

Supplementary Material

Ring-closing metathesis in flavonoid synthesis, part 1: flavenes

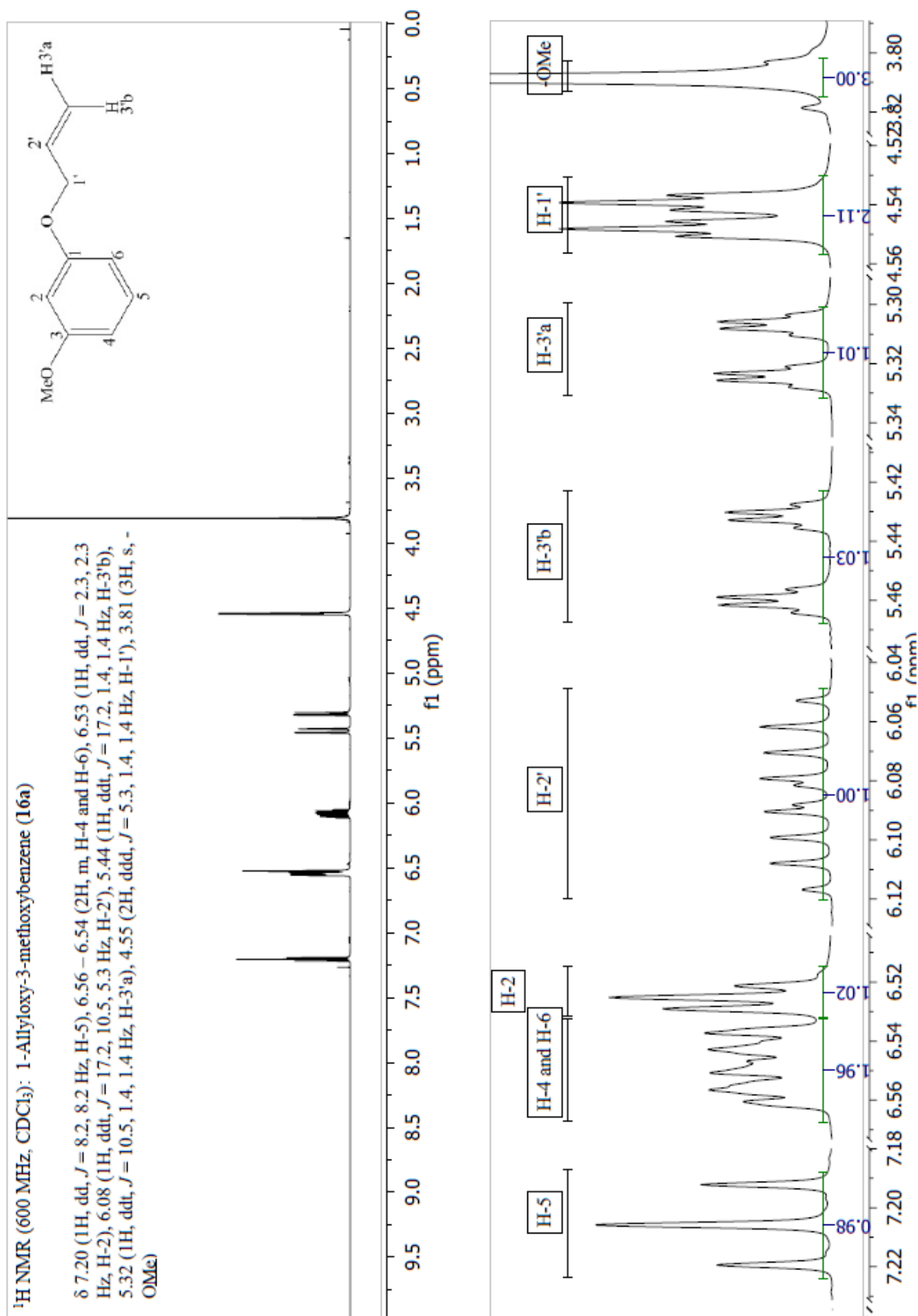
Tanya Pieterse, Charlene Marais,* and Barend C. B. Bezuidenhoudt*

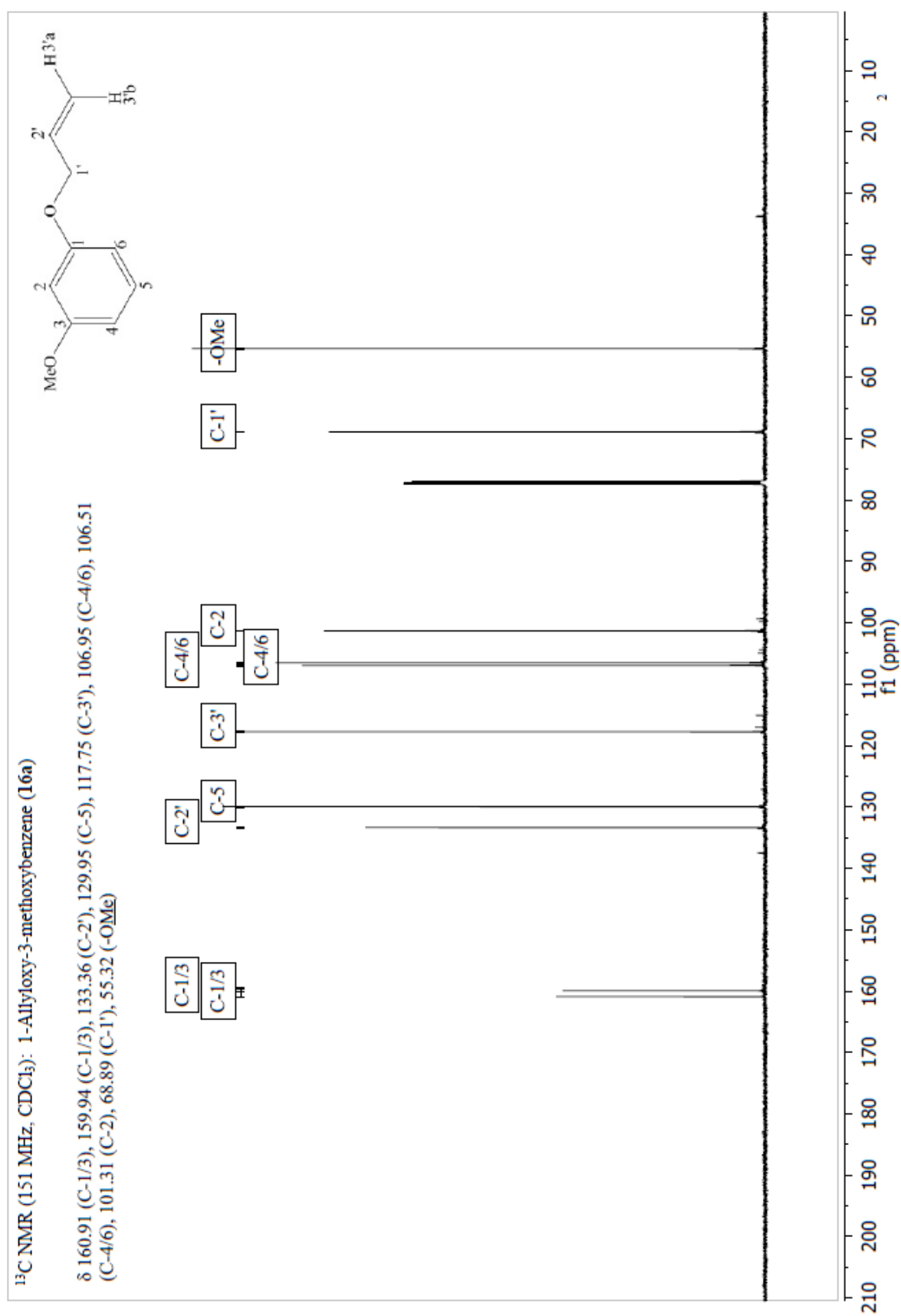
Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9300,
South Africa

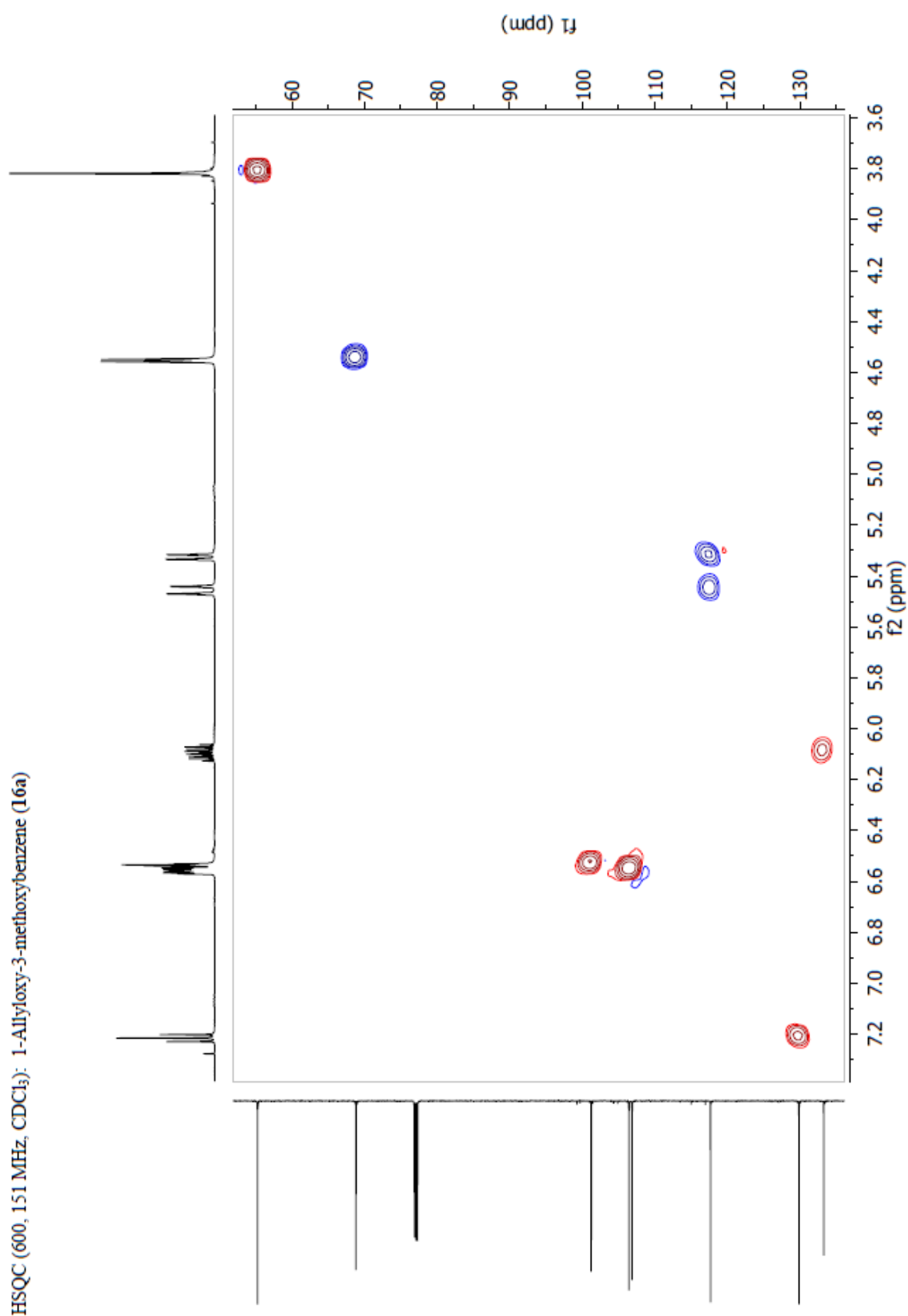
Email: MaraisC@ufs.ac.za; BezuidBC@ufs.ac.za or bcbbez@gmail.com

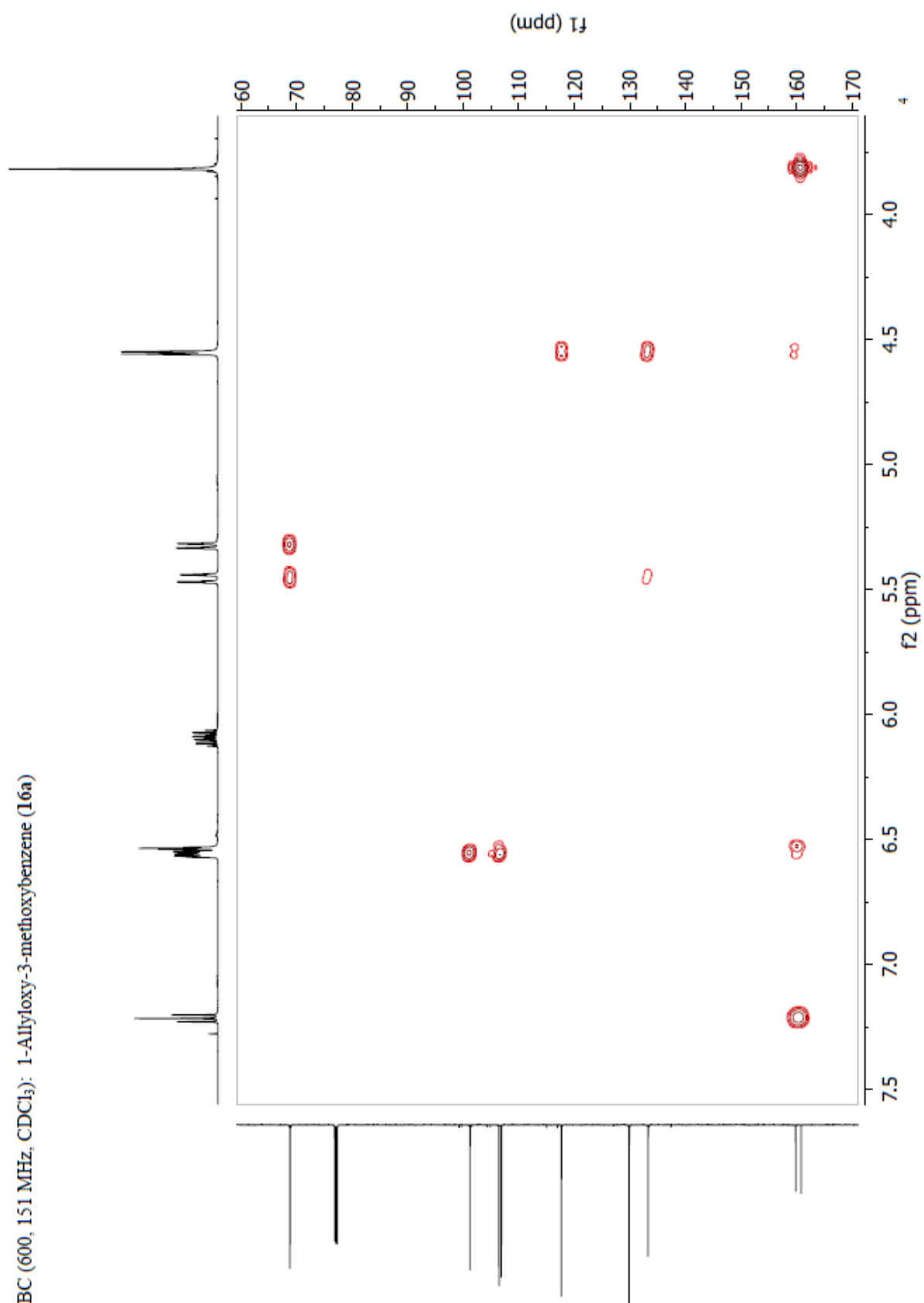
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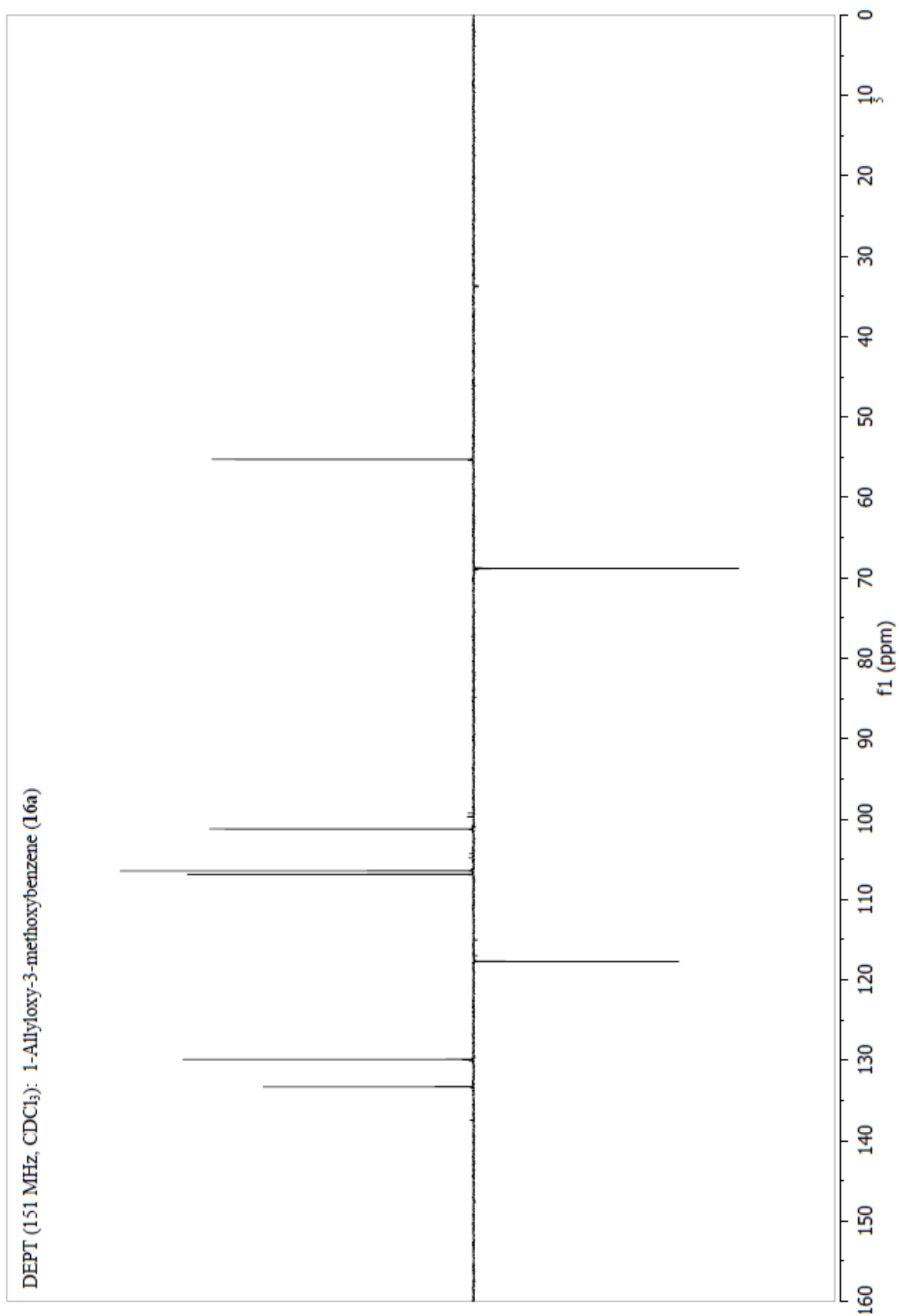
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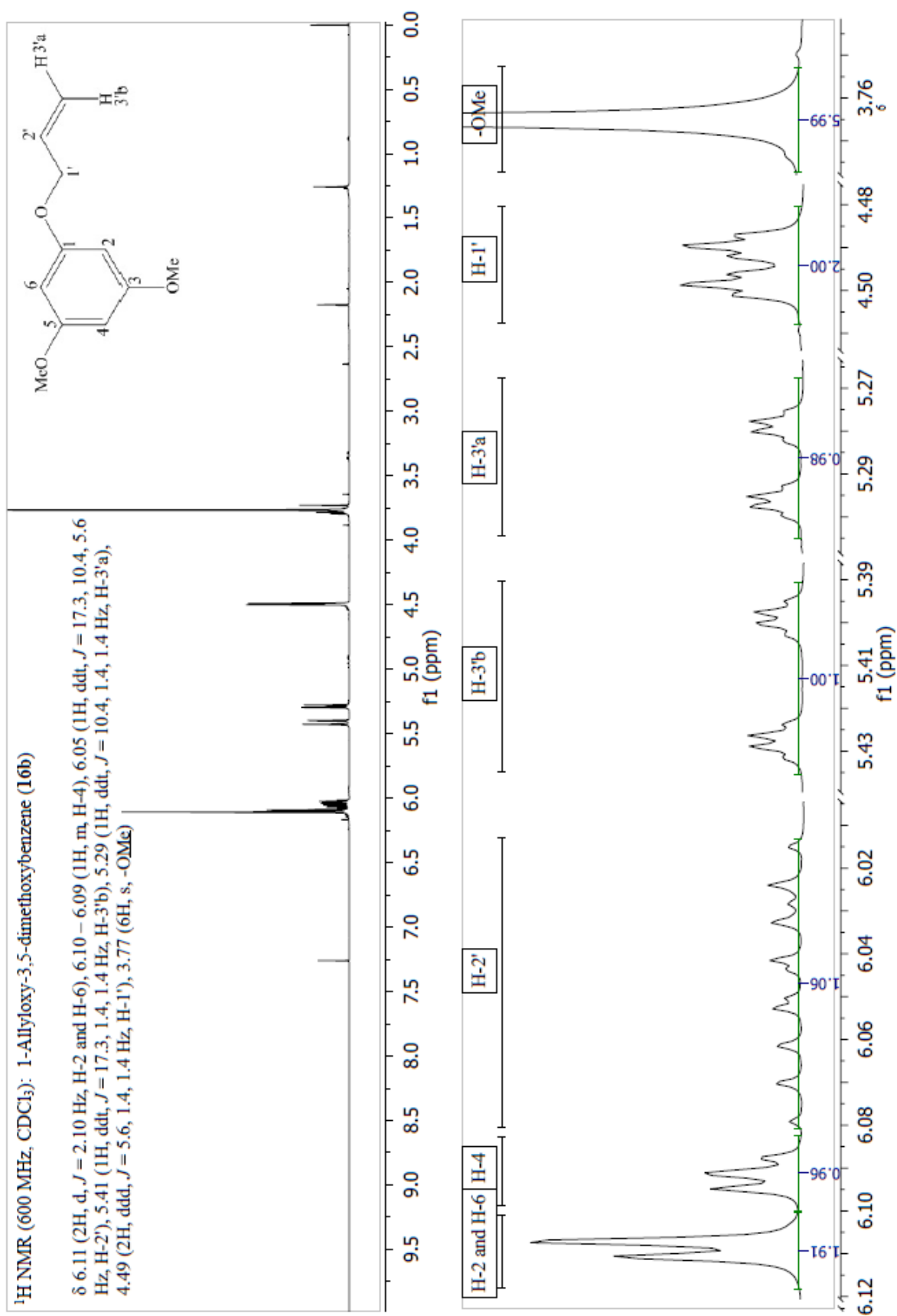


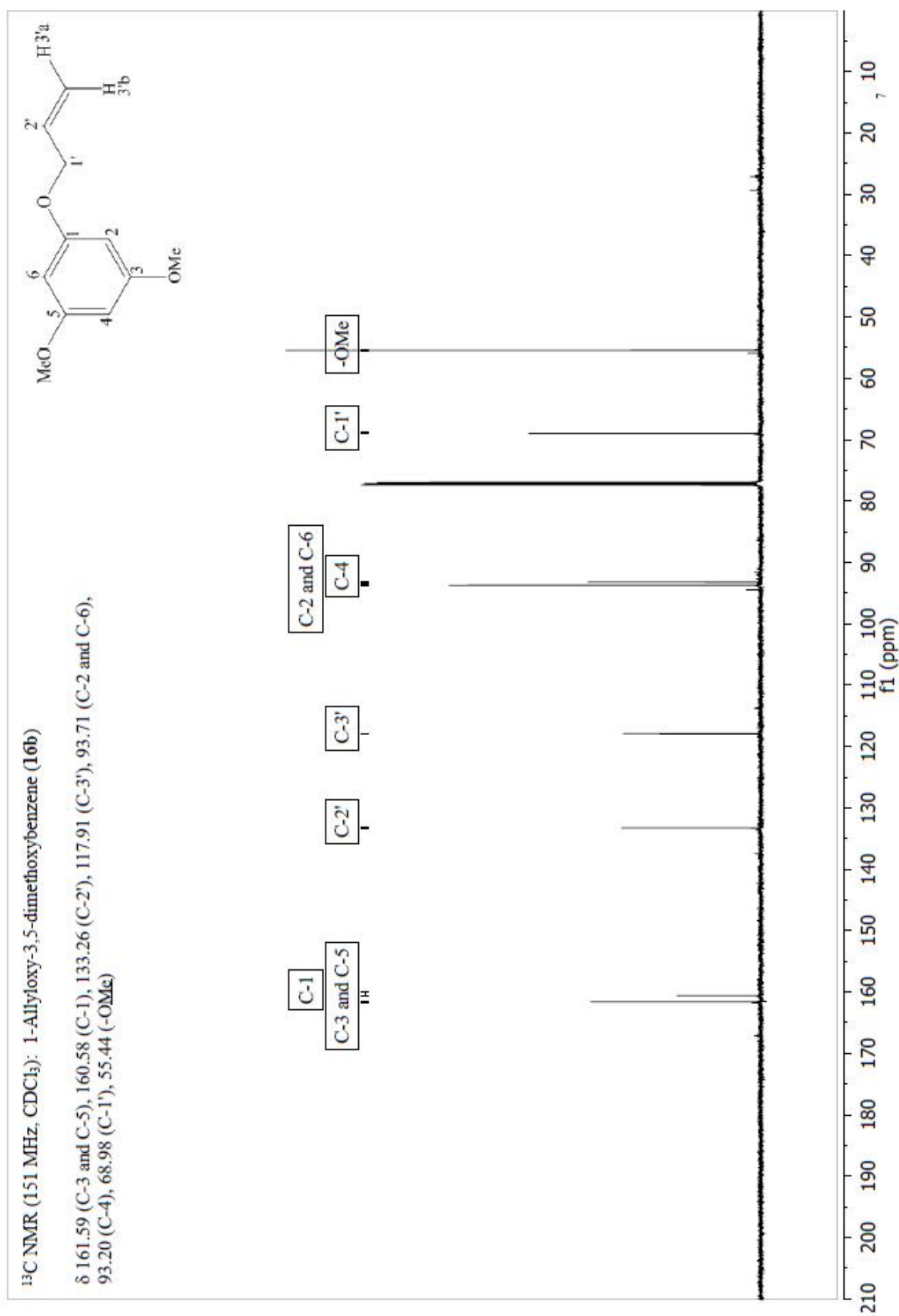


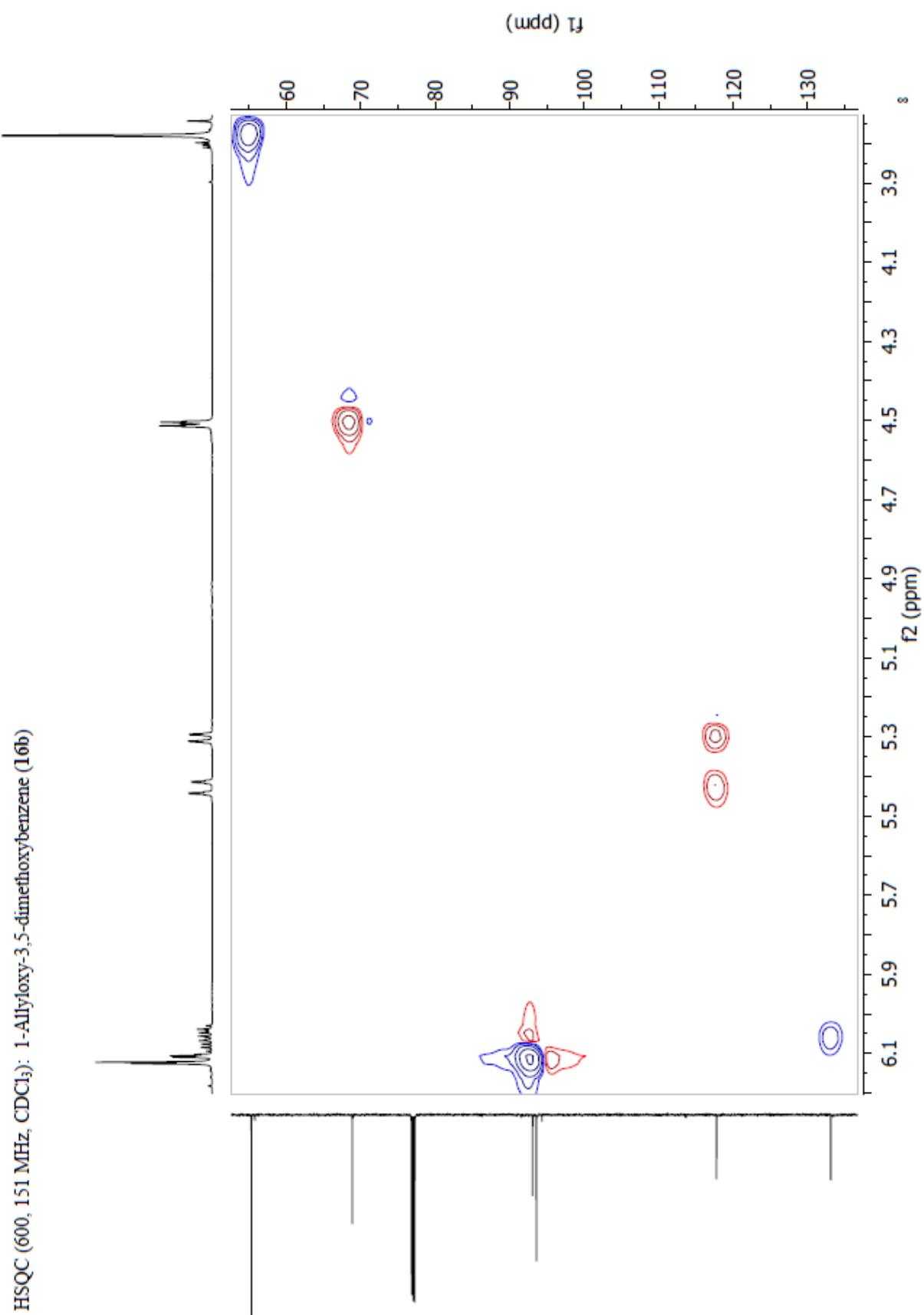


HMBC (600, 151 MHz, CDCl₃): 1-Allyloxy-3-methoxybenzene (16a)

