Supporting Information

Triethylsilane-Indium(III) Chloride System as a Radical Reagent

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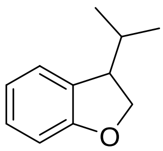
General:

IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All the ^{1}H and ^{13}C-NMR spectra were recorded with a JEOL JNM-GSX-270 (270 and 67 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using Fuji Davison silica gel FL-100DX.

A typical experimental procedure of the dehalogenation:

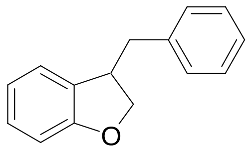
The 10 mL of round bottom flask charged with $InCl_3$ (0.022 g, 0.1 mmol) was heated at 110 °C under reduced pressure for 1 h. After nitrogen was filled, MeCN (2 mL) and Et_3SiH (2.0 mmol) was added and the mixture was stirred at rt for 5 min. Then halide [alkyl halide, alkyl or aryl halide and olefin, or haloalkene (1.0 mmol)] and 1M Et_3B in hexane (0.1 mL) were added, and the resulting mixture was stirred at rt for 2 h. After deionized water was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over $MgSO_4$ and concentrated. Yield of product was determined by ^{1}H NMR. Purification was performed by column chromatography eluting with hexane/EtOAc=9/1. Further purification was performed by TLC eluting with hexane/Et_2O=9/1. Radical cyclization was performed under the same conditions by using haloalkenes **3** as starting materials.

3-Isopropyl-2,3-dihydro-benzofuran (4a)



bp 60 ^{o}C/ 2 mmHg; IR (neat) 1018 (C-O-C), 1234 (C-O-C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.87 (d, *J*= 6.84 Hz, 3H), 0.95 (d, *J*= 6.84 Hz, 3H), 1.97 (qd, *J*= 6.84 and 6.59 Hz, 1H), 3.29-3.36 (m, 1H), 4.38 (dd, *J*= 5.13 and 9.03 Hz, 1H), 4.52 (t, *J*= 9.03 Hz, 1H), 6.76-6.88 (m, 2H), 7.10-7.20 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 18.5, 19.8, 31.7, 48.1, 73.8, 109.3, 120.0, 125.0, 128.1, 129.4, 160.3; MS (EI) m/z 162 (M^+, 24), 119 (M^+ - $CHCH_3CH_3$, 100), 118 (8), 91 (59), 65 (7), 39 (4); HRMS calcd for $C_{11}H_{14}O$: 162.1045, found: m/z 162.1038 (EI, (M^+), -0.7 mmu); Anal. calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70, found: C, 81.15; H, 8.63.

3-Benzyl-2,3-dihydro-benzofuran (4b)



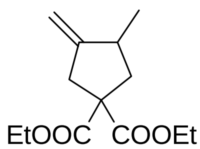
IR (neat) 1230 (C-O-C), 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.83 (dd, *J*= 13.9 and 9.0 Hz, 1H), 3.06 (dd, *J*= 13.9 and 6.4 Hz, 1H), 3.74 (dddd, *J*= 9.0 and 8.8 and 6.4 and 6.0 Hz, 1H), 4.27 (dd, *J*= 8.8 and 6.0 Hz, 1H), 4.51 (t, *J*= 8.8 Hz, 1H), 6.78-6.84 (m, 2H), 6.95-6.98 (m, 1H), 7.09-7.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 41.0, 43.4, 76.3, 109.6, 120.2, 124.5, 126.4, 128.3, 128.5, 128.9, 130.2, 139.1, 159.8; HRMS calcd for $C_{15}H_{14}O$: 210.10, found: m/z 210.10 (M^+,-0.1 mmu).

A typical experimental procedure of the reduction of alkyne:

The 10 mL of round bottom flask charged with $InCl_3$ (0.442 g, 2.0 mmol) was heated at 110 °C under reduced pressure for 1 h. After nitrogen was filled, MeCN (2 mL) and Et_3SiH (2.0 mmol) was added and the mixture was stirred at 0 ° C for 5 min. Then alkyne (1.0 mmol) and 1M Et_3B in hexane (0.1 mL) were added, and the resulting mixture was stirred at 0 ° C for 2 h. After deionized water was added, the reaction mixture was extracted with ether (10 mL x 3). The combined organic layer was dried over $MgSO_4$ and concentrated. Yield of product was determined by ^{1}H NMR. Purification was performed by column chromatography eluting with hexane/EtOAc=9/1. Further purification was performed by TLC eluting with hexane/Et_2O=9/1.

4,4-Bis(ethoxycarbonyl)-1-methyl-2-methylenecyclopentane (8a)

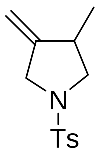
Reference : Crich, D.; Hwang, J.; Gastaldi, S.; Recupero, F.; Wink, D. J. *J. Org. Chem.* **1999**, *64*, 2877-2882.



