Supplementary Material (ESI) for Chemical Communications

"Superacid promoted reactions of *N*-acyliminium salts and evidence for the involvement of superelectrophiles"

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Computational Methods

All calculations were performed with the GAUSSIAN (G98) code.[1] Cations **6**, **7b**, **10**, and **11** were fully optimized without constraints at the HF/6-31+G(d) level. The resulting structures were examined by analytical frequency analysis at this level, and demonstrated to be minima (no imaginary frequencies). The structures were then reoptimized at the HF/6-311+G(d) level; these structures were used as starting points for optimizations at the MP2/6-311+G(d) level.[2] Relative energies were corrected using unscaled zero point energies from the frequency analysis. Cation **10** proved unstable to dissociation during optimization at the MP2/6-311+G(d) level. To estimate its relative energy, the C2–C7 and C7–H22 distances were fixed at their optimized HF/6-311+G(d) values, and all other structural parameters were optimized at the MP2/6-311+G(d) level. The calculated energy was used to estimate the endothermicity of the formation of **10** from **6** + benzene. NMR calculations employed the gauge-independent atomic orbital (GIAO) approach.

1. Cartesian Coordinates (MP2/6-311+G(d) level) for **6** and **10**.

N	0.033572	-0.037197	0.252438
C	1.319955	0.037897	0.242494
C	-0.586664	1.350196	0.154706
C	1.837659	1.432044	0.140476
C	0.579322	2.305812	0.081483
O	-1.766689	1.475783	0.149972
C	-0.818445	-1.227824	0.341351
H	1.934458	-0.858756	0.304843
H	2.480604	1.643612	1.002172
H	2.475504	1.517913	-0.746298
H	0.501865	3.011271	0.913067
H	0.495868	2.883832	-0.842720
H	-1.445806	-1.132797	1.227564
H	-1.453082	-1.259966	-0.544189
H	-0.191711	-2.115580	0.402522

N	0.083159	-0.061863	-0.174783
C	1.408556	-0.343390	0.253181
C	-0.205362	1.310768	-0.224981
C	1.844430	0.954034	0.964274
C	1.052111	2.036851	0.229032
O	-1.269761	1.777739	-0.561942
C	2.398836	-0.639068	-0.974728
C	-0.946942	-1.079017	-0.299535
C	1.736852	-1.529347	-1.917128
C	3.653769	-1.119169	-0.408376
C	2.173248	-2.826635	-2.115713
C	4.069620	-2.423286	-0.596118
C	3.321084	-3.274313	-1.434982
H	1.430075	-1.234424	0.890598
H	1.514373	0.885689	2.005334
H	2.923045	1.120808	0.965885
H	0.781799	2.889912	0.853274
H	1.579181	2.433898	-0.647215
H	-1.074925	-1.613164	0.646626
H	-1.877742	-0.573992	-0.560767
H	-0.709567	-1.807656	-1.081513
H	2.498388	0.365035	-1.403936
H	0.866626	-1.151294	-2.447913
H	4.231809	-0.457795	0.232758
H	1.649693	-3.492385	-2.795465
H	4.975493	-2.789746	-0.122537
H	3.649980	-4.303029	-1.572599

2. Cartesian Coordinates (MP2/6-311+G(d) level) for **7b** and **11**.

N	0.014290	0.021890	0.248034
C	1.334419	0.064185	0.240945
C	-0.479955	1.330478	0.152365
C	1.872666	1.426949	0.138393
C	0.621438	2.315555	0.075675
O	-1.731526	1.442480	0.148910
C	-0.864157	-1.186696	0.339807
H	1.909283	-0.861246	0.307702
H	2.530455	1.631003	0.998506
H	2.526809	1.501824	-0.745050
H	0.546042	3.032988	0.906963
H	0.541395	2.901738	-0.852474
H	-1.479594	-1.092527	1.234794
H	-1.482401	-1.227337	-0.557271
H	-0.218263	-2.060541	0.404756
H	-2.100841	2.351555	0.081175