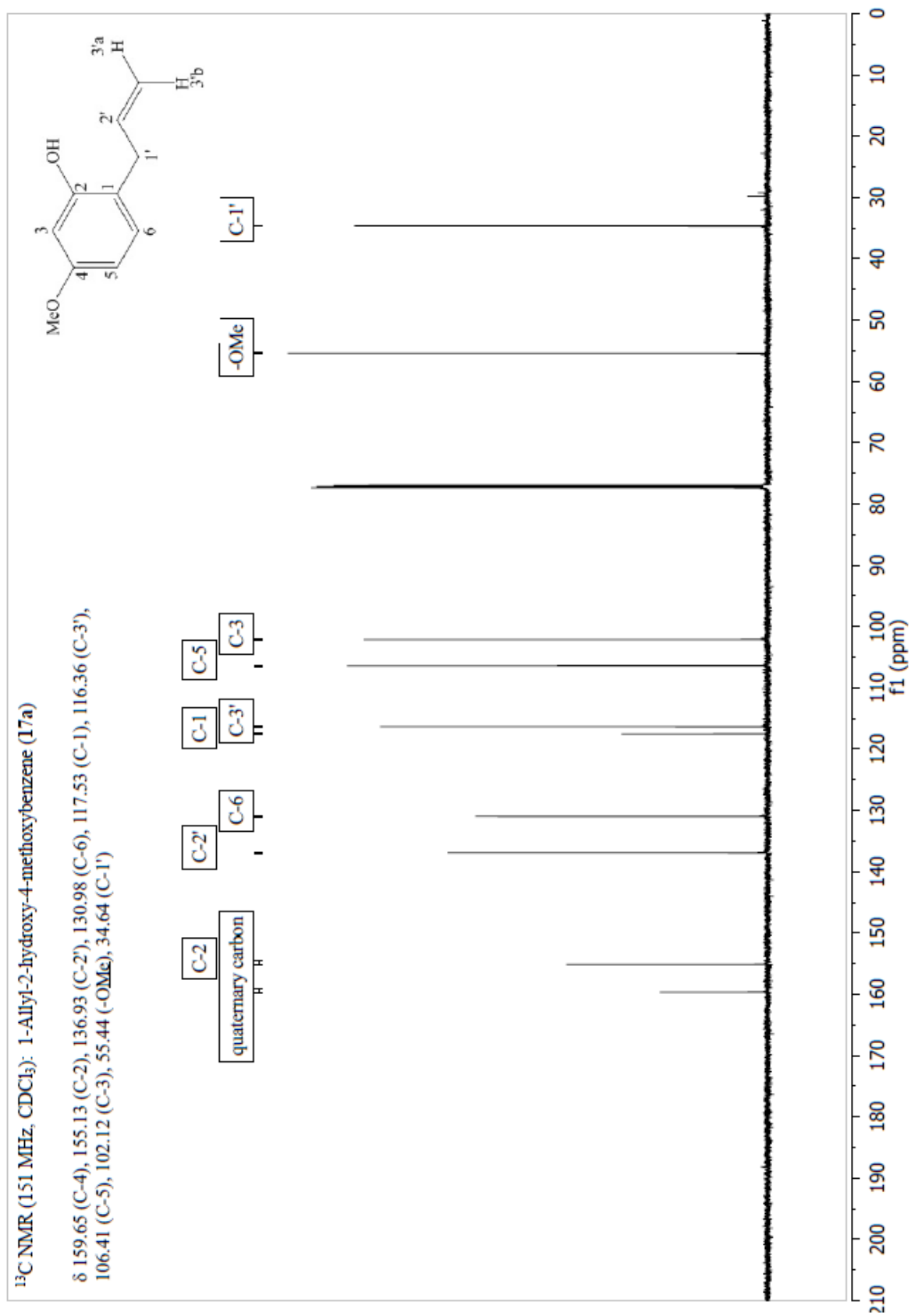


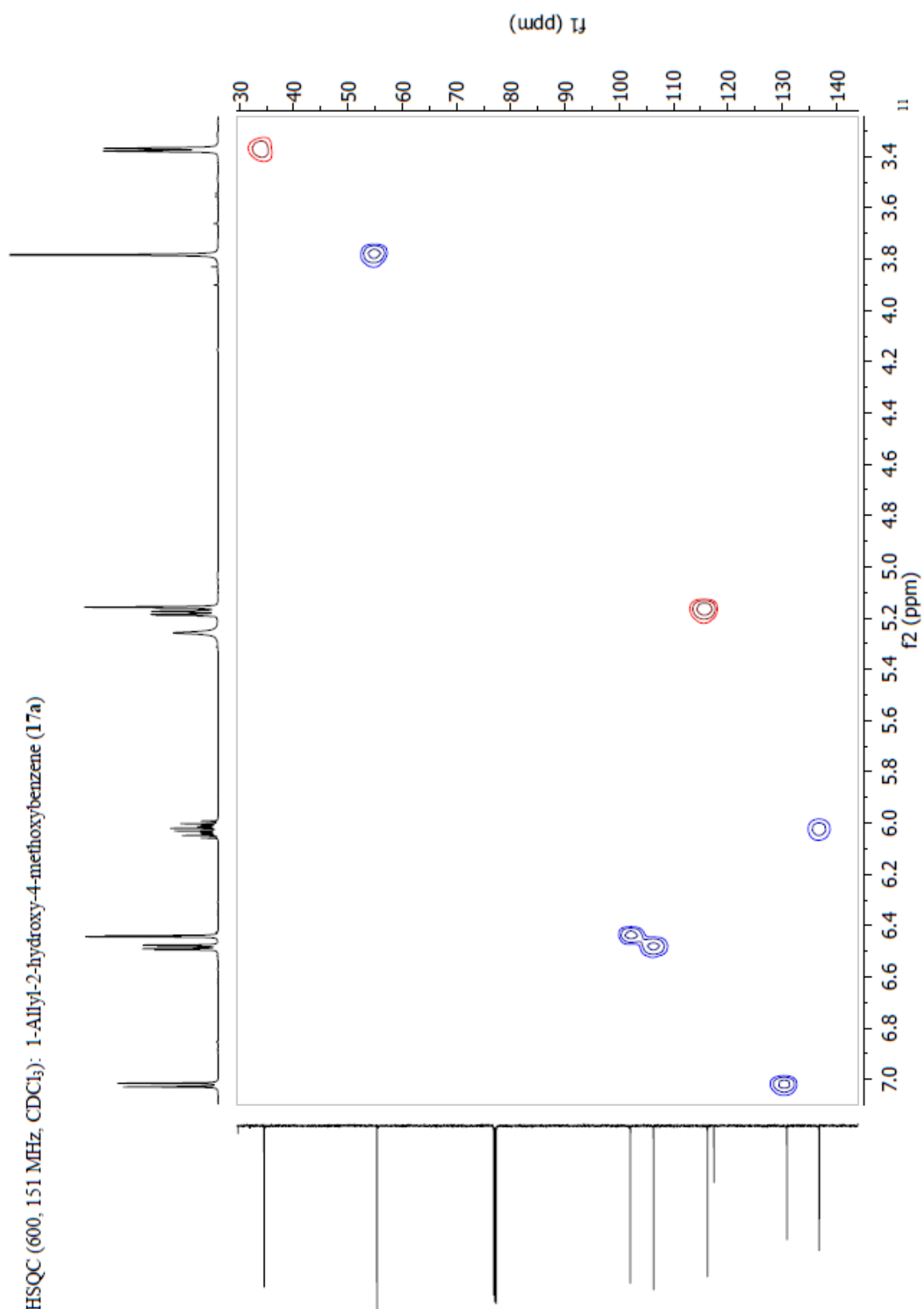


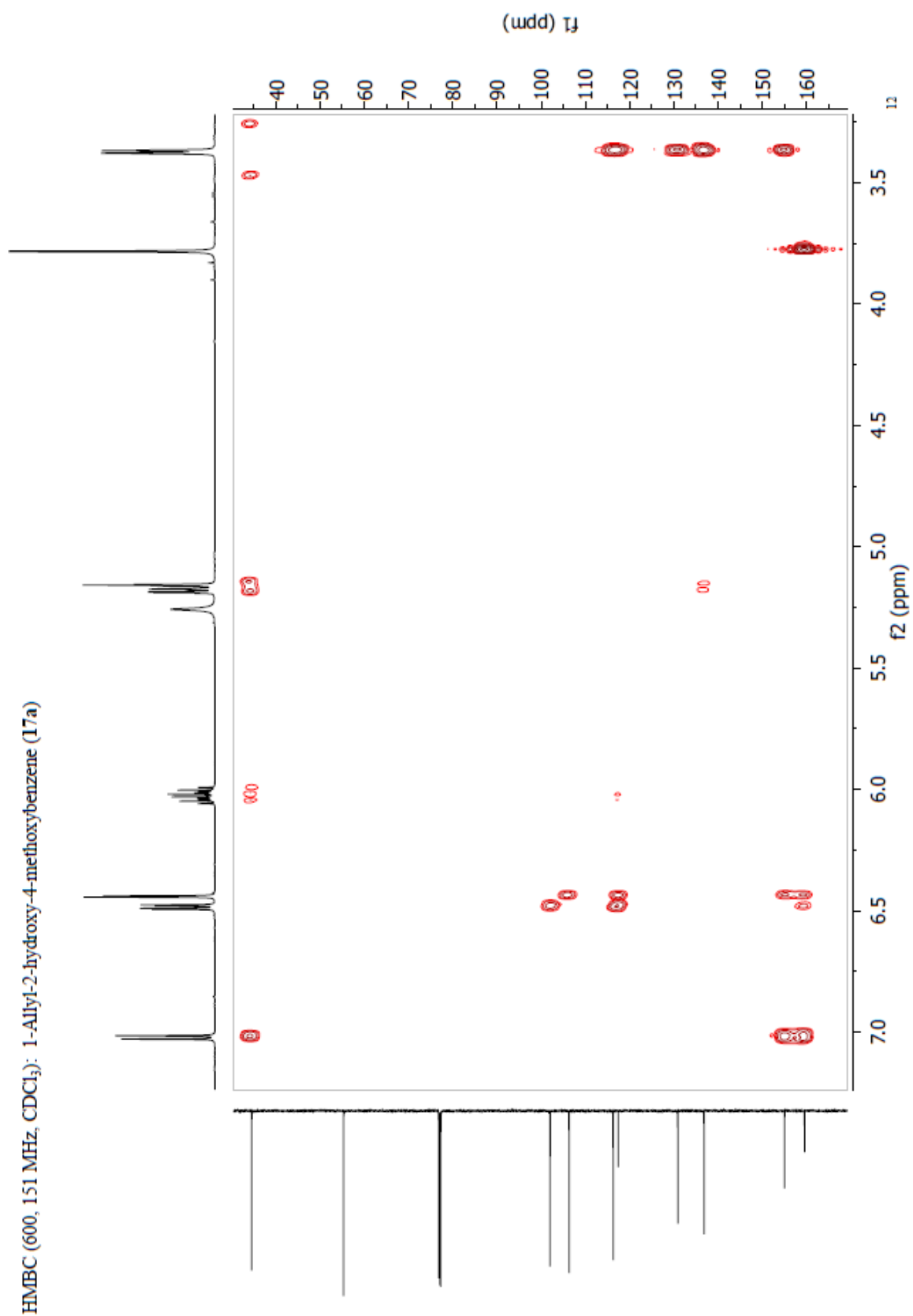


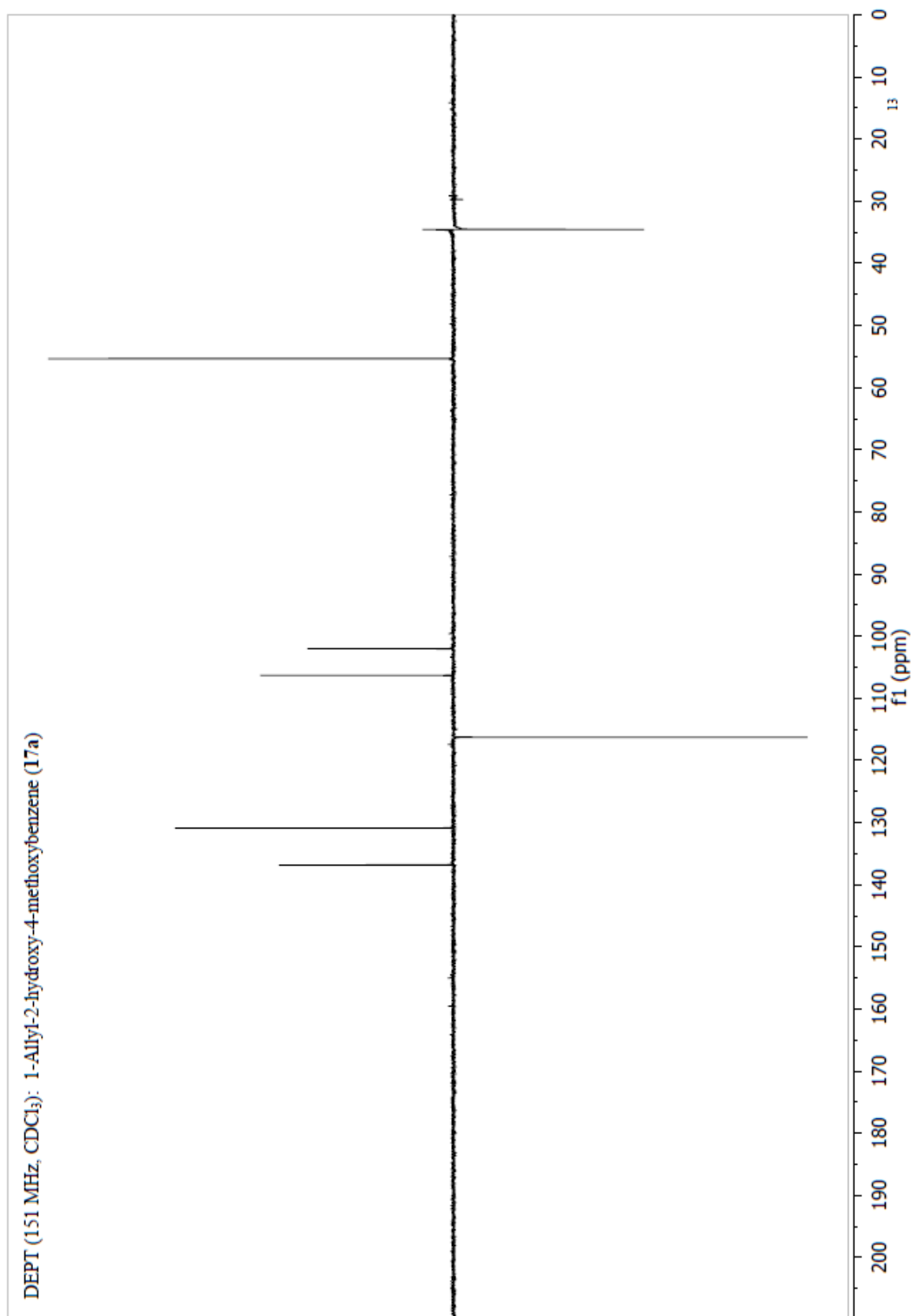


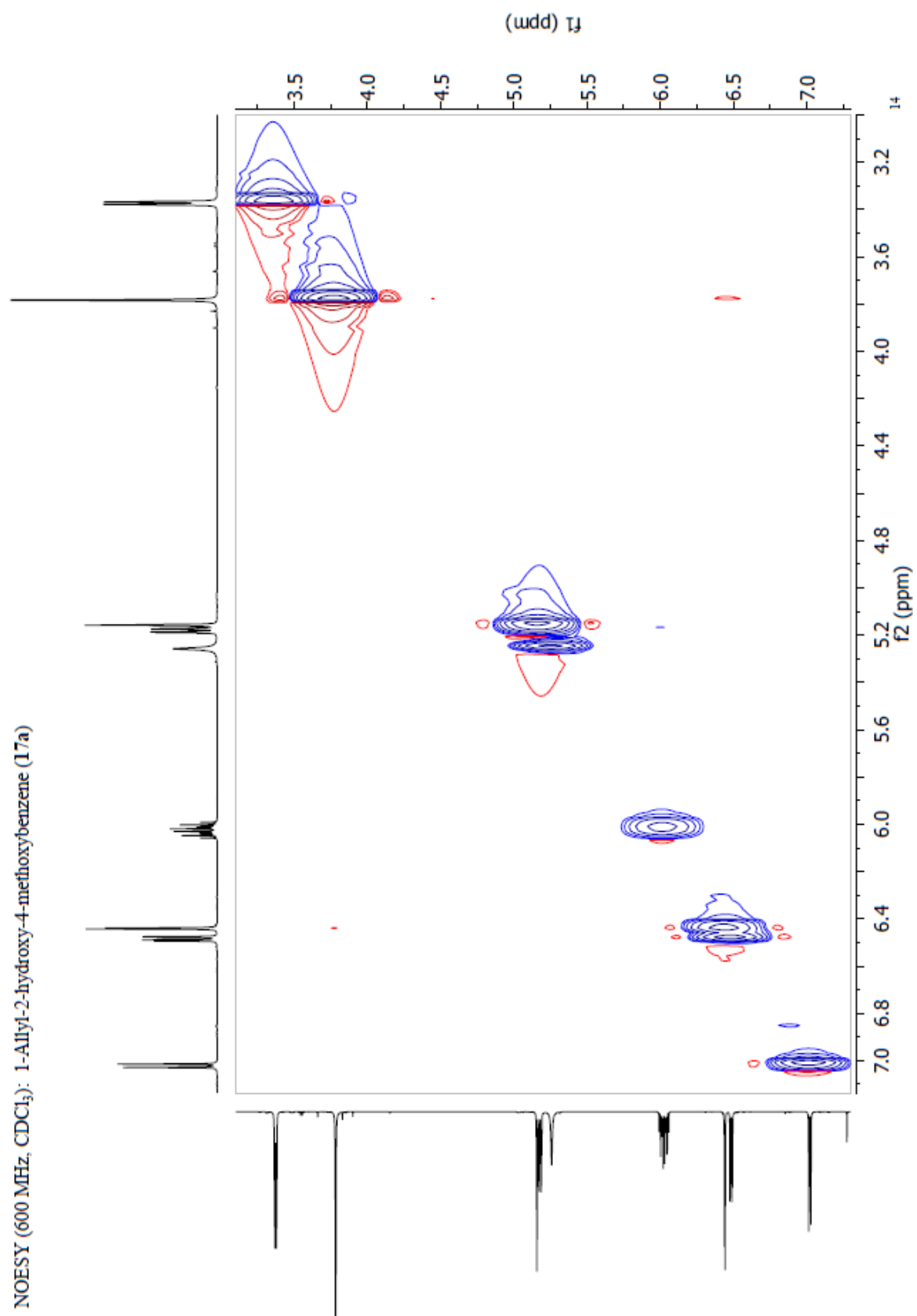


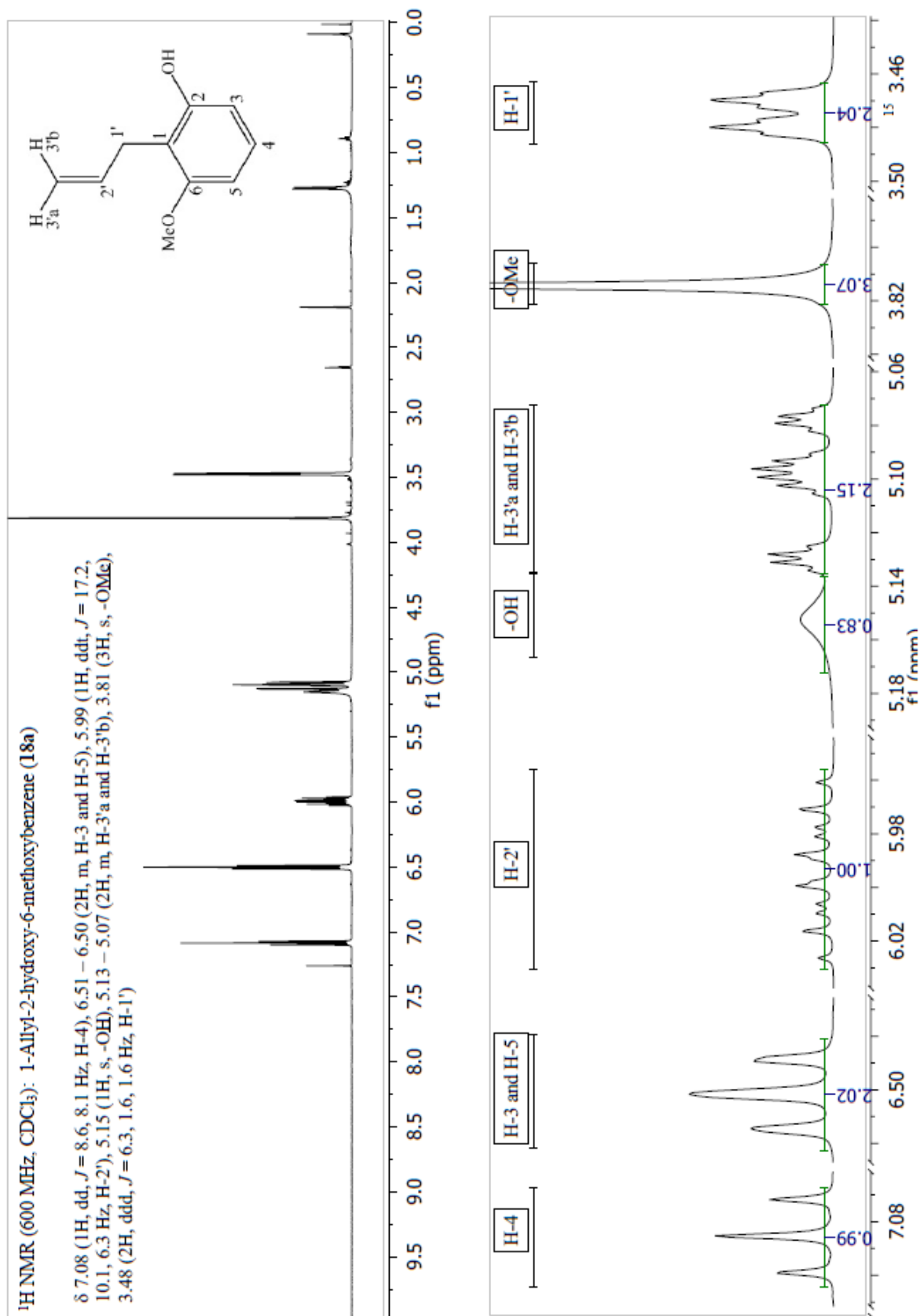


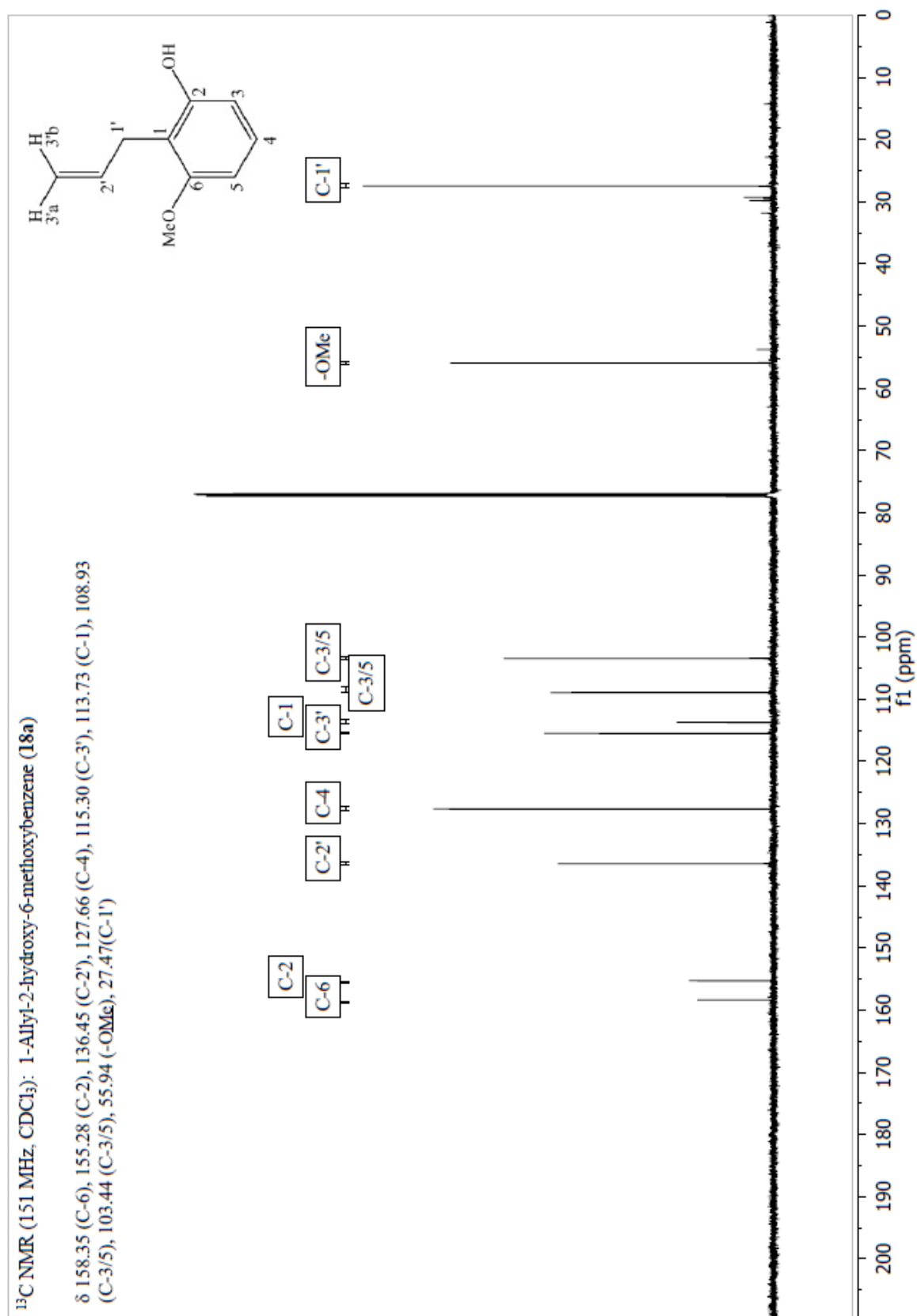
HSQC (600, 151 MHz, CDCl₃): 1-Allyl-2-hydroxy-4-methoxybenzene (17a)

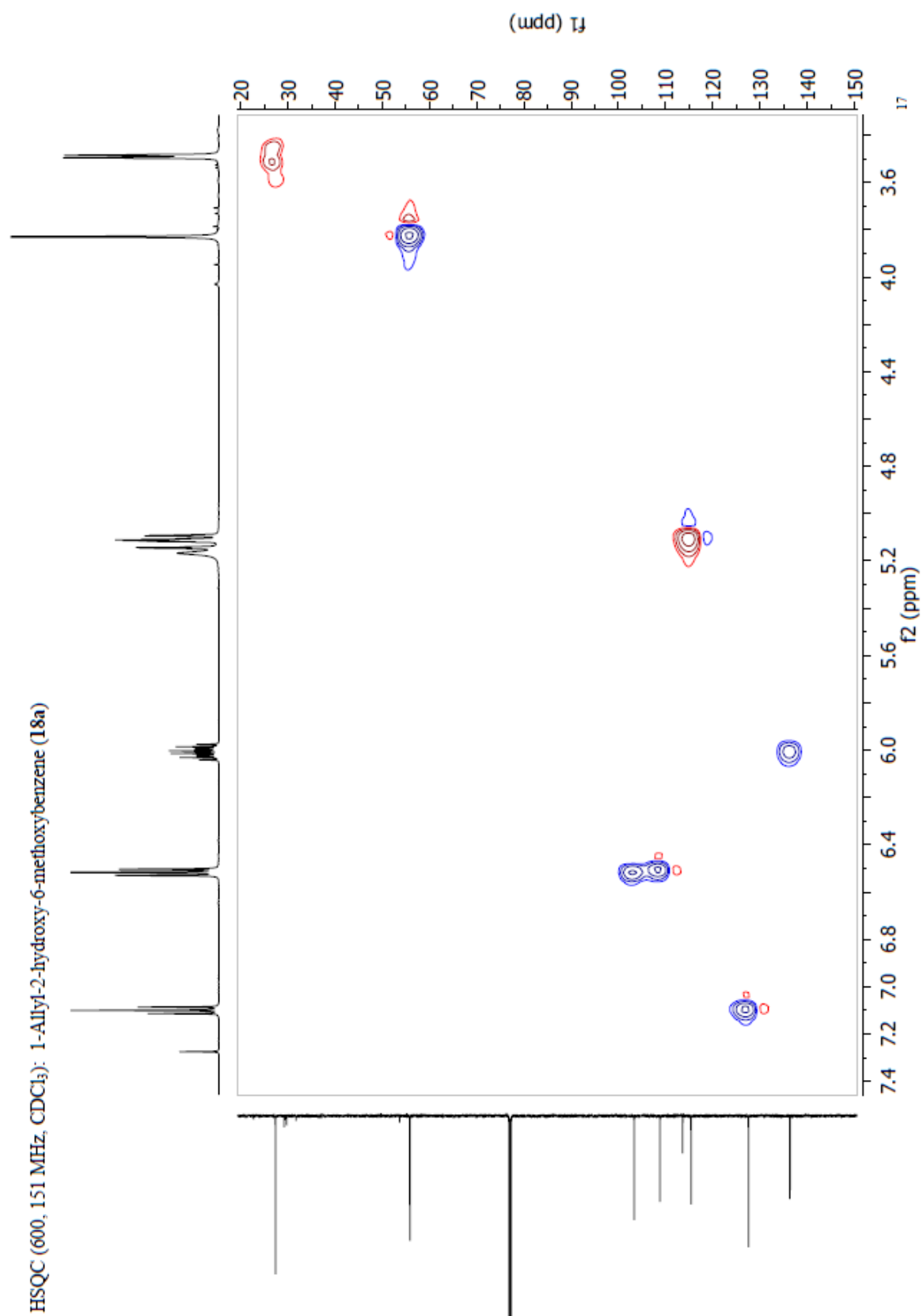


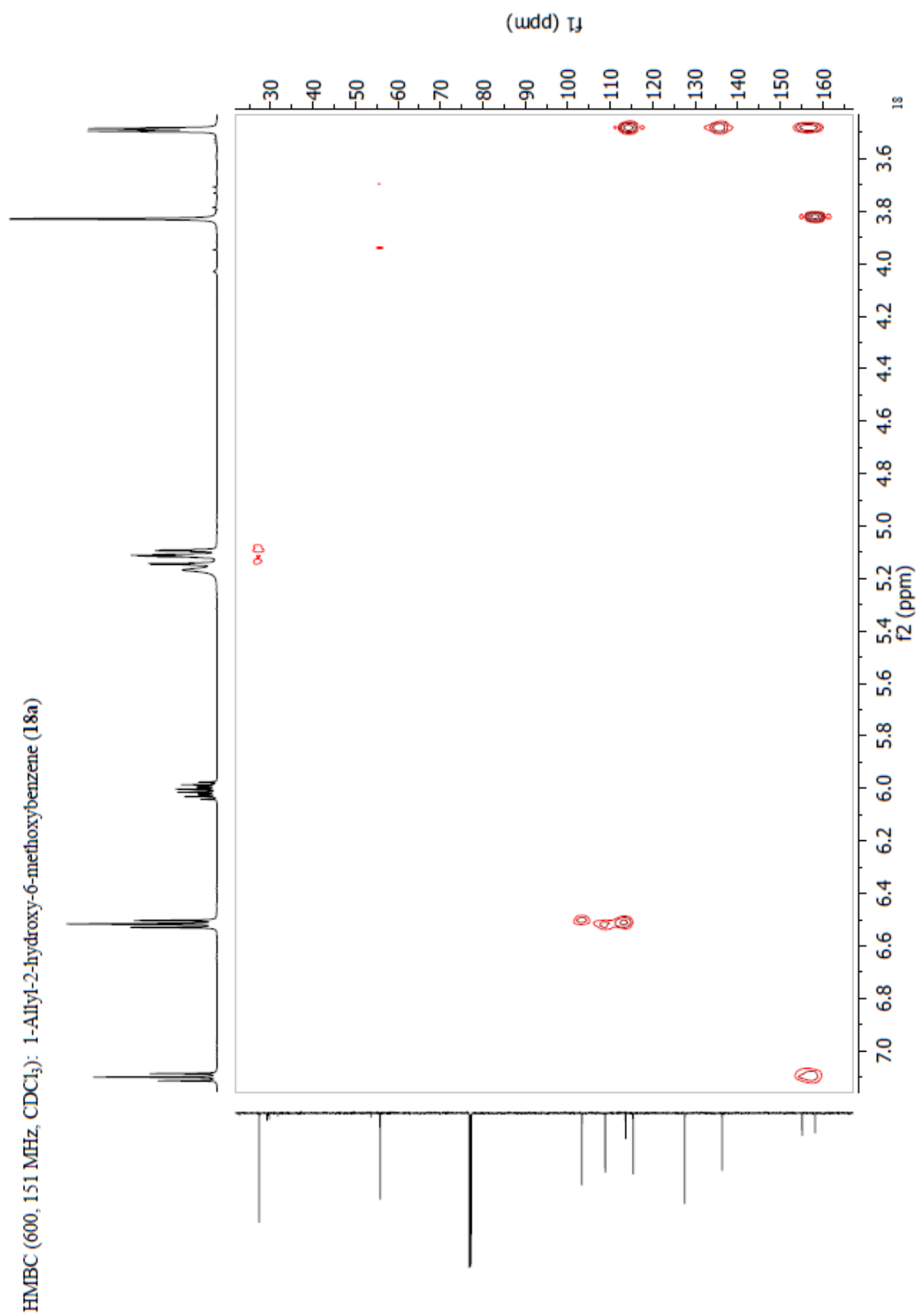


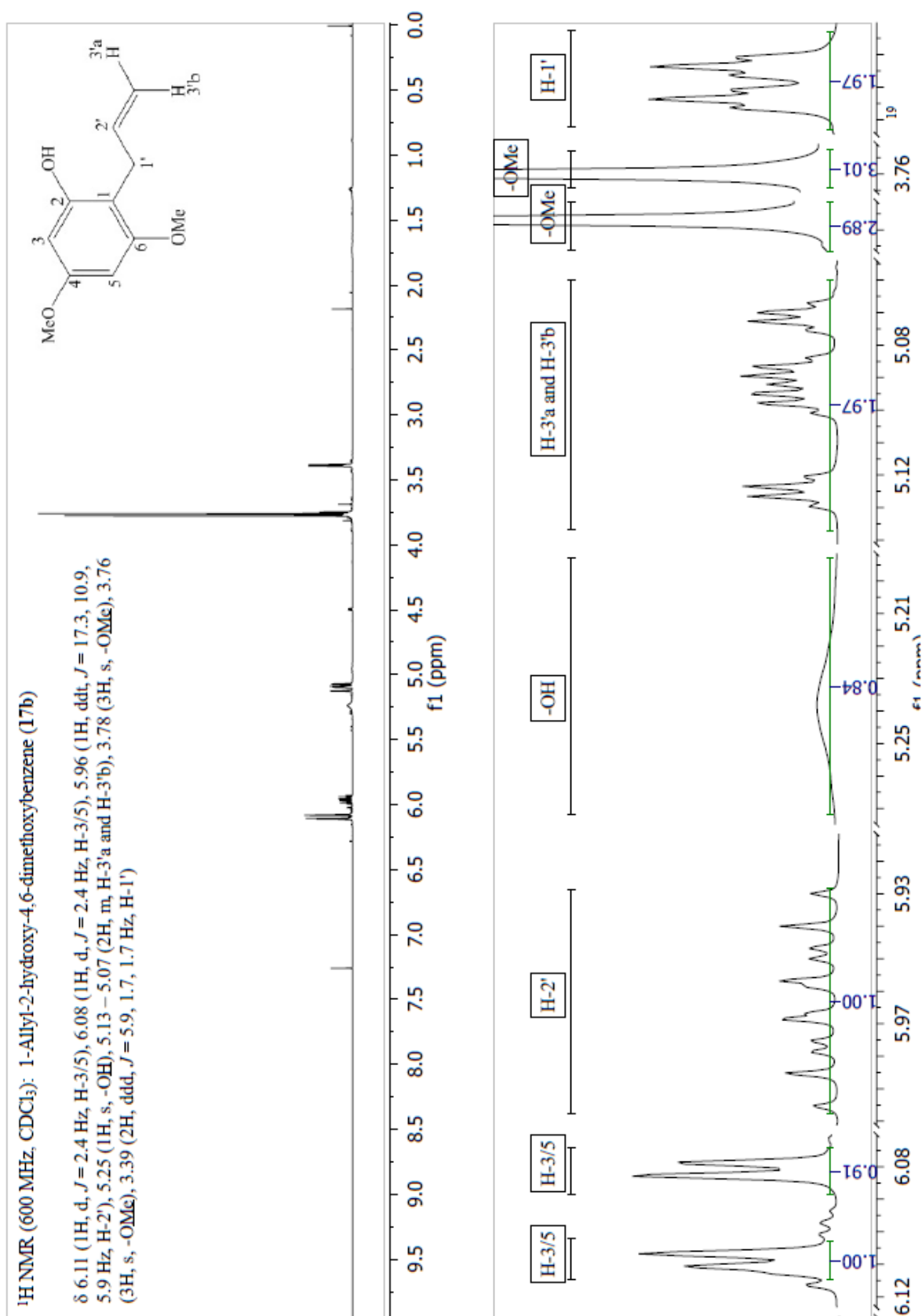
NOESY (600 MHz, CDCl₃): 1-Allyl-2-hydroxy-4-methoxybenzene (**17a**)

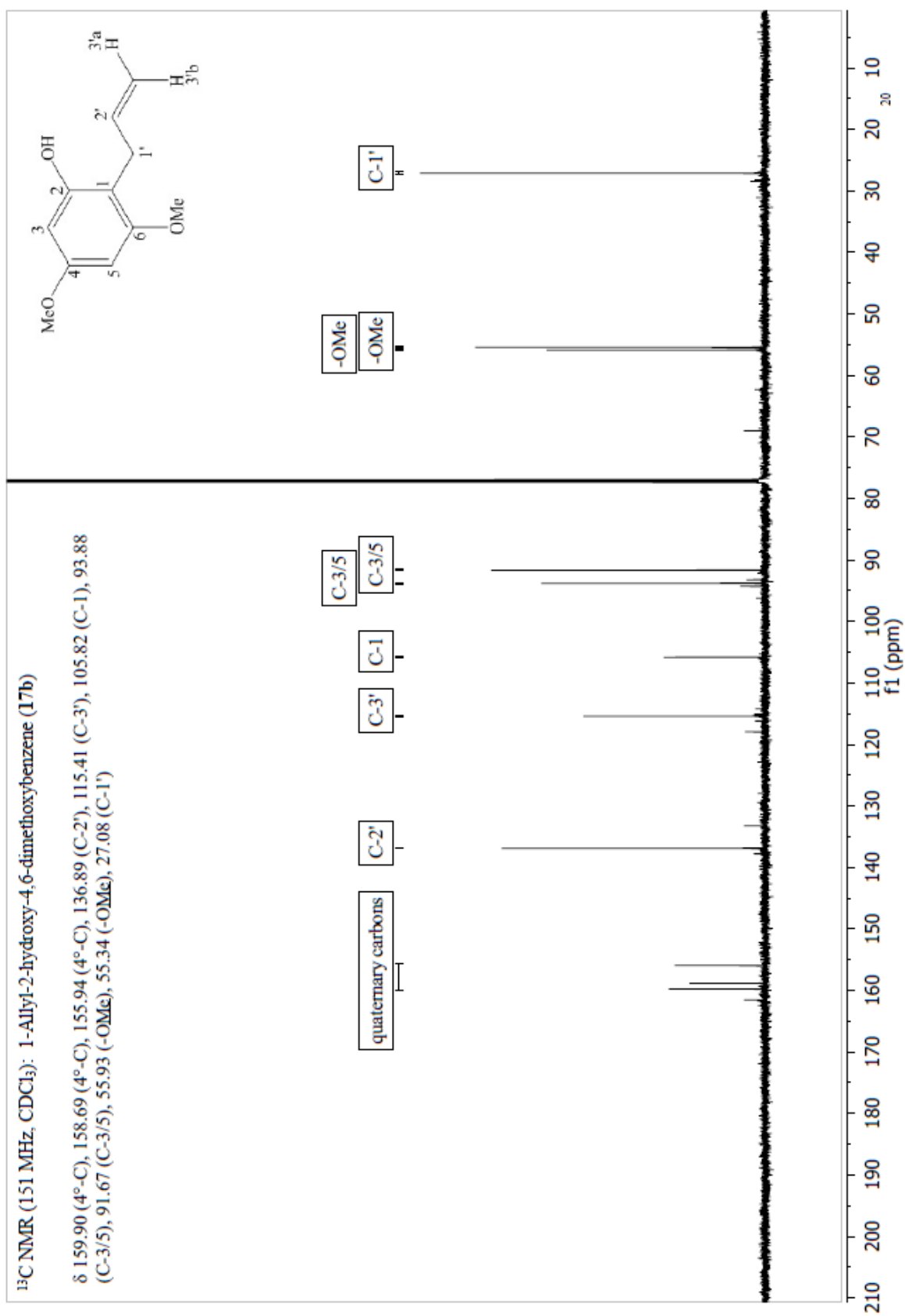


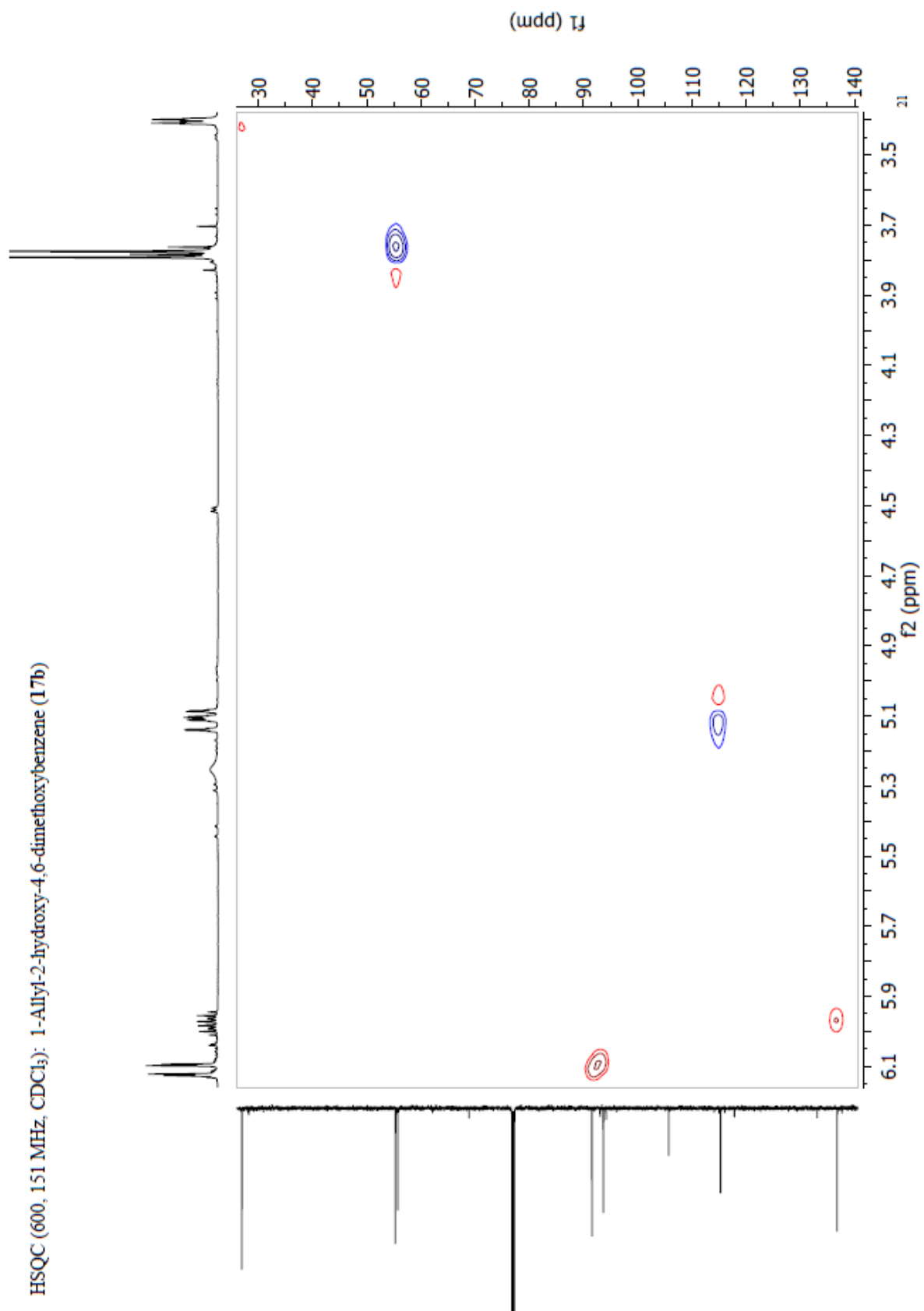


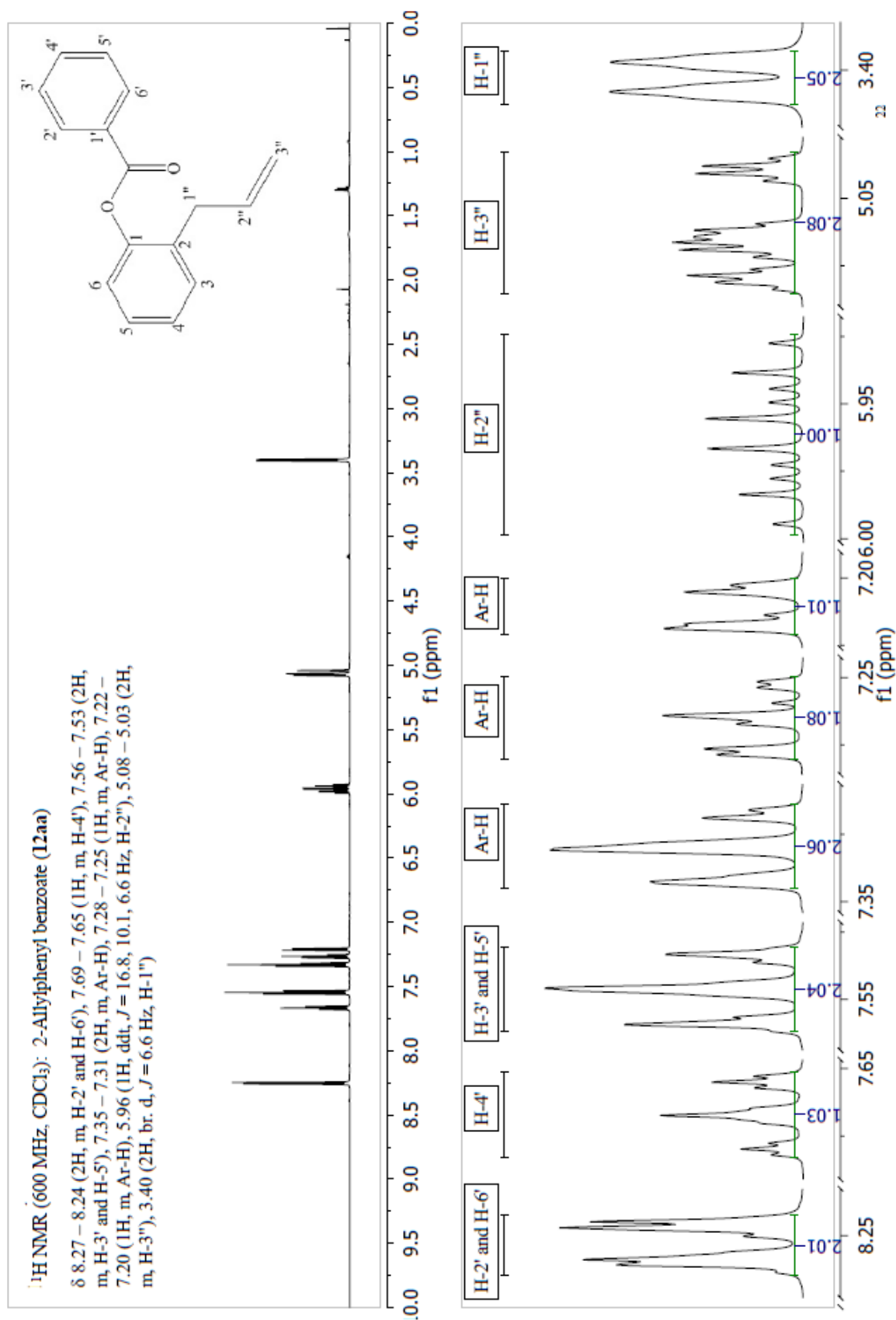
HSQC (600, 151 MHz, CDCl₃): 1-Allyl-2-hydroxy-6-methoxybenzene (18a)