IR (neat) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.10 (d, *J*= 6.4 Hz, 3H), 1.25 (t, *J*= 7.3 Hz, 6H), 1.75 (t, *J*= 14.7 Hz, 1H), 2.57 (m, 2H), 3.00 (q, *J*= 17.1 Hz, 2H), 4.18 (m, 4H), 4.80 (d, *J*= 2.0 Hz, 1H), 4.91 (d, *J*= 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.9 MHz) δ 14.0, 18.0, 37.3, 40.5, 42.1, 58.2, 61.4, 105.3, 153.4, 170.8.

3-Methyl-4-methylene-1-(toluene-4-sulfonyl)-pyrrolidine (8b)

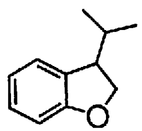
Reference : Radetich, B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1998**, *120*, 8007-8008.



IR (neat) 1165, 1346 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.04 (d, *J*= 6.4 Hz, 3H), 2.44 (s, 3H), 2.67-2.73 (m, 2H), 3.51-3.62 (m, 1H), 3.73 (dd, *J*= 13.9 and 1.8 Hz, 1H), 3.95 (d, *J*= 13.9 Hz, 1H), 4.85 (dd, *J*= 4.4 and 2.2 Hz, 1H), 4.90 (dd, *J*= 4.0 and 2.2 Hz, 1H), 7.33 (d, *J*= 8.6 Hz, 2H), 7.71 (d, *J*= 6.6 Hz, 2H); ^{13}C NMR (CDCl3, 67.9 MHz) δ 16.1, 21.6, 37.4, 52.2, 55.1, 105.9, 127.7, 129.6, 132.7, 143.5, 149.2.

\\Excalibur\my documents\abc–Ñ,Ì'ª'è,Ó,Ÿ,¢,é\500-599\hh598TLC2.GXD
4a

^{1}H NMR



4a

NO.	PPM	NO.	PPM
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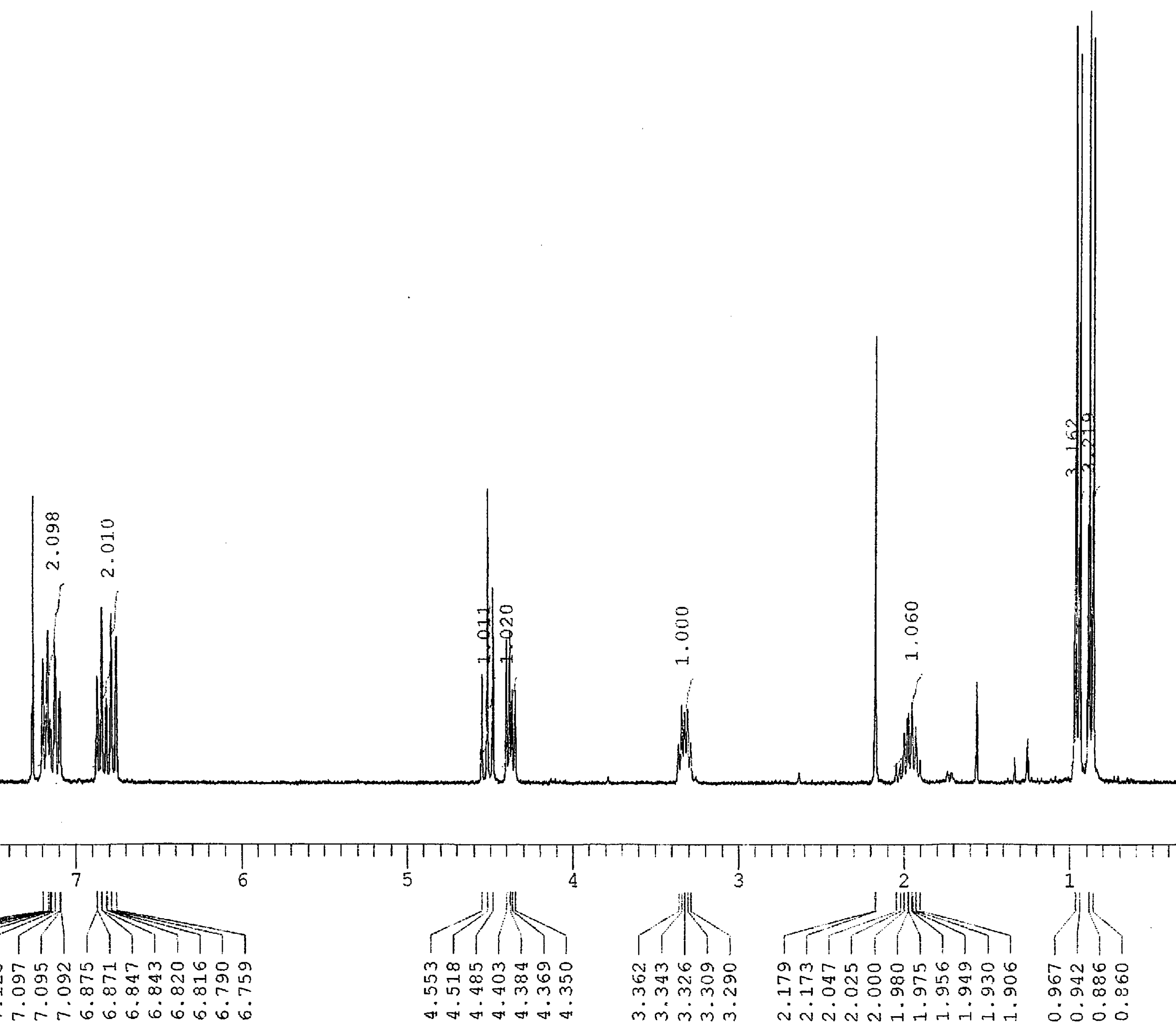
2	7.16880	22	4.38369
3	7.15434	23	4.36923
4	7.15253	24	4.35026
5	7.14711	25	3.36164
6	7.12452	26	3.34267
7	7.09741	27	3.32640
8	7.09470	28	3.30923
9	7.09199	29	3.29026
10	6.87511	30	2.17874
11	6.87149	31	2.17332
12	6.84709	32	2.04681
13	6.84348	33	2.02512
14	6.81998	34	1.99982
15	6.81637	35	1.97994
16	6.79016	36	1.97451
17	6.75944	37	1.95554
18	4.55268	38	1.94921
19	4.51834	39	1.93023
20	4.48490	40	1.90584
		41	0.96692
		42	0.94162
		43	0.88559
		44	0.86029