N	0.004109	-0.033460	0.008721
C	1.385039	-0.338488	0.434217
C	-0.210248	1.258467	-0.055969
C	1.857958	1.005706	1.026920
C	0.994045	2.062977	0.312468
O	-1.389488	1.670910	-0.409452
C	2.280442	-0.834509	-0.761246
C	-1.068271	-1.038599	-0.147991
C	1.623697	-1.697060	-1.763069
C	3.595270	-1.298668	-0.274452
C	2.249179	-2.817151	-2.268750
C	4.197231	-2.427735	-0.790209
C	3.517554	-3.189870	-1.766327
H	1.334908	-1.136600	1.181076
H	1.646536	1.018018	2.099049
H	2.926326	1.185547	0.896827
H	0.735342	2.911042	0.953647
H	1.455101	2.473337	-0.595656
H	-1.791397	-0.913750	0.660252
H	-1.571802	-0.902828	-1.105872
H	-0.624761	-2.031128	-0.088046
H	-1.491346	2.637465	-0.395879
H	2.525018	0.082659	-1.356242
H	0.664724	-1.386063	-2.172196
H	4.107423	-0.720863	0.493407
H	1.772586	-3.420151	-3.036612
H	5.173752	-2.745518	-0.435786
H	3.992322	-4.090438	-2.154671

References:

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, A D.; Rabuck, K. D.; Raghavachari, K; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople. J. A. *Gaussian 98*, Revision A.11.4, Gaussian, Inc.: Pittsburgh PA, 1998.

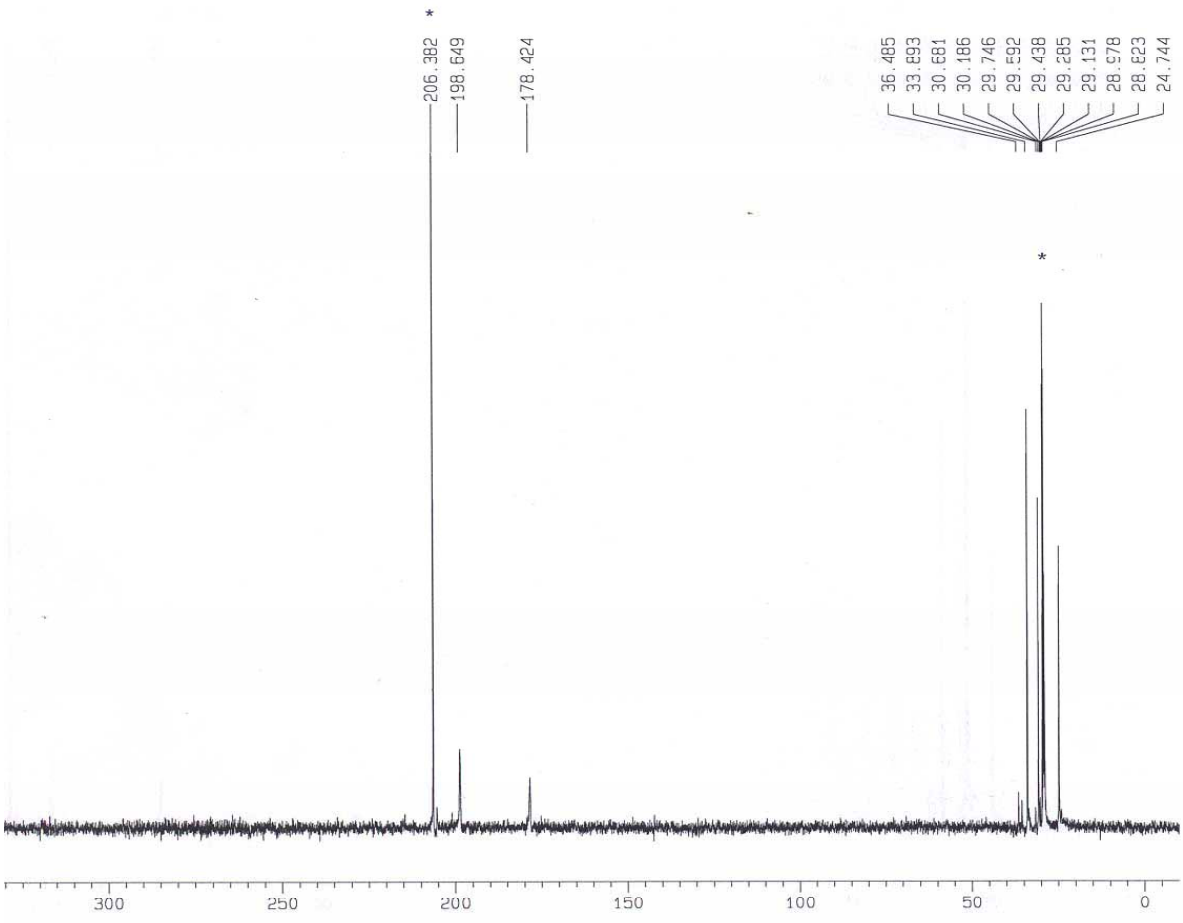
[2]Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618 - 622.