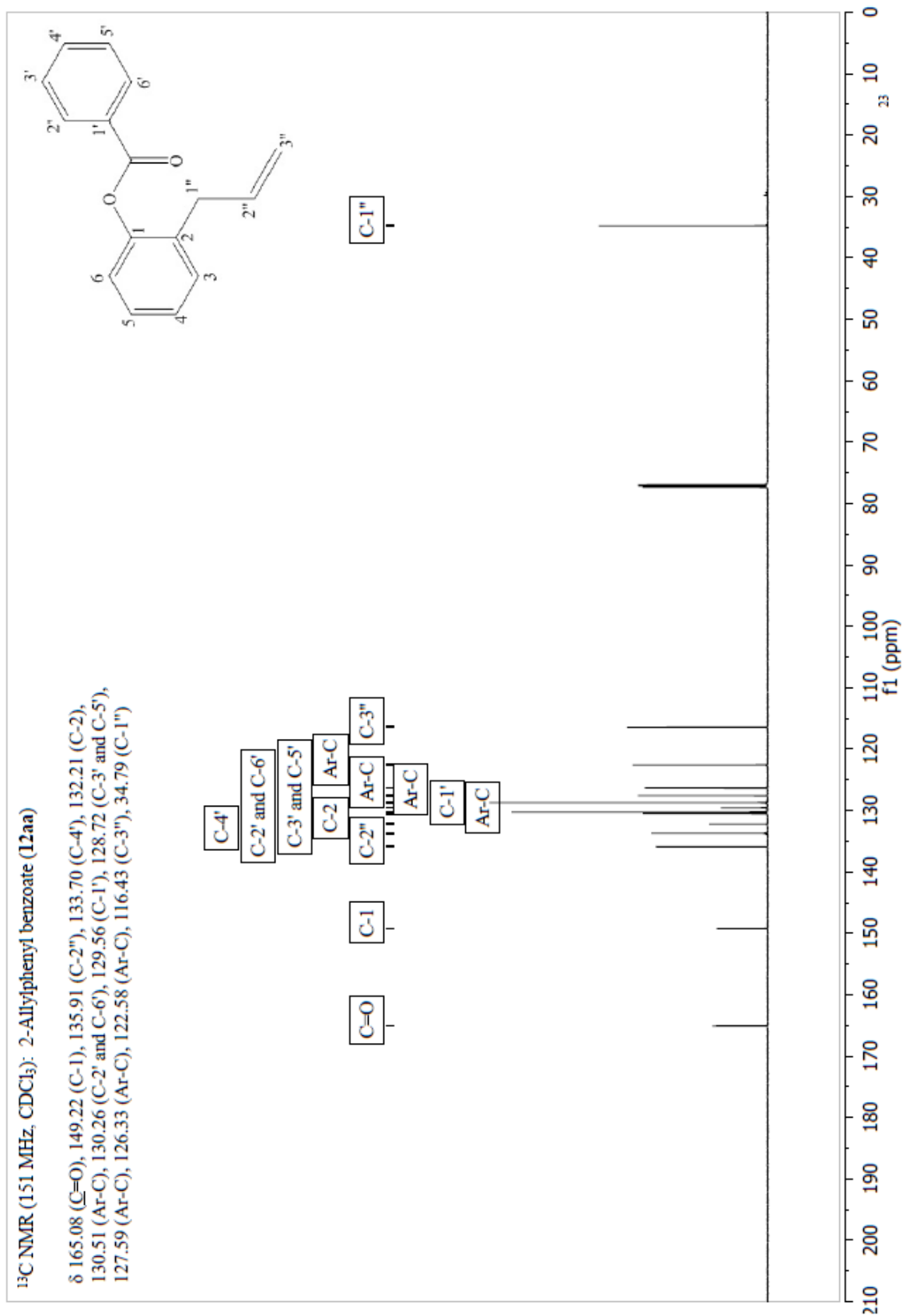


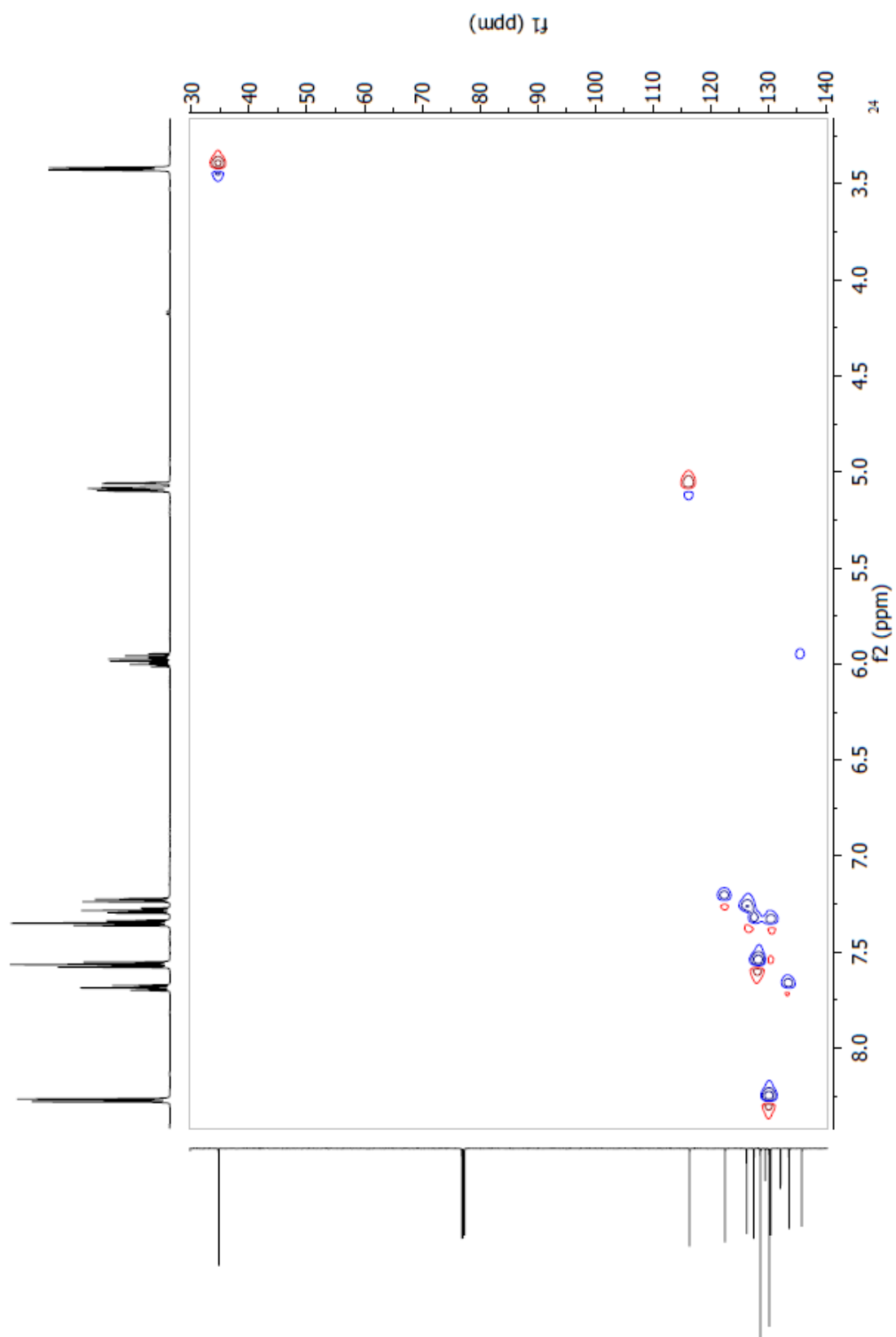


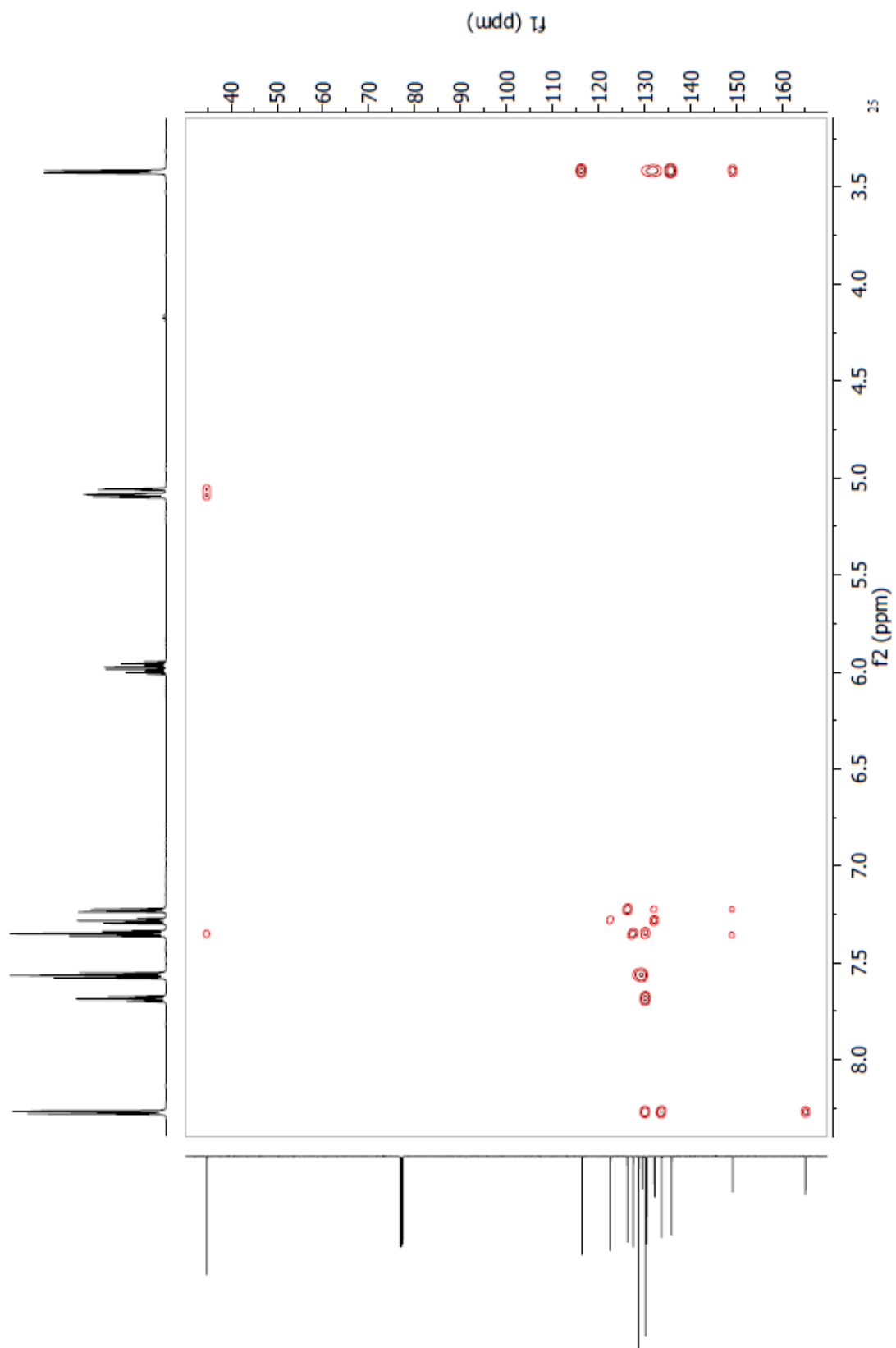


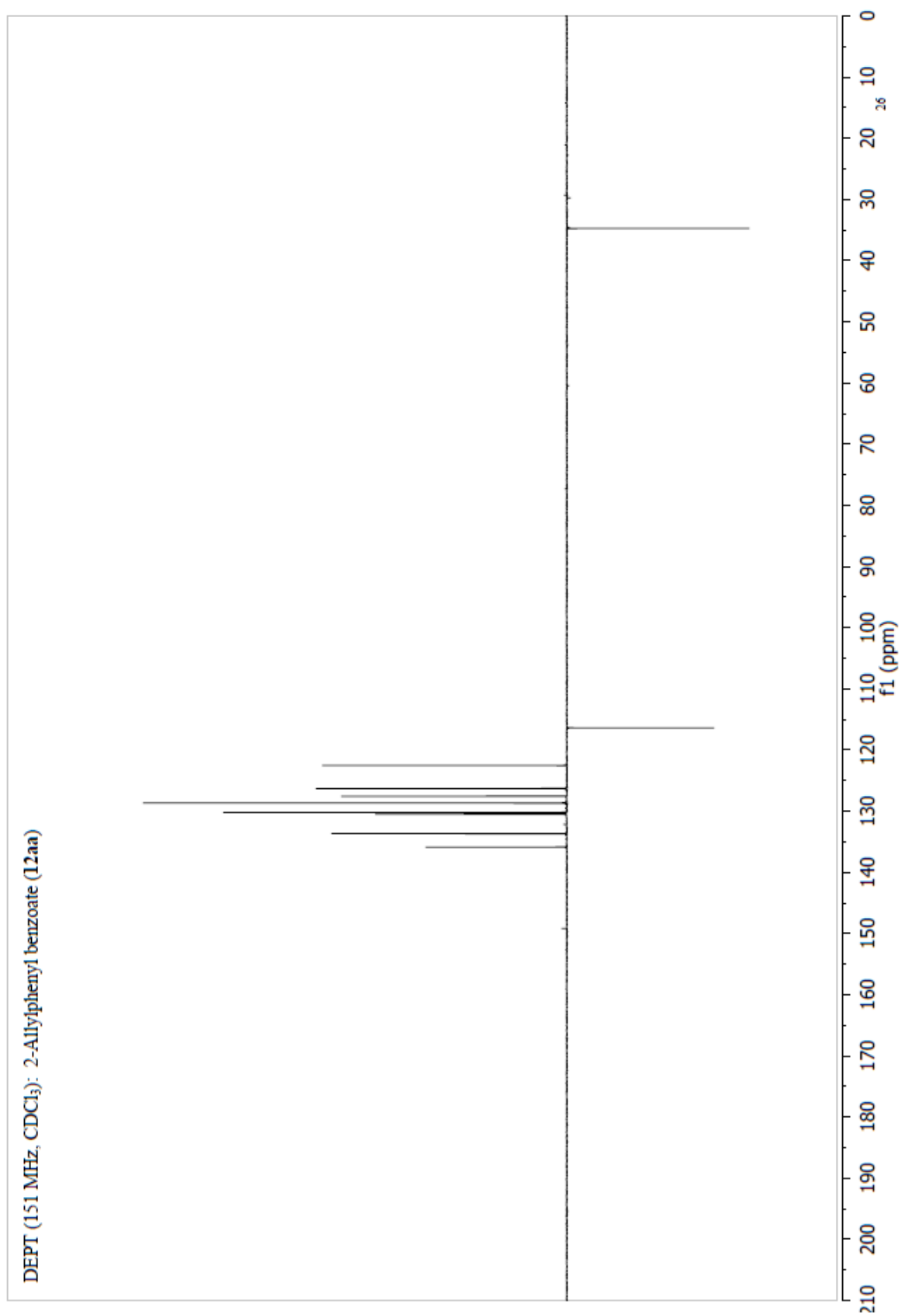


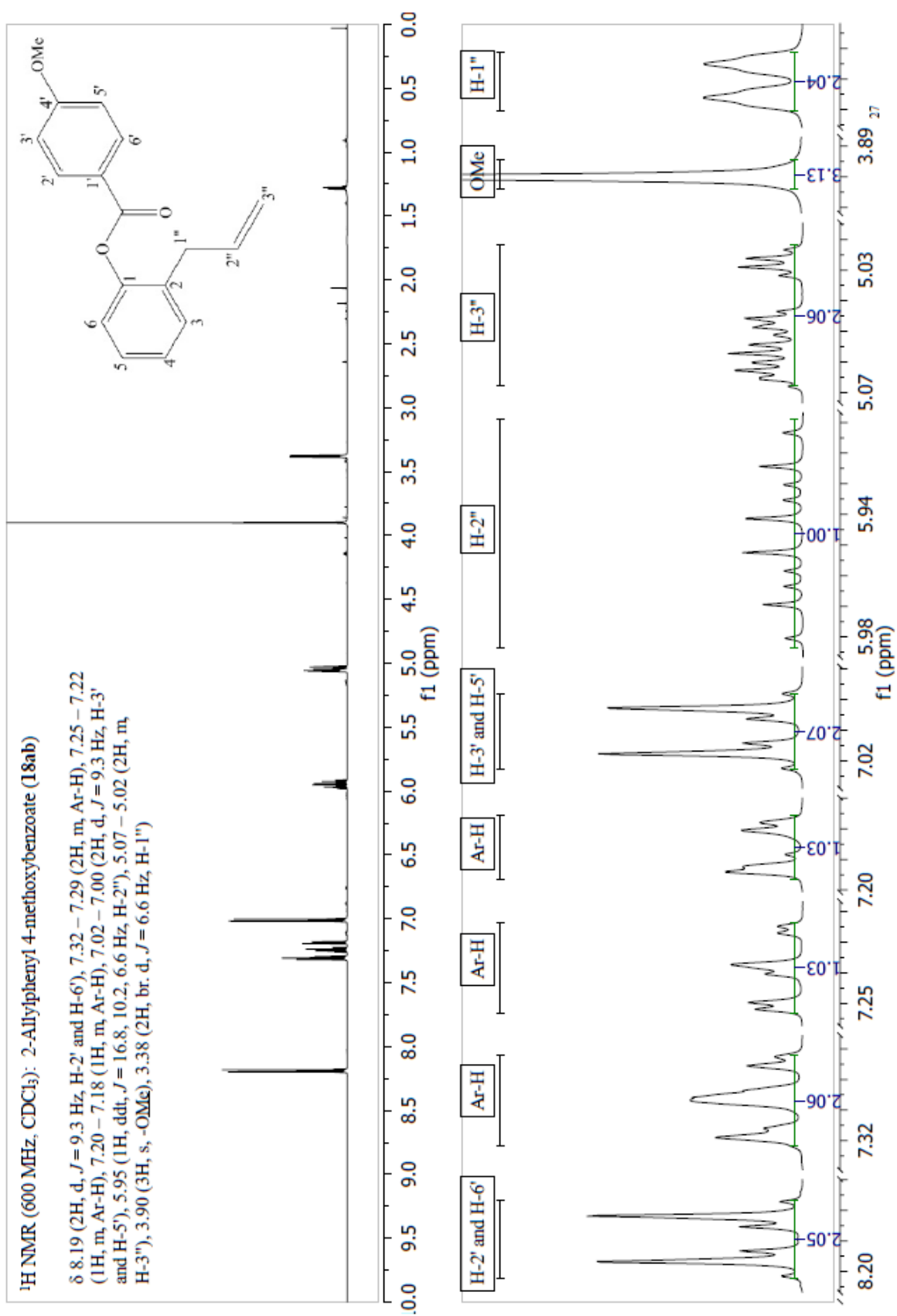


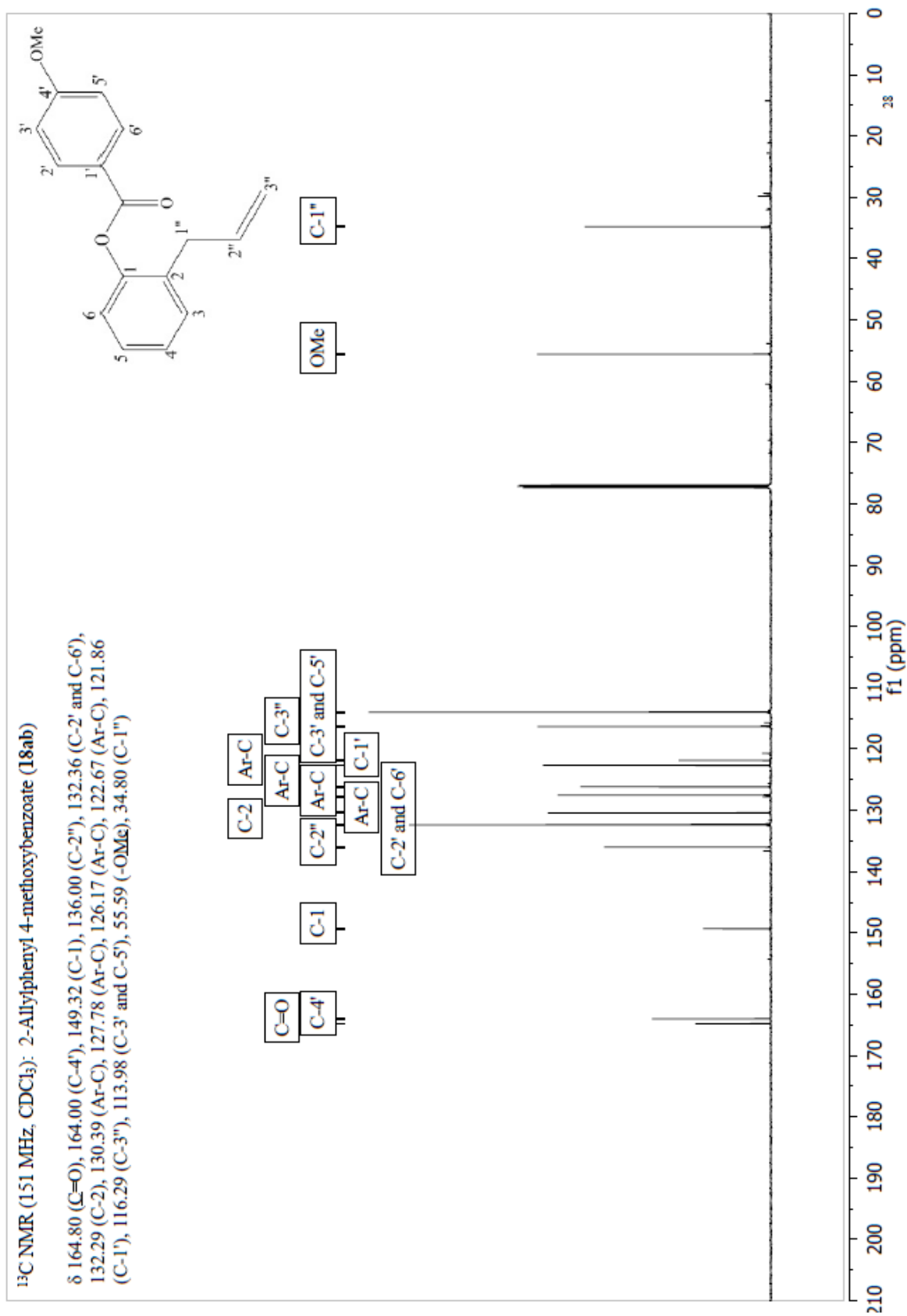


HSQC (600, 151 MHz, CDCl₃): 2-Allylphenyl benzoate (12aa)

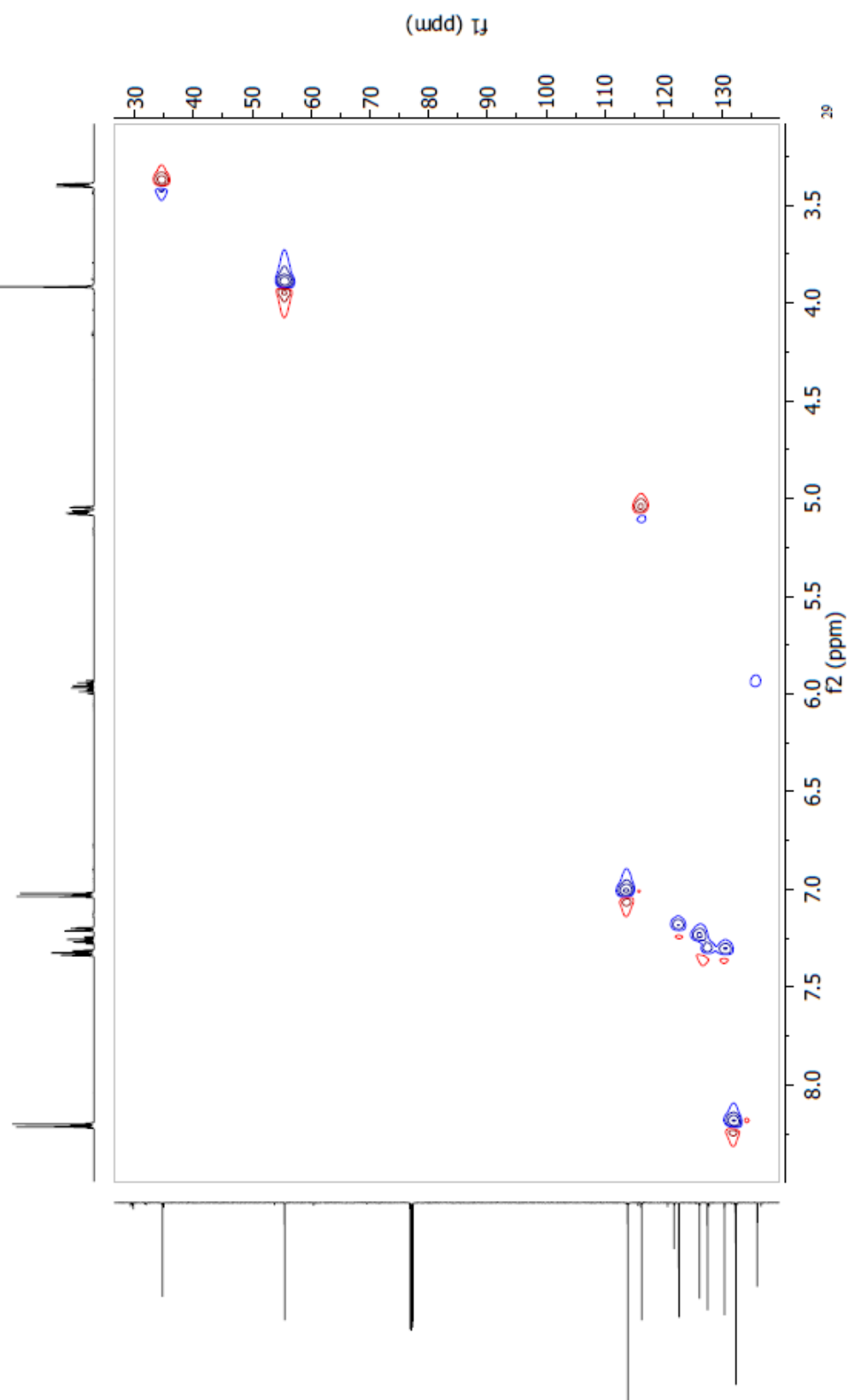
HMBC (600, 151 MHz, CDCl₃): 2-Allylphenyl benzoate (12aa)