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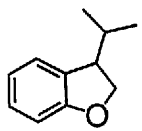
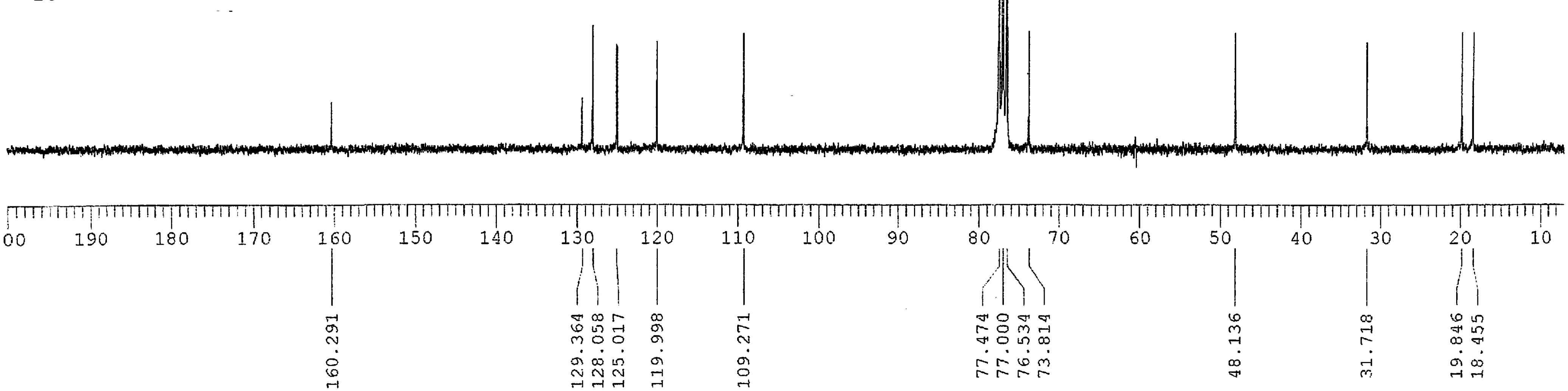
4a

^{13}C NMR



4a

NO.	PPM
1	160.29054
2	129.36409
3	128.05767
4	125.01697
5	119.99754
6	109.27107
7	77.47368
8	77.00000
9	76.53396
10	73.81415
11	48.13634
12	31.71812
13	19.84567
14	18.45520



