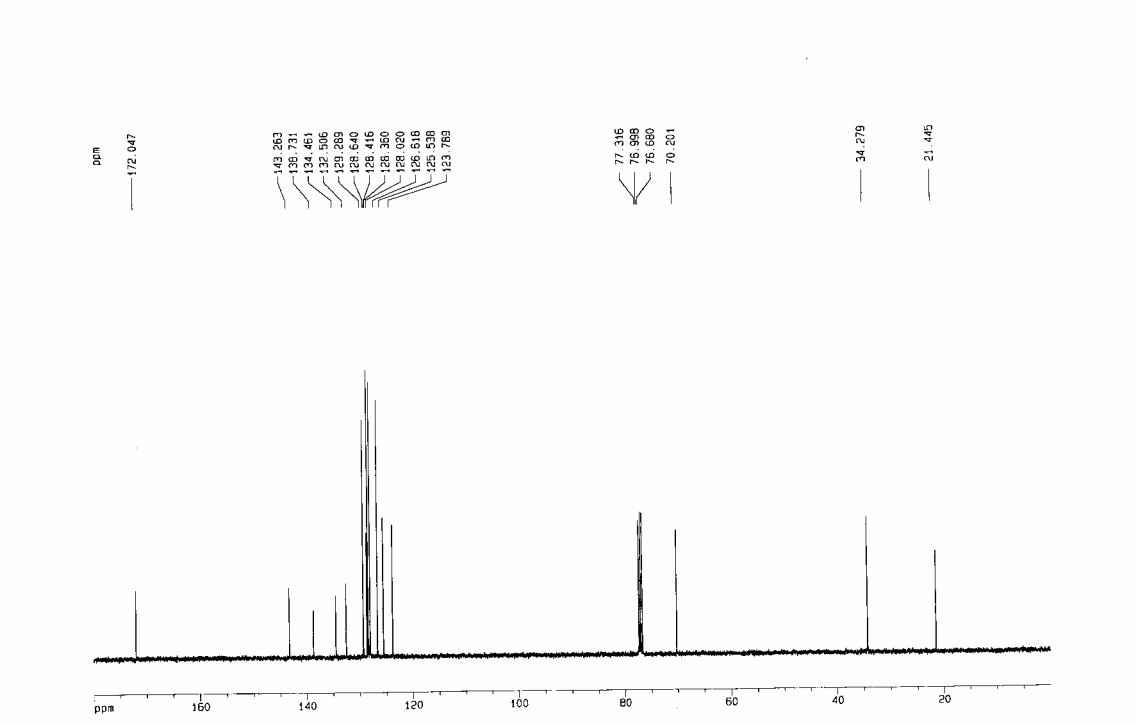
Benzyl *N*-(4-methylbenzensulfonyl)-(4-methoxylphenyl)acetimidate (4r)



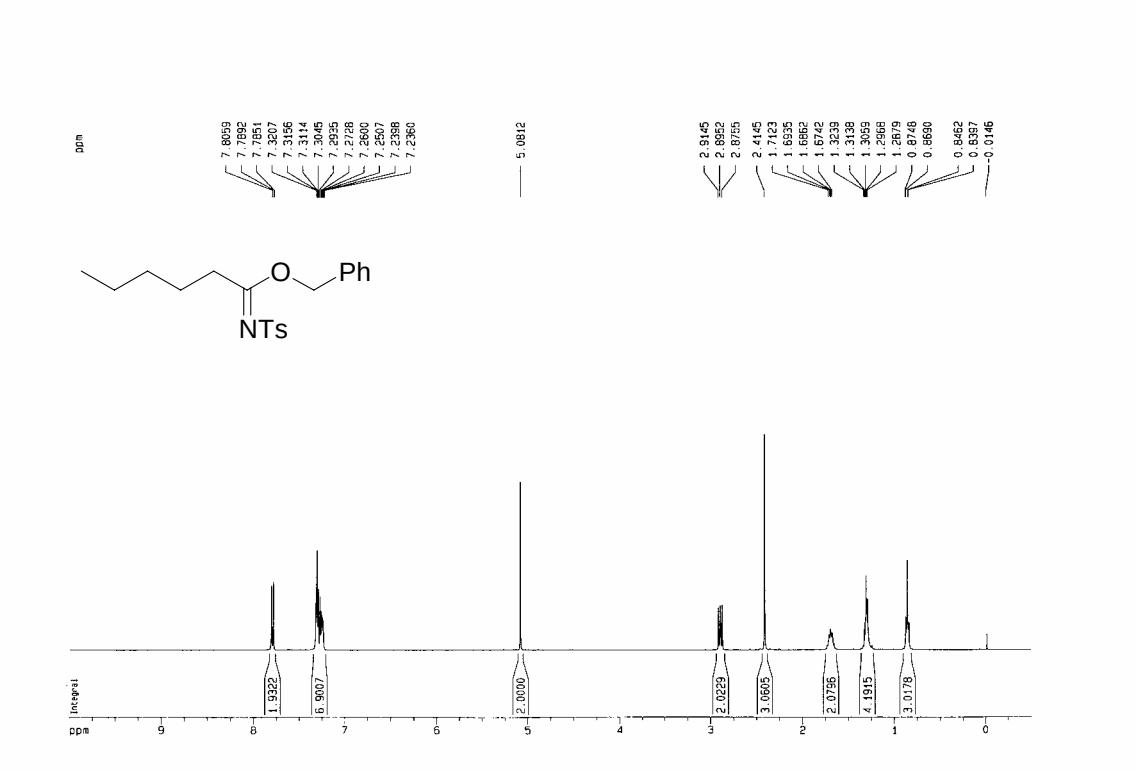


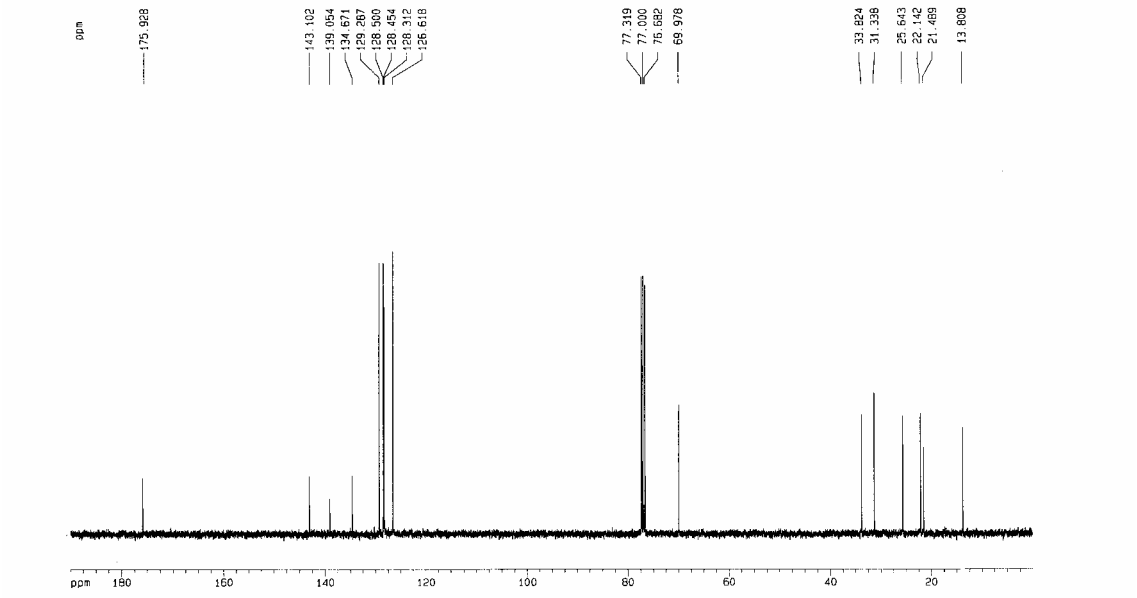
Benzyl *N*-(4-methylbenzensulfonyl)-(thien-3-yl)acetimidate (4s)



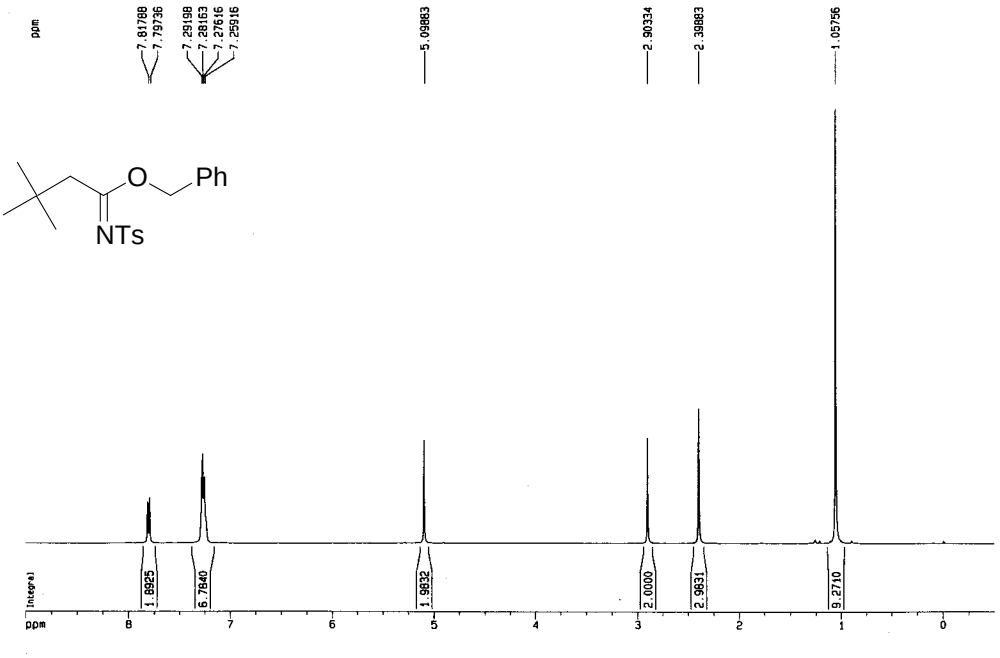


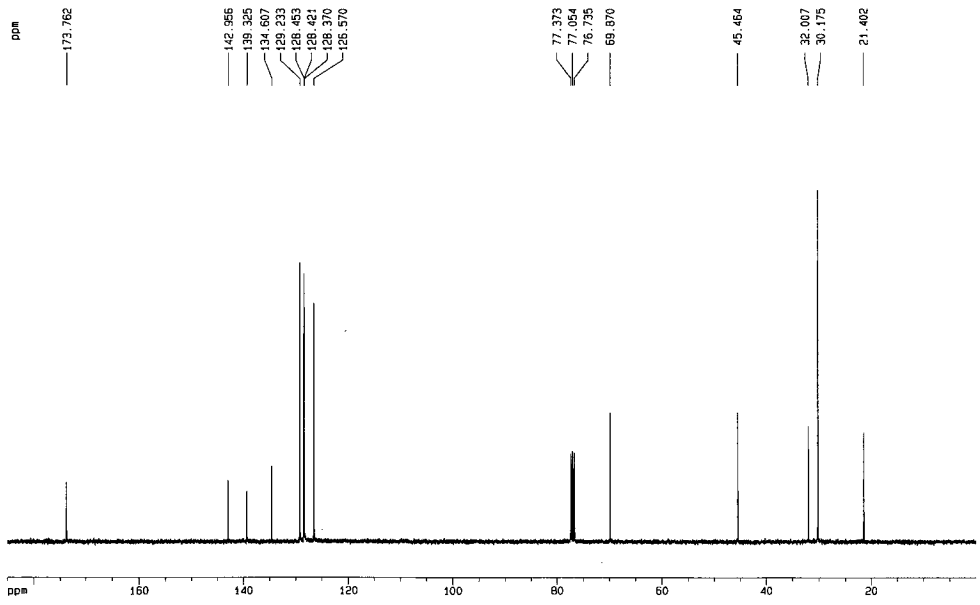
Benzyl *N*-(4-methylbenzensulfonyl)heximidate (4t)