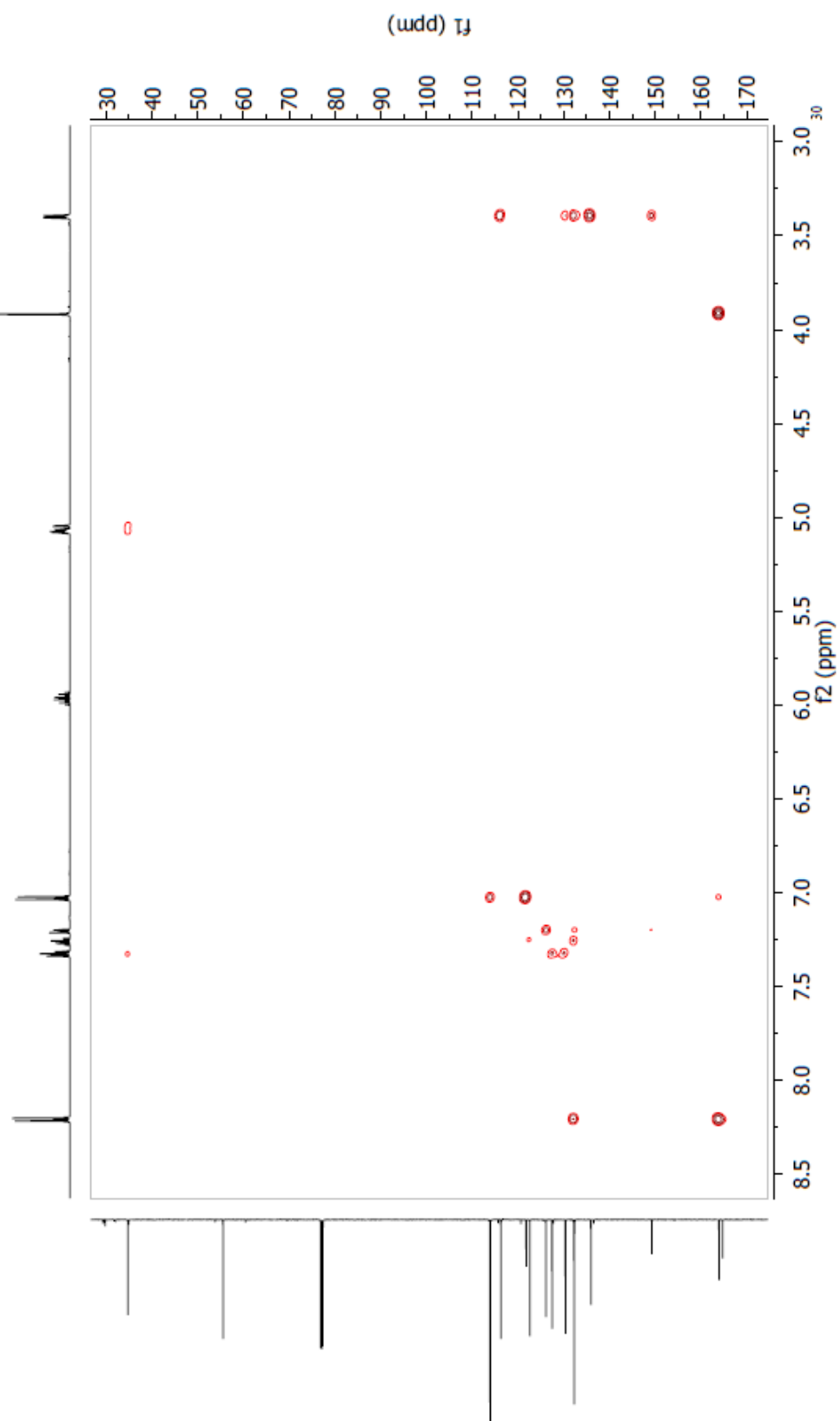


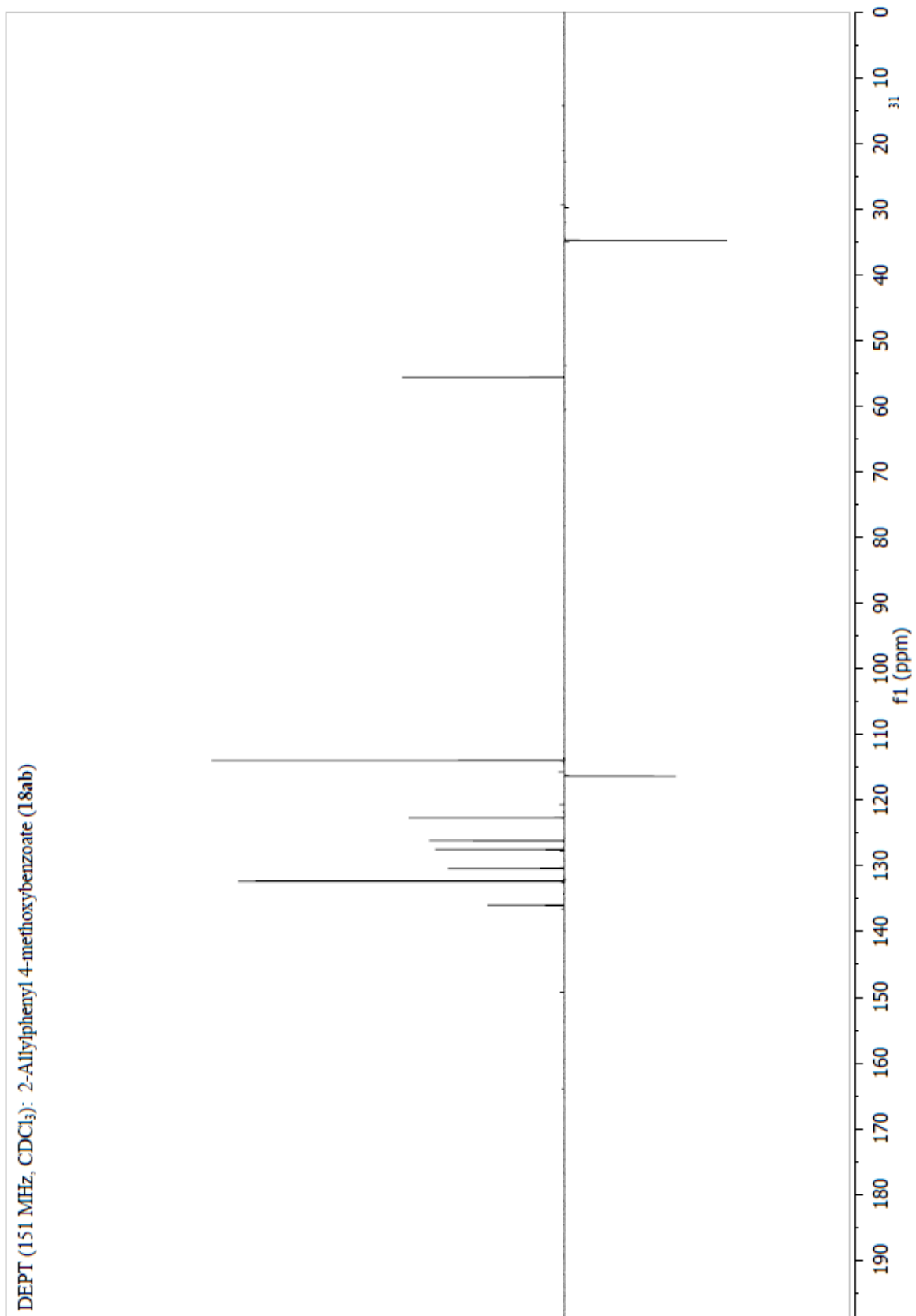


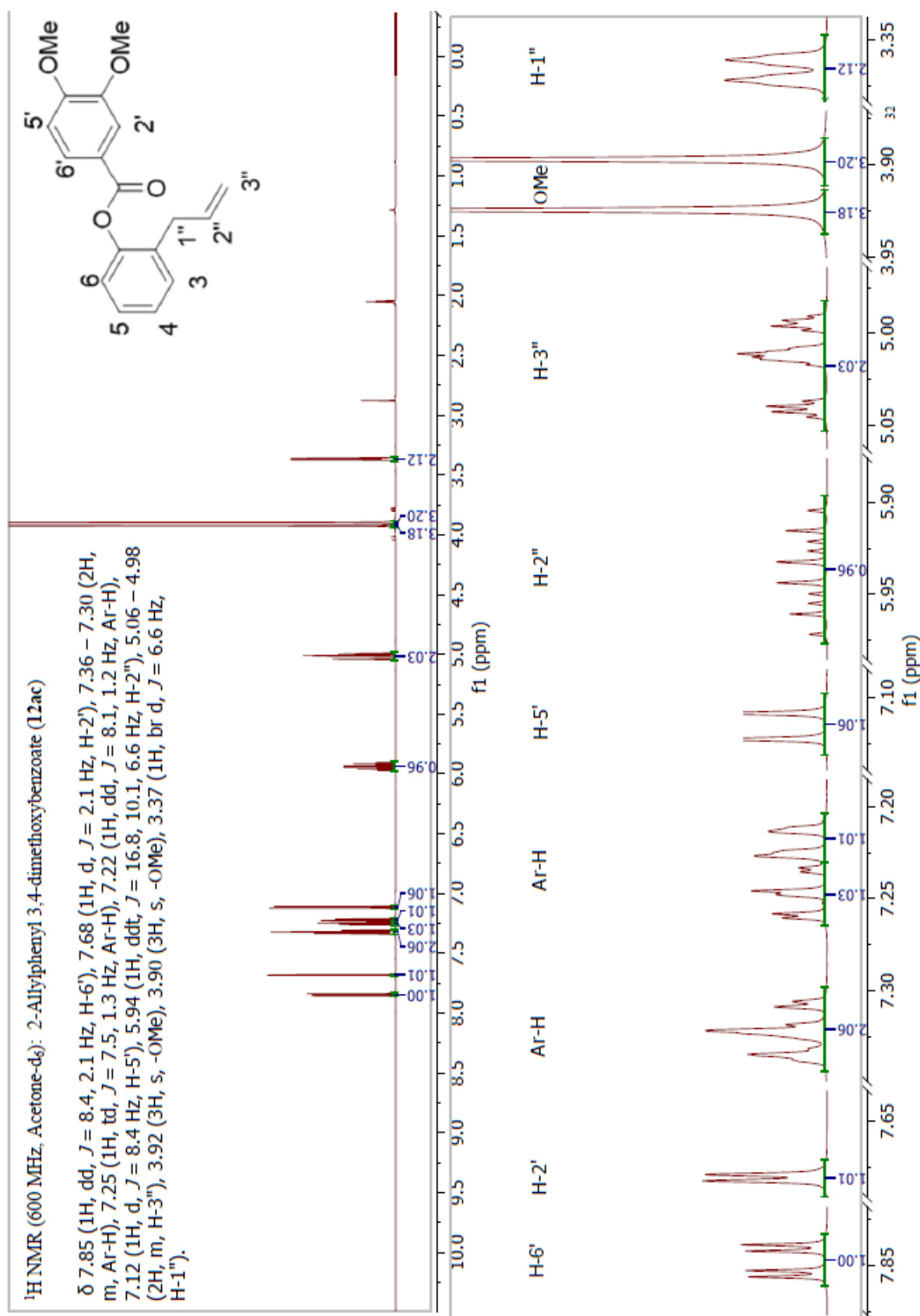


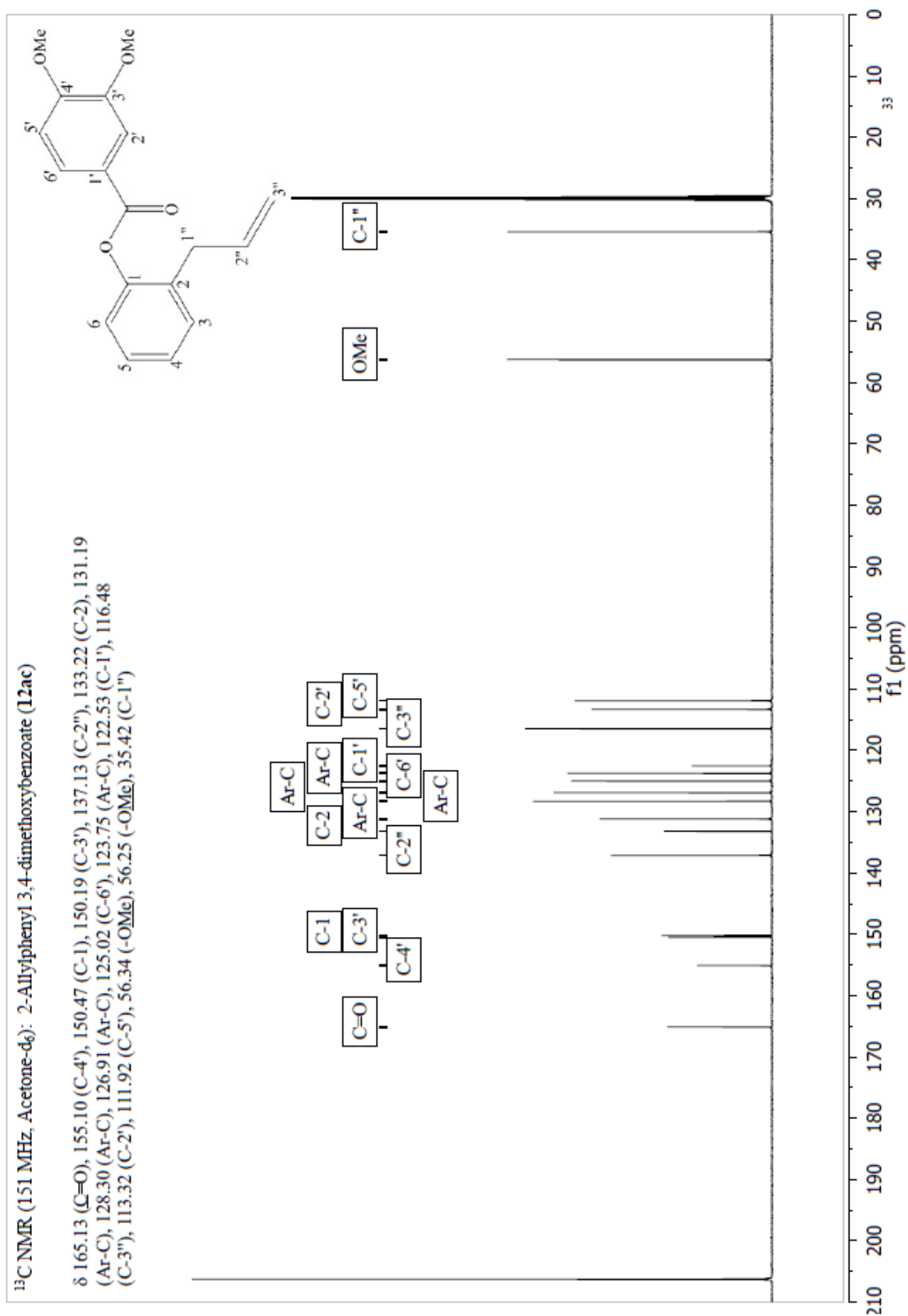
HSQC (600, 151 MHz, CDCl₃): 2-Allylphenyl 4-methoxybenzoate (18ab)

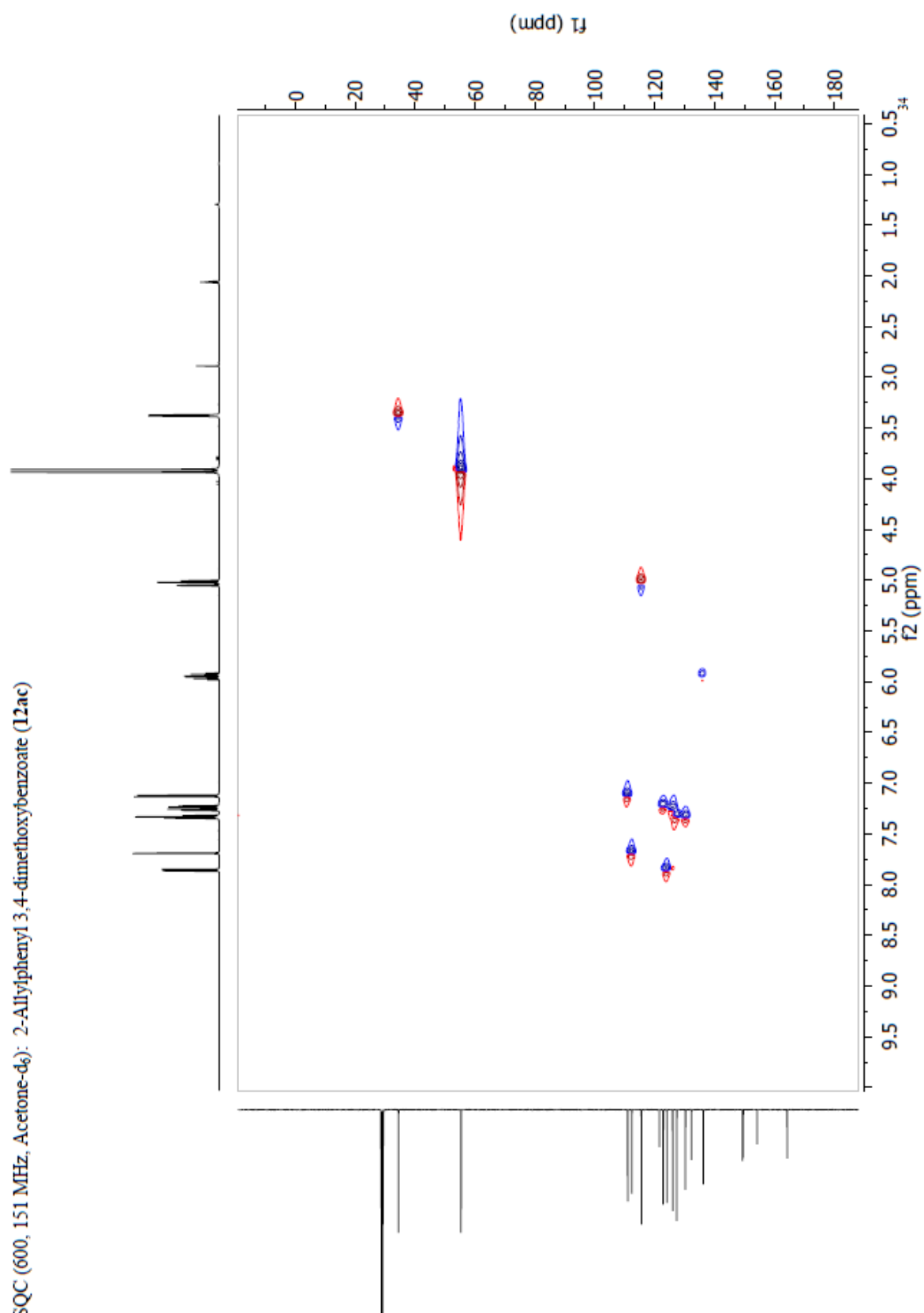


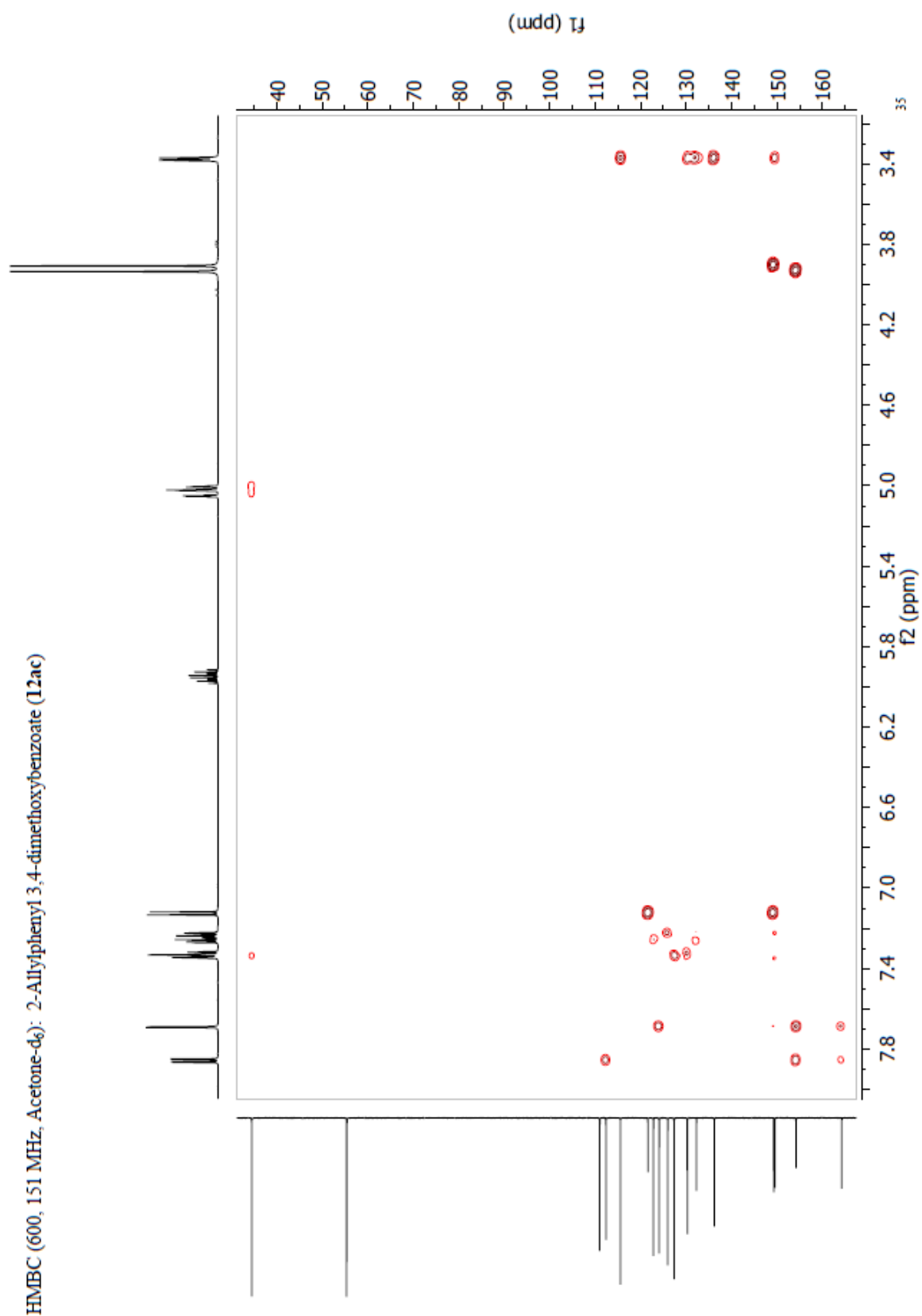
HMBC (600, 151 MHz, CDCl₃): 2-Allylphenyl 4-methoxybenzoate (18ab)

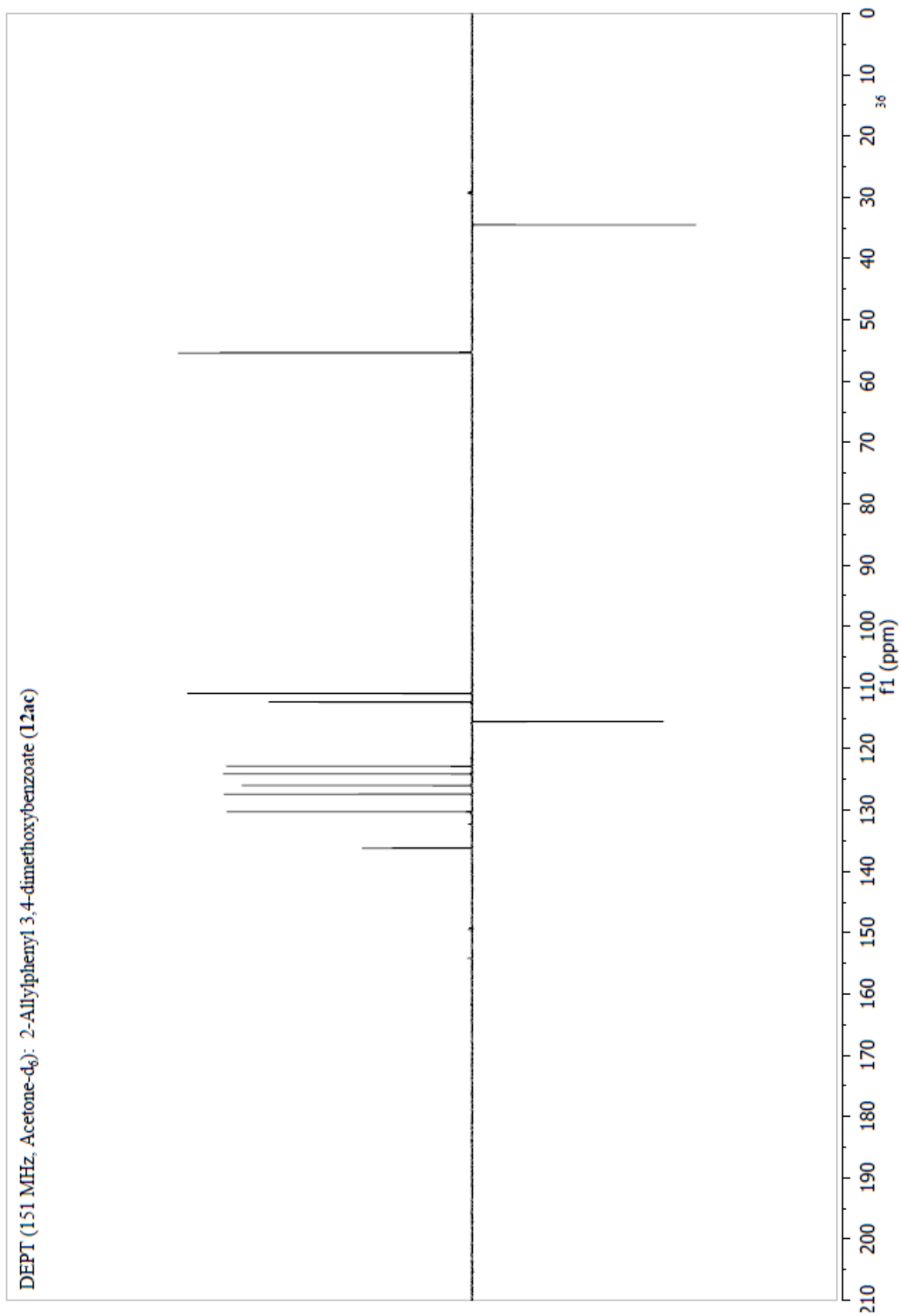


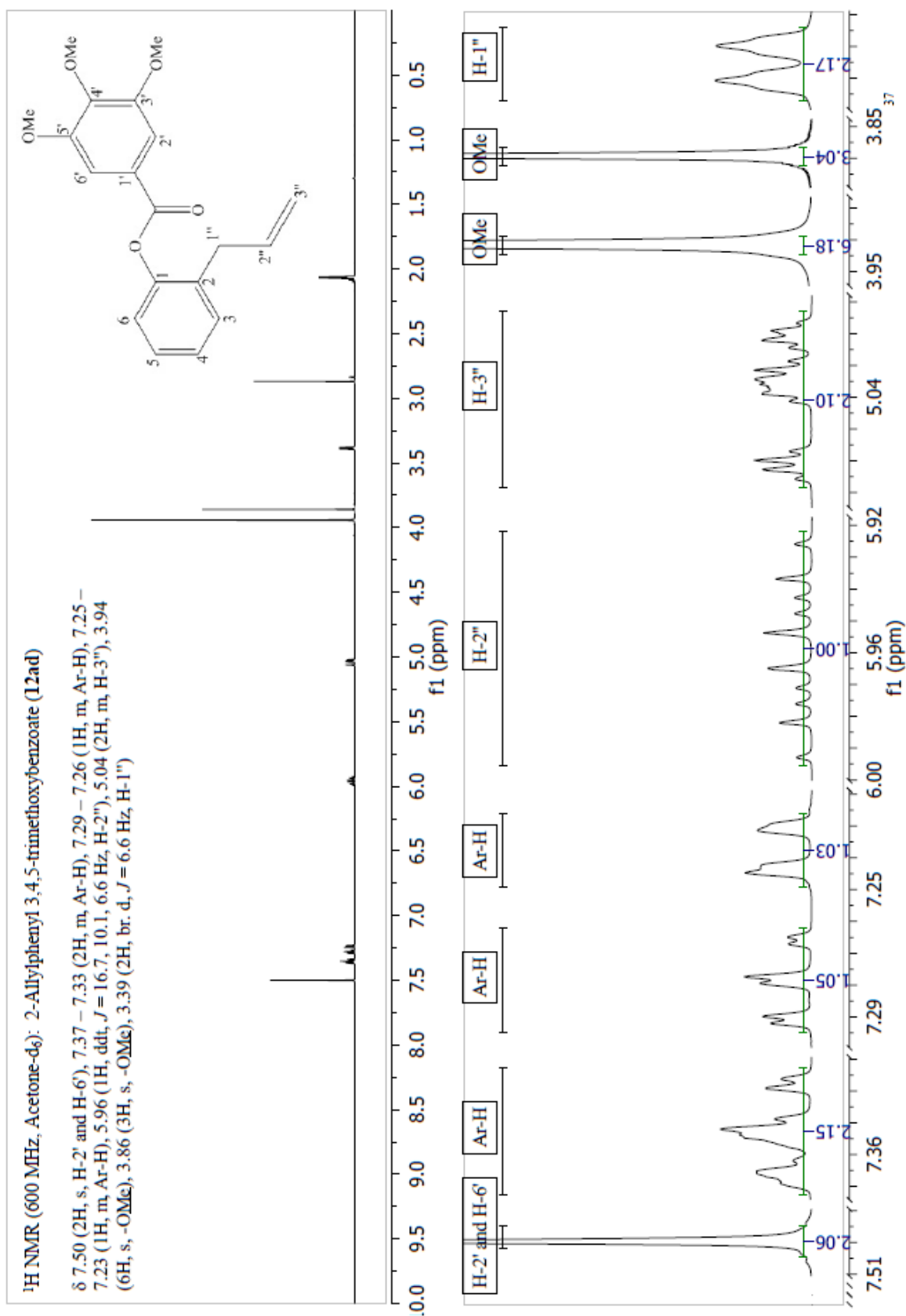


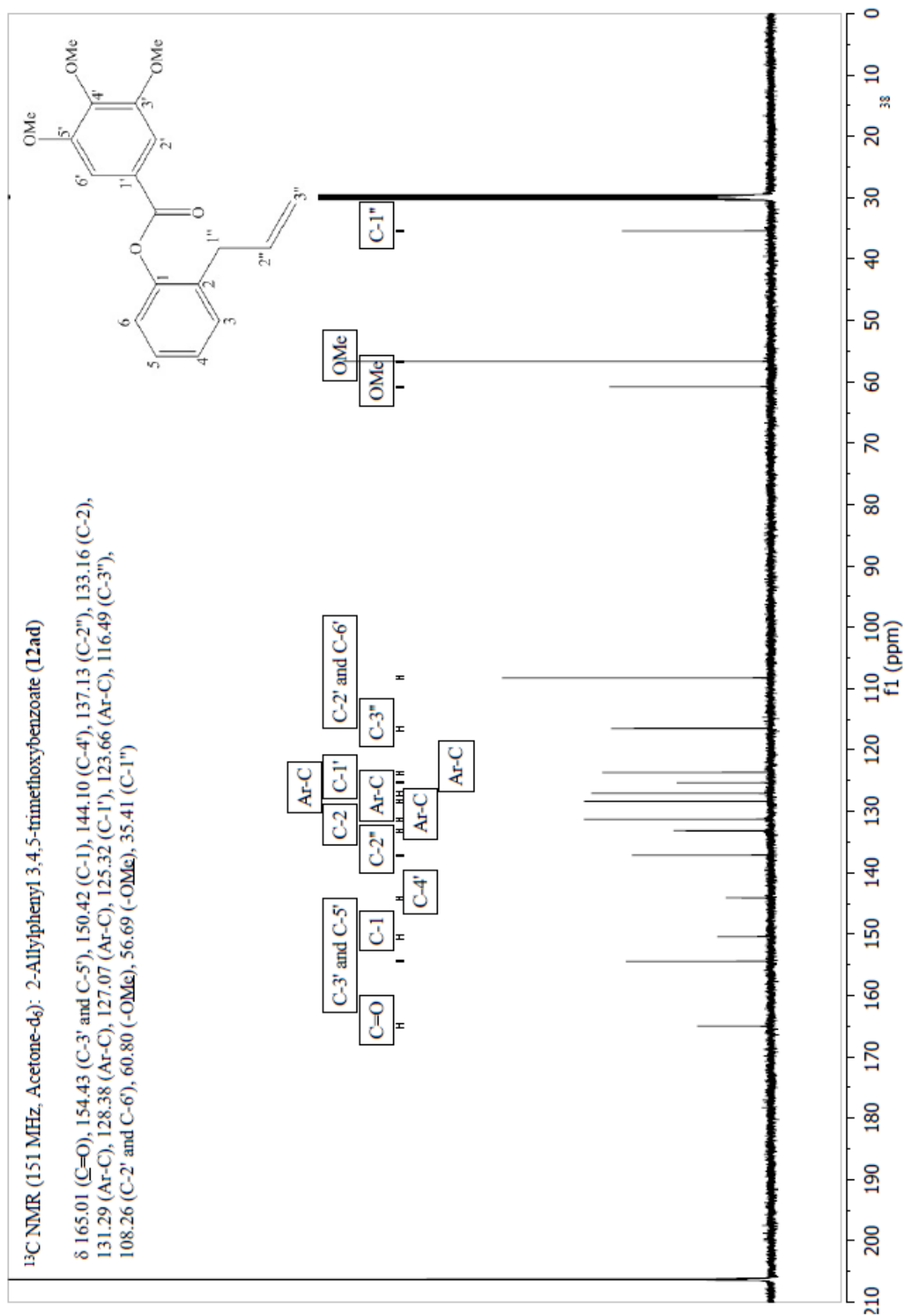


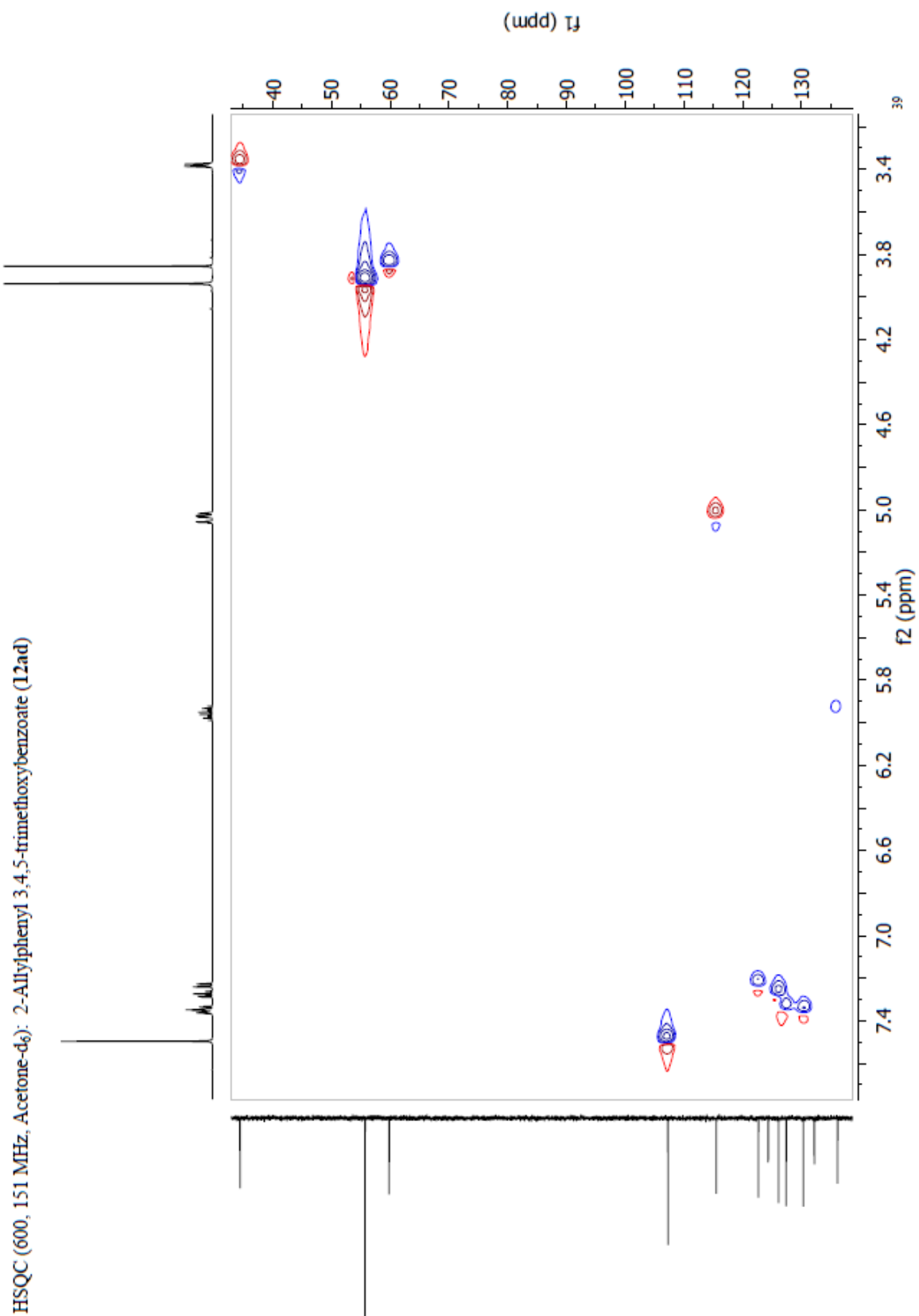
HSQC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 3,4-dimethoxybenzoate (**12ac**)