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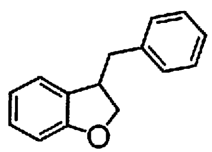
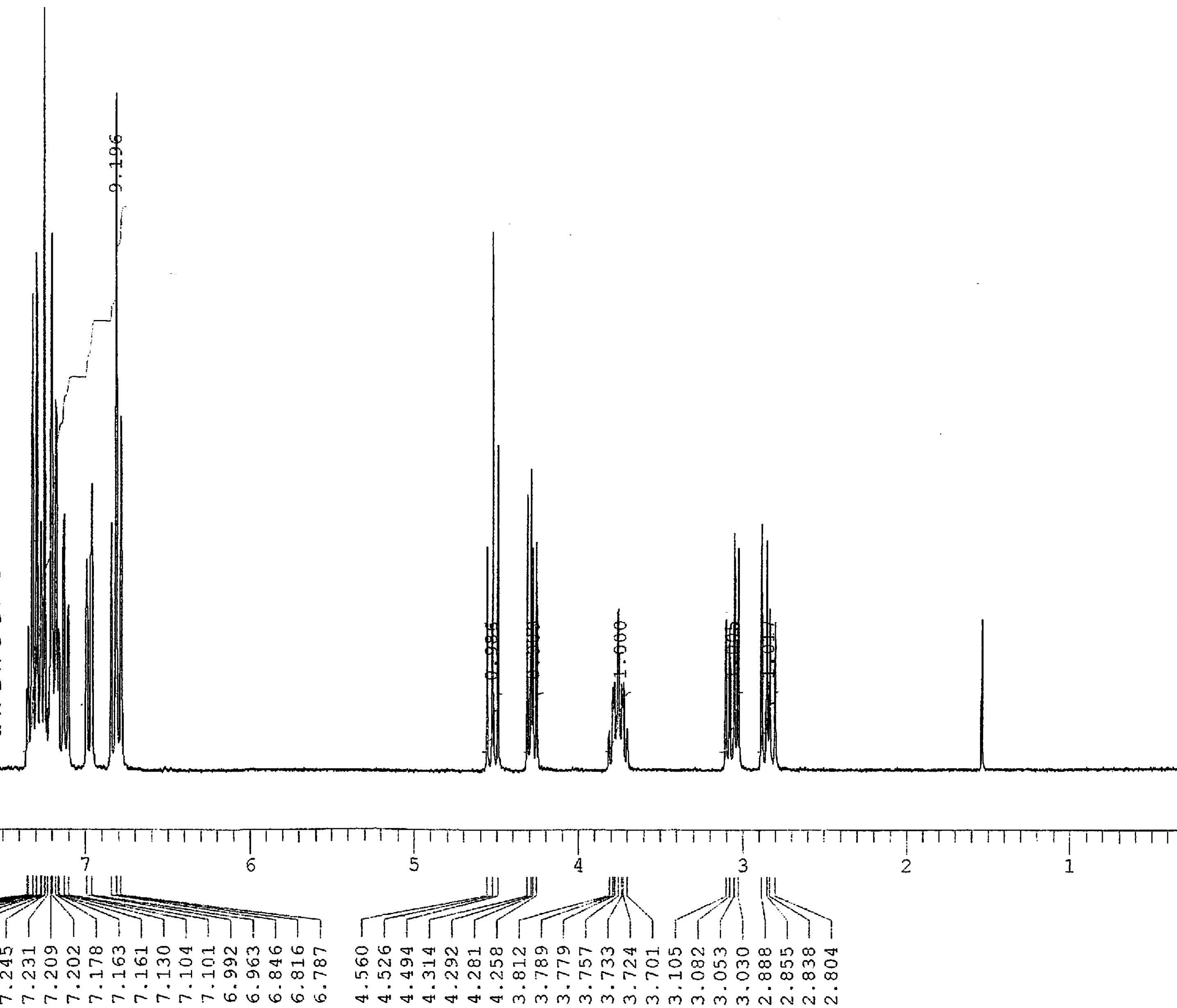
4b

^{1}H NMR



4b

NO.	PPM
1	7.35405
2	7.34772
3	7.32333
4	7.31700
5	7.29441
6	7.27001
7	7.26459
8	7.24832
9	7.24471
10	7.23115
11	7.20856
12	7.20223
13	7.17783
14	7.16338
15	7.16066
16	7.12994
17	7.10373
18	7.10102
19	6.99168
20	6.96276
21	6.84619
22	6.81637
23	6.78655
24	4.55991
25	4.52647
26	4.49394
27	4.31411
28	4.29152
29	4.28068
30	4.25808
31	3.81167
32	3.78908
33	3.77914
34	3.75655
35	3.73305
36	3.72402
37	3.70142
38	3.10500
39	3.08151
40	3.05349
41	3.03000
42	2.88812
43	2.85469
44	2.83752
45	2.80408