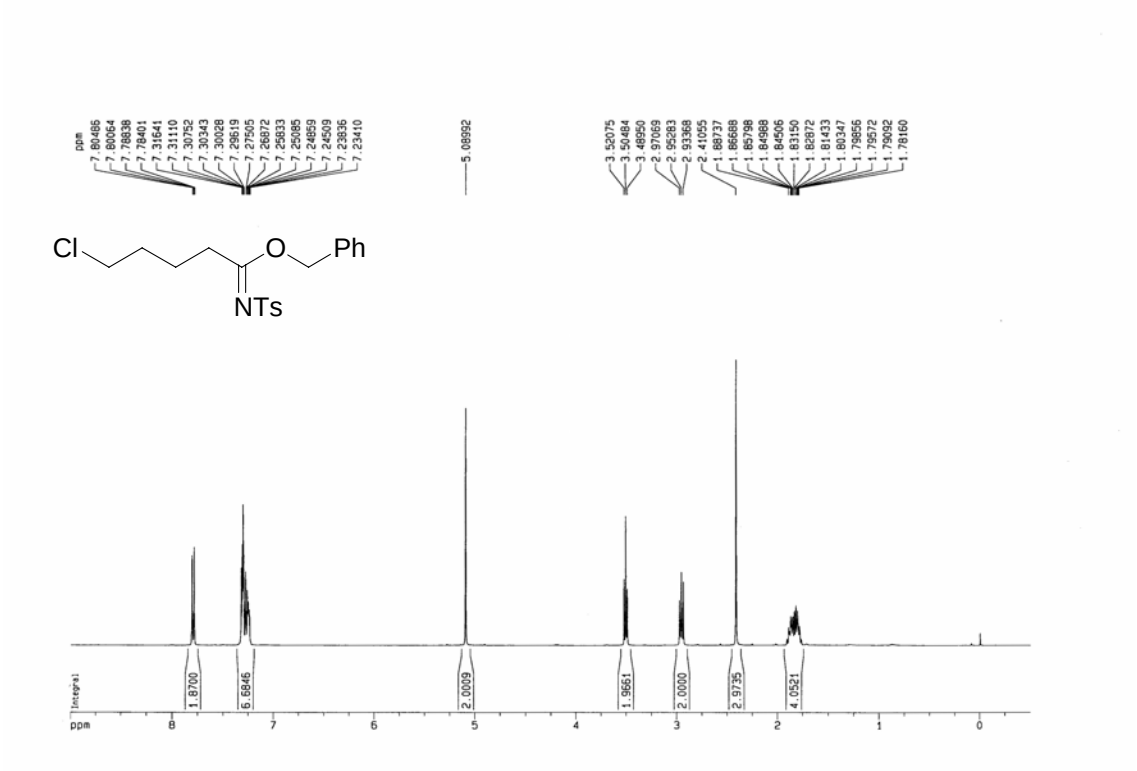


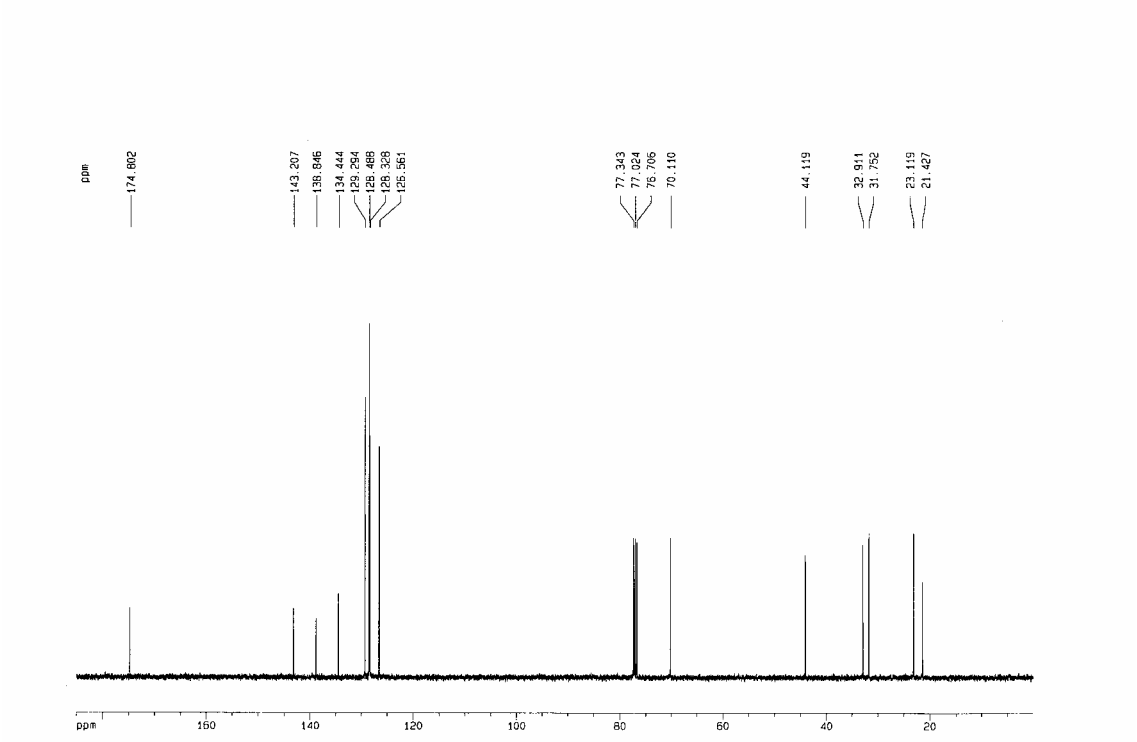
Benzyl *N*-(4-methylbenzenesulfonyl)-(3,3-dimethyl)butyrimidate (4u)



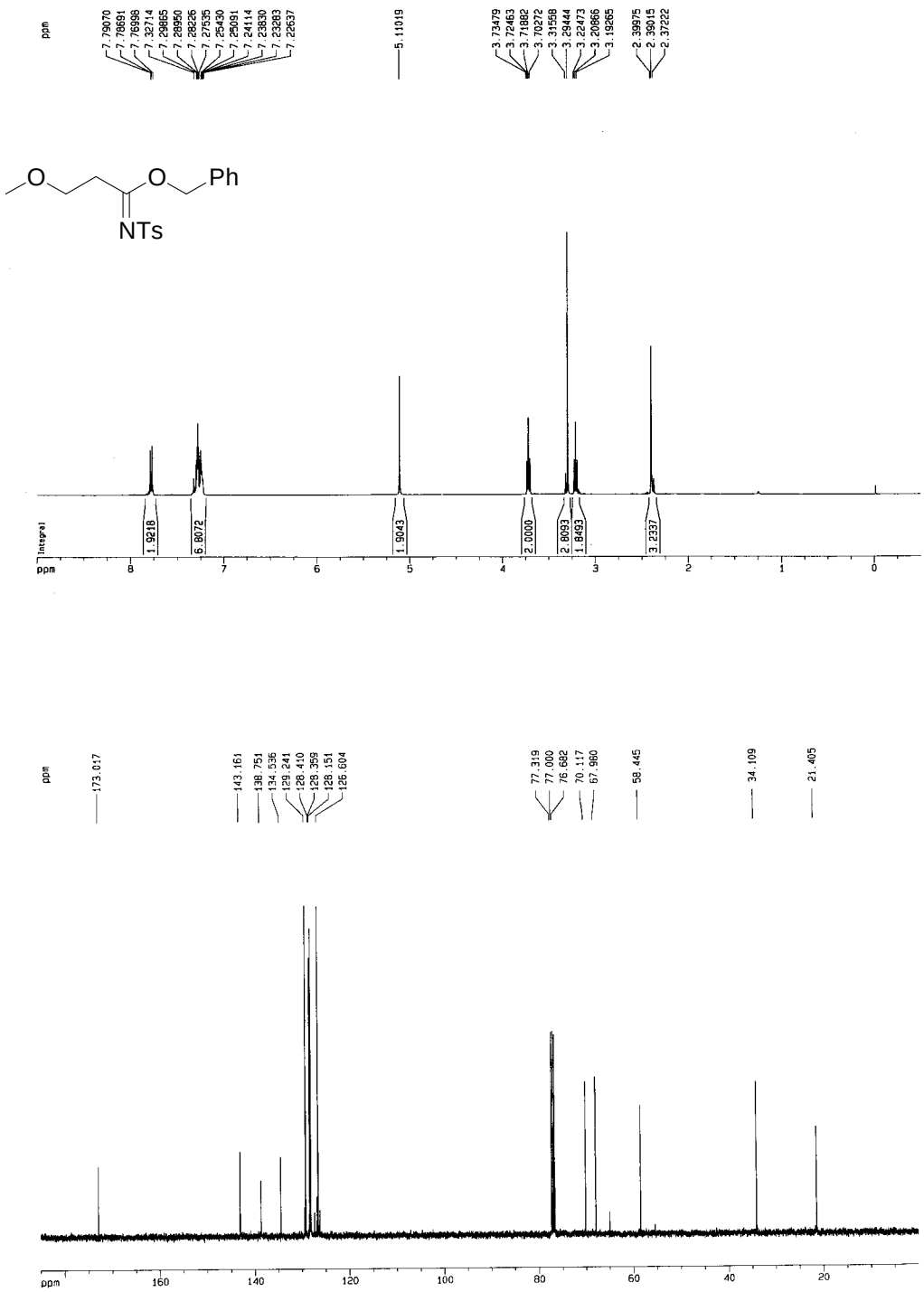


Benzyl *N*-(4-methylbenzensulfonyl)-(5-chloro)valerimidate (4v)