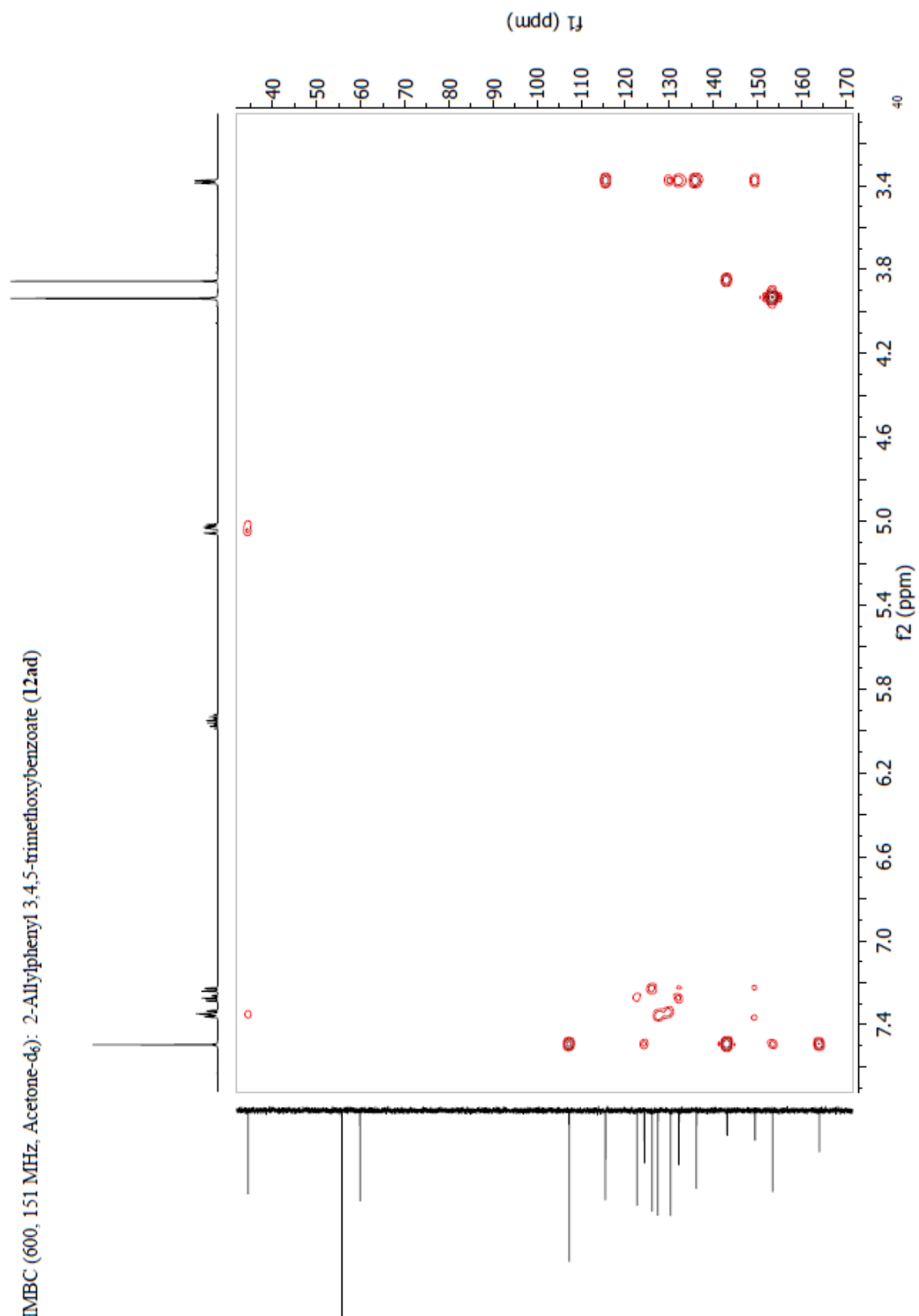


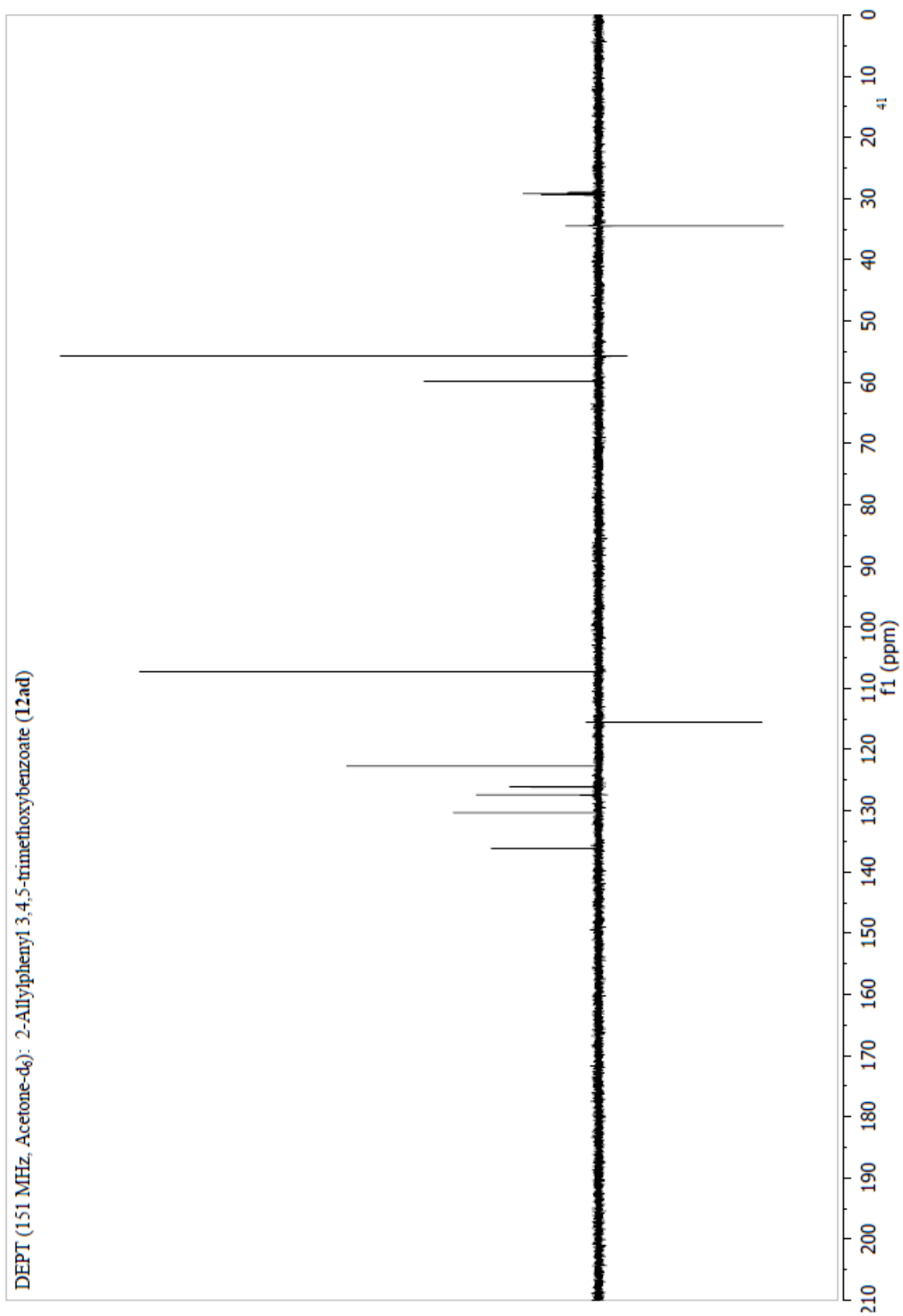


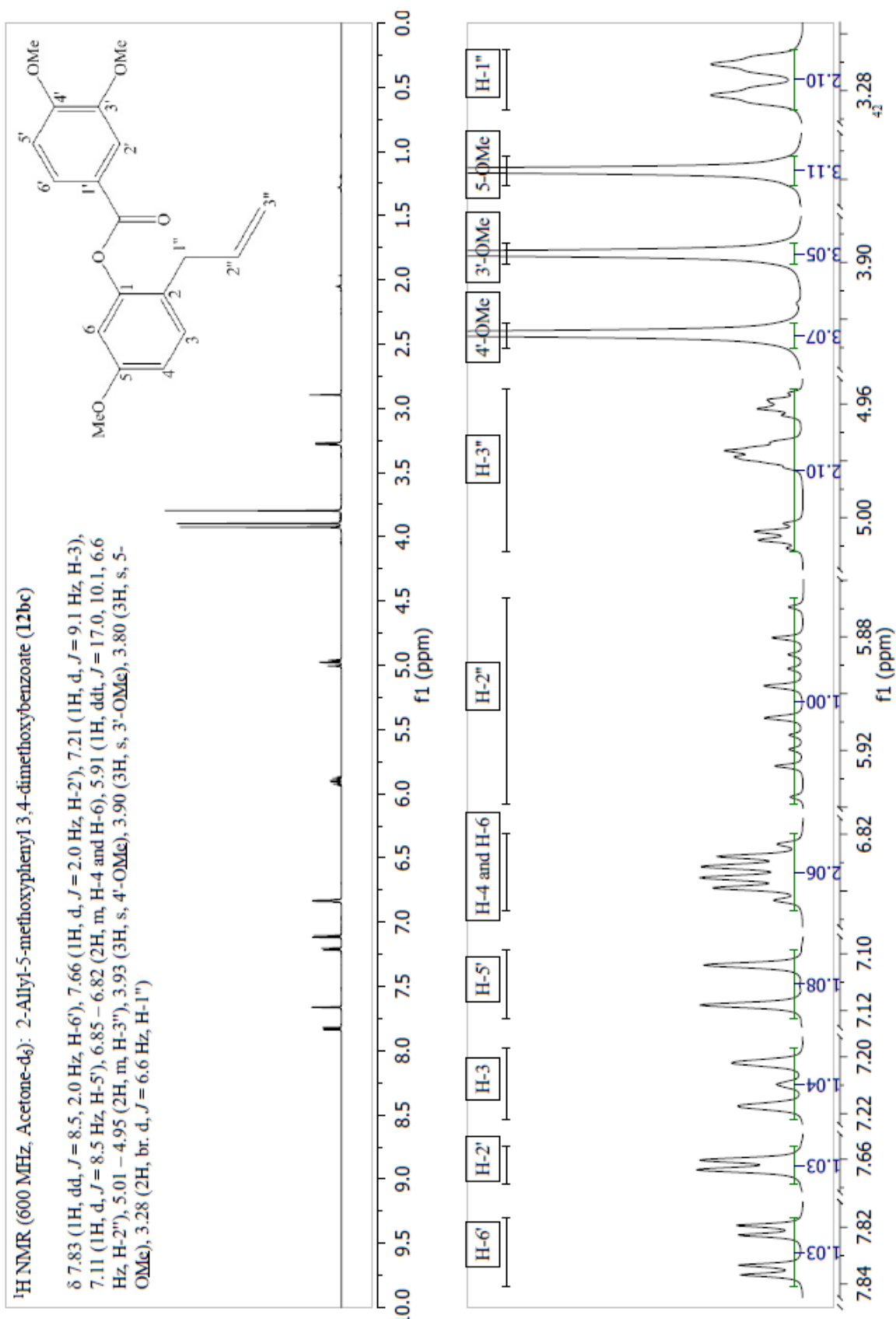


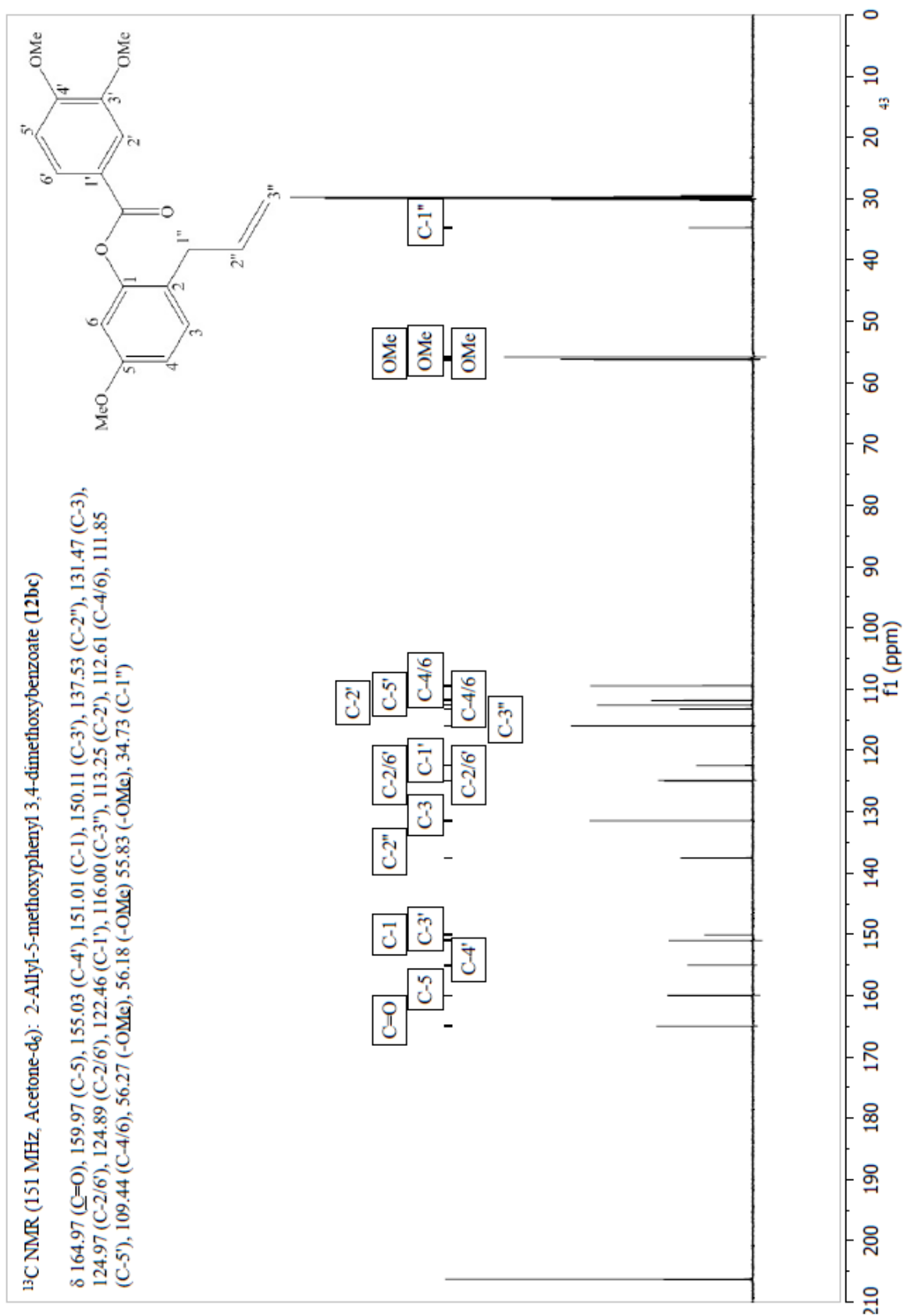


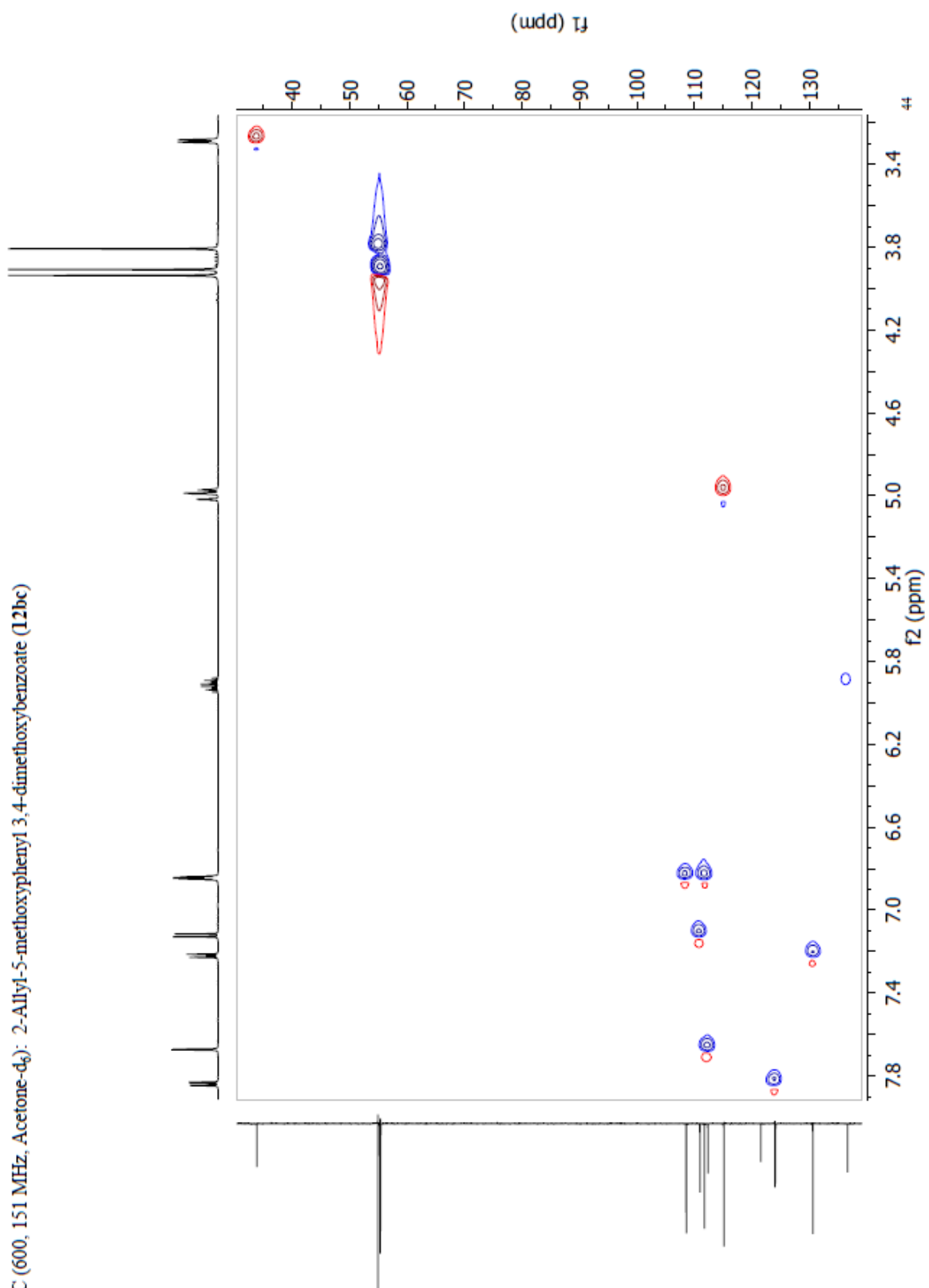


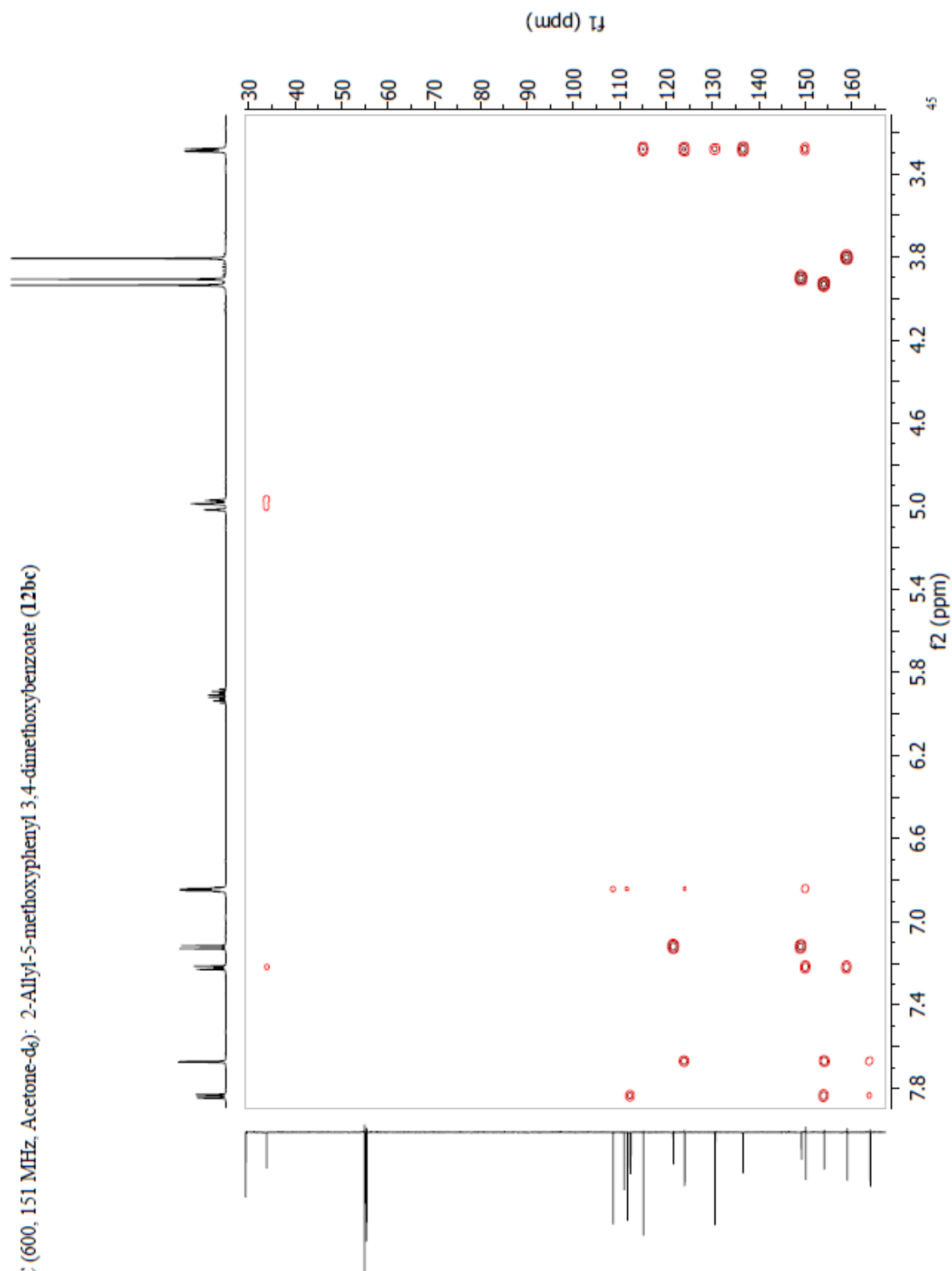
HMBC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 3,4,5-trimethoxybenzoate (12ad)

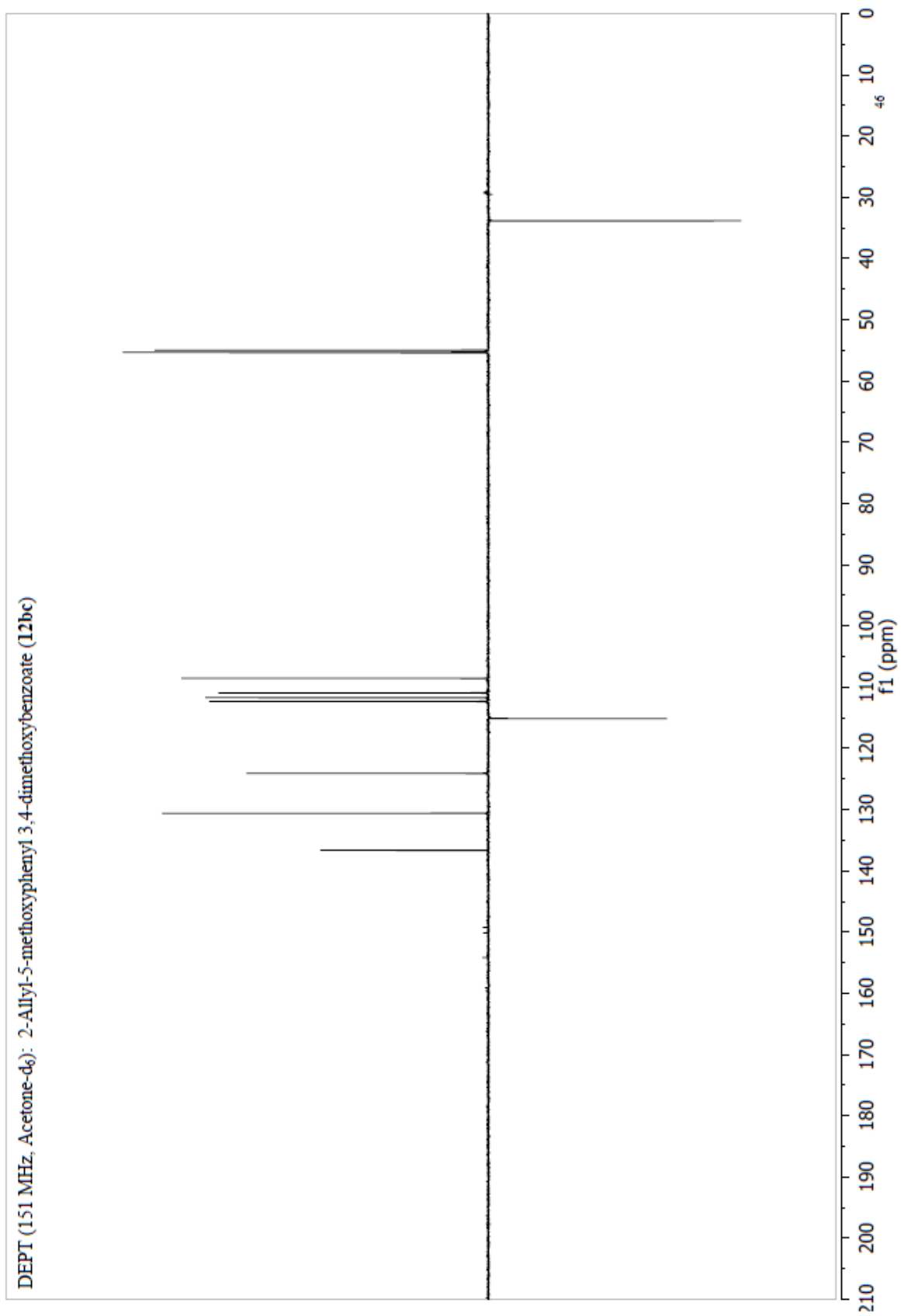


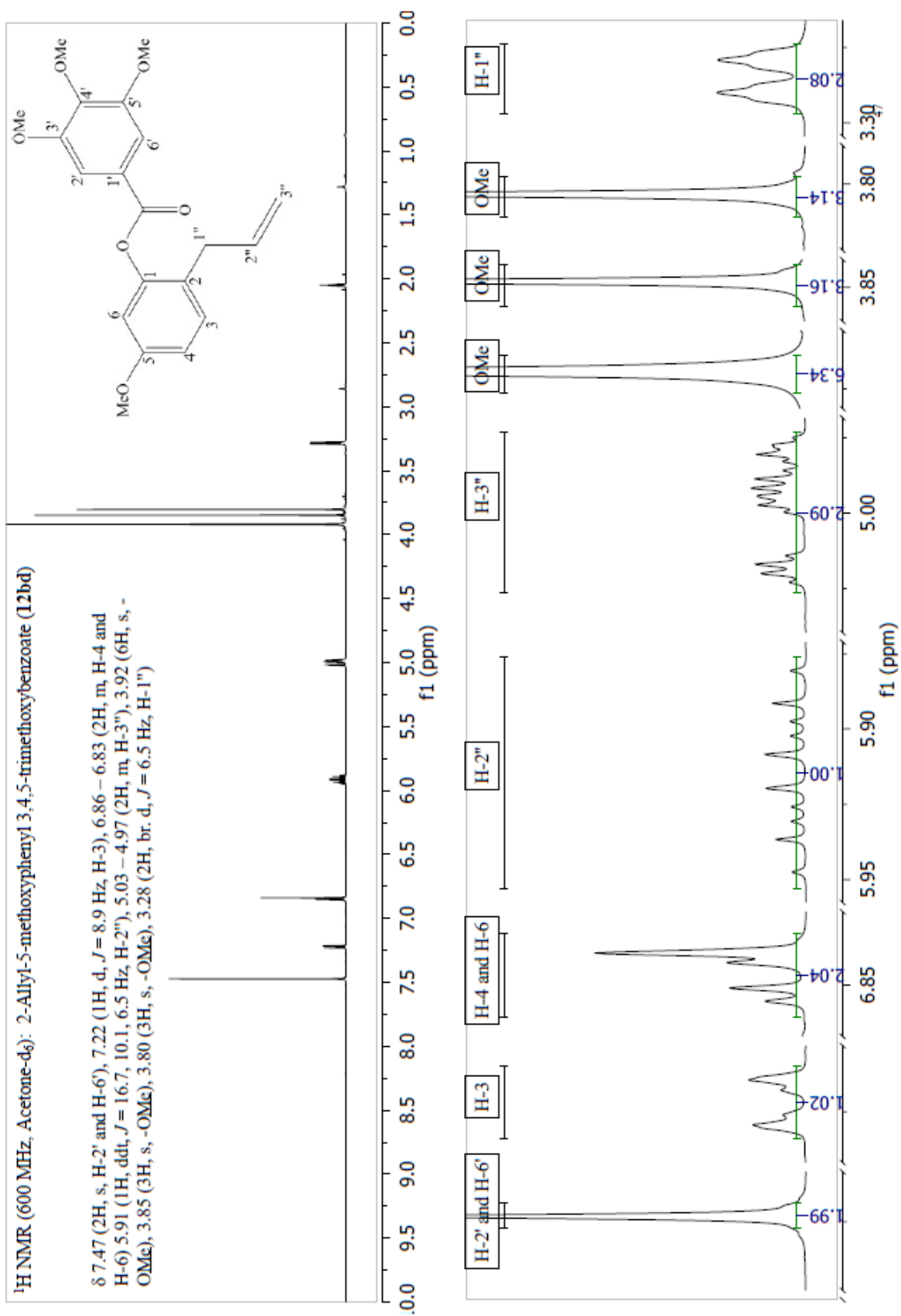




HSQC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 3,4-dimethoxybenzoate (**12bc**)

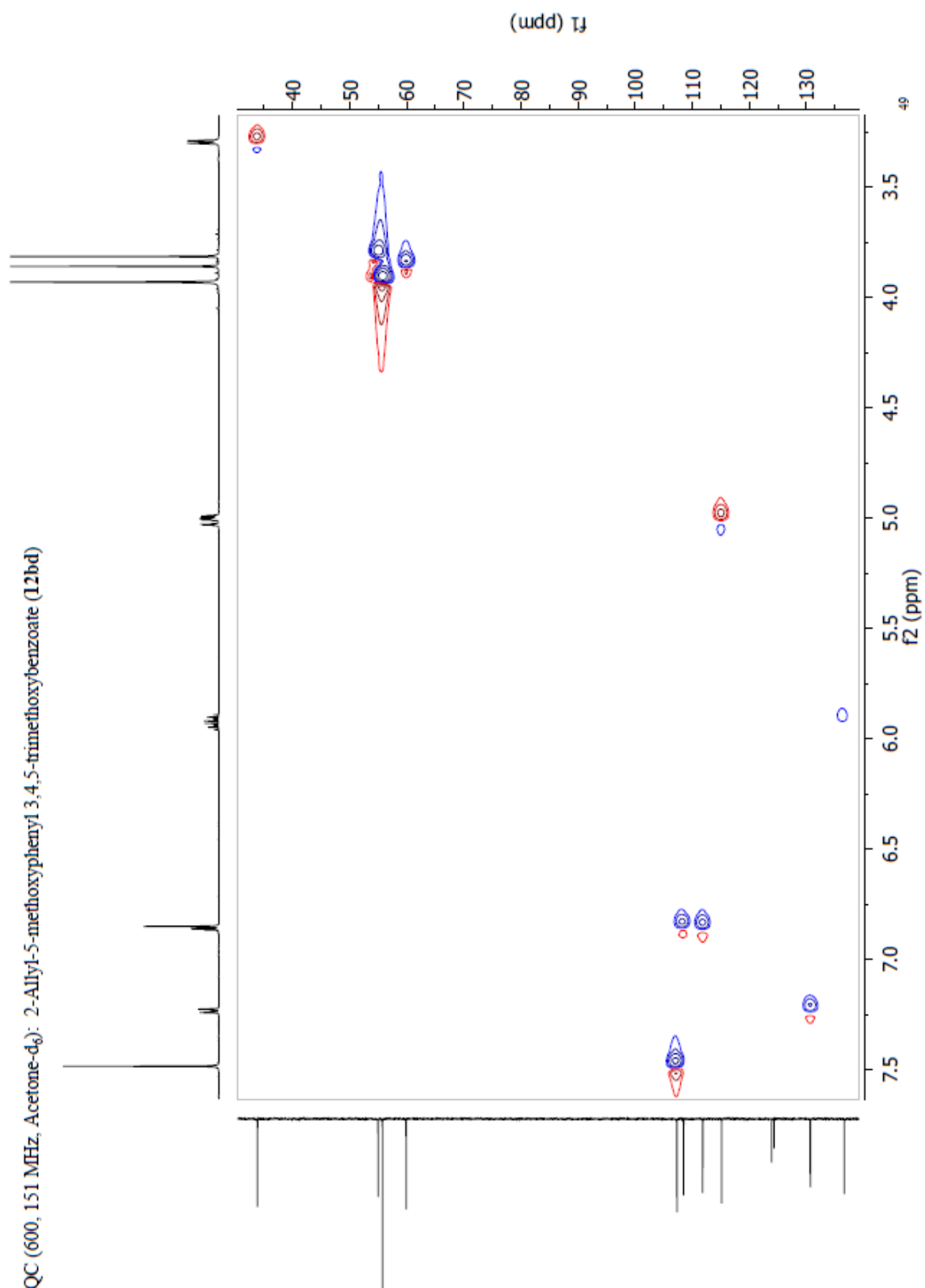
HMBC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 3,4-dimethoxybenzoate (**12bc**)



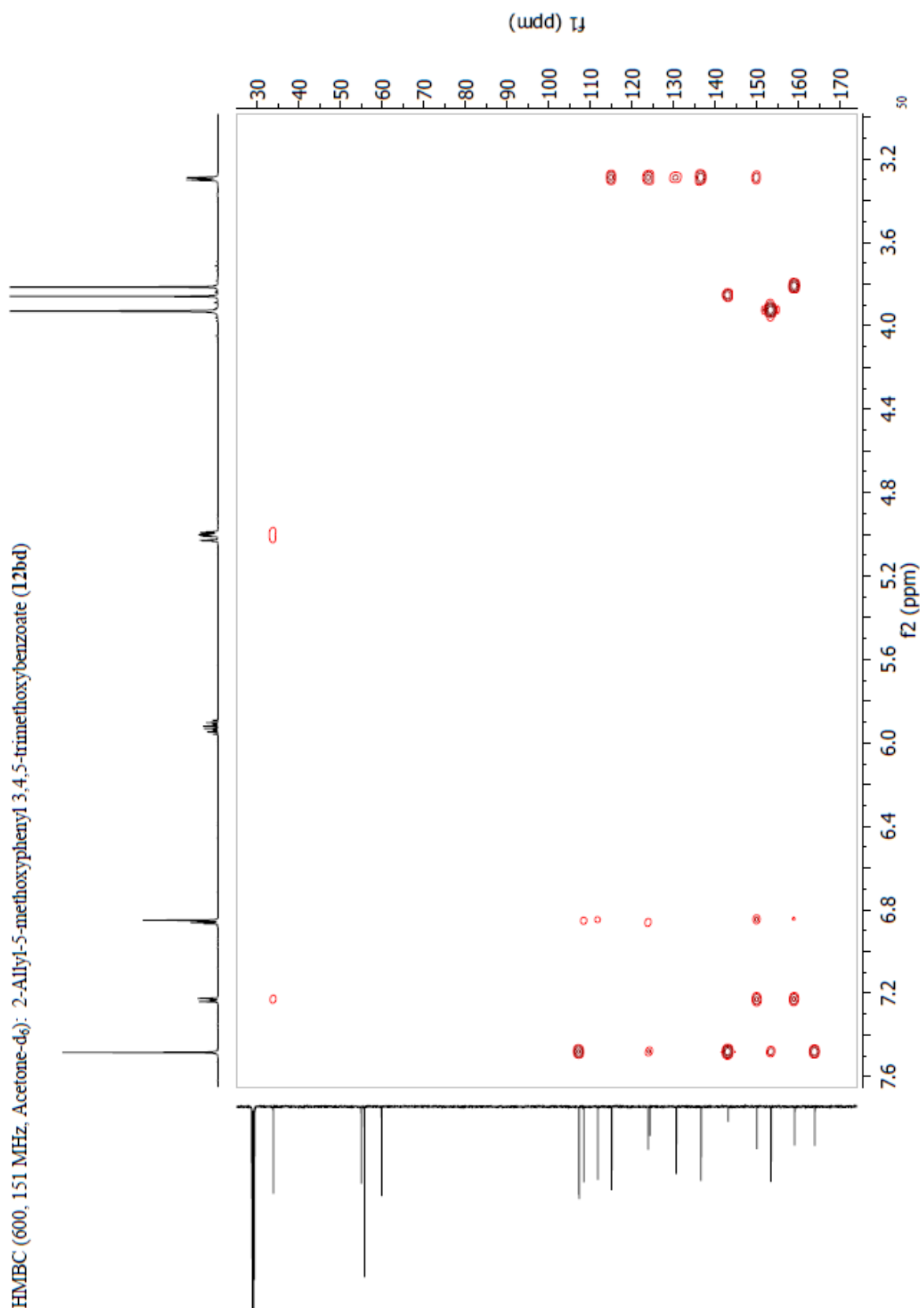


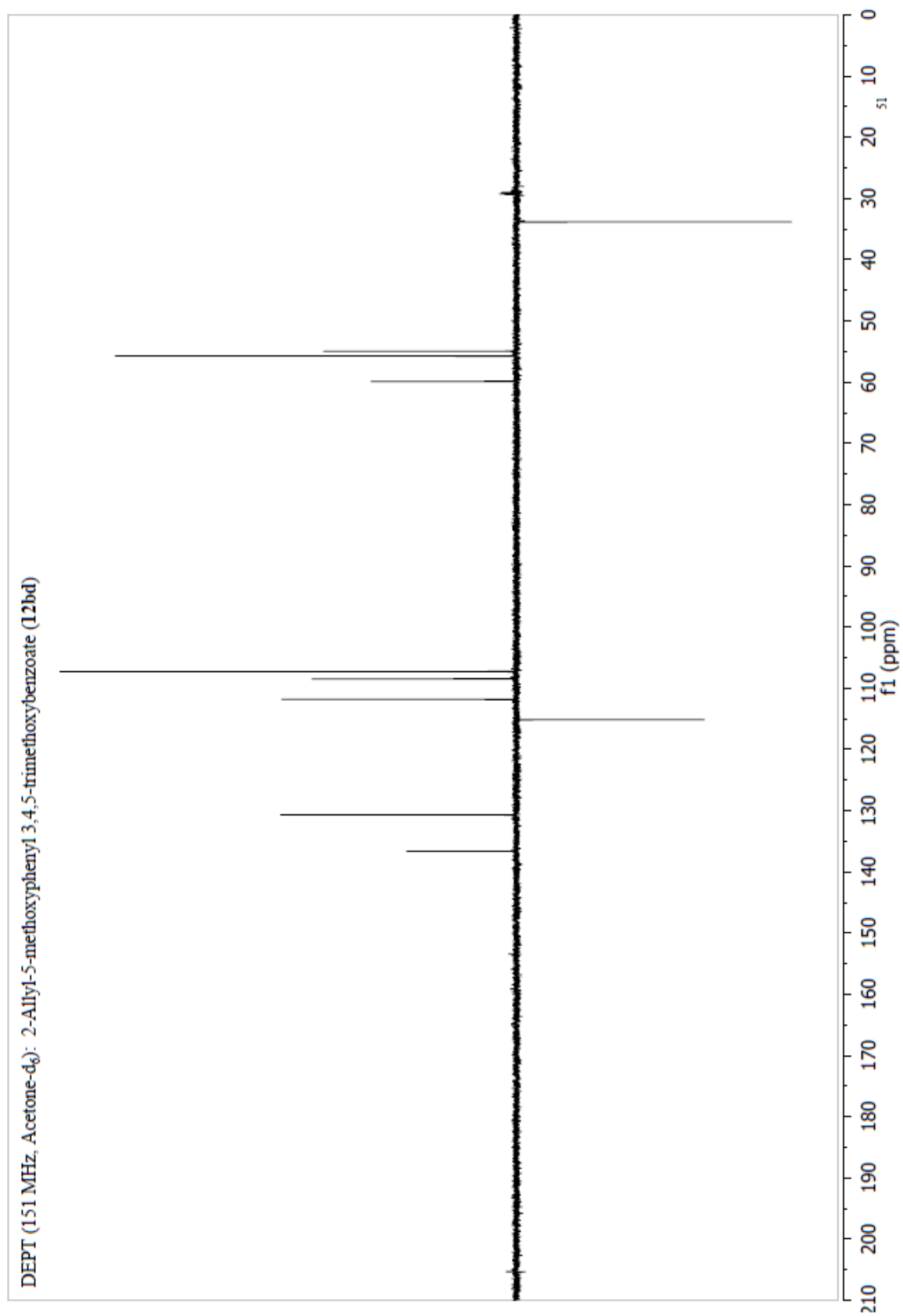


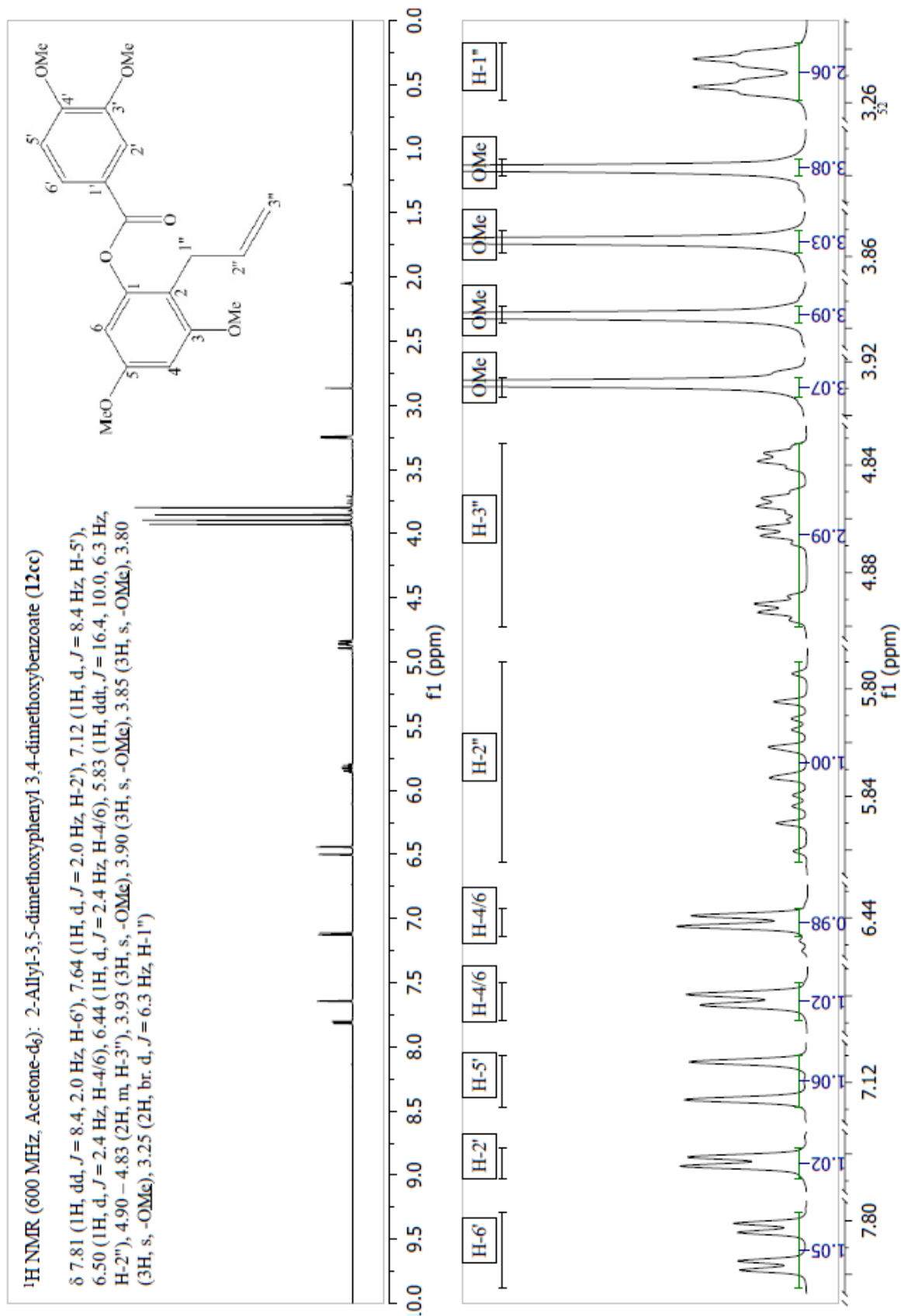
HSQC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 3,4,5-trimethoxybenzoate (**12bd**)