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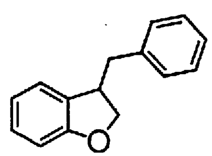
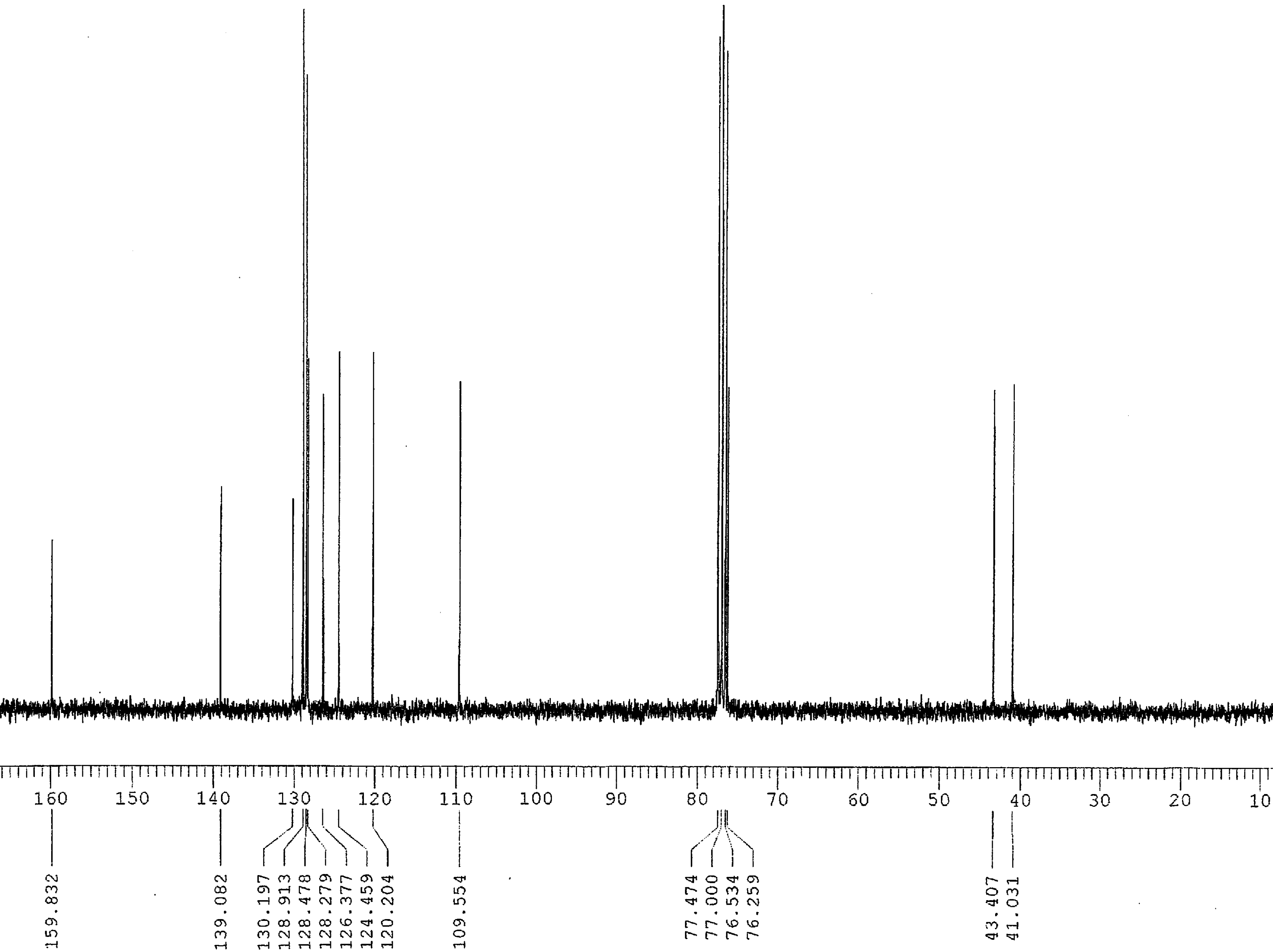
4b

^{13}C NMR



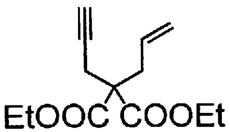
4b

NO.	PPM
1	159.83214
2	139.08208
3	130.19684
4	128.91333
5	128.47786
6	128.27922
7	126.37688
8	124.45925
9	120.20381
10	109.55375
11	77.47368
12	77.00000
13	76.53396
14	76.25893
15	43.40722
16	41.03120

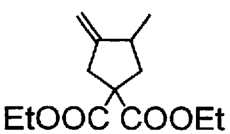


\\Excalibur\my documents\abc-Ñ,Ì'ª'è,Ó,Ÿ,¢,é\1200-1299\hh1220kqurge12(after3day).GXD
8a