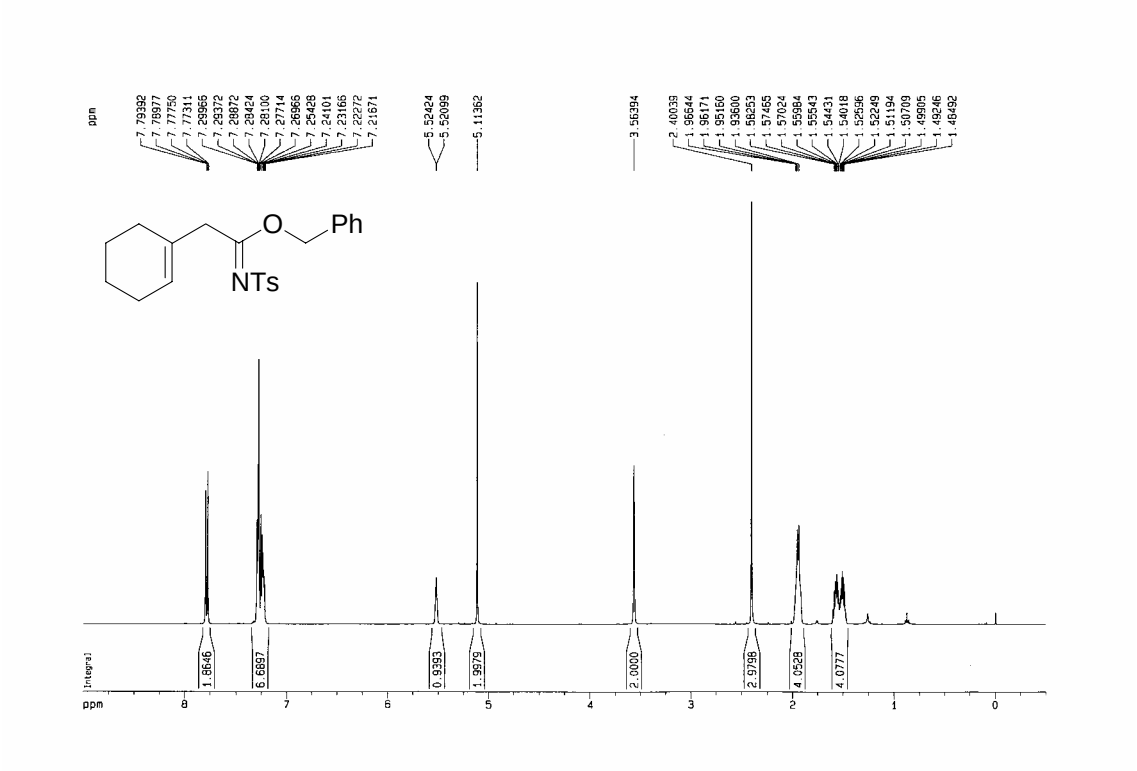


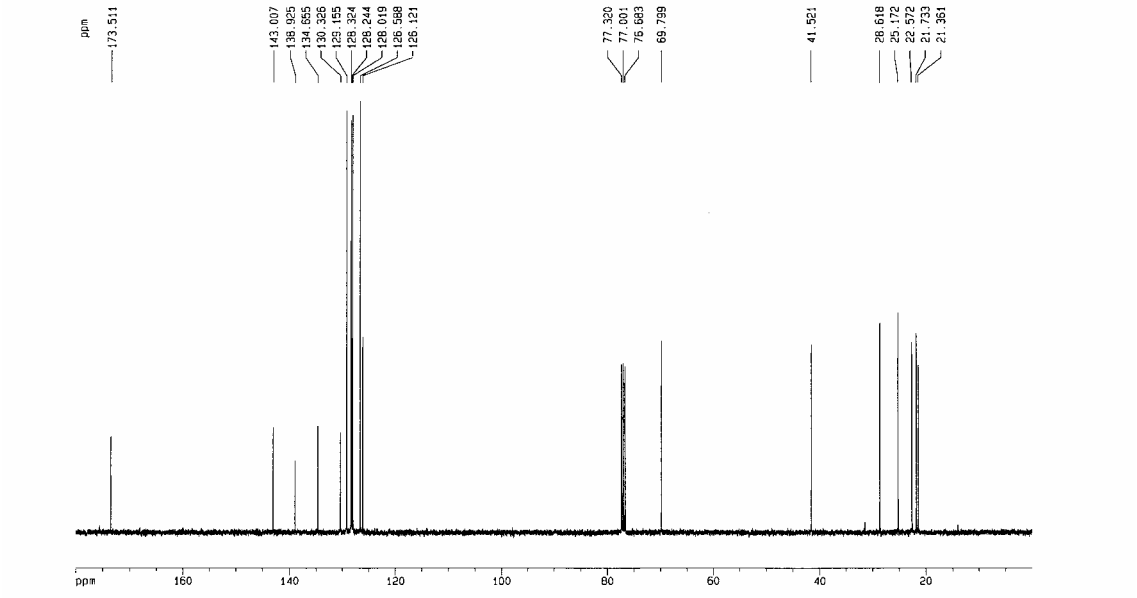


Benzyl *N*-(4-methylbenzenesulfonyl)-(3-methoxy)propionimidate (4w)

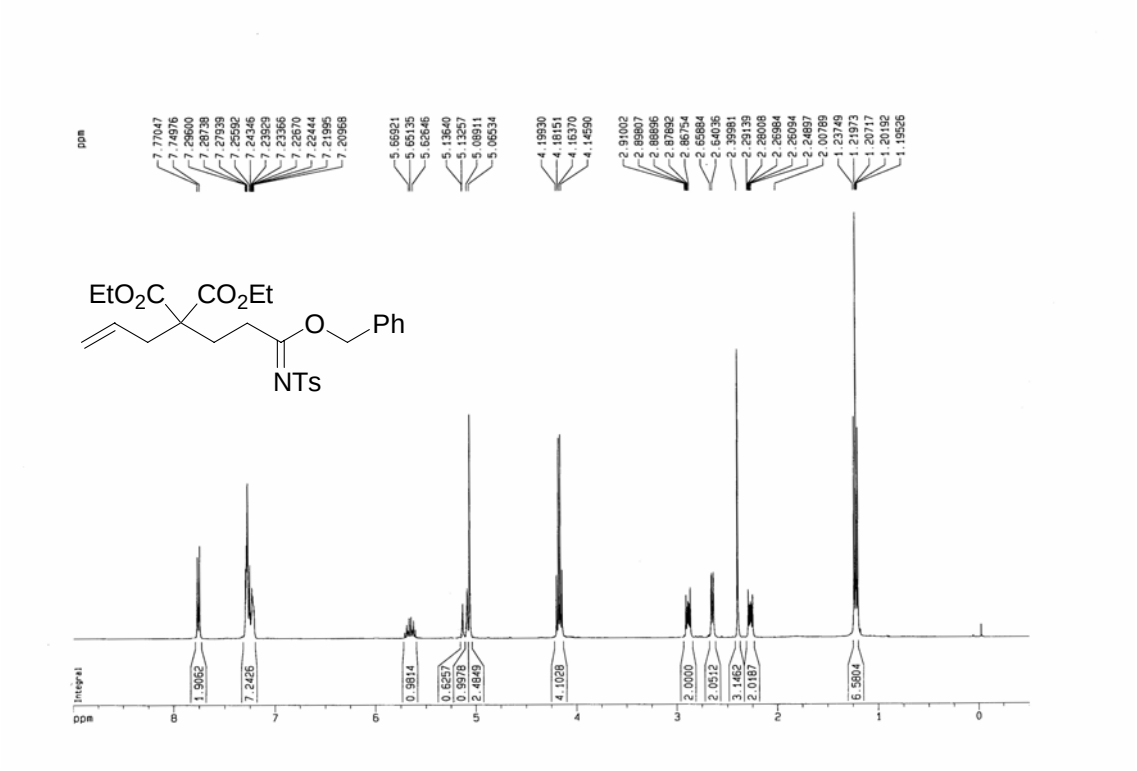


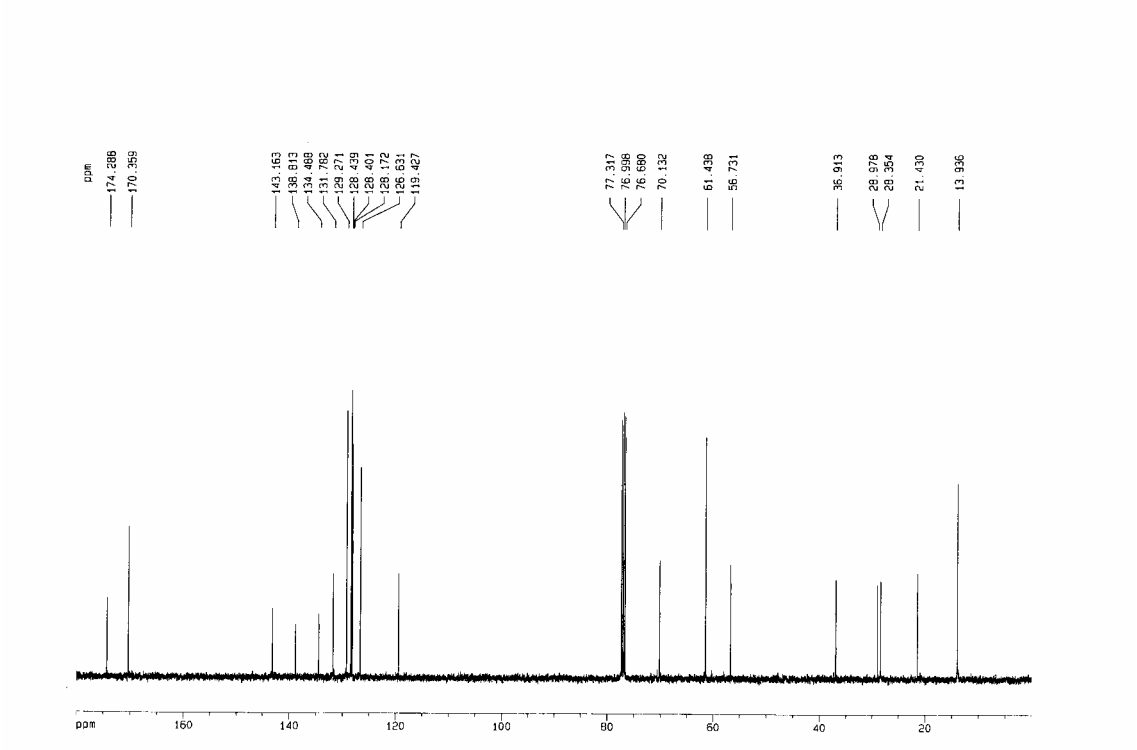
Benzyl *N*-(4-methylbenzenesulfonyl)-(1-cyclohexenyl)acetimidate (4x)



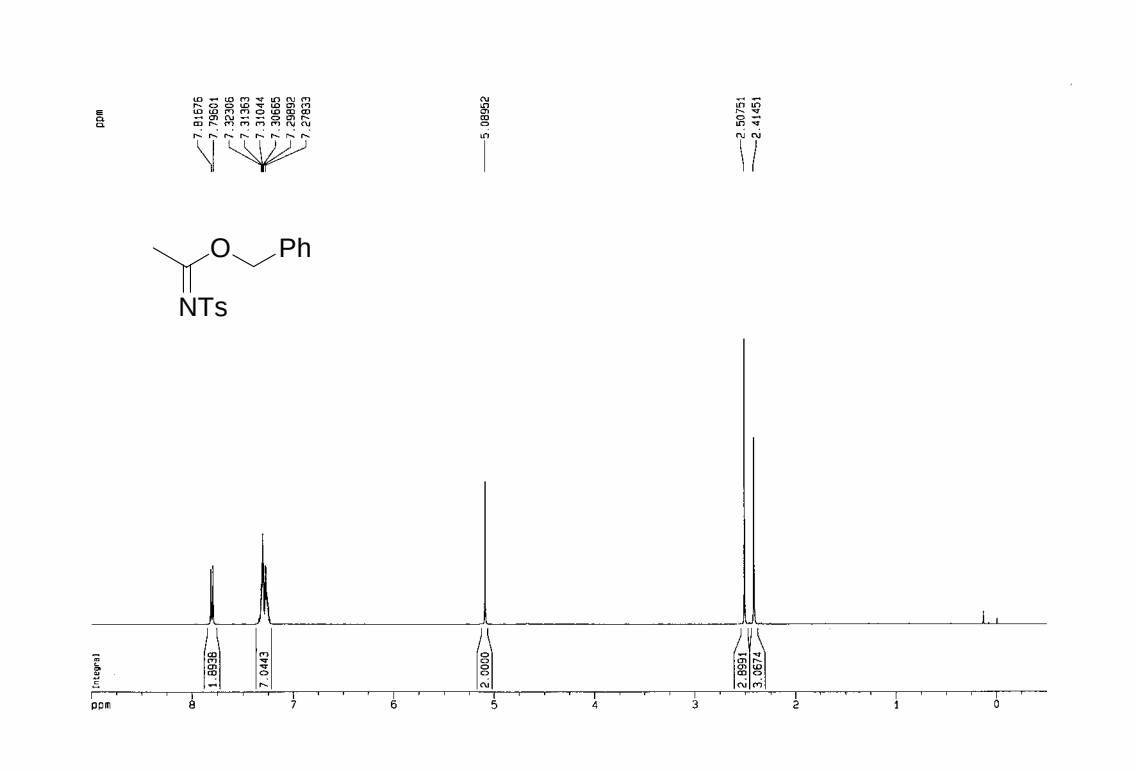


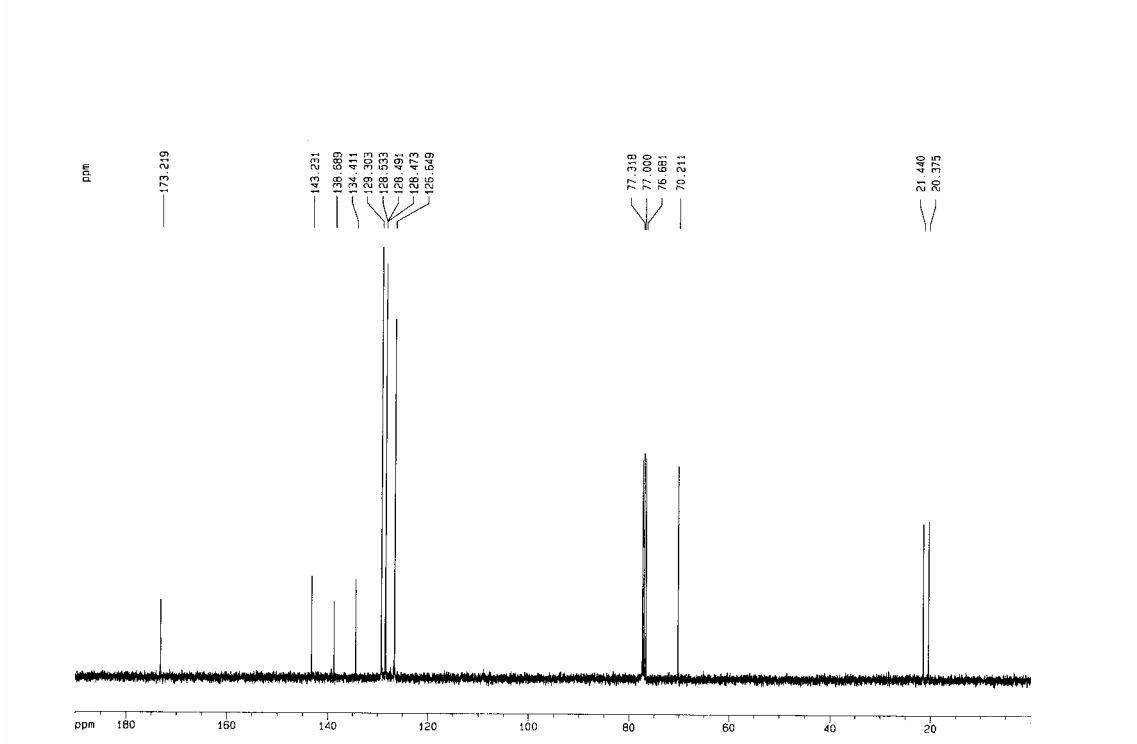
Benzyl *N*-(4-methylbenzenesulfonyl)-[4,4-bis(ethoxycarbonyl)]-6-heptimidate (4y)