HMBC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 3,4,5-trimethoxybenzoate (12bd)

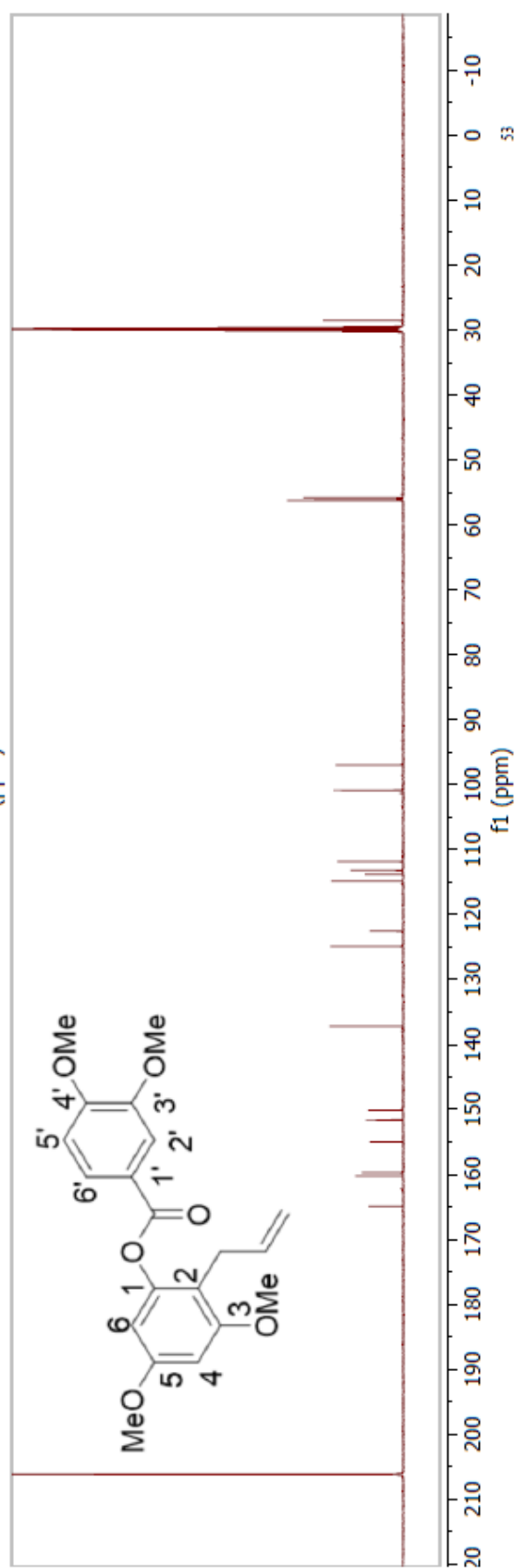
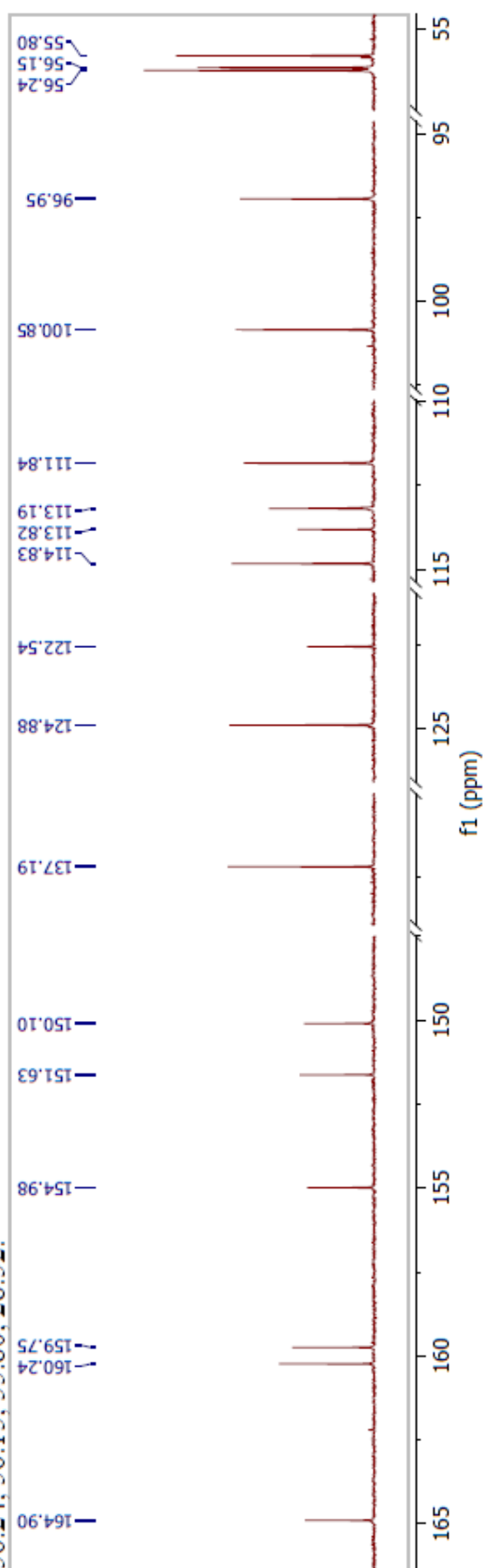




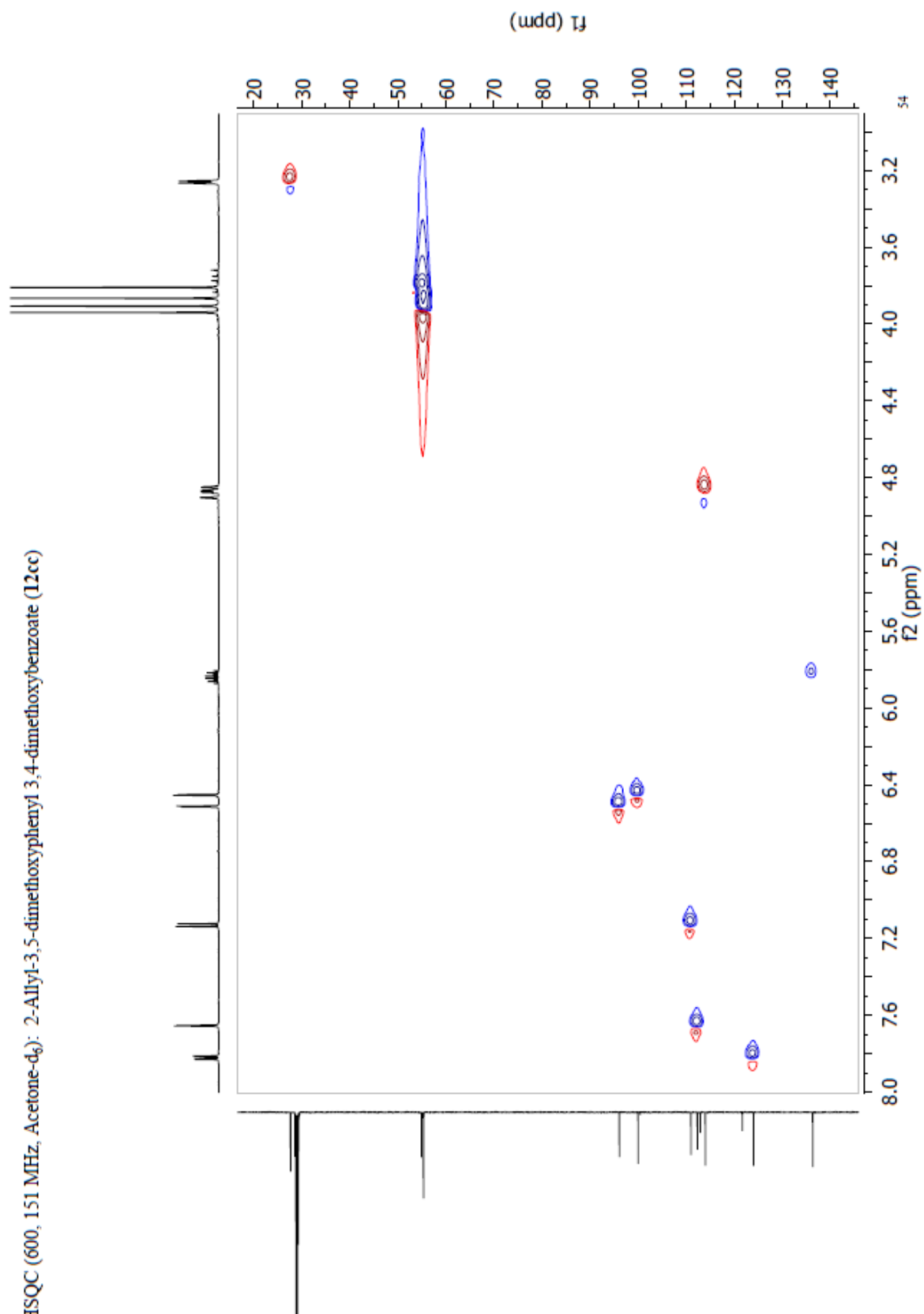


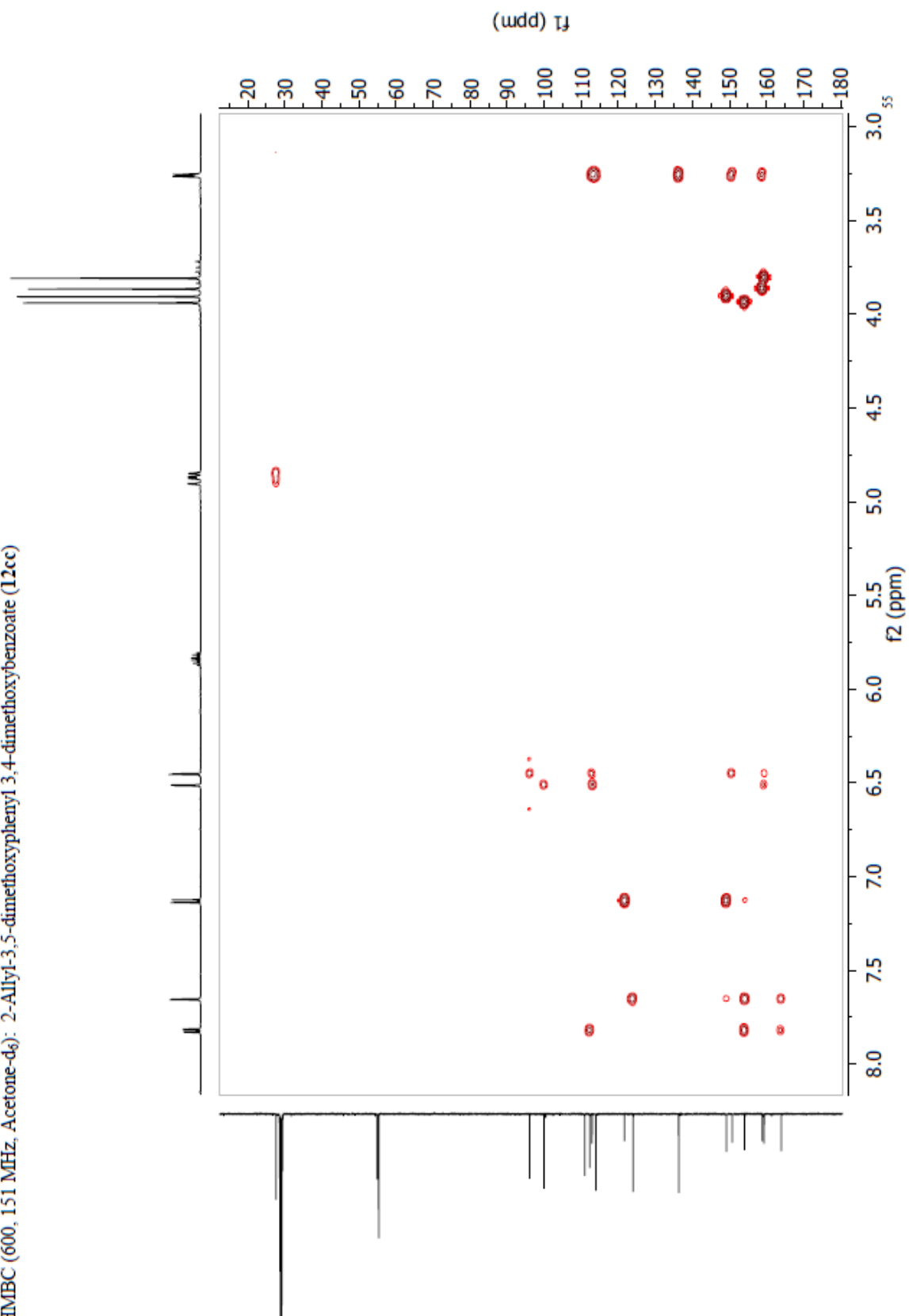
¹³C NMR (151 MHz, Acetone-d₆): 2-Allyl-3,5-dimethoxyphenyl 3,4-dimethoxybenzoate (12cc)

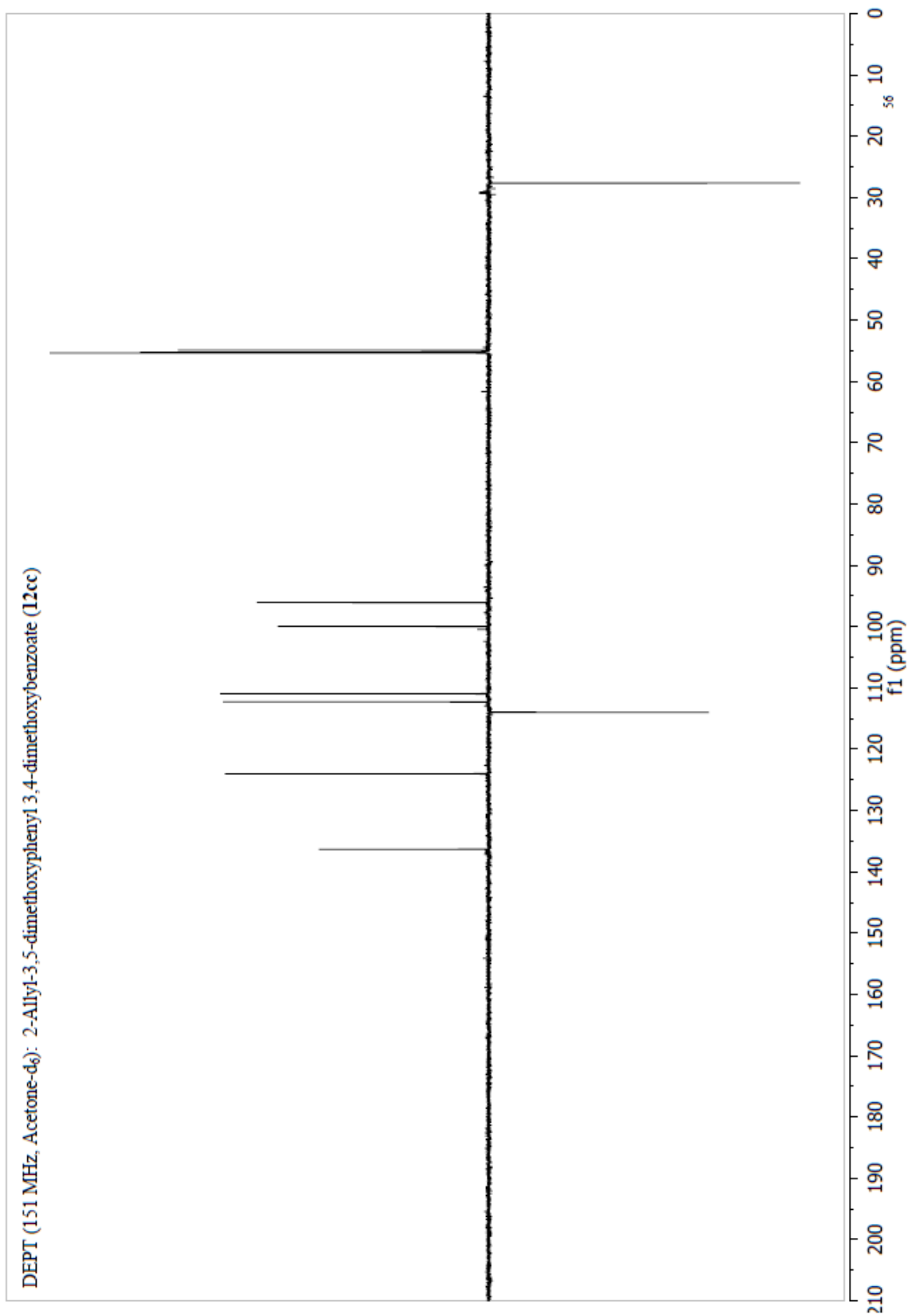
δ 164.90, 160.24, 159.75, 154.98, 151.63, 150.10, 137.19, 124.88, 122.54, 114.83, 113.82, 113.19, 111.84, 100.85, 96.95, 56.24, 56.15, 55.80, 28.52.

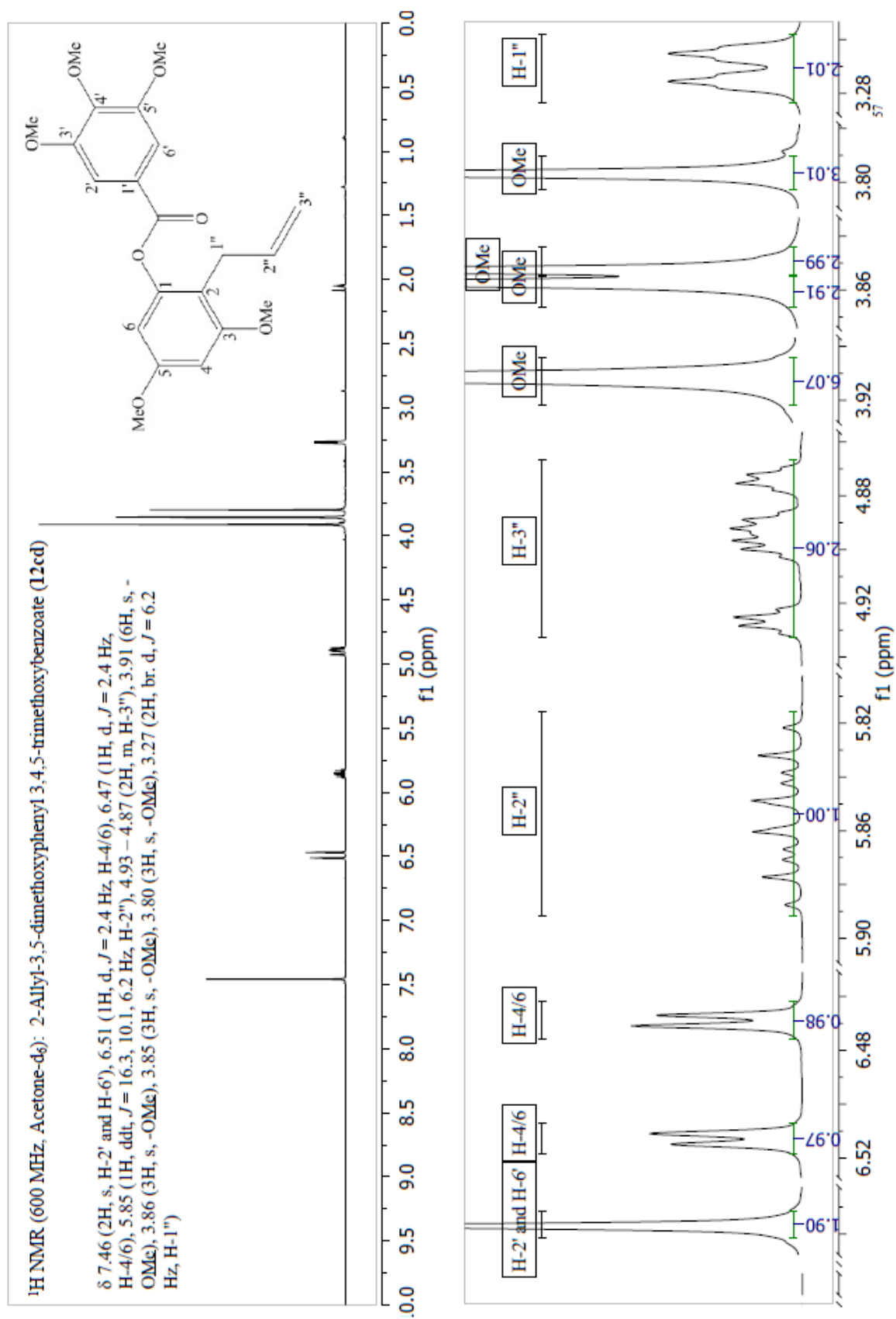


HSQC (600, 151 MHz, Acetone- d_6): 2-Allyl-3,5-dimethoxyphenyl 3,4-dimethoxybenzoate (12cc)



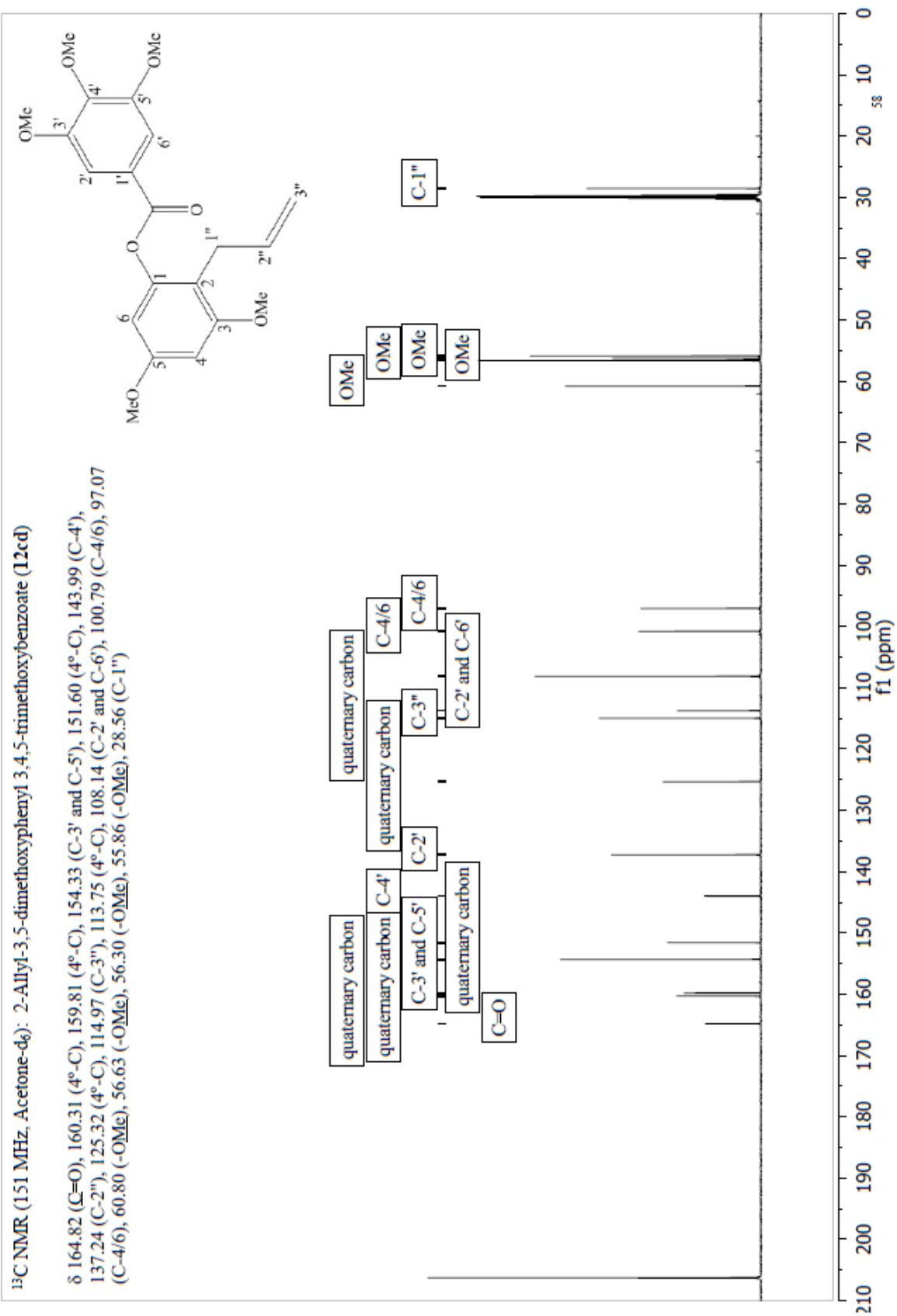
HMBC (600, 151 MHz, Acetone- d_6): 2-Allyl-3,5-dimethoxyphenyl 3,4-dimethoxybenzoate (**12cc**)



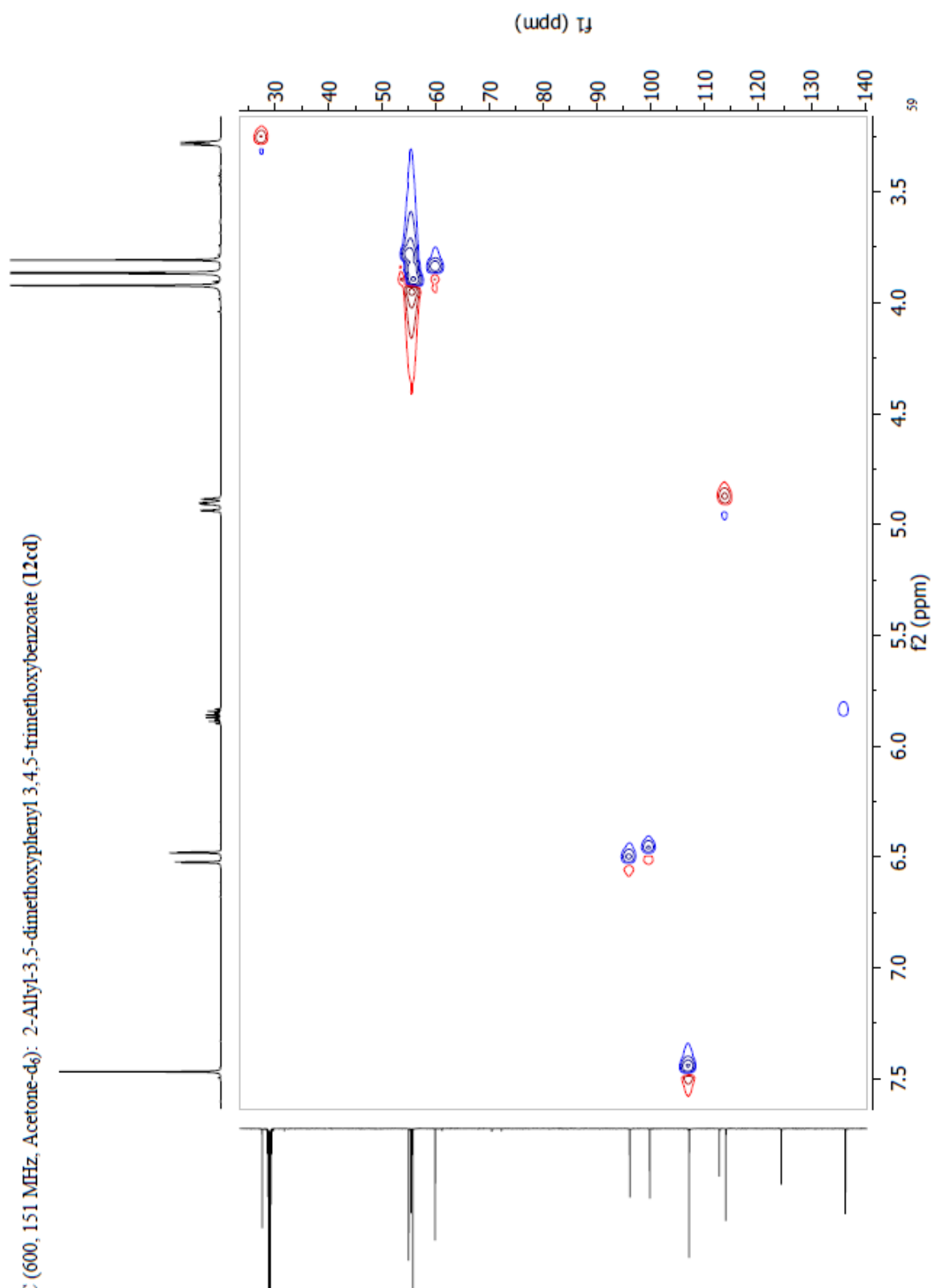


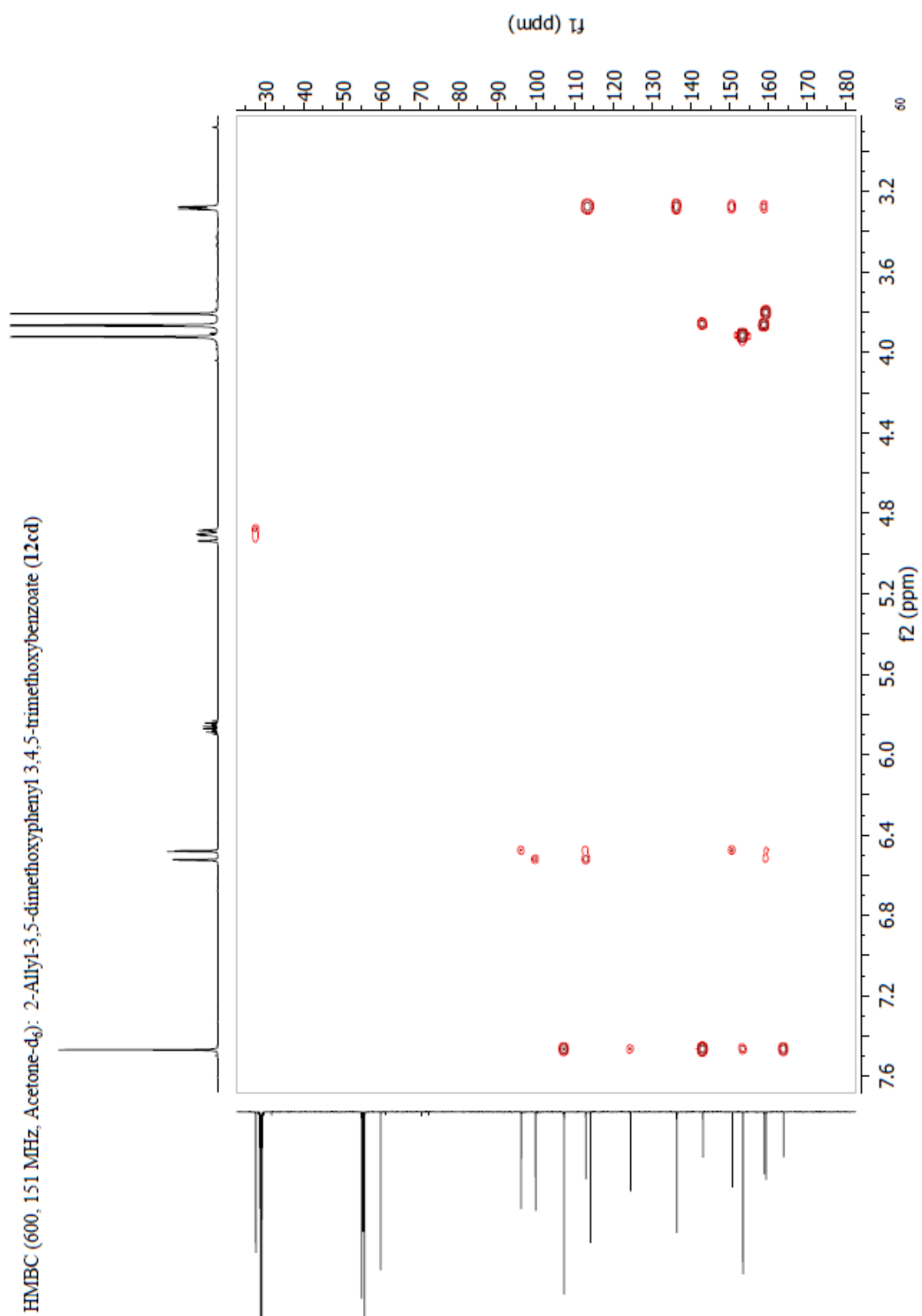
¹³C NMR (151 MHz, Acetone-d₆): 2-Allyl-3,5-dimethoxyphenyl 3,4,5-trimethoxybenzoate (**12cd**)