***N*-Benzhydryl-*N*-phenyl-acetamide** (**4**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.98 (s, 3H), 6.84-6.88 (m, 2H), 7.16-7.28 (m, 13H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.6, 64.0, 127.3, 127.9, 128.0, 128.9, 129.6, 130.2, 139.1, 140.9, 170.7. Low resolution mass spectra (EI): m/z: 301 (M+), 167, 152, 77. HRMS: m/z (EI) calculated for $C_{21}H_{19}NO$: 329.1780, measured: 329.1777. Known compound, see: Venkov, A. P.; Mollov, N. M. *Synthesis* **1982**, 216.

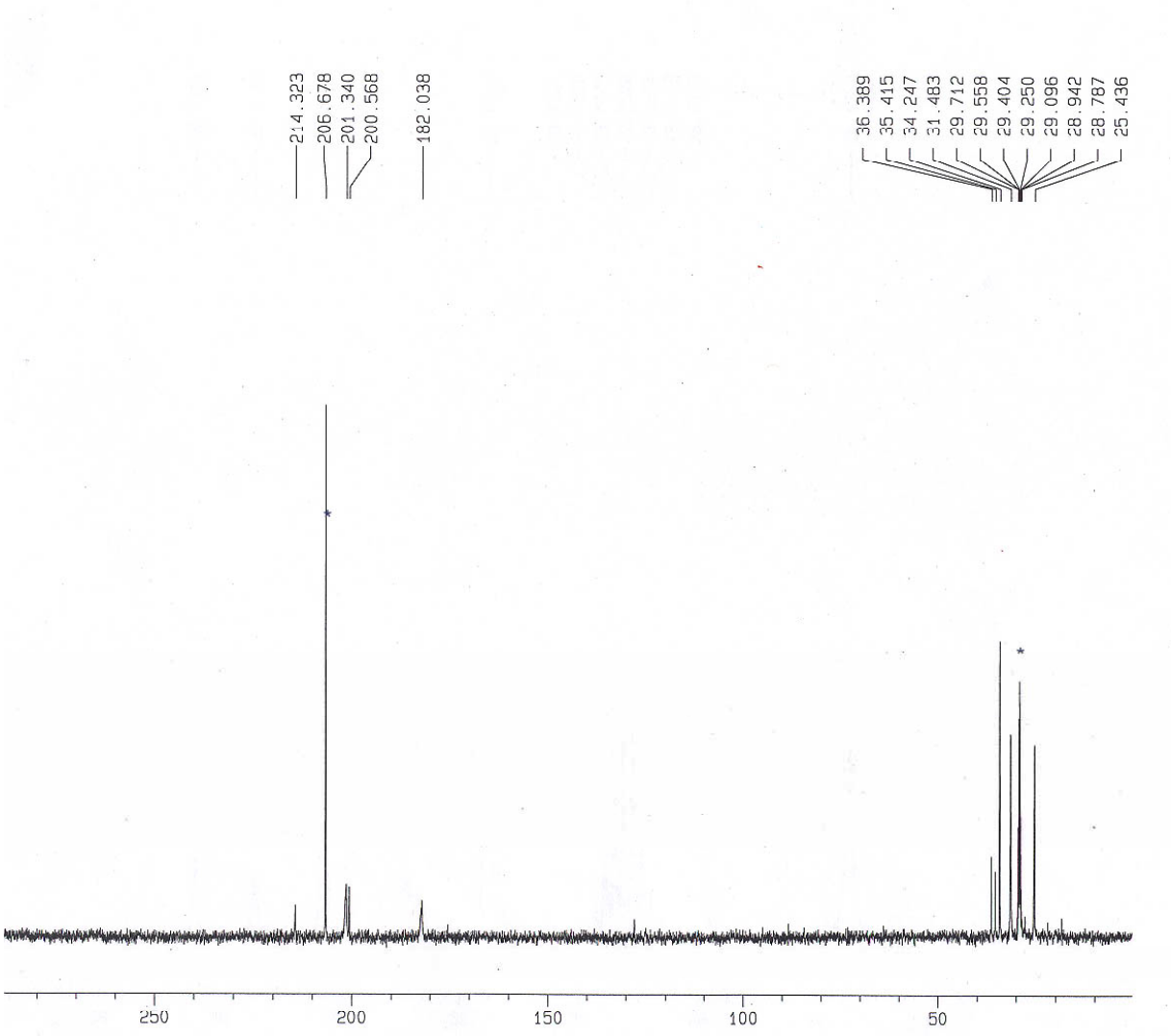
5-(2,5-Dimethoxyphenyl)-1-methylpyrrolidin-2-one (9): Colorless crystals, MP 70-72°C (diethyl ether). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.77-1.86 (m, 1H), 2.35-2.56 (m, 3H), 2.70 (s, 3H), 3.73 (s, 3H), 3.78 (s, 3H), 4.86-4.90 (m, 1H), 6.57 (d, 1H, *J* = 2.9 Hz), 6.74-6.78 (m, 1H), 6.82 (d, 1H, *J* = 8.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 26.6, 28.5, 29.9, 55.7, 56.0, 59.3, 112.0, 112.8, 112.9, 129.9, 151.2, 153.9, 176.1. Low resolution mass spectra (EI): m/z: 235 (M+), 220, 164, 98. HRMS: m/z (EI) calculated for $C_{13}H_{17}NO_3$: 235.1208, measured: 235.1207. Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.39; H, 7.33; N, 6.03.

1-Methyl-5-phenyl-pyrrolidin-2-one: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.77-1.84 (m, 1H), 2.33-2.56 (m, 3H), 2.59 (s, 3H), 4.44-4.47 (m, 1H), 7.12 (d, 2H, *J* = 7.2 Hz), 7.22-7.26 (m, 1H), 7.30 (dd, 1H, *J* = 7.2 Hz, 7.7 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 28.1, 28.4, 30.1, 64.5, 126.3, 128.0, 129.0, 141.1, 175.5. Low resolution mass spectra (EI): m/z: 175 (M+), 118, 98. Known compound, see: Rigo, B.; Fasseur, D.; Cherepy, N.; Couturier, D. *Tetrahedron Lett.* 1989, **30**, 7057.