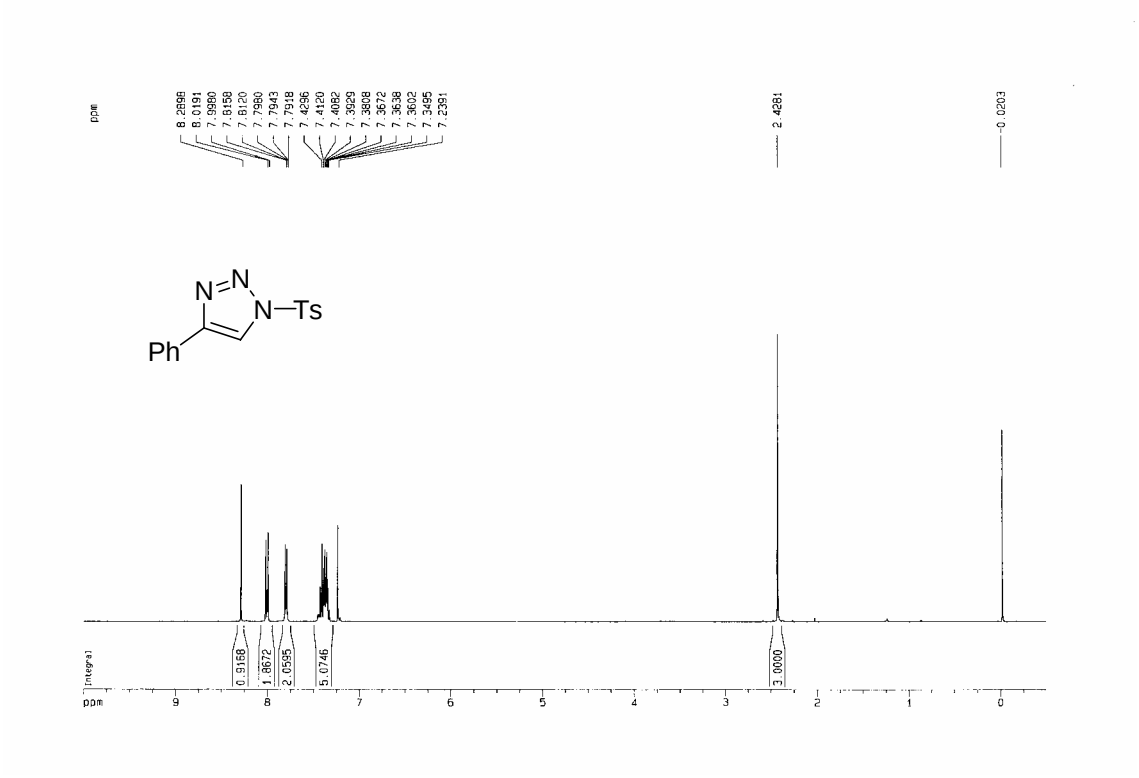


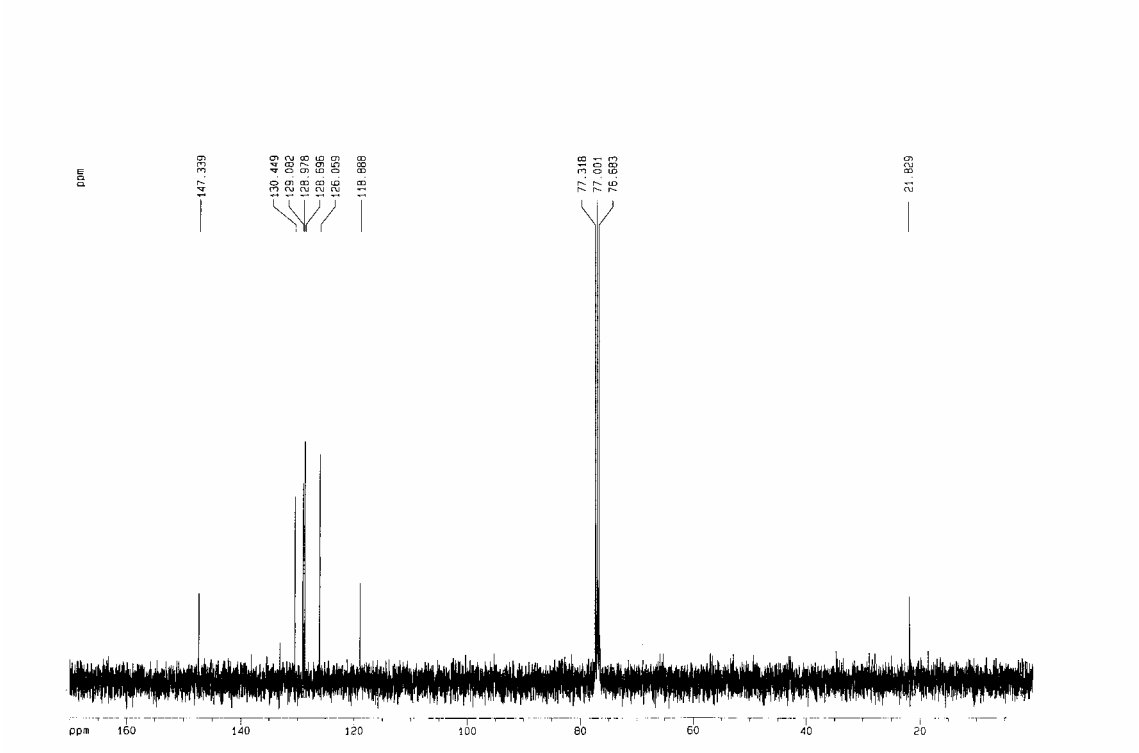
Benzyl *N*-(4-methylsulfonylbenzen)acetimidate (4z)



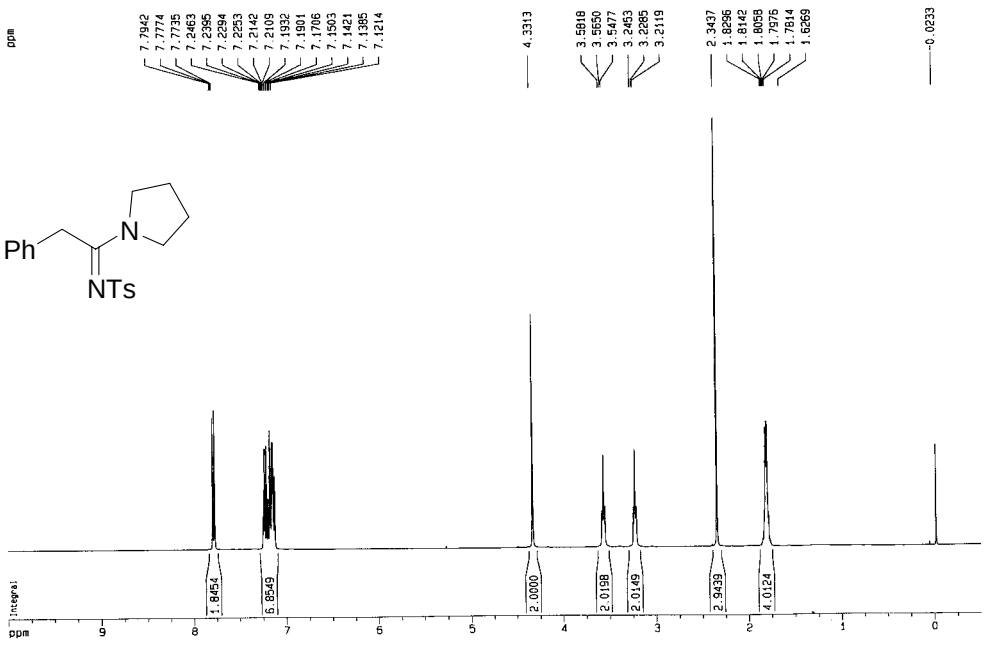


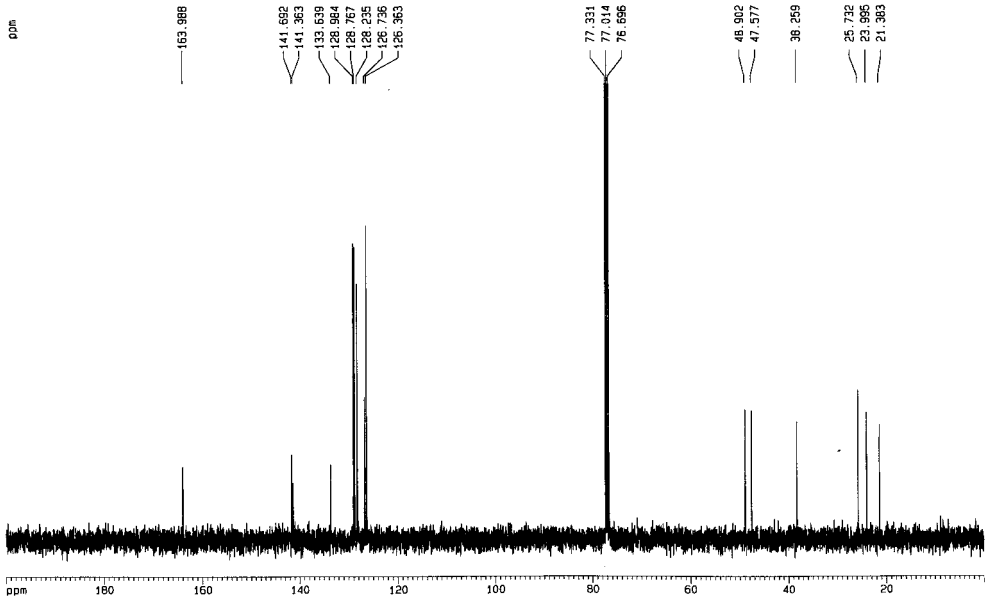
1-(4-Methylbenzensulfonyl)-4-phenyl-1,2,3-triazole (5a)