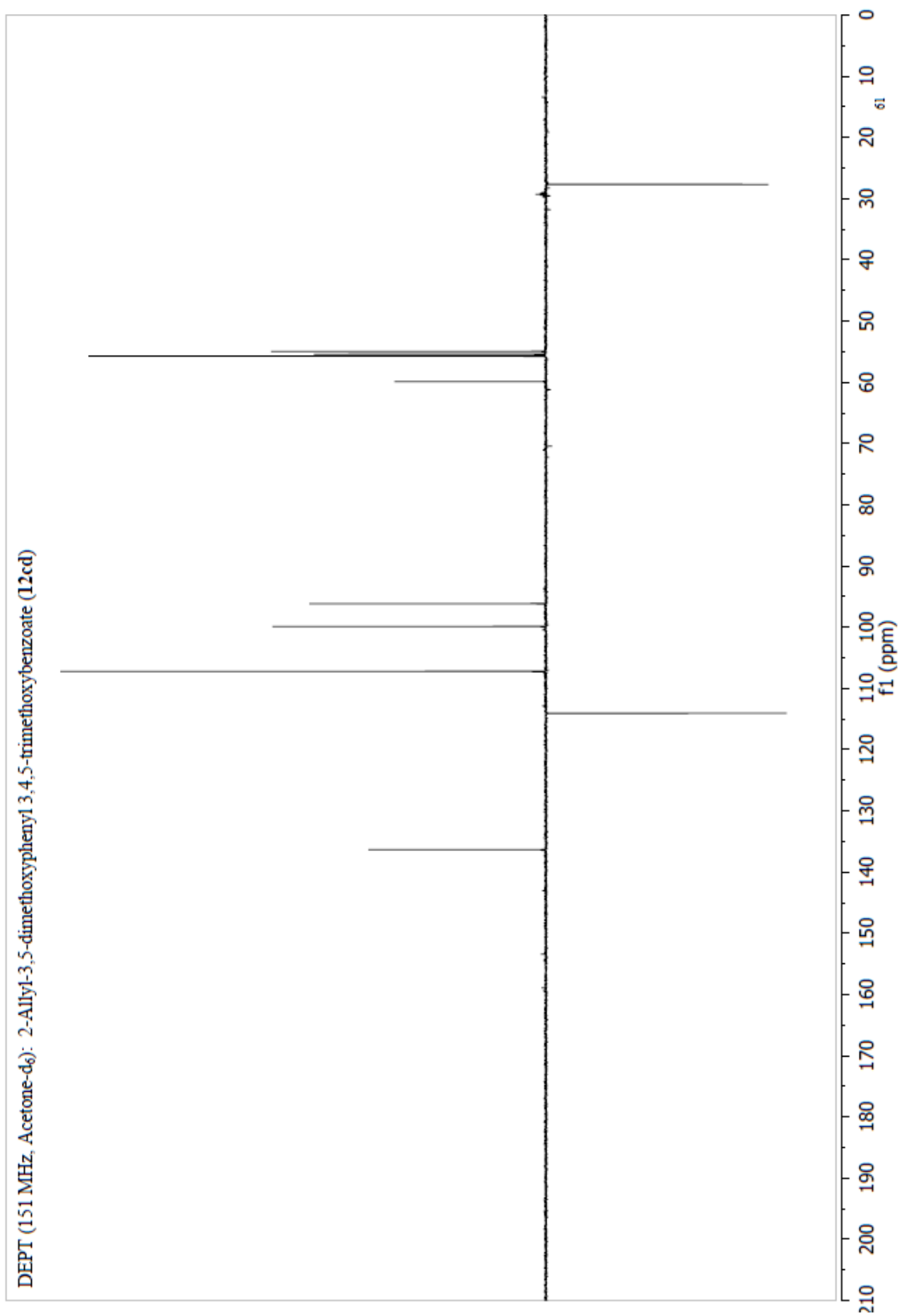
δ 164.82 (C=O), 160.31 (4^o-C), 159.81 (4^o-C), 154.33 (C-3' and C-5'), 151.60 (4^o-C), 143.99 (C-4'), 137.24 (C-2''), 125.32 (4^o-C), 114.97 (C-3''), 113.75 (4^o-C), 108.14 (C-2' and C-6'), 100.79 (C-4/6), 97.07 (C-4/6), 60.80 (-OMe), 56.63 (-OMe), 55.86 (-OMe), 28.56 (-OMe), 28.56 (C-1'')

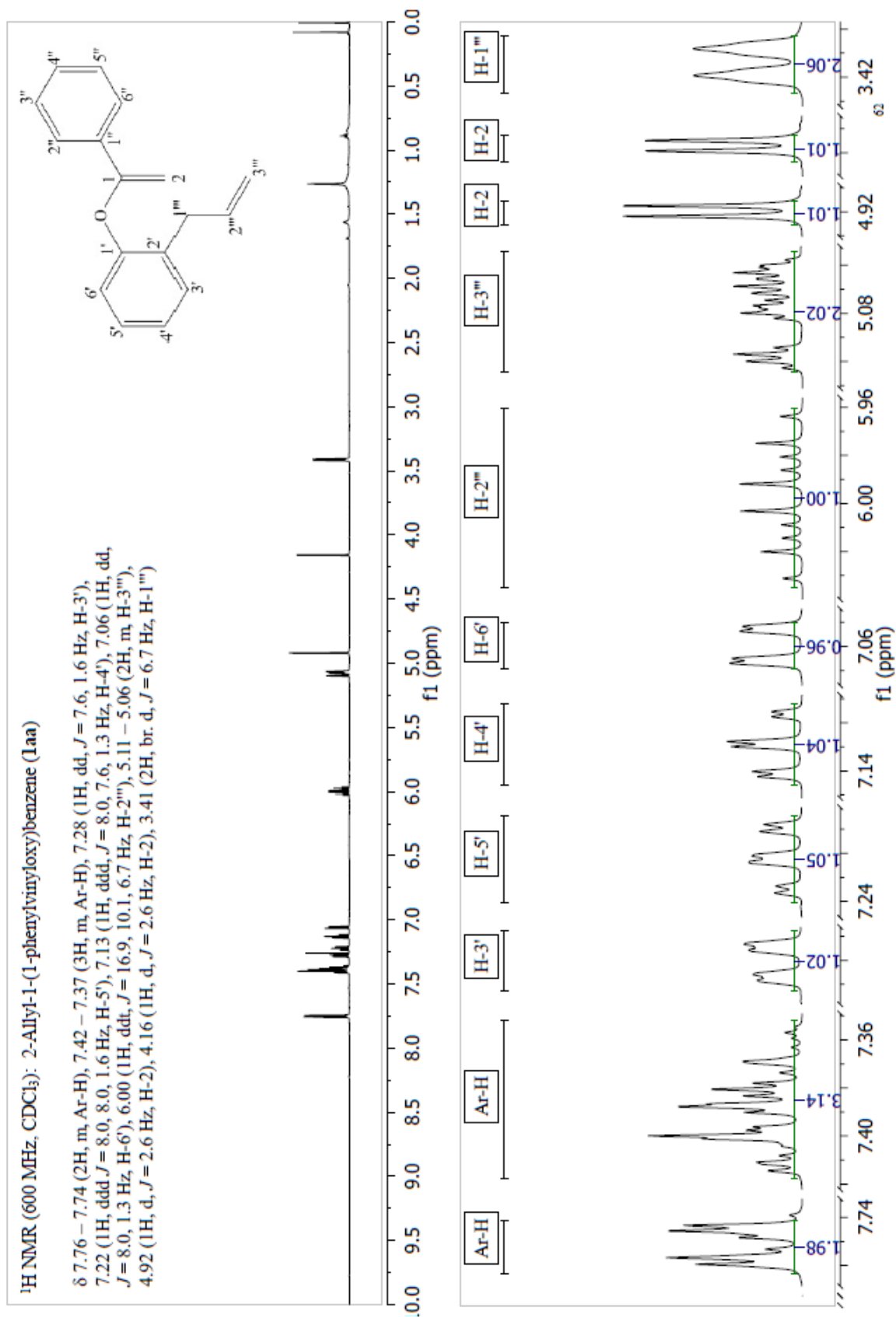


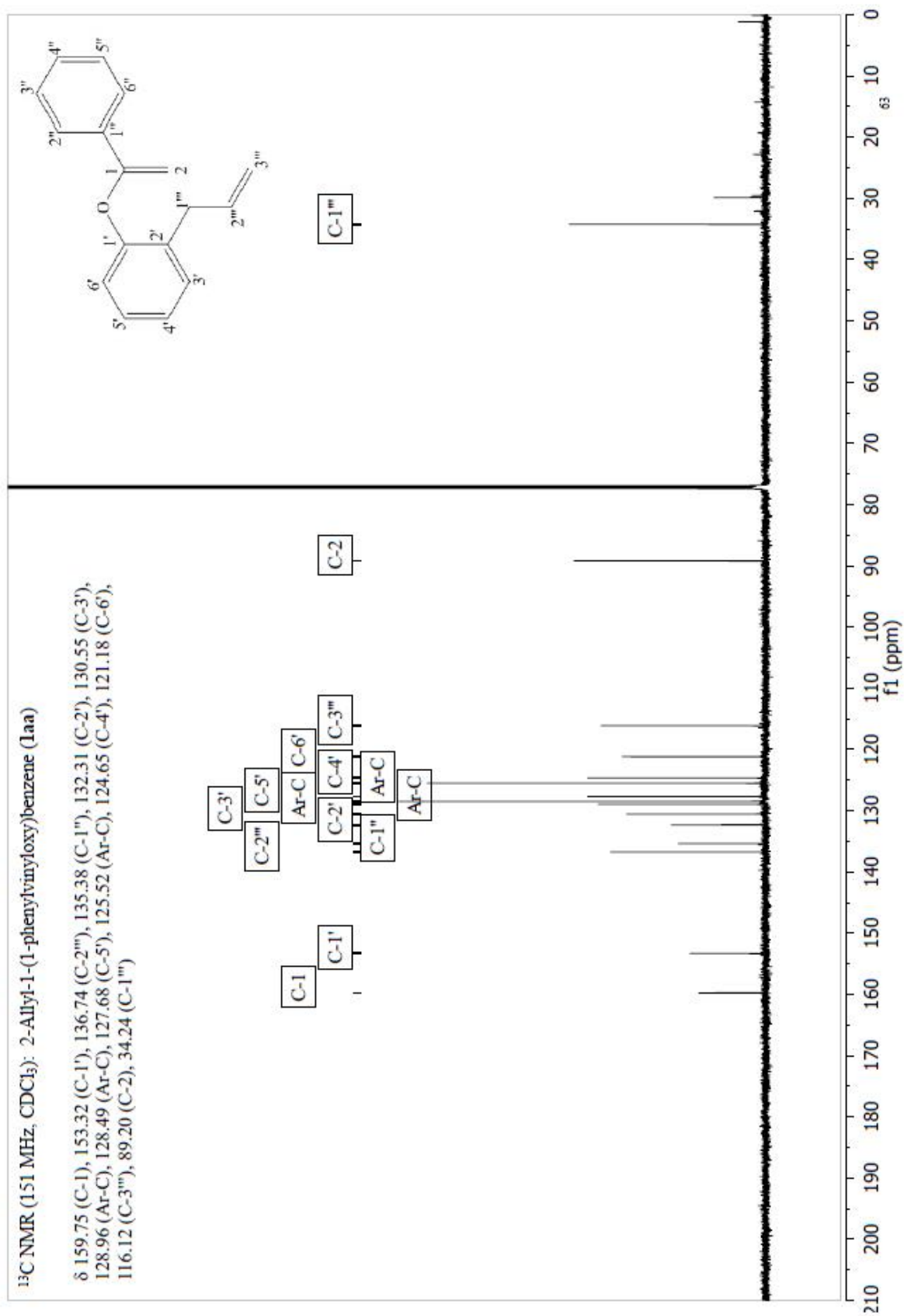
HSQC (600, 151 MHz, Acetone- d_6): 2-Allyl-3,5-dimethoxyphenyl 3,4,5-trimethoxybenzoate (**12cd**)

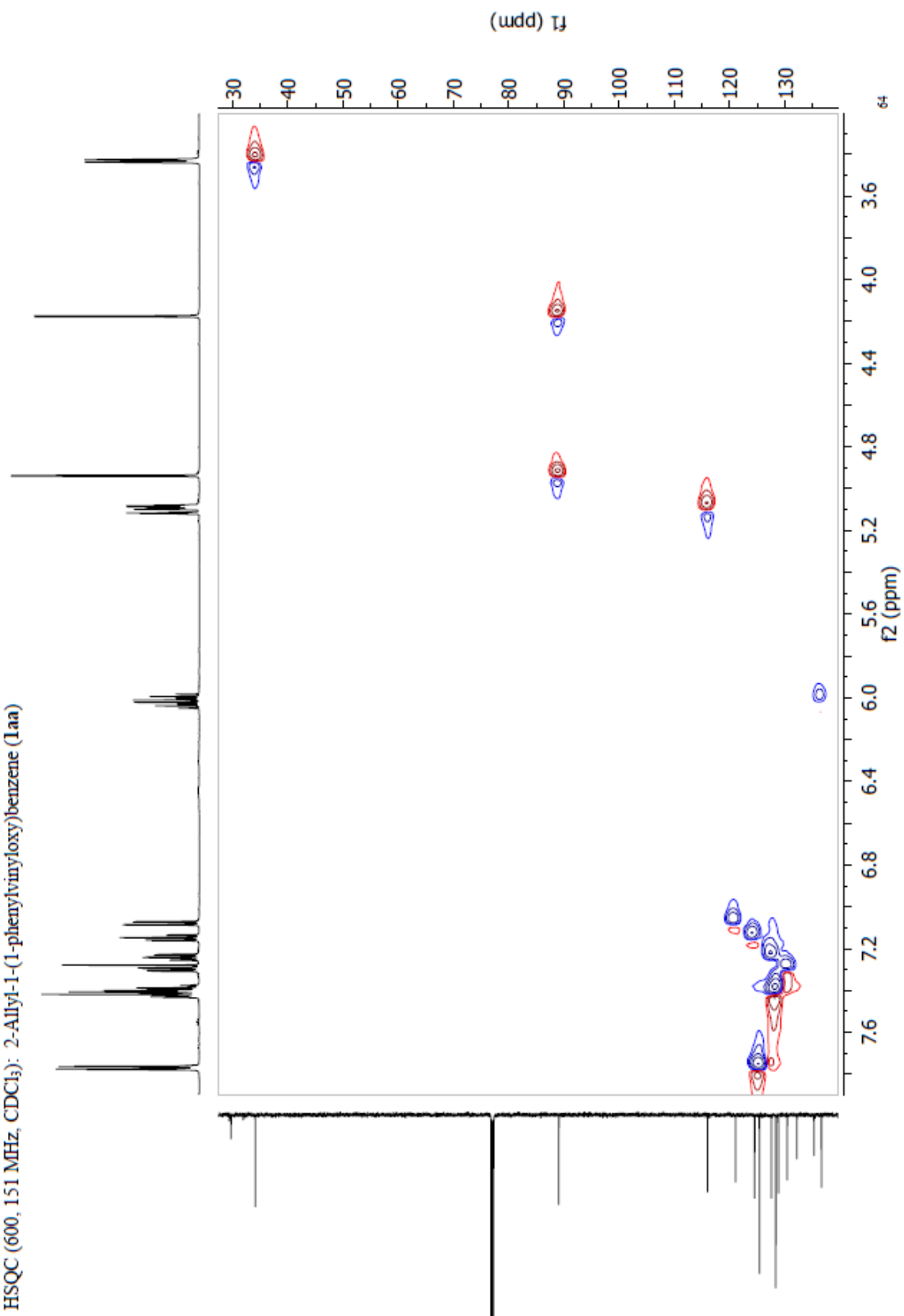


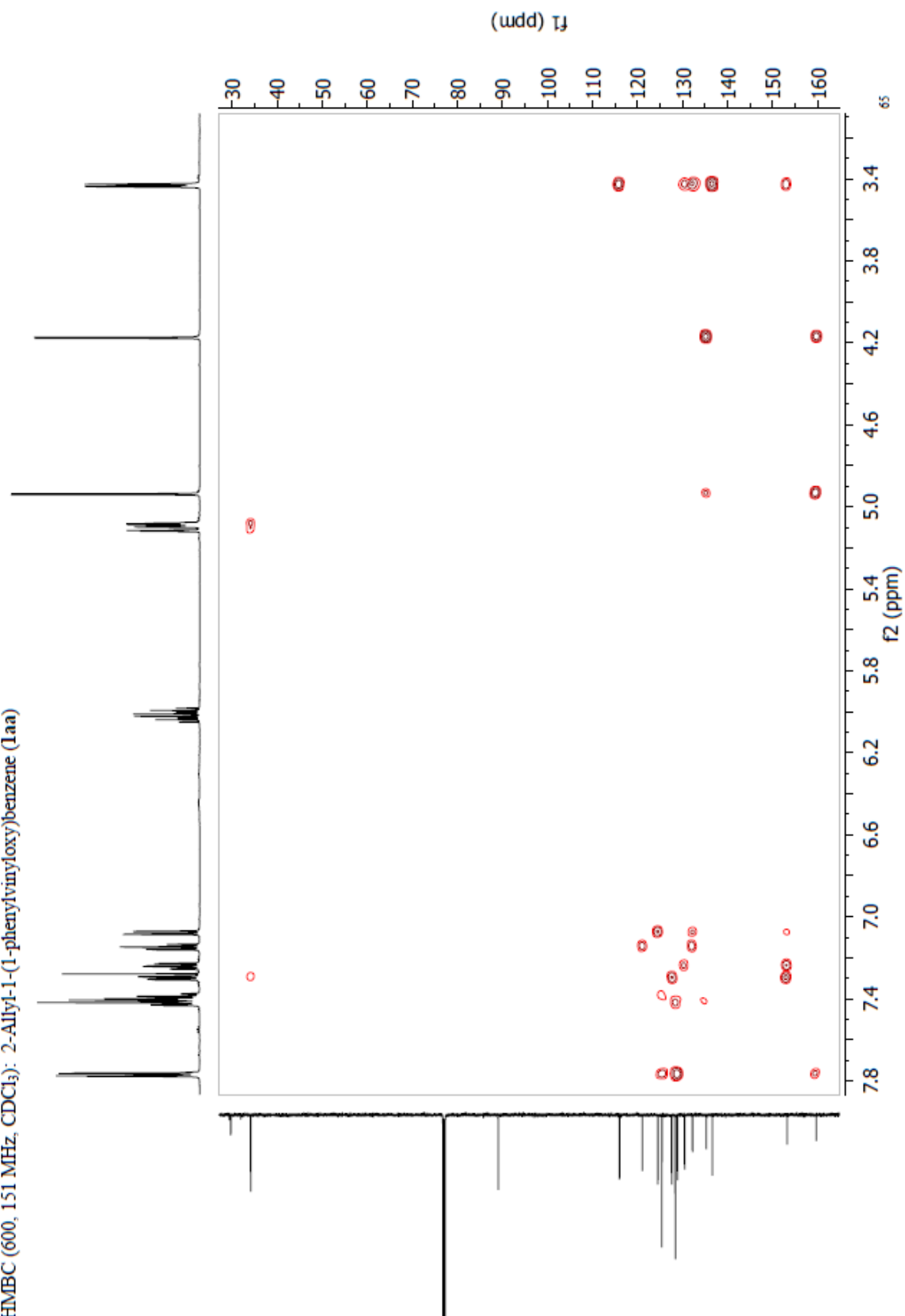


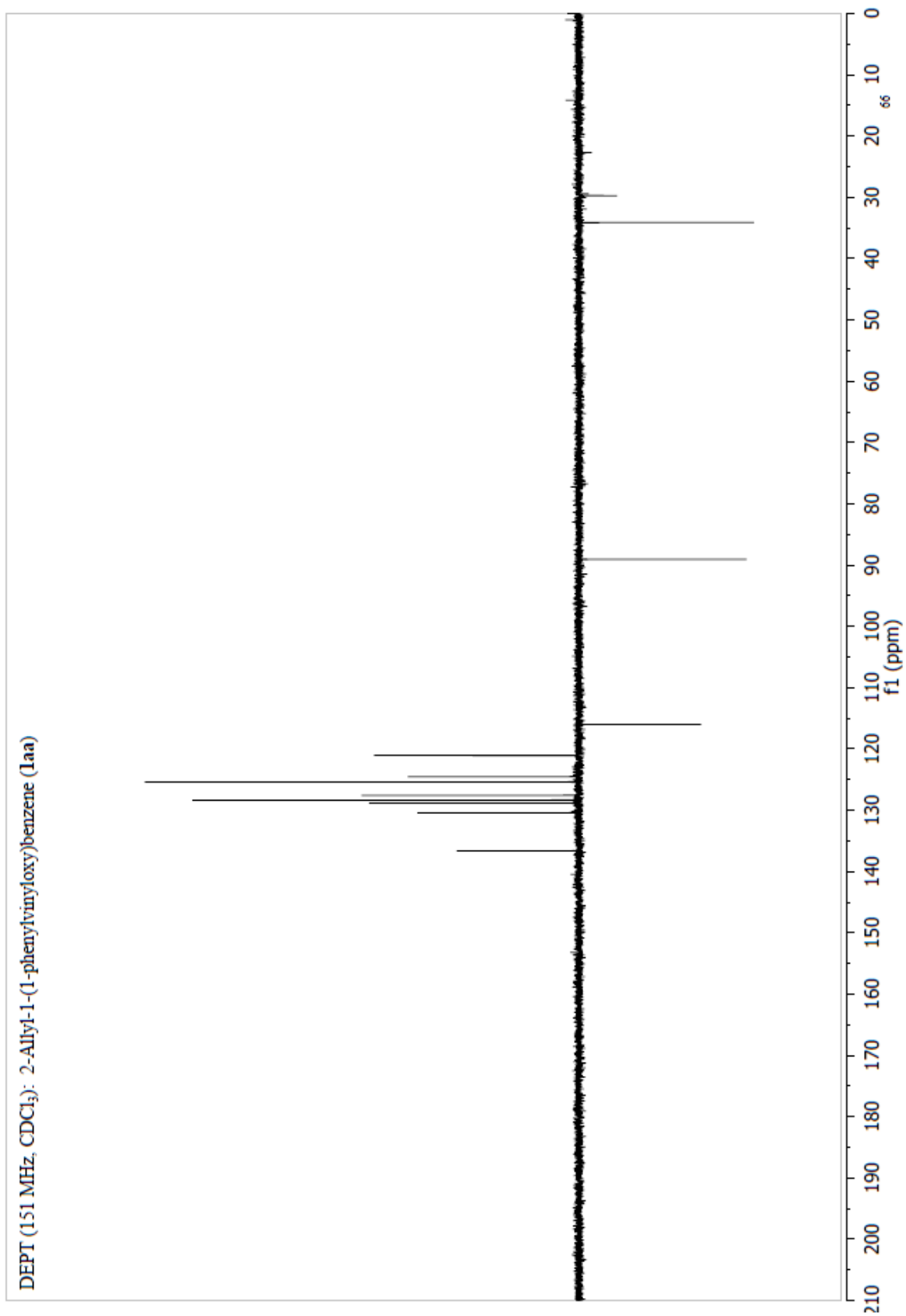


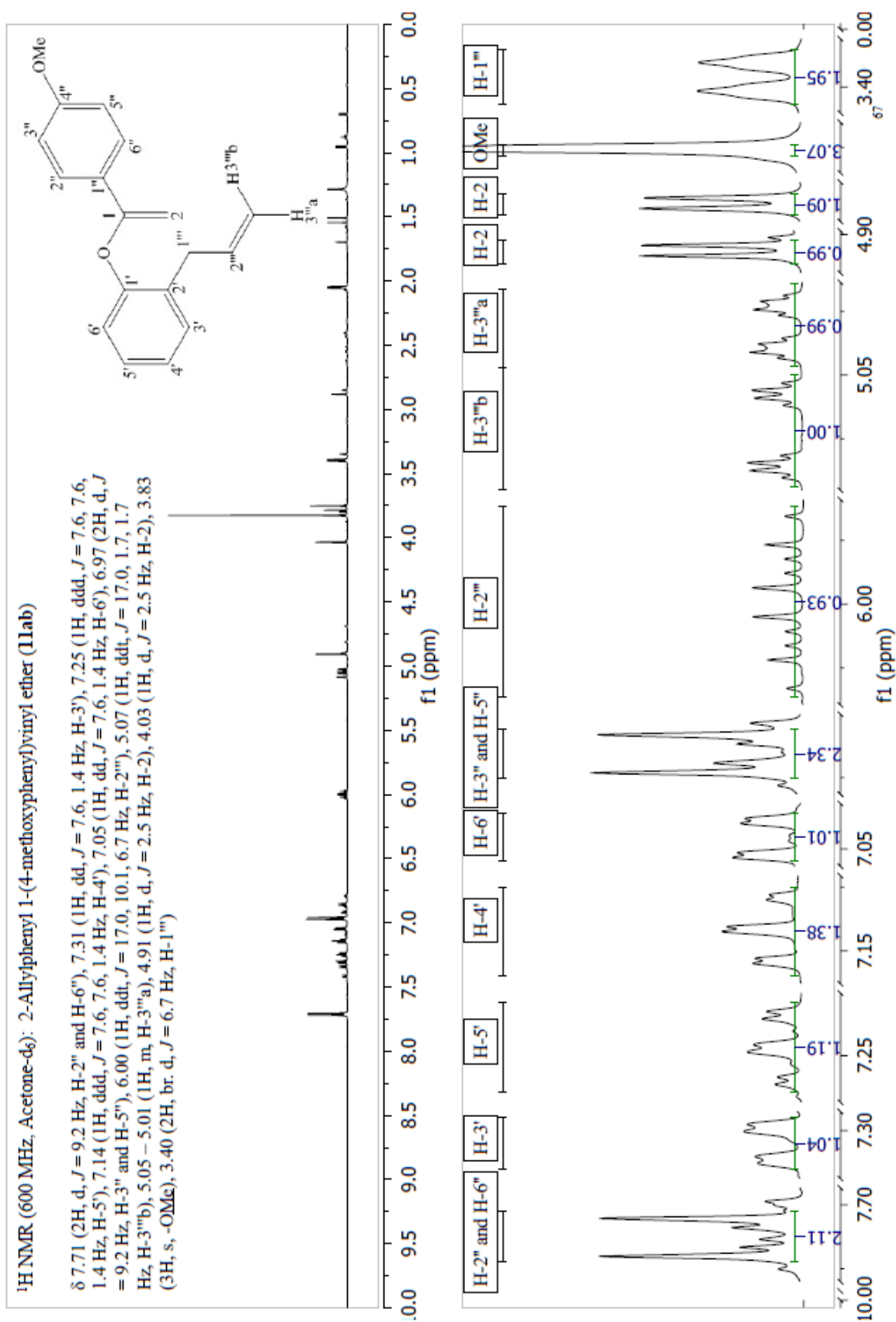


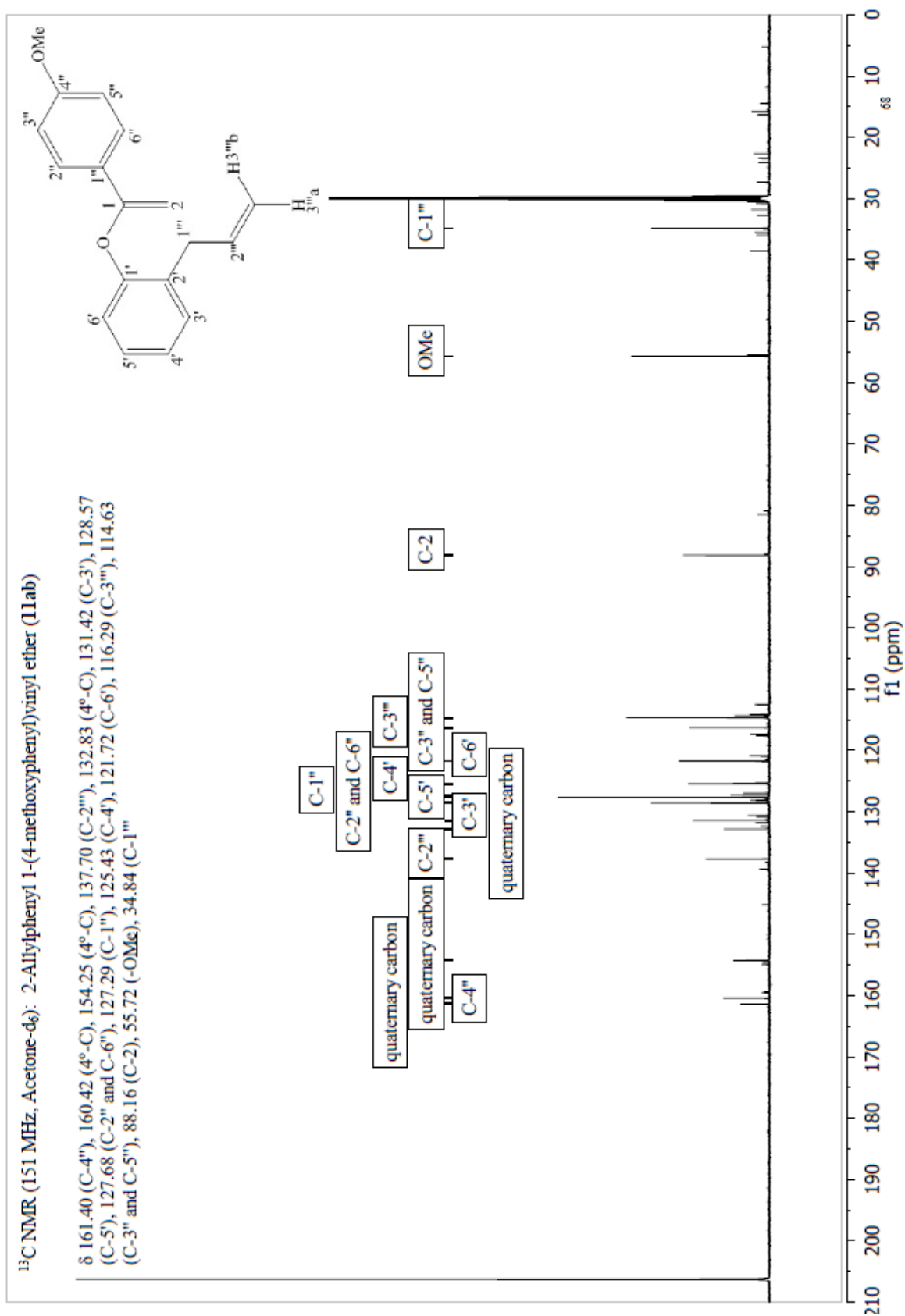


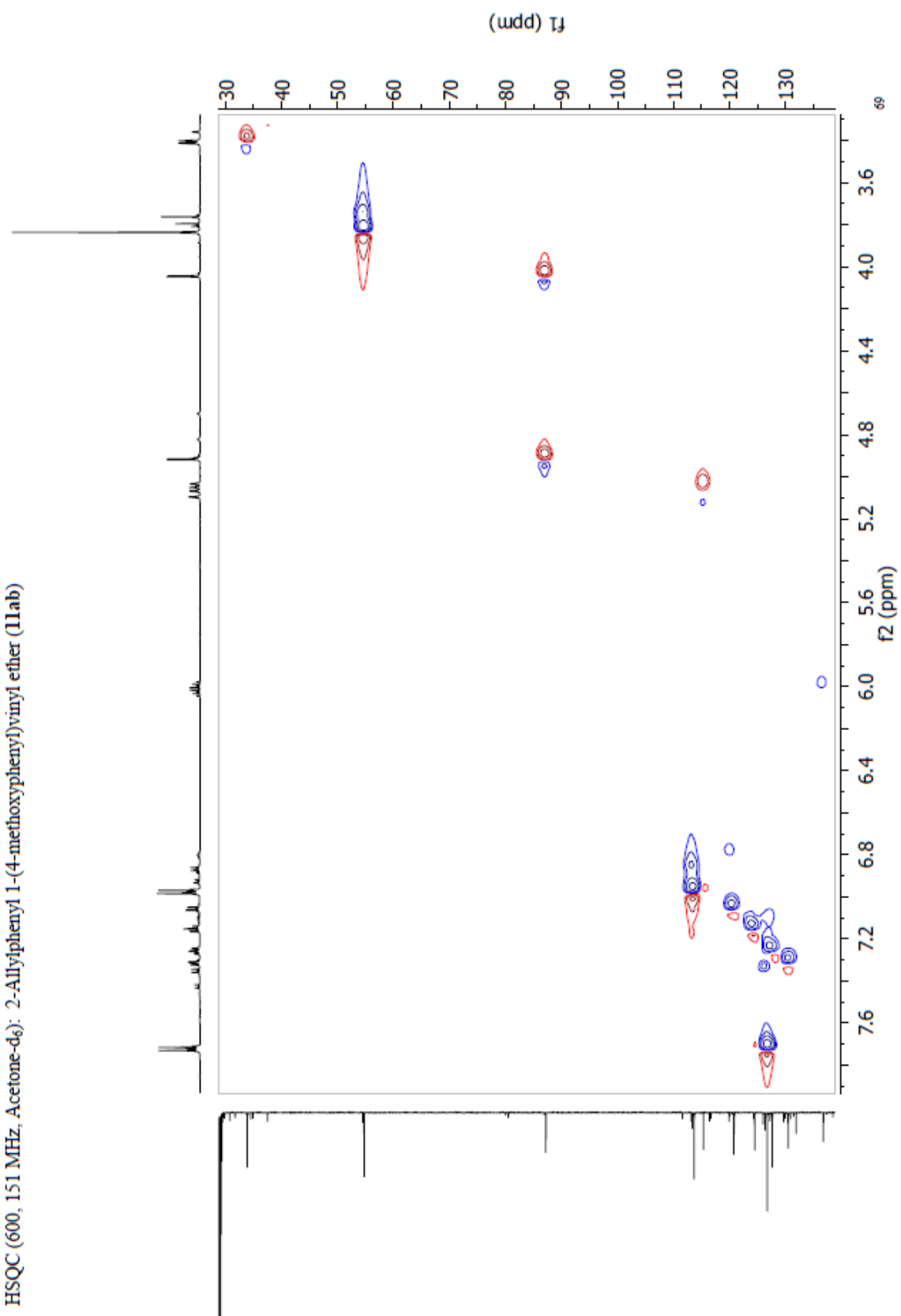
HSQC (600, 151 MHz, CDCl₃): 2-Allyl-1-(1-phenylvinylloxy)benzene (1aa)

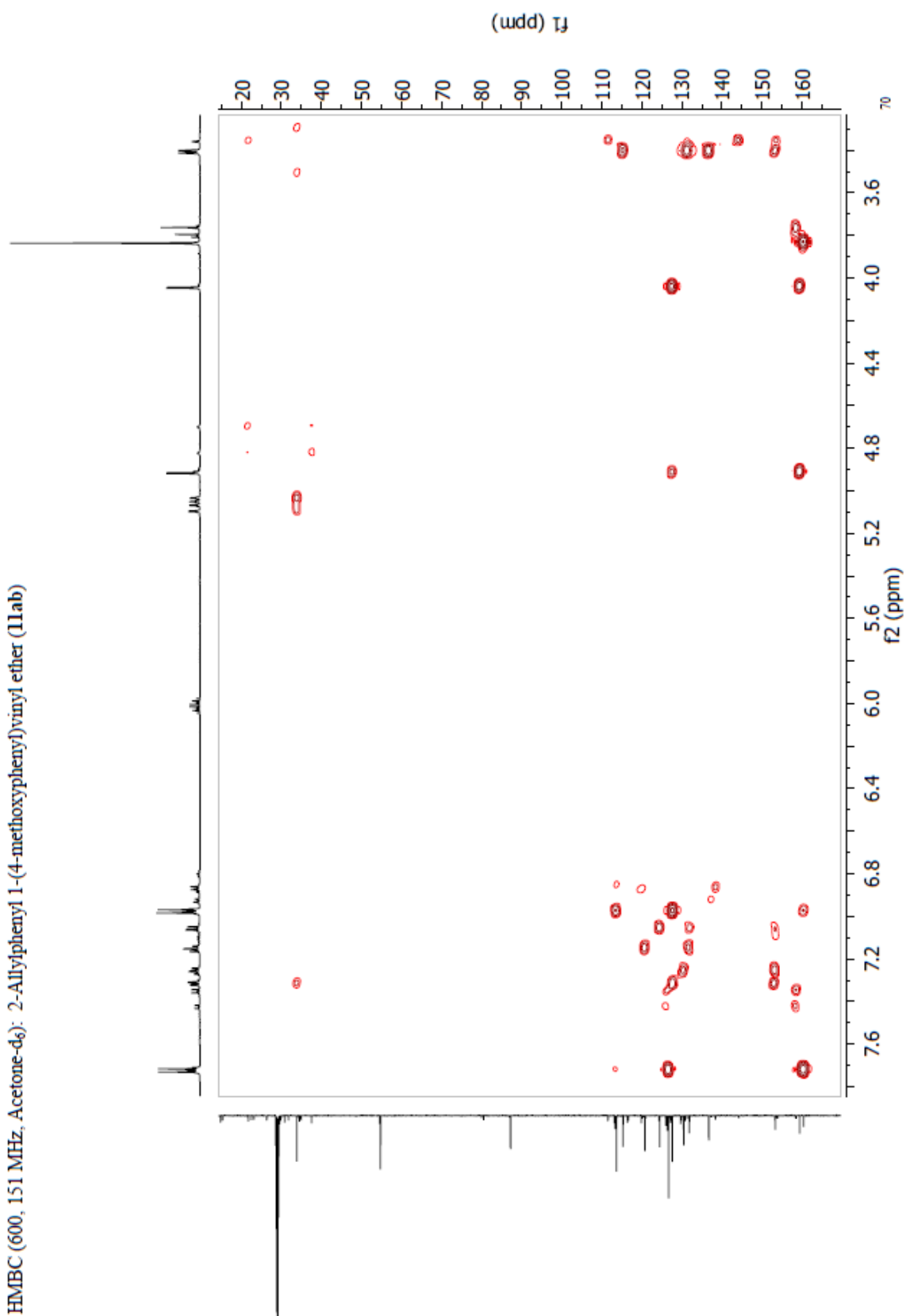
HMBC (600, 151 MHz, CDCl₃): 2-Allyl-1-(1-phenylvinyl)oxy)benzene (1aa)