^{1}H NMR

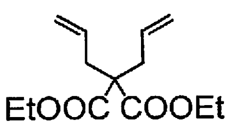


7a ○



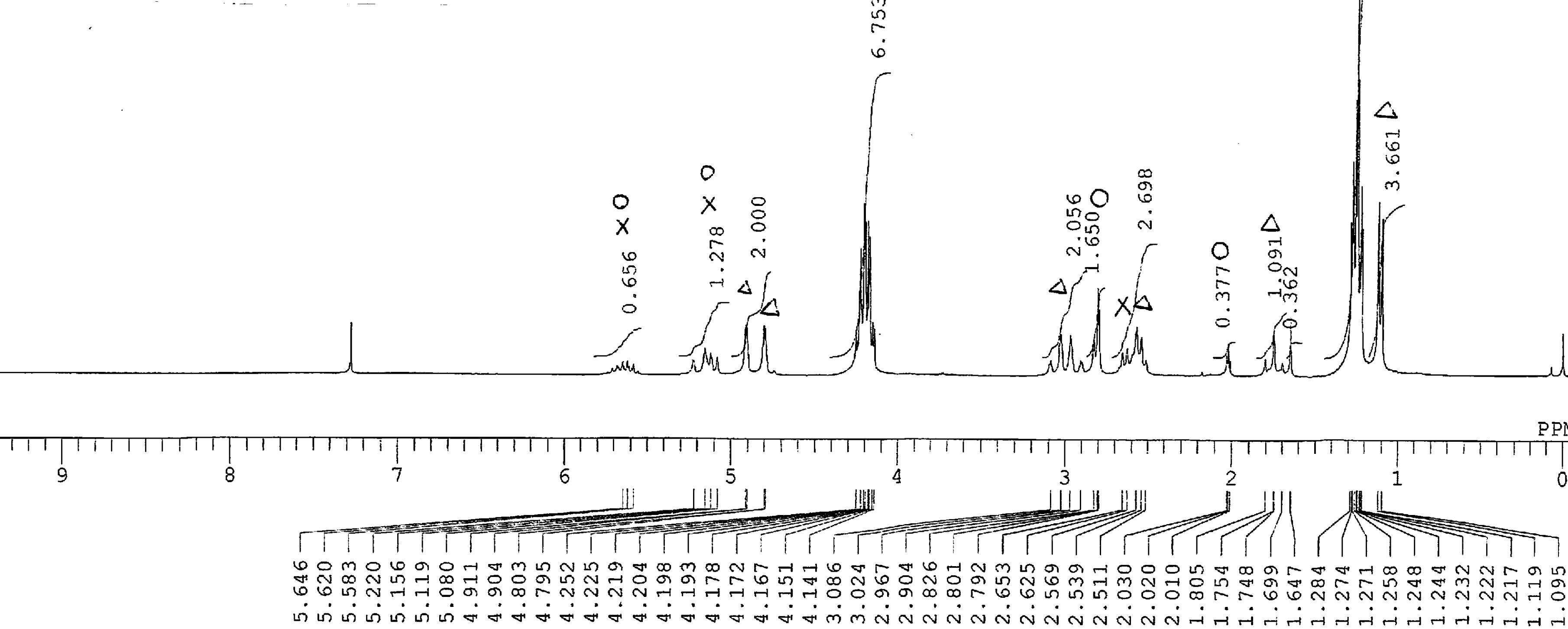
8a △

Reference : Crich, D.; Hwang, J.; Gastaldi, S.; Recupero, F.; Wink, D. J. *J. Org. Chem.* **1999**, *64*, 2877-2882.



9a X

NO.	PPM	NO.	PPM	NO.	PPM	NO.	PPM
1	5.64612	13	4.22465	26	2.90439	39	1.75402
2	5.61991	14	4.21923	27	2.82577	40	1.74769
3	5.58286	15	4.20386	28	2.80137	41	1.69890
4	5.22049	16	4.19844	29	2.79233	42	1.64739
5	5.15633	17	4.19302	30	2.65317	43	1.28411
6	5.11928	18	4.17766	31	2.62516	44	1.27417
7	5.08042	19	4.17224	32	2.56913	45	1.27056
8	4.91144	20	4.16681	33	2.53931	46	1.25791
9	4.90421	21	4.15145	34	2.51129	47	1.24797
10	4.80300	22	4.14061	35	2.02964	48	1.24435
11	4.79486	23	3.08603	36	2.01970	49	1.23170
12	4.25176	24	3.02367	37	2.00976	50	1.22176
		25	2.96674	38	1.80462	51	1.21724
						52	1.11874
						53	1.09525



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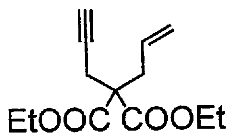
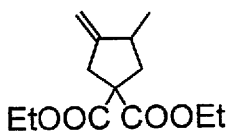
8a

^{13}C NMR

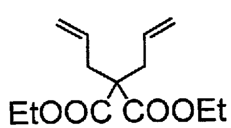


7a O



8a △

Reference : Crich, D.; Hwang, J.; Gastaldi, S.; Recupero, F.; Wink, D. J. *J. Org. Chem.* **1999**, *64*, 2877-2882.