^{13}C NMR spectrum of ion **6** (–40°C; FSO_3H-SO_2ClF solvent, acetone-d_6 external standard, marked with *):



^{13}C NMR spectrum of ion **6** and **7** (–40°C; FSO_3H-SbF_5-SO_2ClF (1:1:1) solvent, acetone-d_6 external standard, marked with *):



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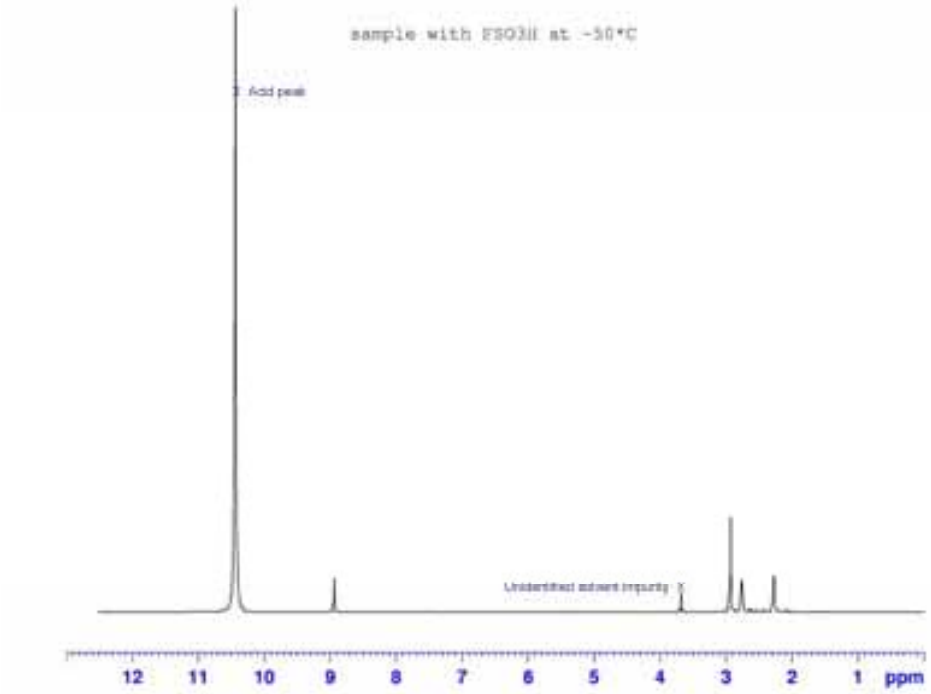
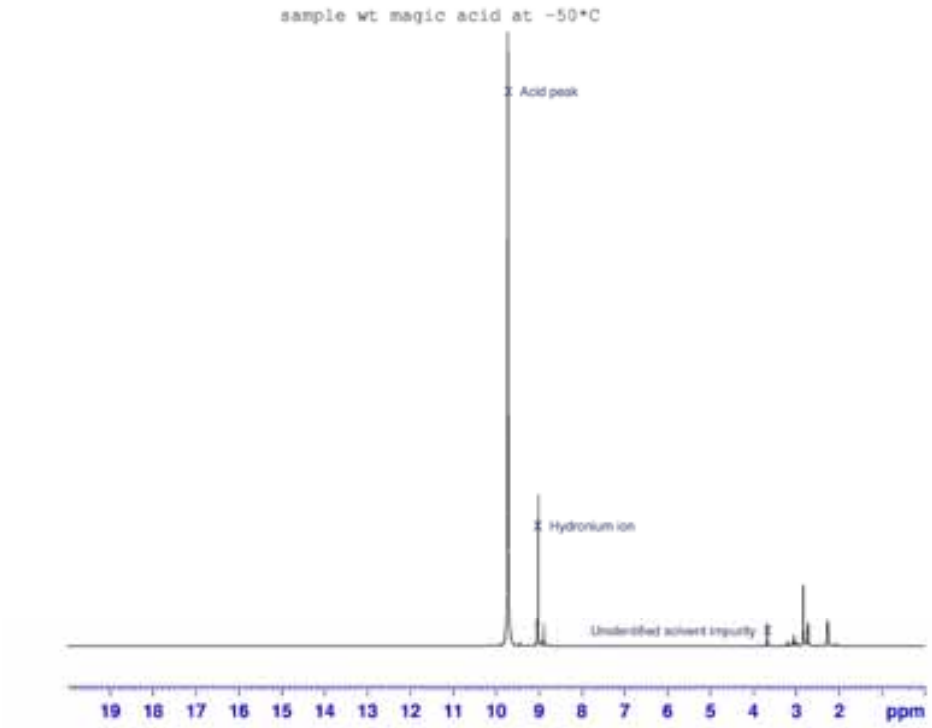
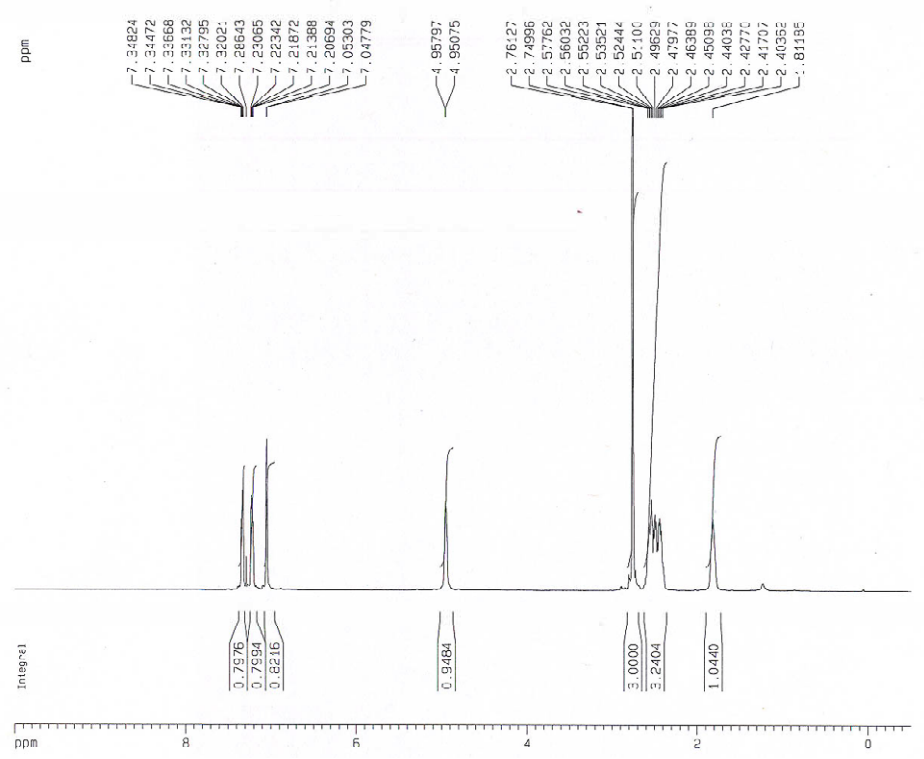