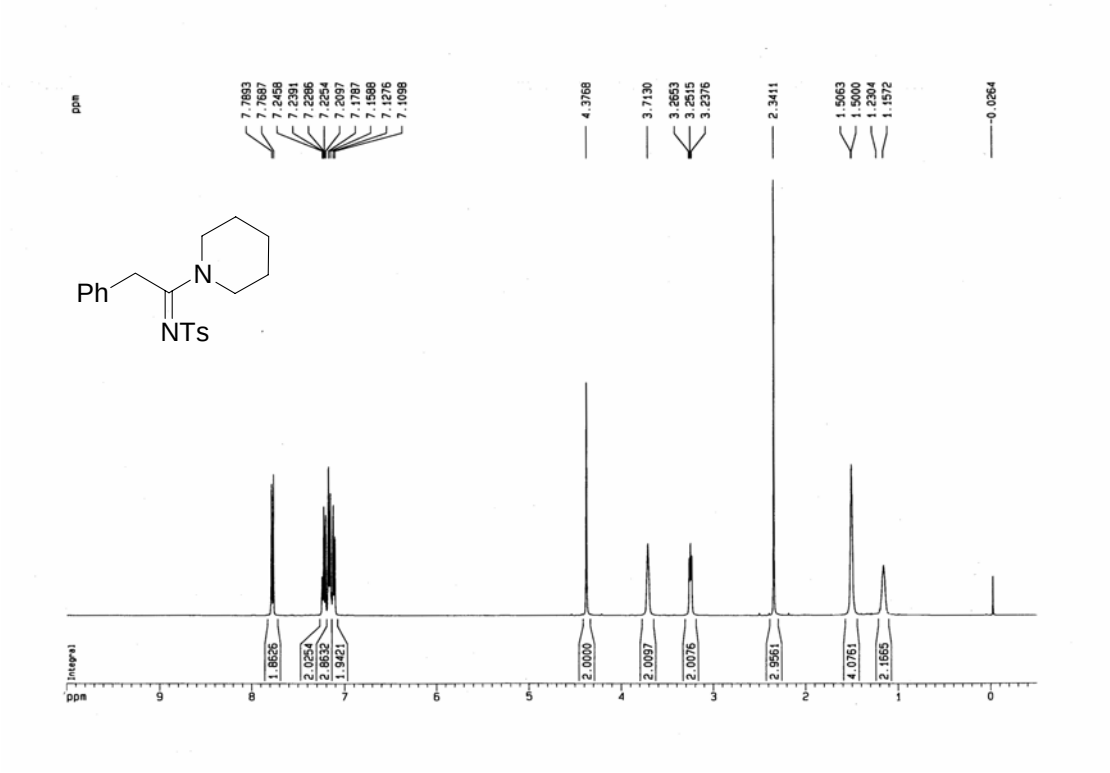


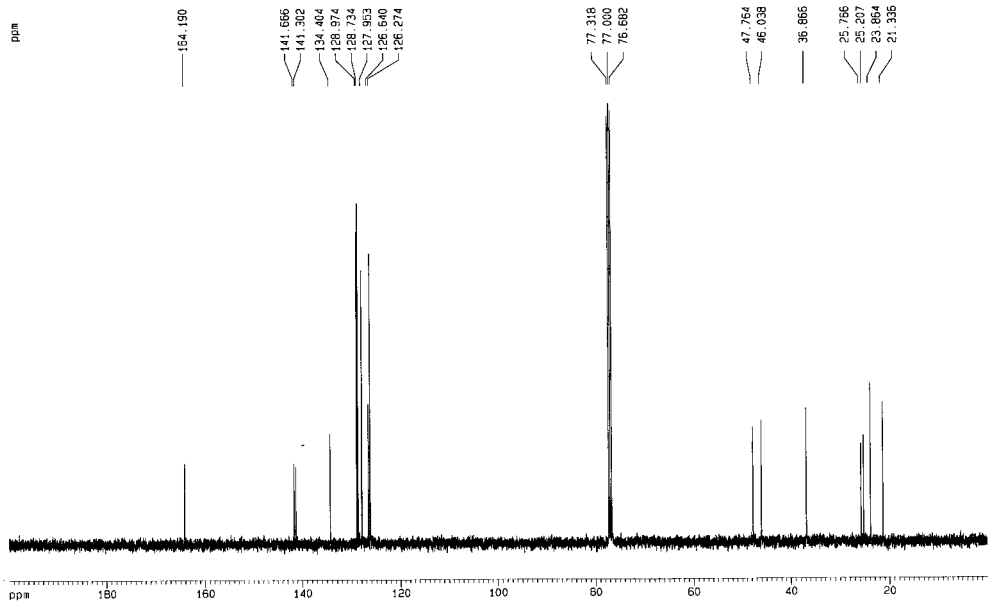
N^1-Pyrrolidinyl-N^2-(4-methylbenzensulfonyl)-2-phenylacetamidine (6a)



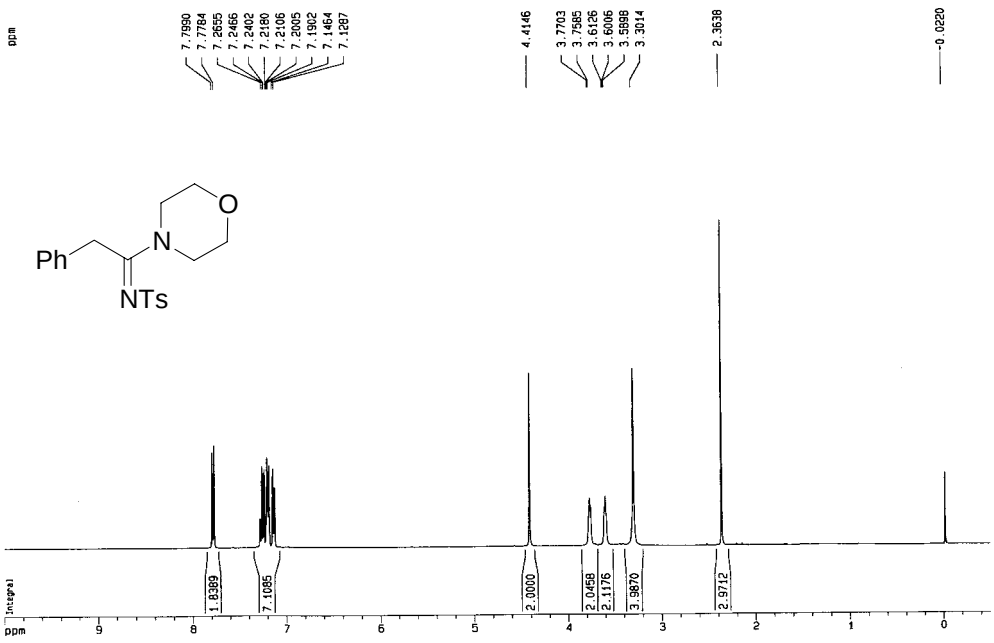


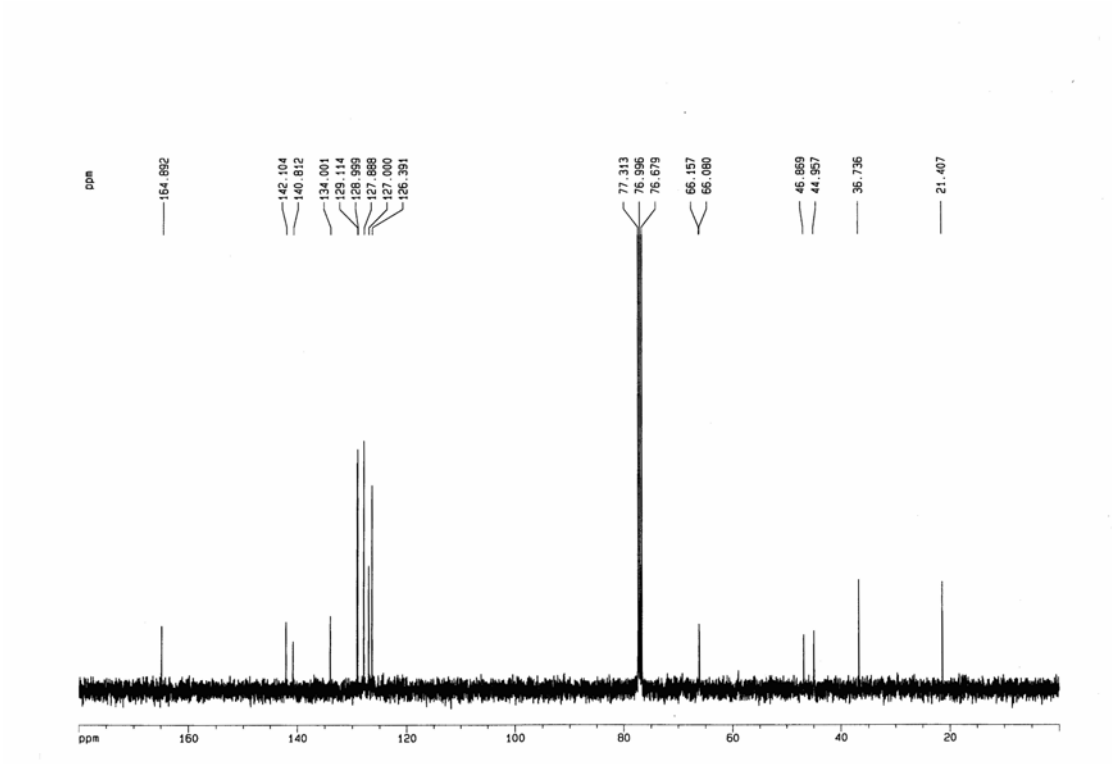
N^1-Piperidinyl-N^2-(4-methylbenzensulfonyl)-2-phenylacetamidine (6b)



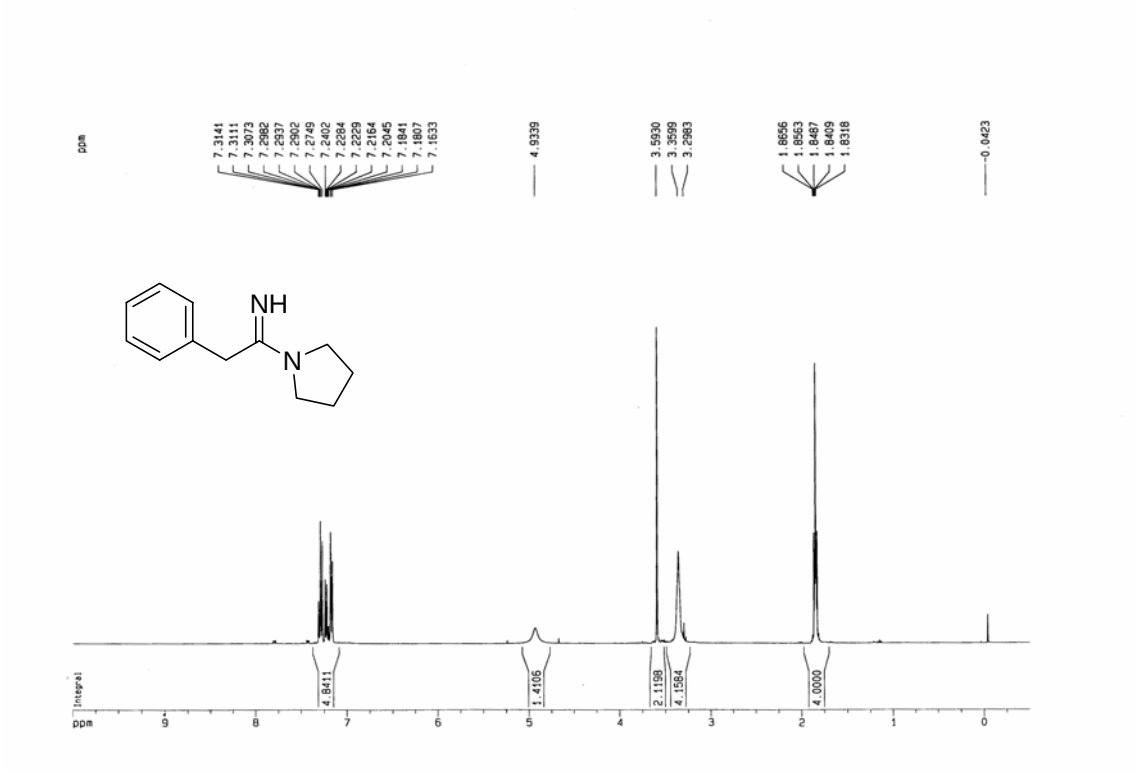


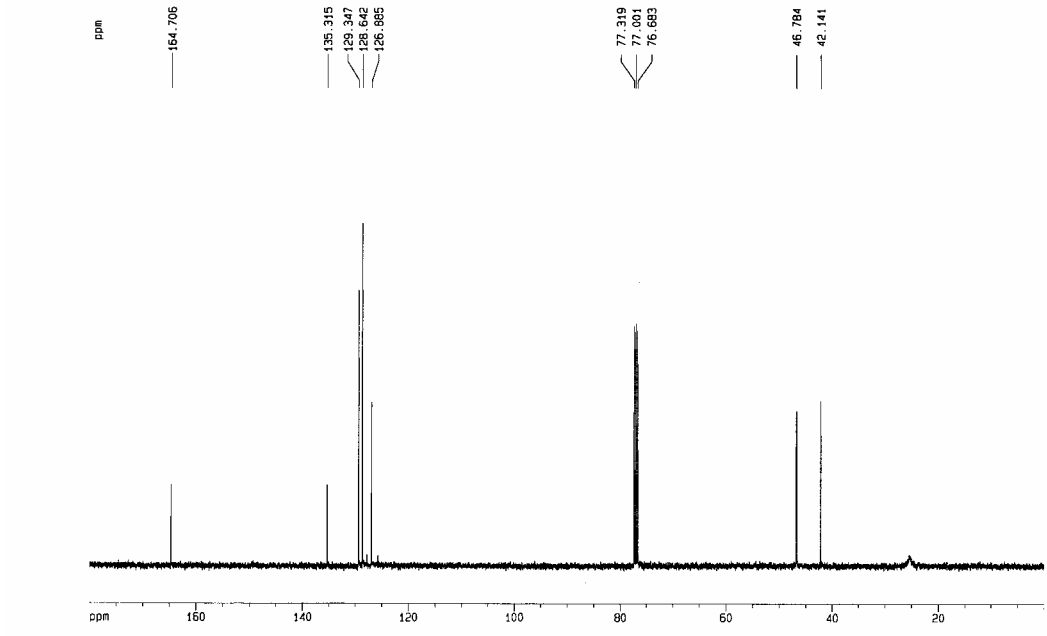
N^1-Morpholinyl-N^2-(4-methylbenzensulfonyl)-2-phenylacetamidine (6c)