9a X

NO.	PPM	NO.	PPM
1	171.88795	16	61.64374
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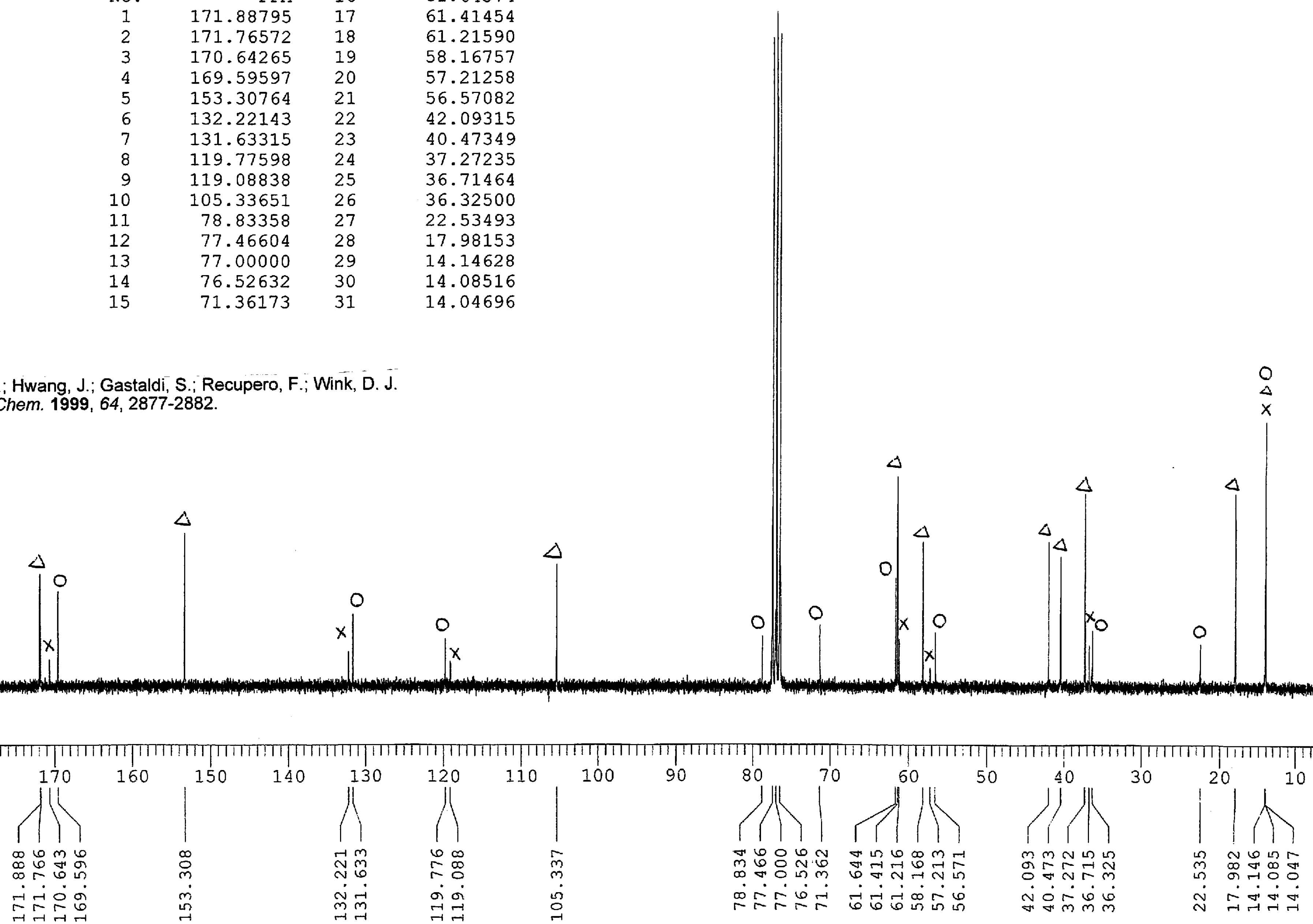
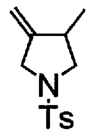
3	170.64265	18	61.21590
4	169.59597	19	58.16757
5	153.30764	20	57.21258
6	132.22143	21	56.57082
7	131.63315	22	42.09315
8	119.77598	23	40.47349
9	119.08838	24	37.27235
10	105.33651	25	36.71464
11	78.83358	26	36.32500
12	77.46604	27	22.53493
13	77.00000	28	17.98153
14	76.52632	29	14.14628
15	71.36173	30	14.08516
		31	14.04696



85

\\Excalibur\my documents\abc–Ñ,Ì'ª'è,Ó,Ÿ,¢,é\1200-1299\hh1217TLC4.GXD
8b

^{1}H NMR



8b

Reference : Radetich, B.; RajanBabu, T. V.
J. Am. Chem. Soc. **1998**, *120*, 8007-8008.