^{1}H NMR spectrum of ion **6** and **7** (–40°C; FSO_3H-SbF_5-SO_2ClF (1:1:1) solvent, acetone-d_6 external standard):

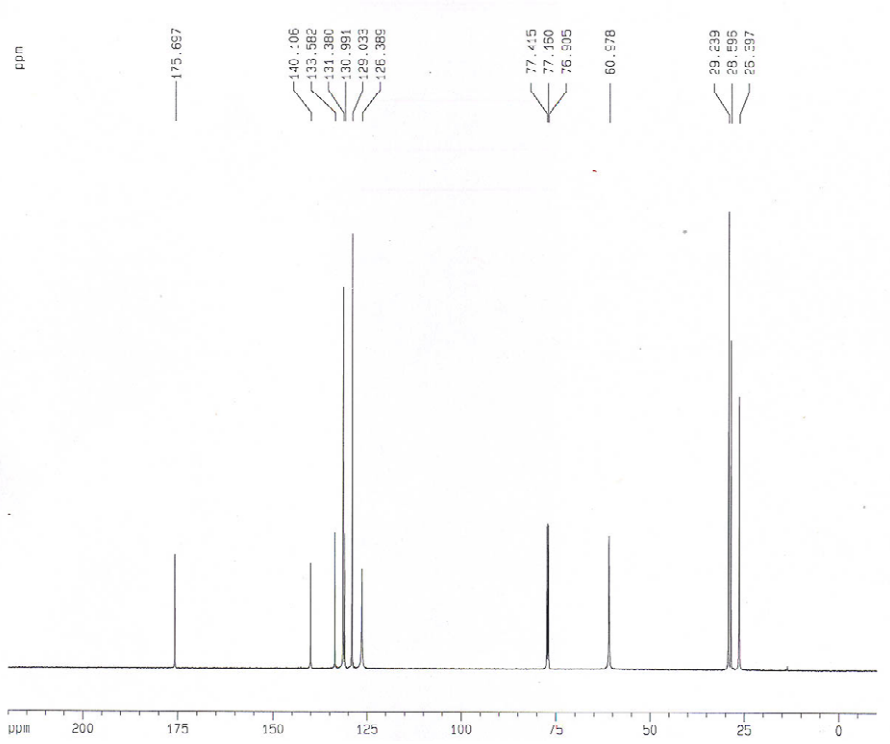


NMR spectra for compound **8:**

^{1}H NMR



^{13}C NMR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131.380
130.991
129.033
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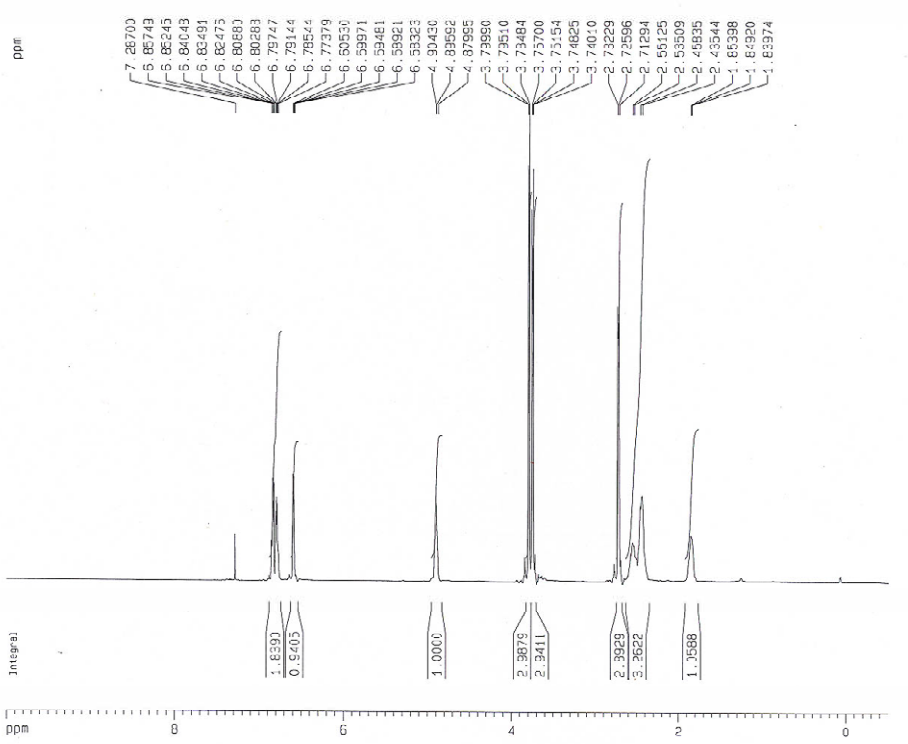
77.415
77.150
76.895
60.578
29.239
28.695
25.397
ppm
200
175
150
125
100
75
50
25
0

NMR spectra for compound **9:**

^{1}H NMR



^{13}C NMR