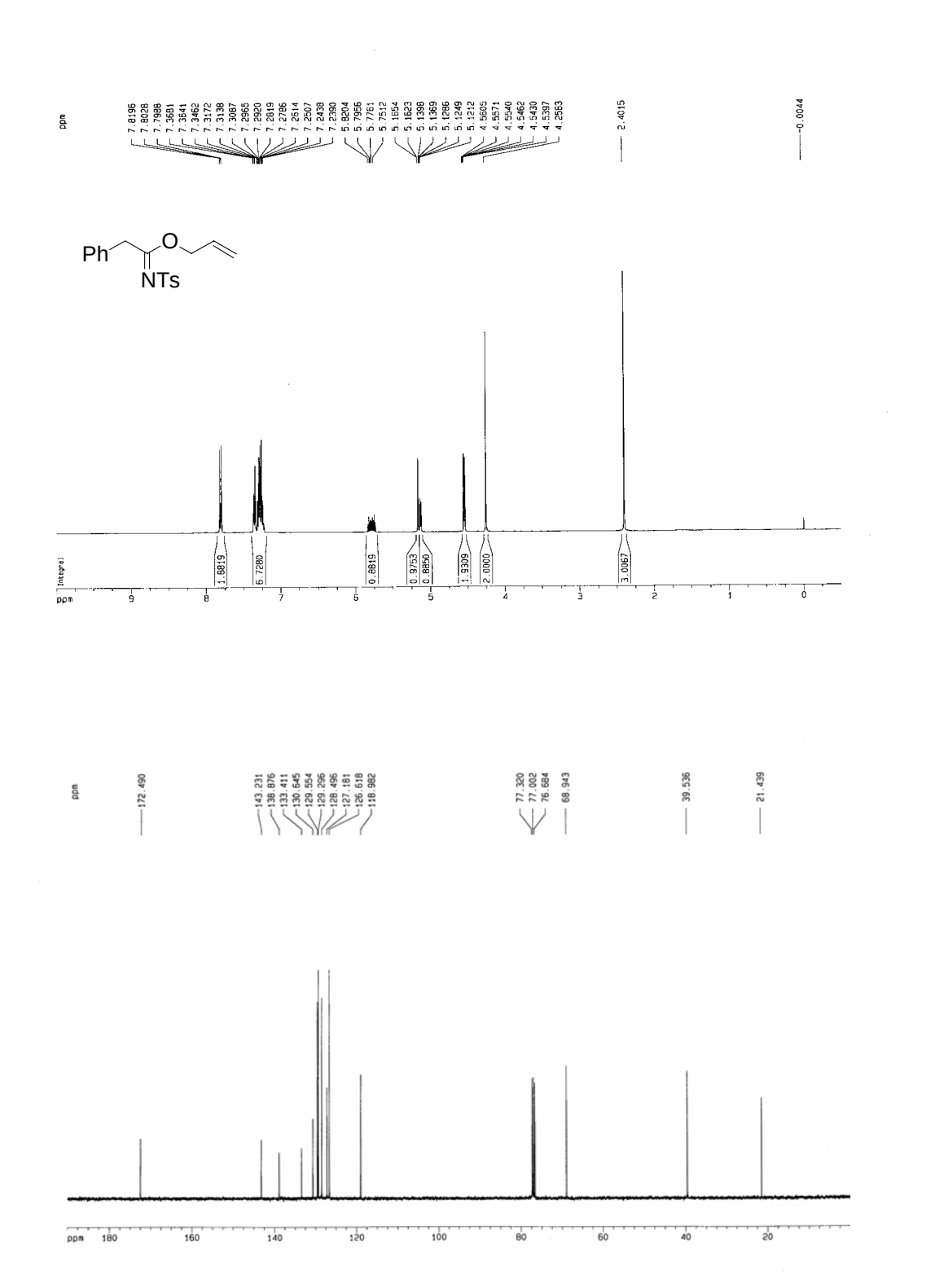


N-Pyrrolidinyl-2-phenylacetamidine (7a)

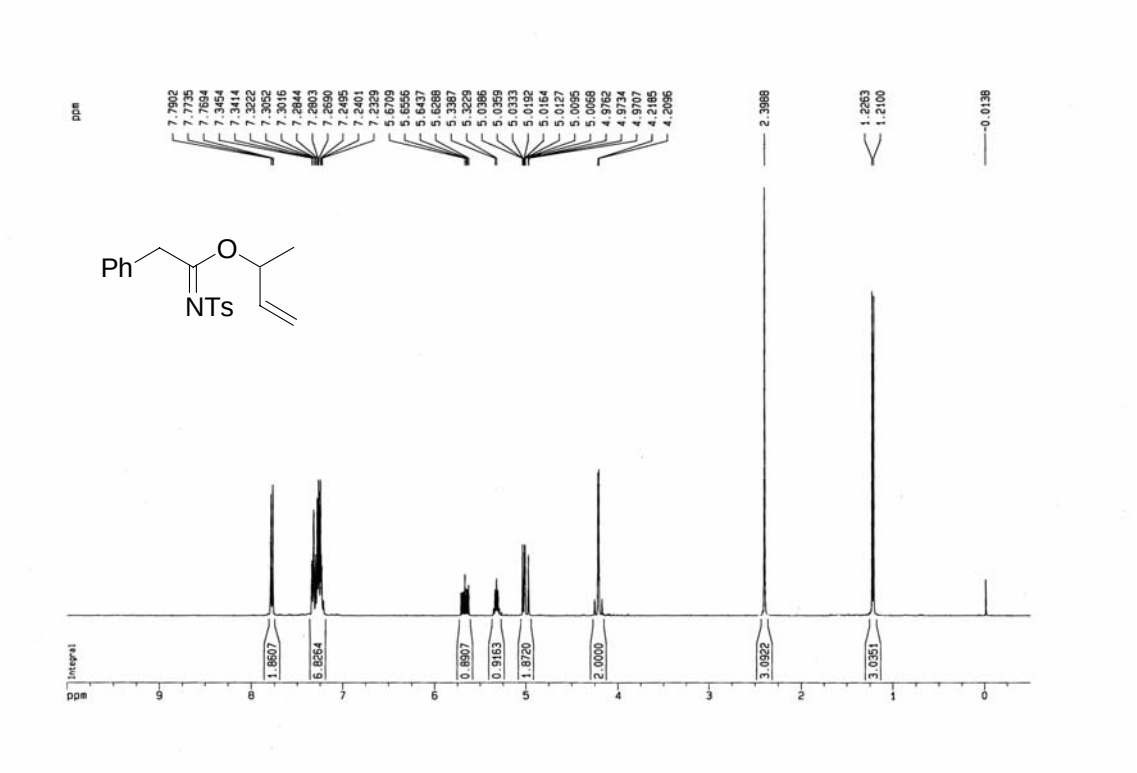


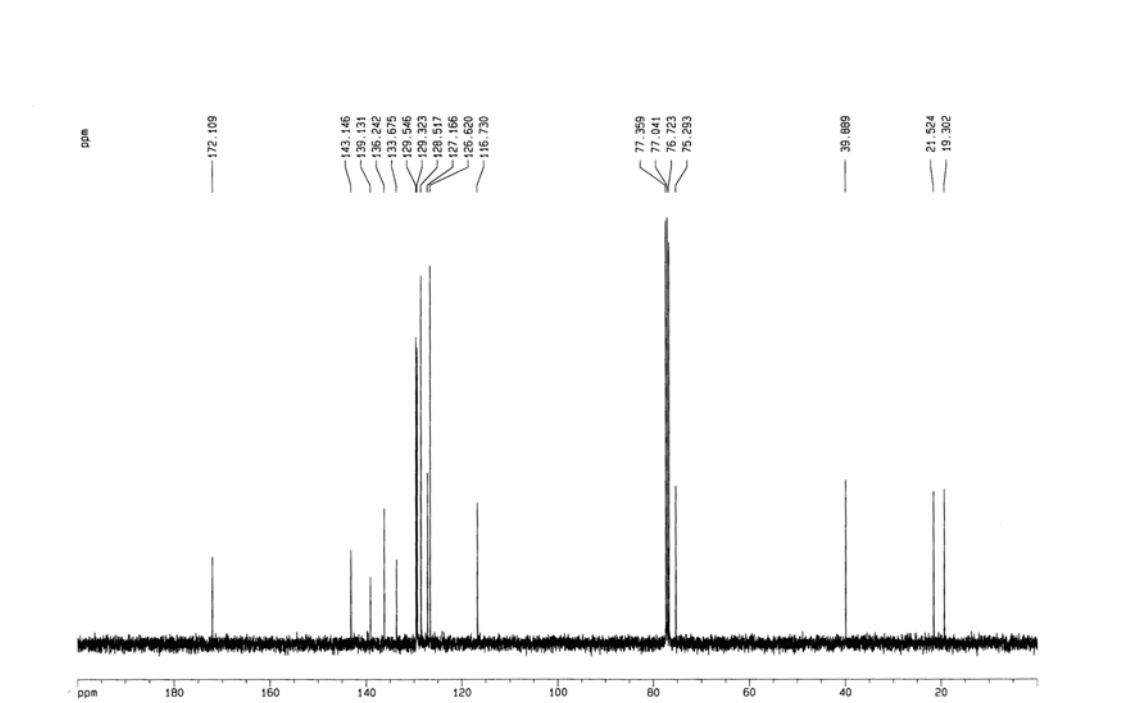


2-Propenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (8a)