NO.	PPM
1	7.72184
2	7.71552
3	7.69744
4	7.69112
5	7.68389
6	7.34772
7	7.31881
8	4.91324
9	4.90601
10	4.89878
11	4.89155
12	4.86354
13	4.85450
14	4.84637
15	4.83824
16	3.97524
17	3.92373
18	3.76287
19	3.75564
20	3.71046
21	3.70414
22	3.57853
23	3.57220
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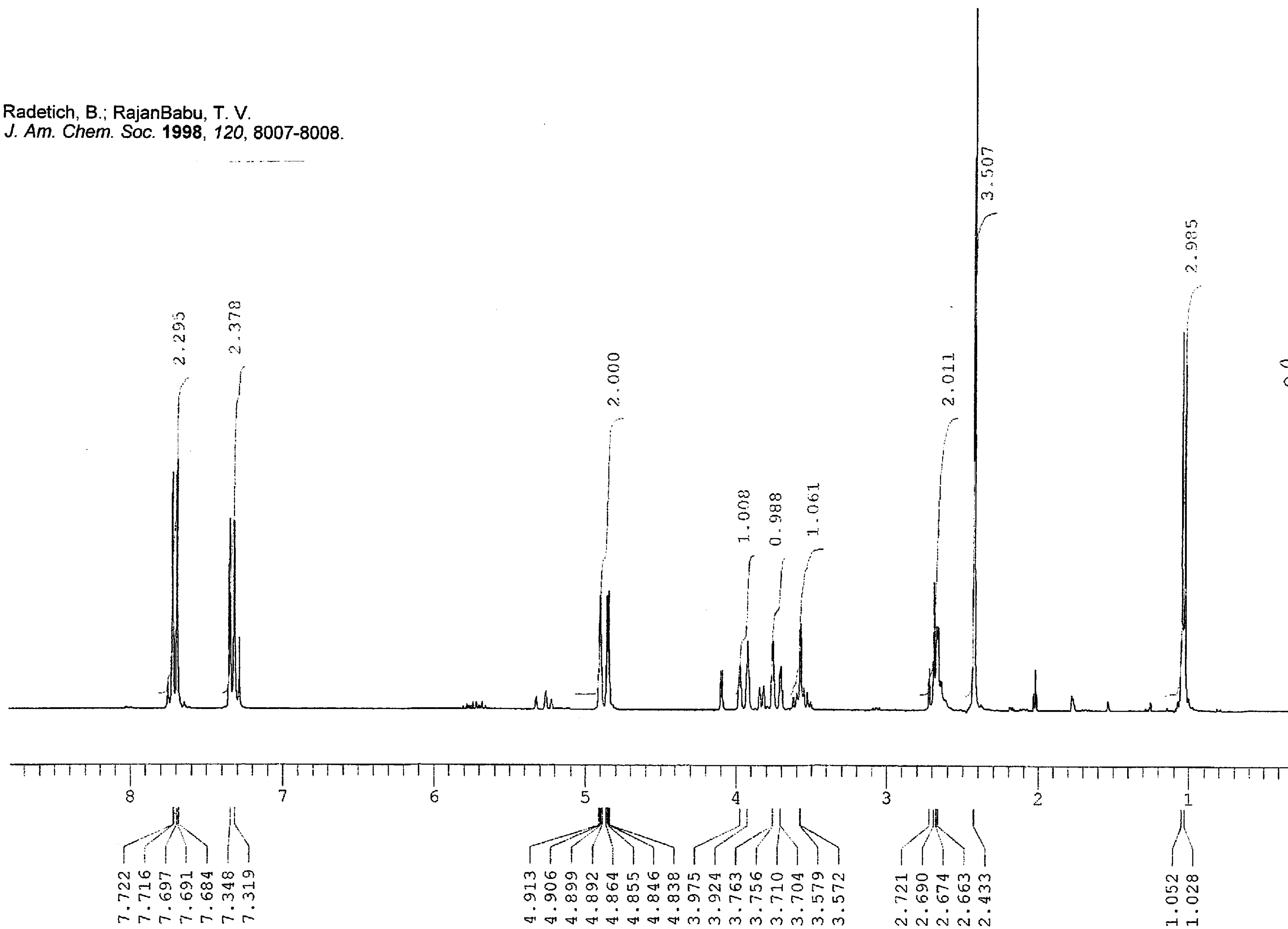
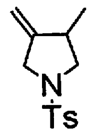
29	1.05187
30	1.02837



\\Excalibur\my documents\abc–Ñ,Ì'ª'è,Ó,Ÿ,¢,é\1200-1299\hc1217isolated(TLC5).GXD
8b

^{13}C NMR



8b

Reference : Radetich, B.; RajanBabu, T. V.
J. Am. Chem. Soc. **1998**, *120*, 8007-8008.

NO.	PPM
1	149.16680
2	143.49797
3	132.73330
4	129.58565
5	127.69859
6	105.94006
7	77.47368
8	77.00000
9	76.53396
10	55.05048
11	52.14730
12	37.43279
13	21.55702
14	16.06390