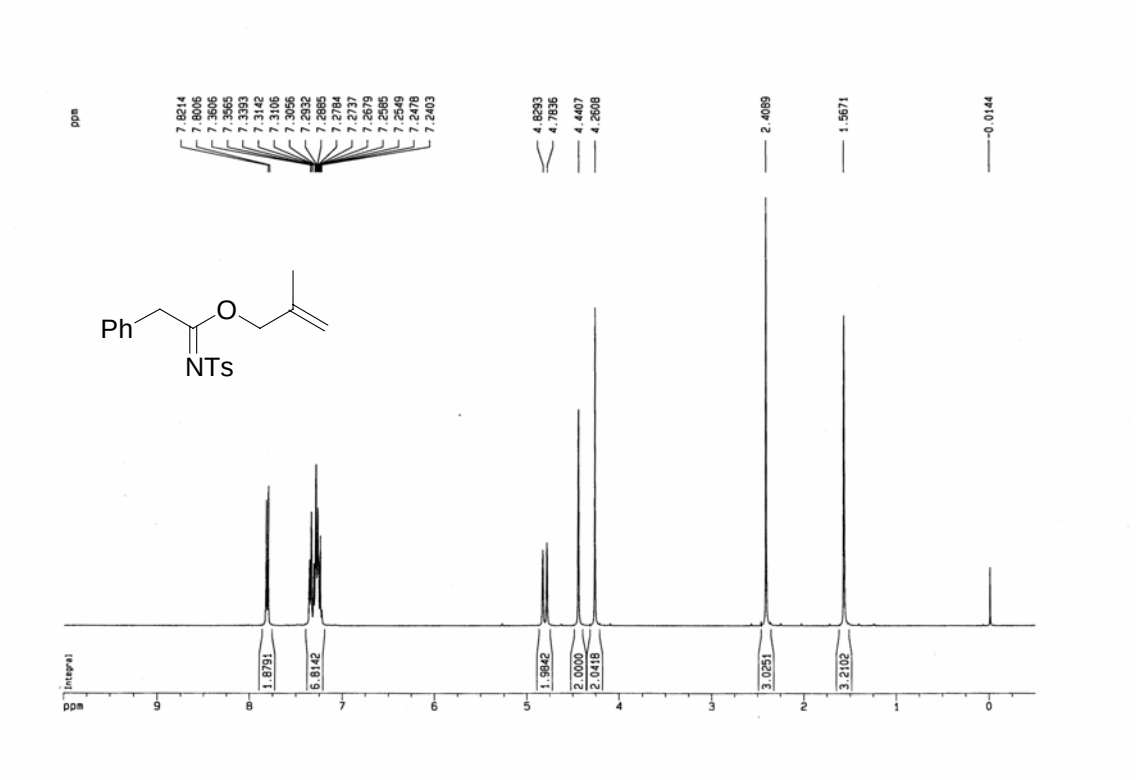


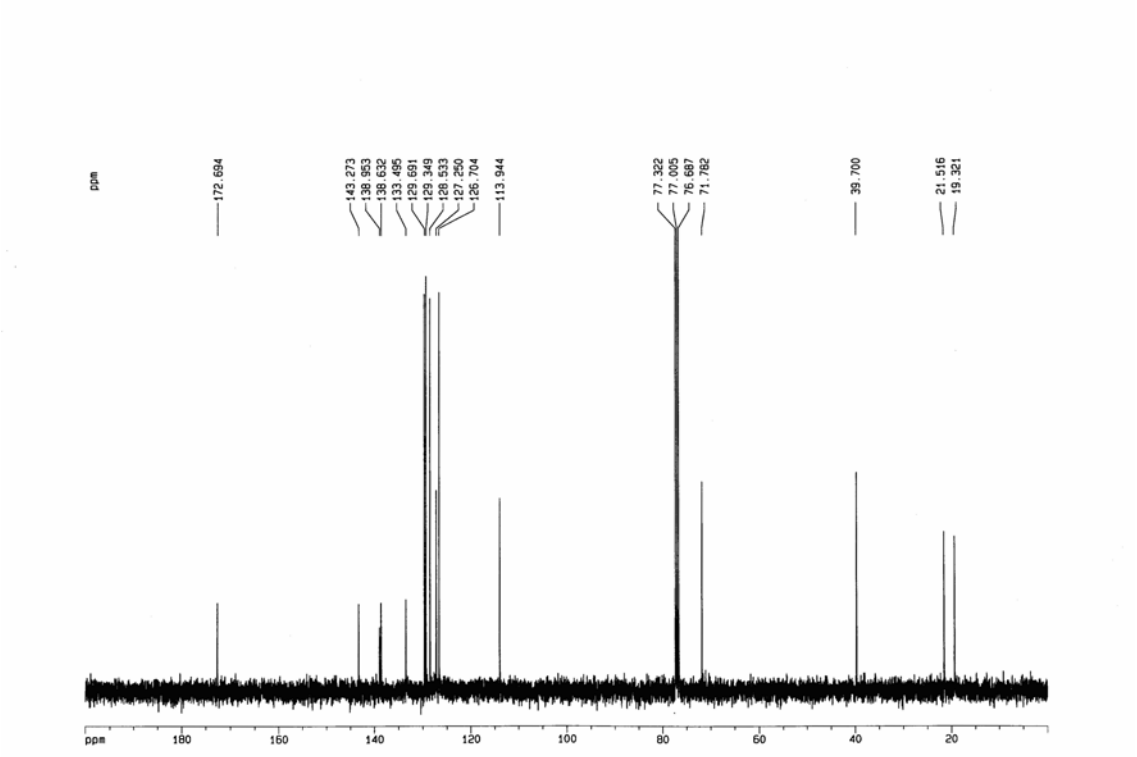
2-(3-Butenyl) *N*-(4-methylbenzensulfonyl)phenylacetimidate (8b)



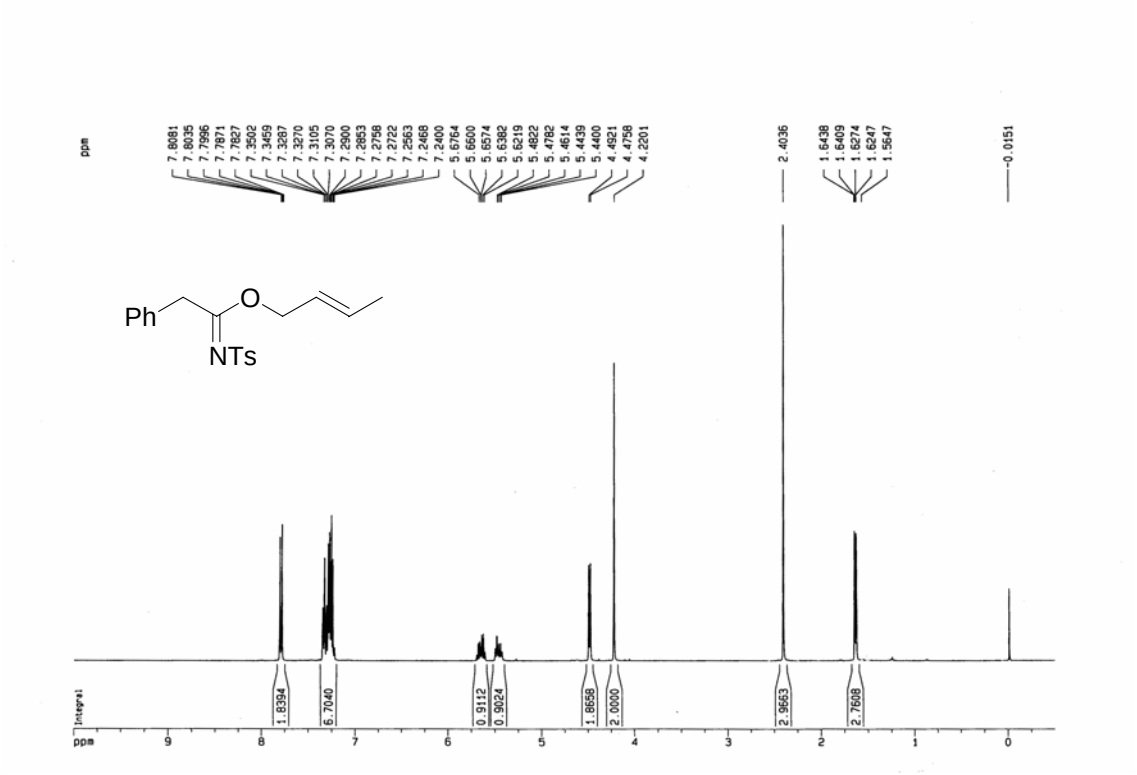


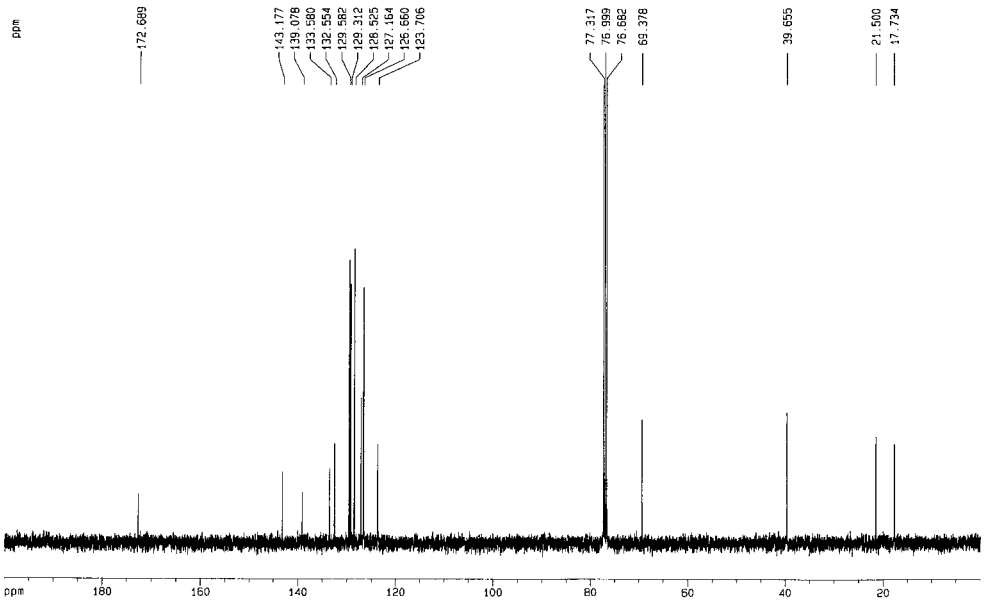
2-Methyl-2-propenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (8c)



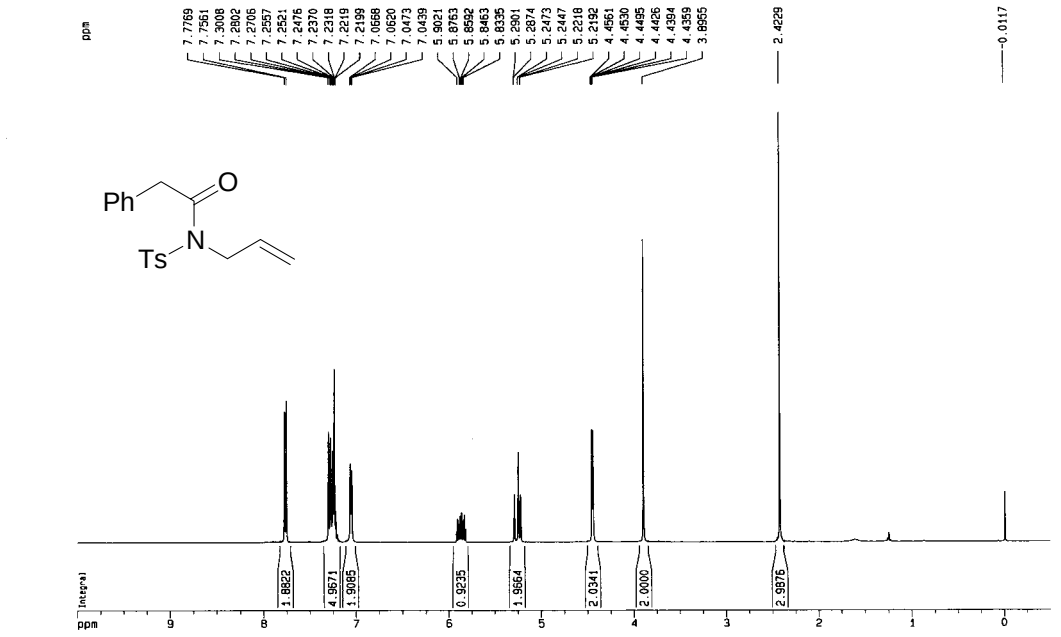


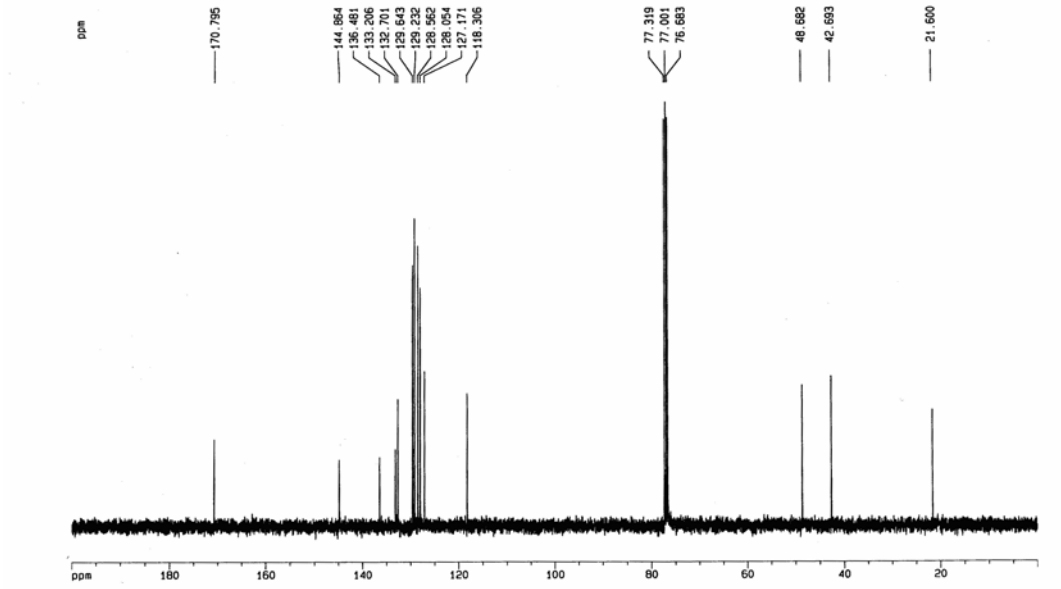
(*E*)-2-Butenyl *N*-(4-methylbenzensulfonyl)phenylacetimidate (8d)



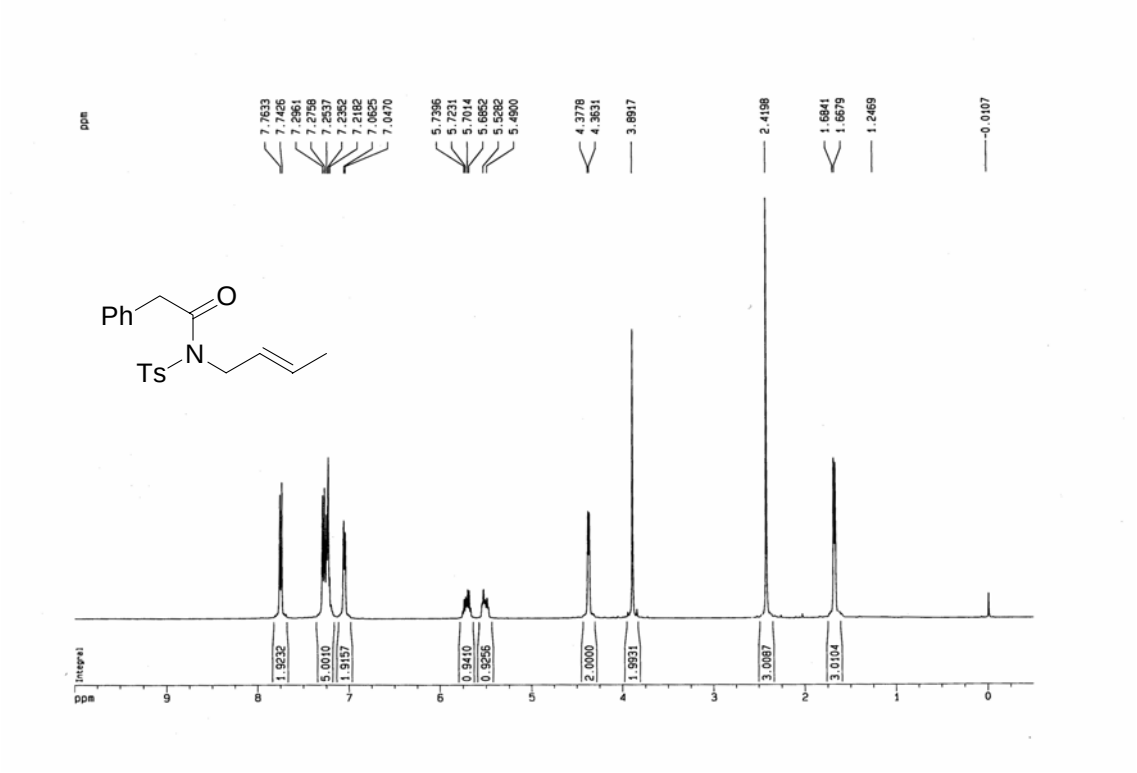


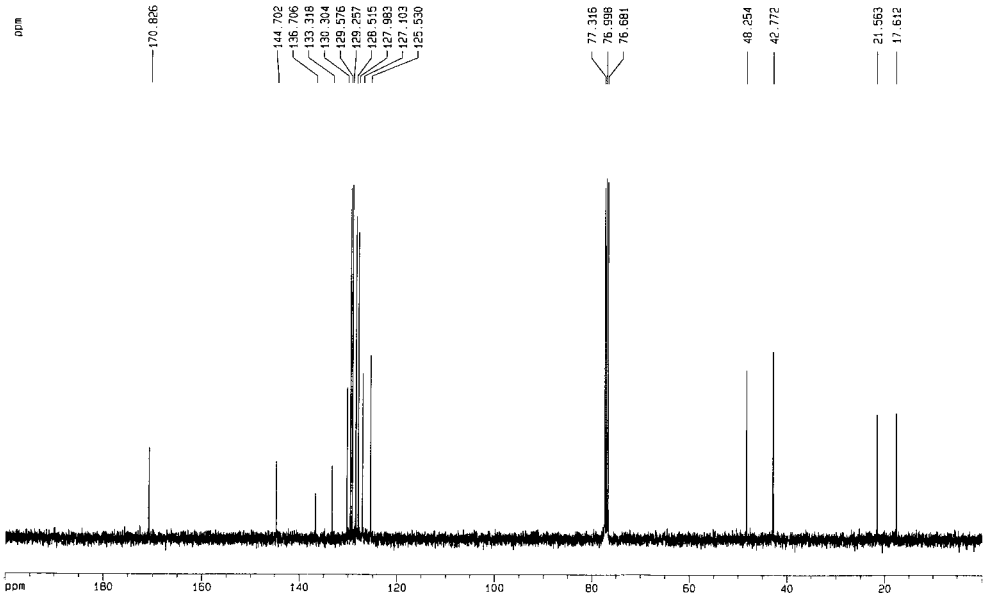
4-Methyl-*N*-(phenylacetyl)-*N*-(2-propenyl)benzenesulfonamide (9a)



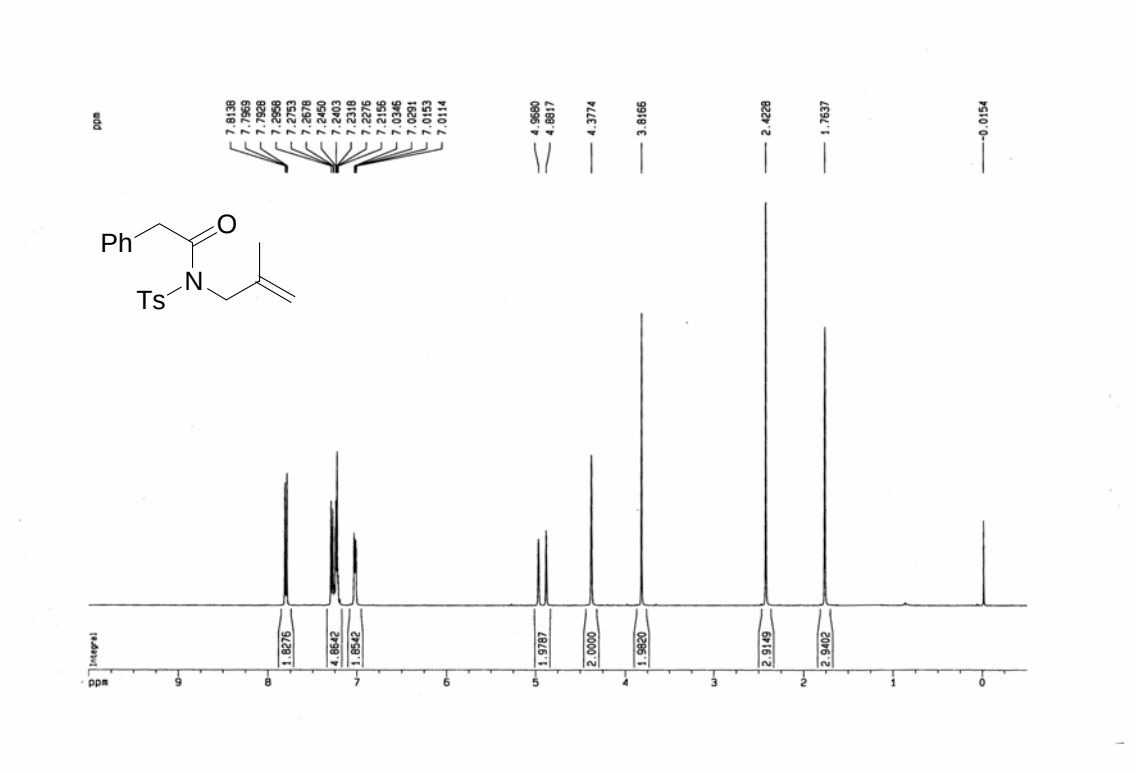


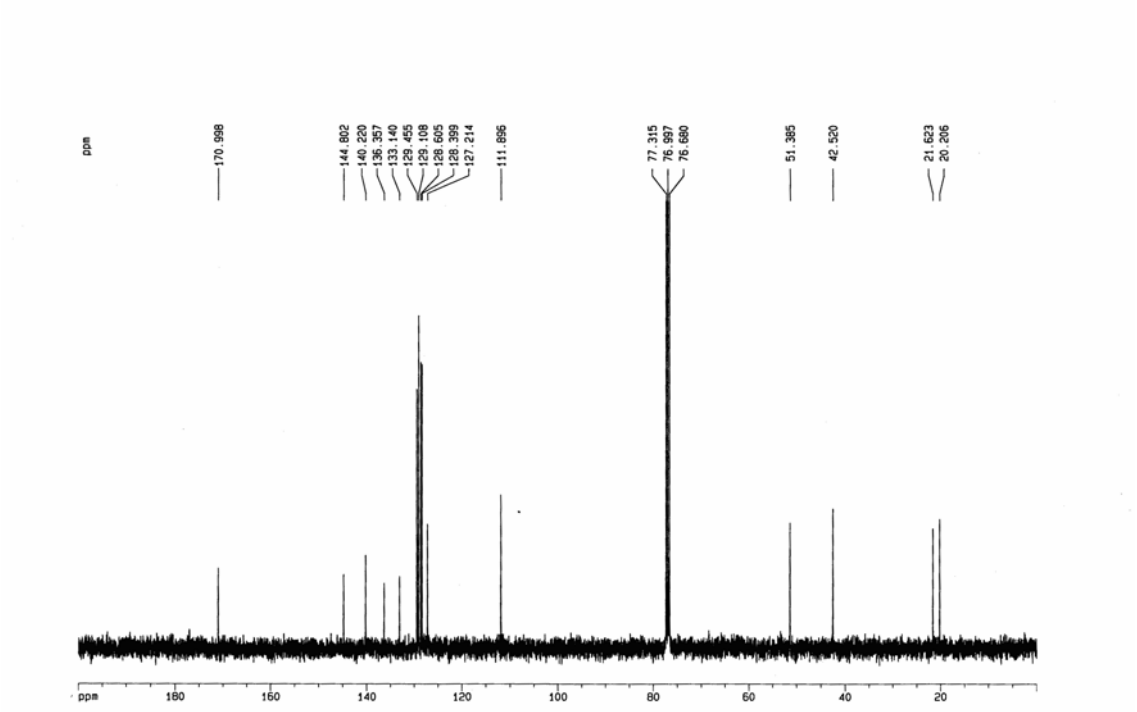
4-Methyl-*N*-[(*E*)-2-butenyl]-*N*-(phenylacetyl)benzenesulfonamide (9b)





4-Methyl-*N*-(2-methyl-2-propenyl)-*N*-(phenylacetyl)benzenesulfonamide (9c)





4-Methyl-*N*-[2-(3-butenyl)]-*N*-(phenylacetyl)benzenesulfonamide (9d)