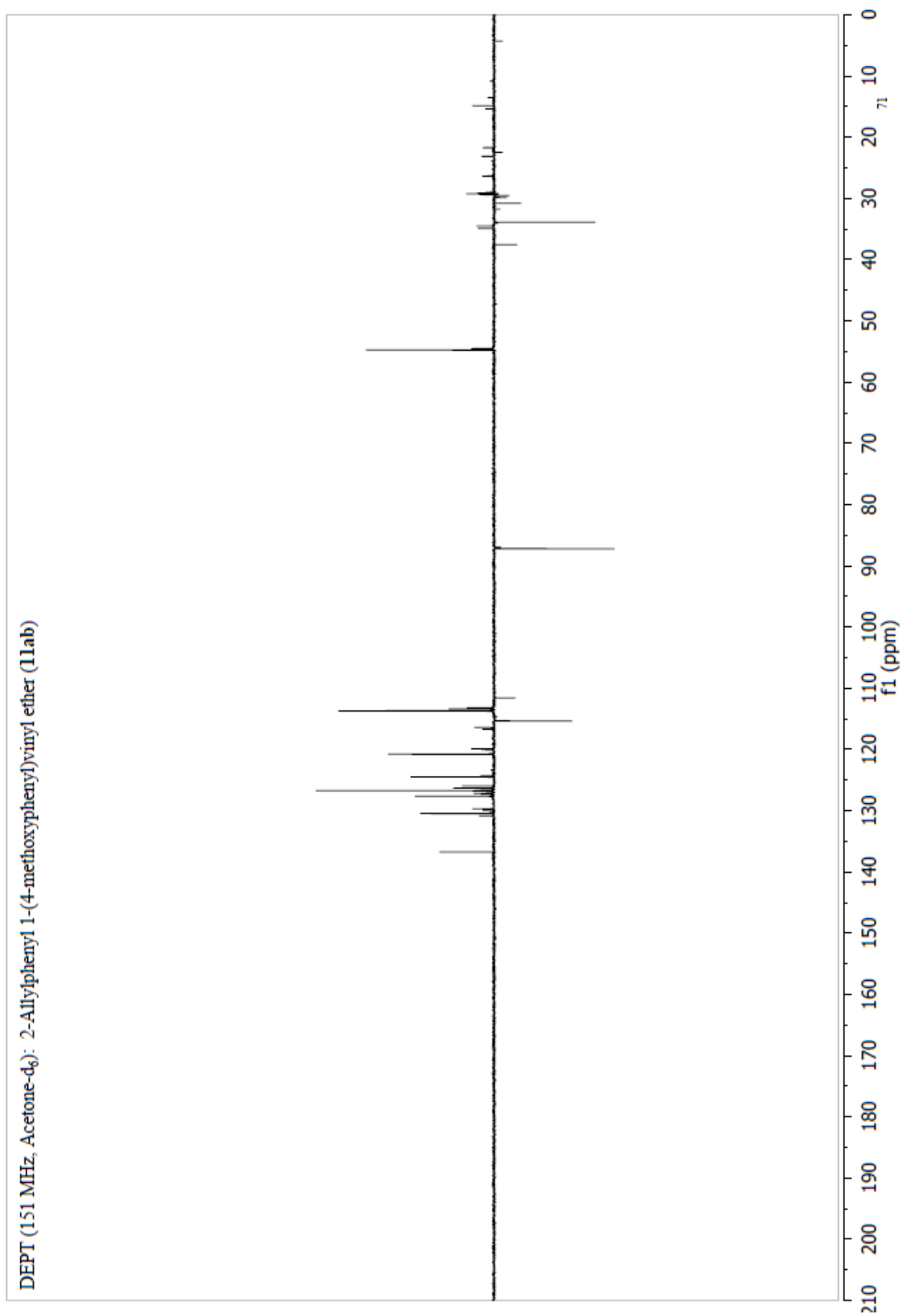


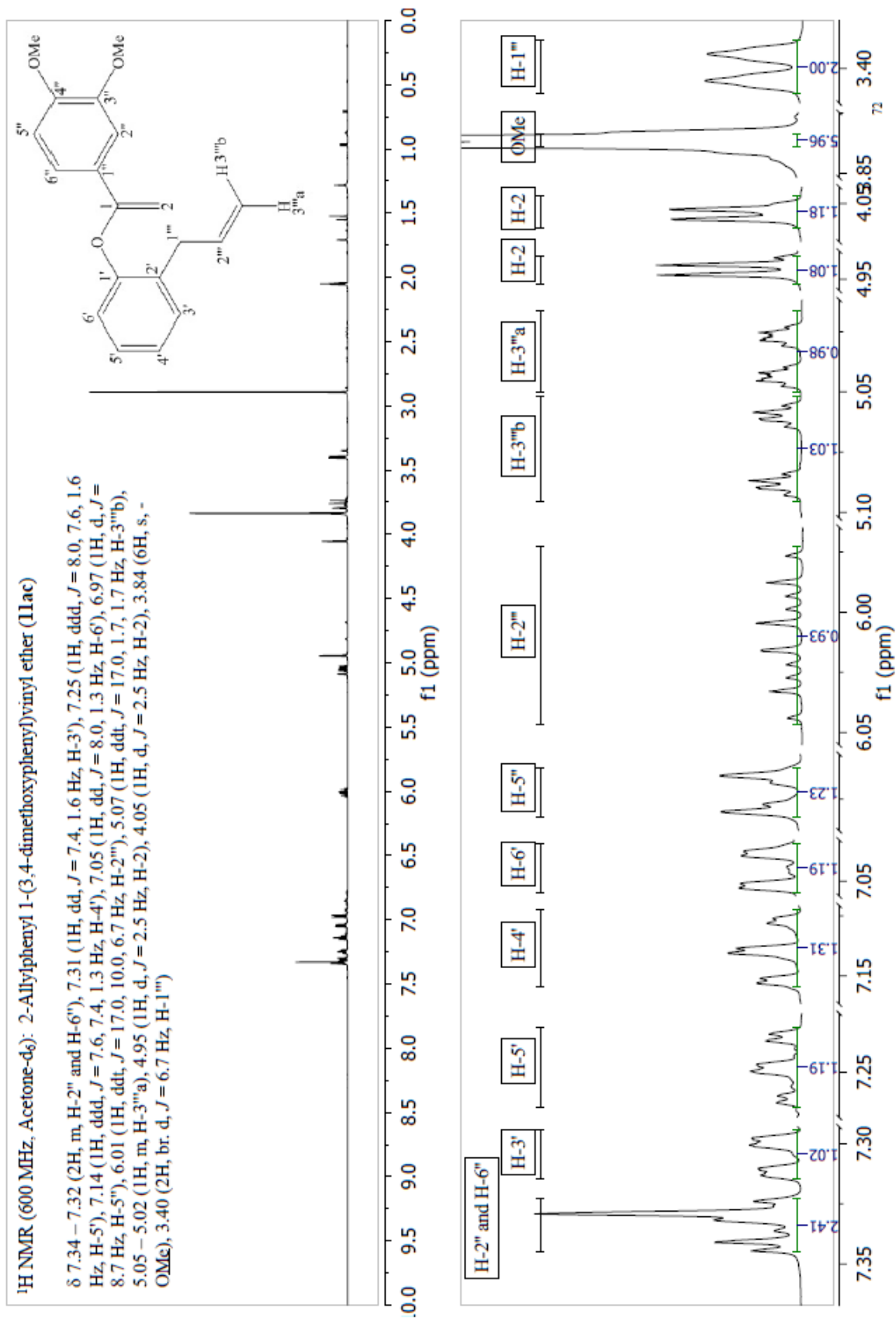


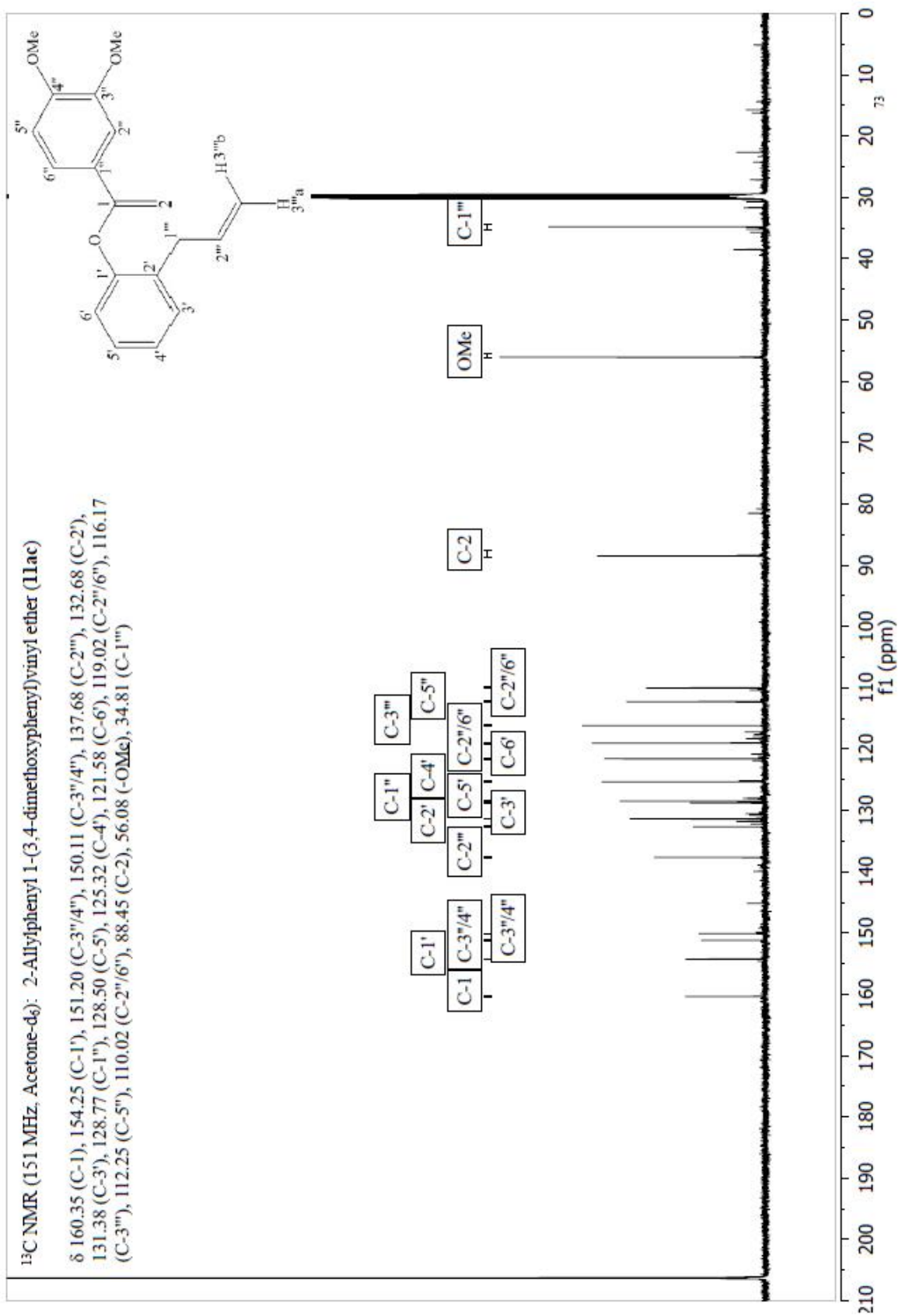


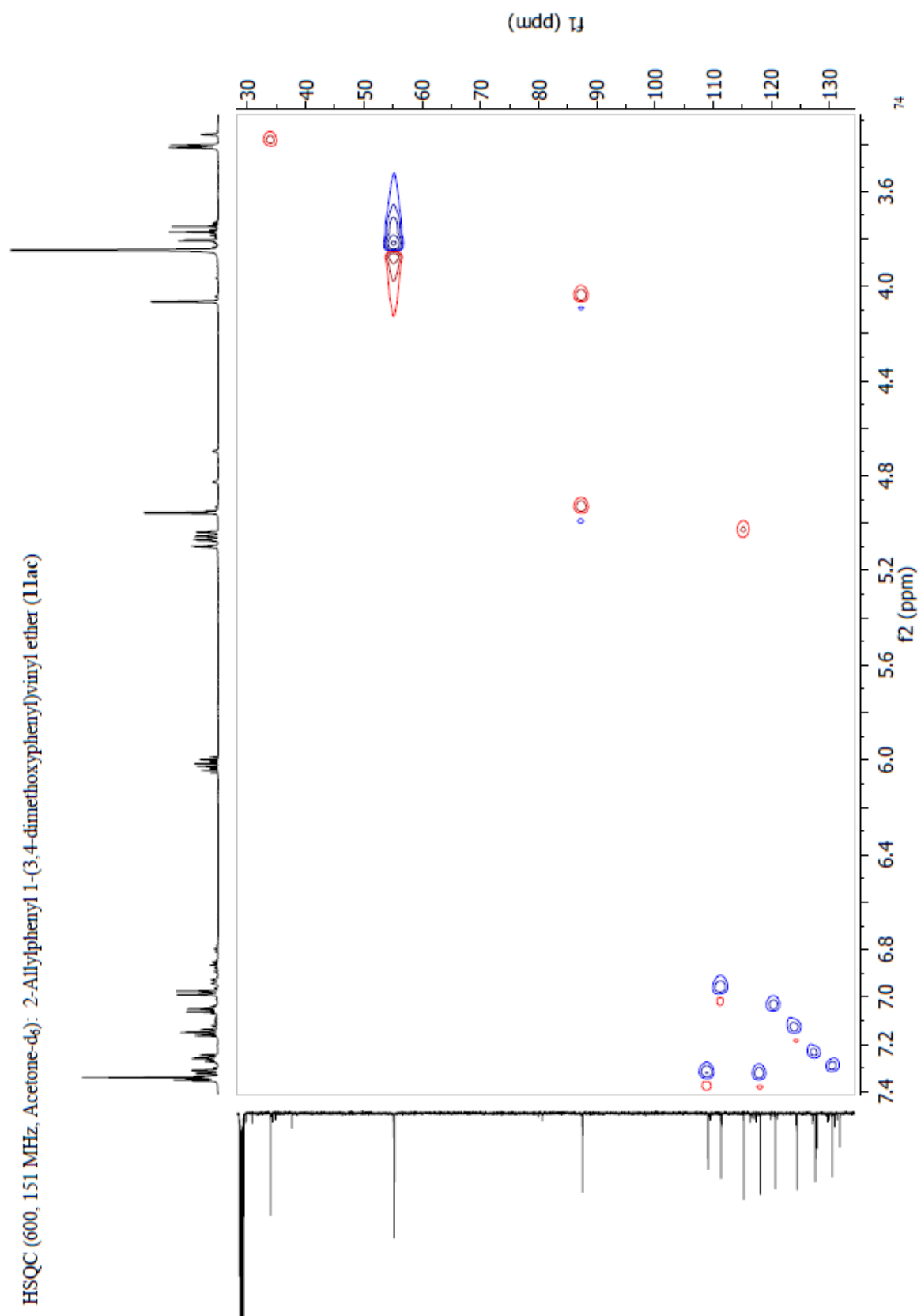
HSQC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 1-(4-methoxyphenyl)vinyl ether (11ab)

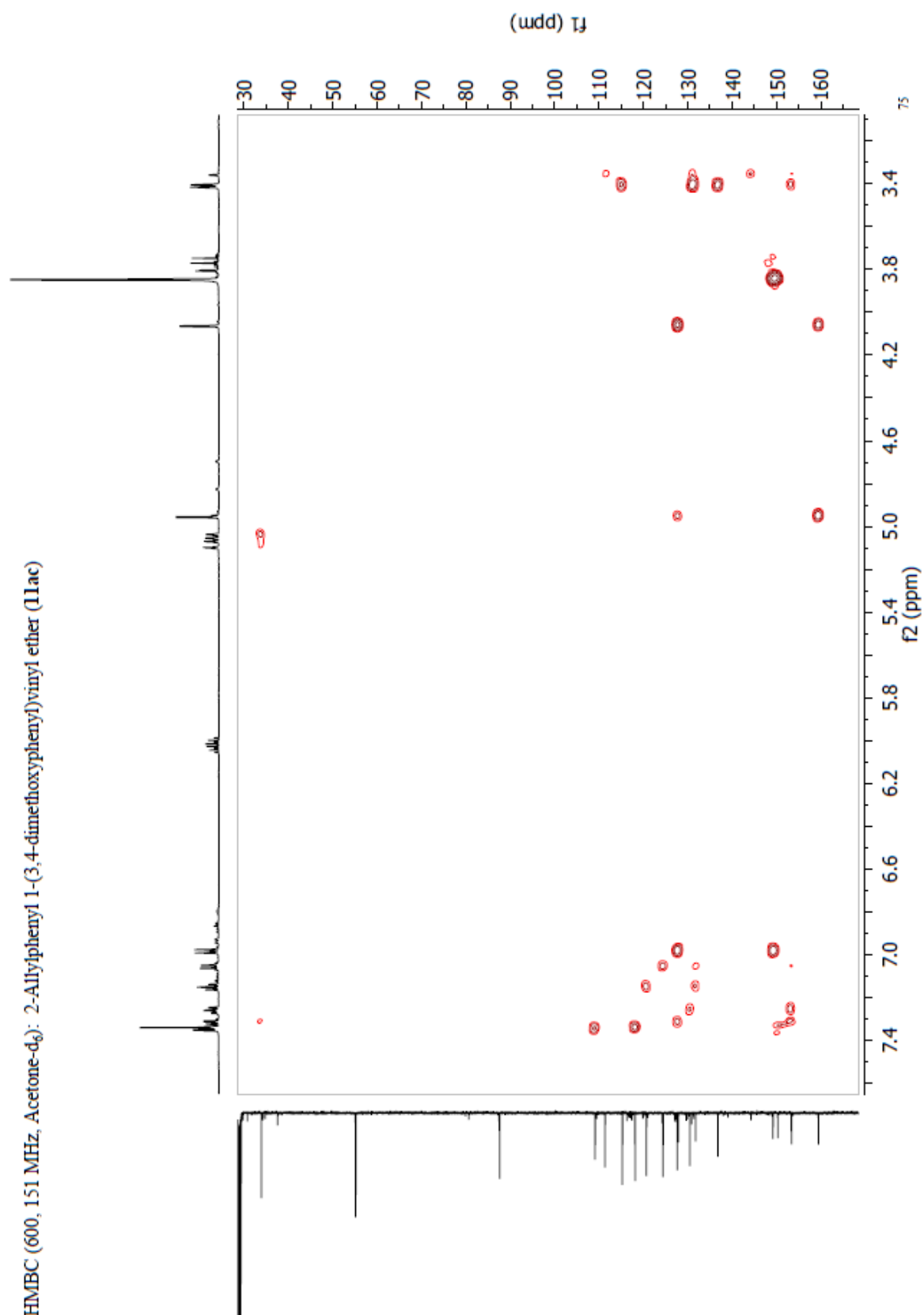
HMBC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 1-(4-methoxyphenyl)vinyl ether (11ab)

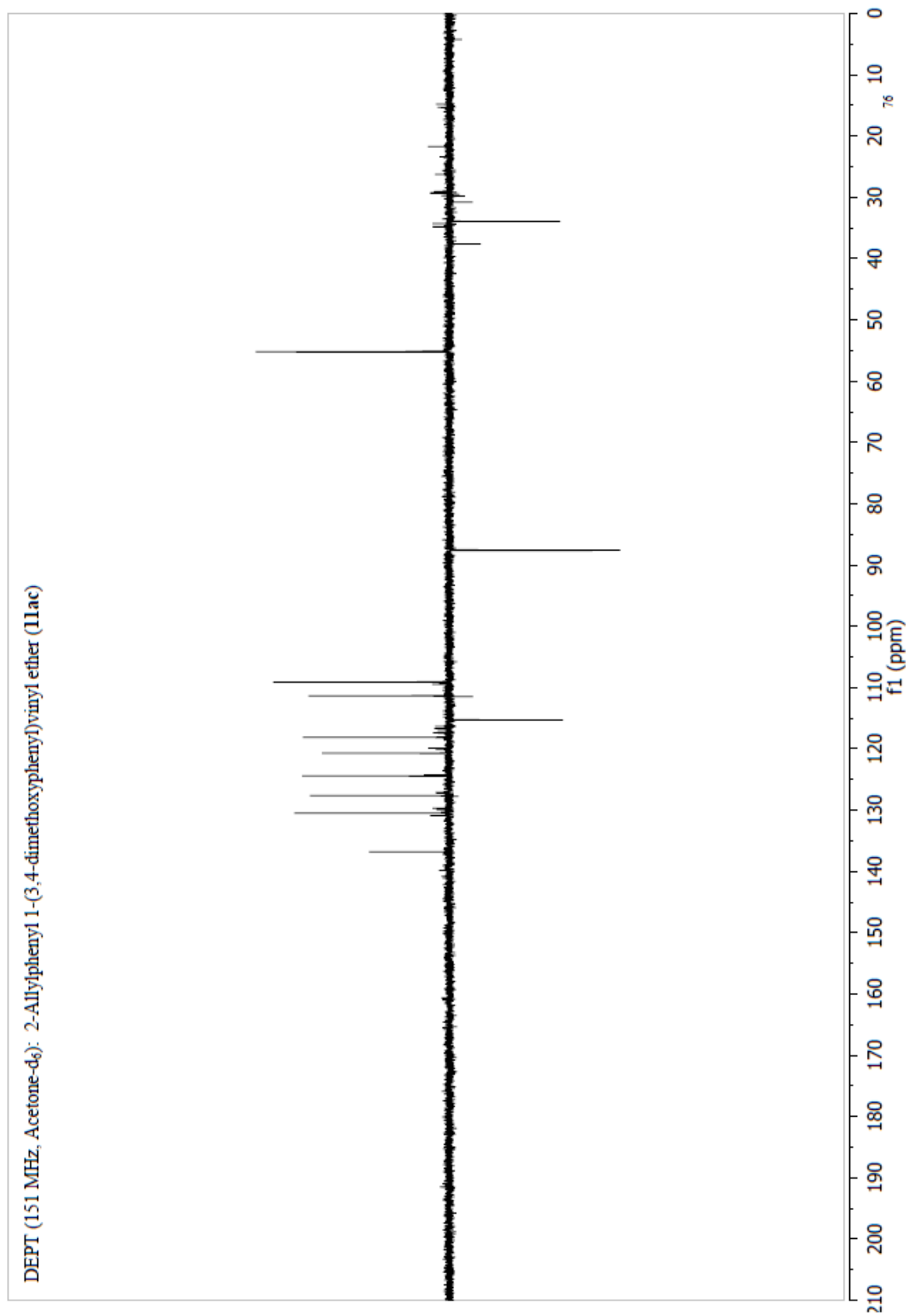


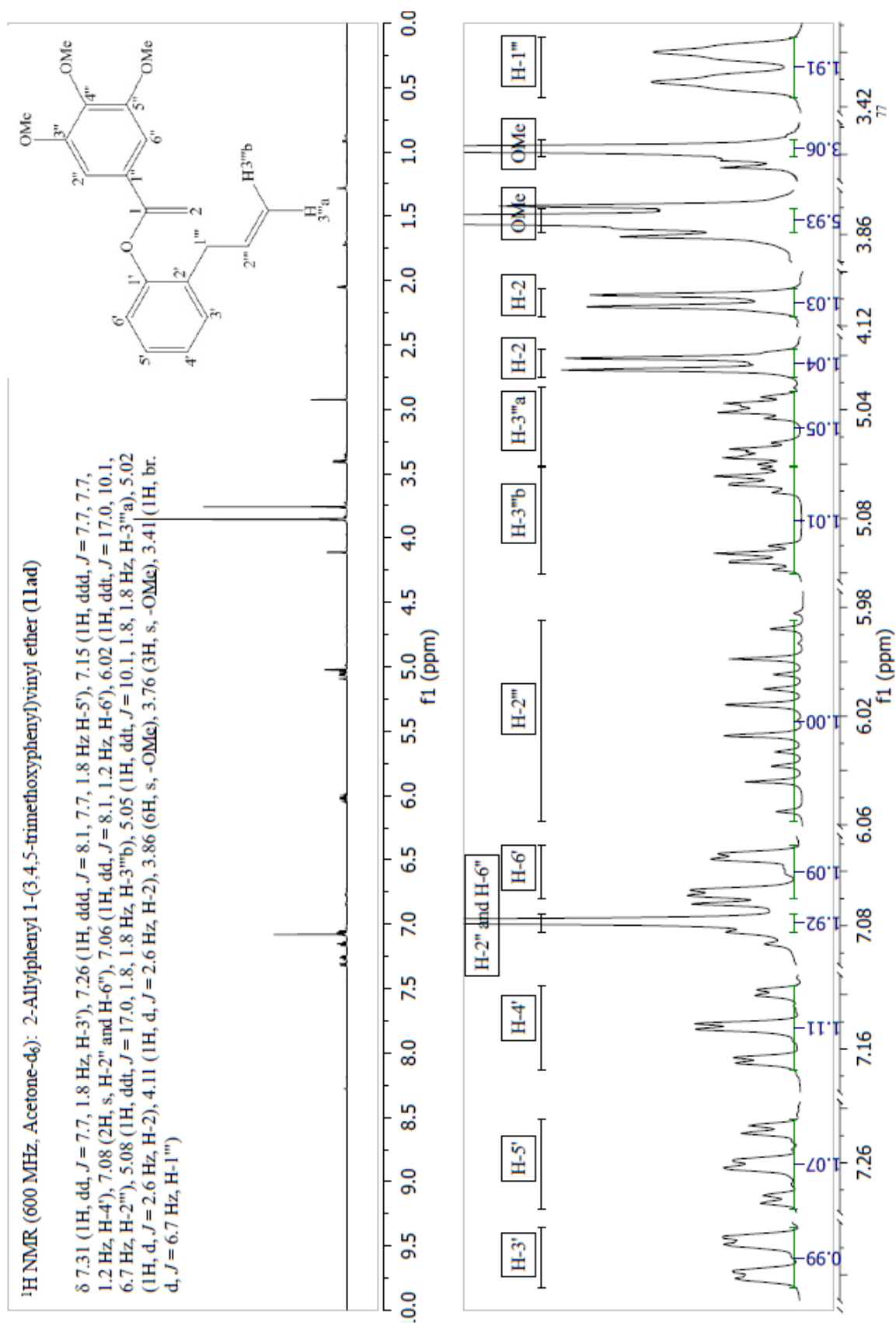




HSQC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 1-(3,4-dimethoxyphenyl)vinyl ether (11ac)

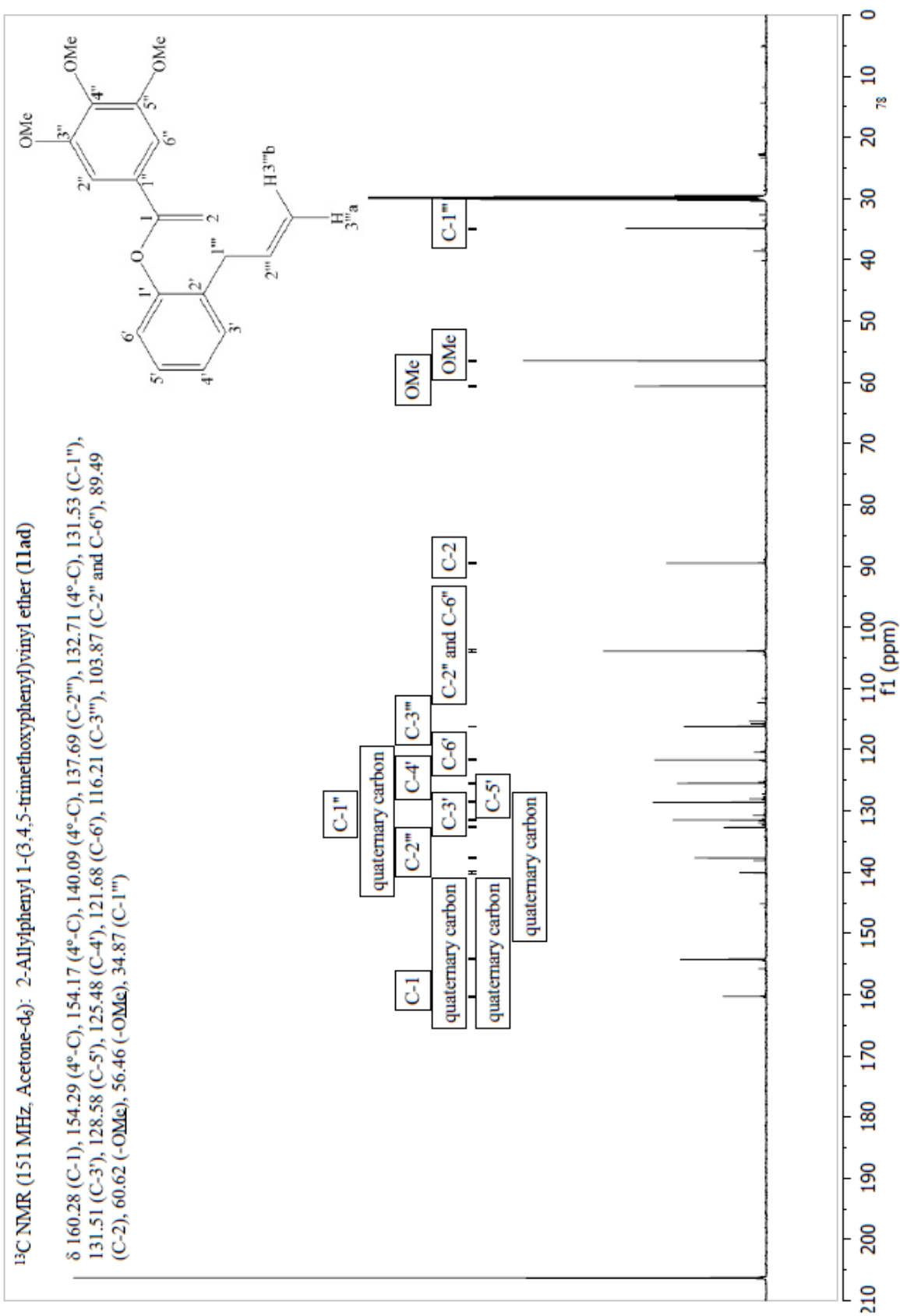
HMBC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 1-(3,4-dimethoxyphenyl)vinyl ether (11ac)

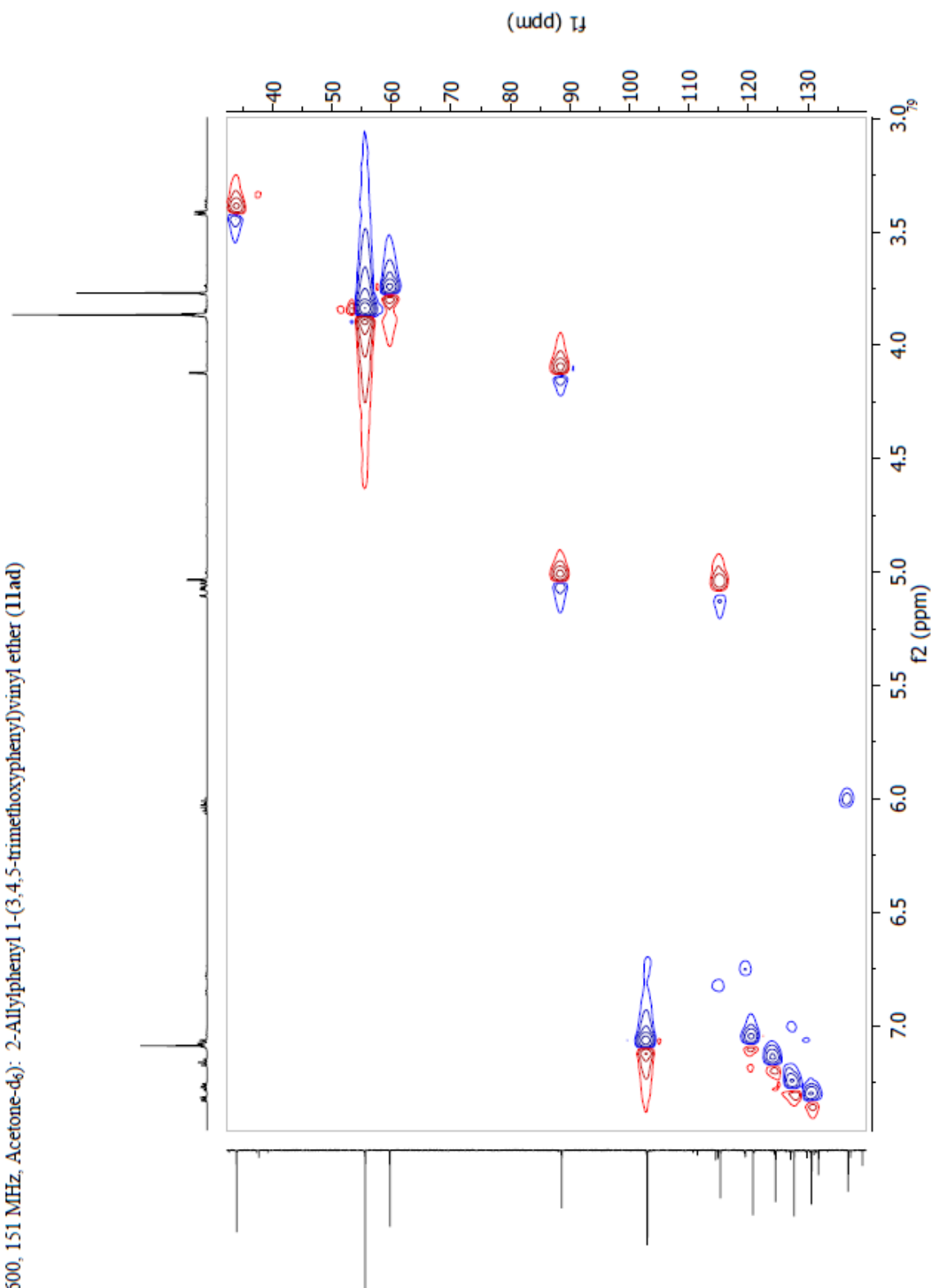


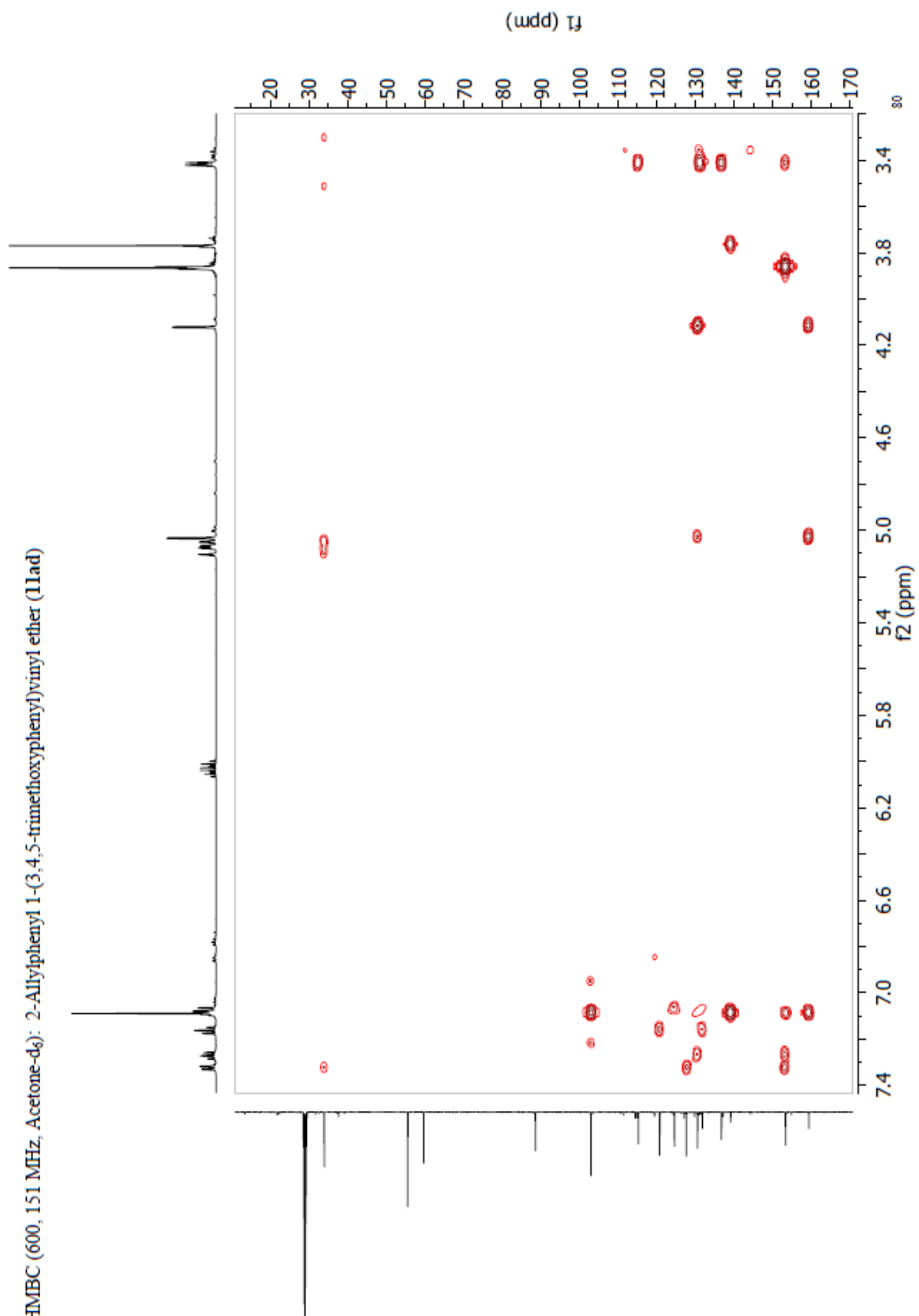


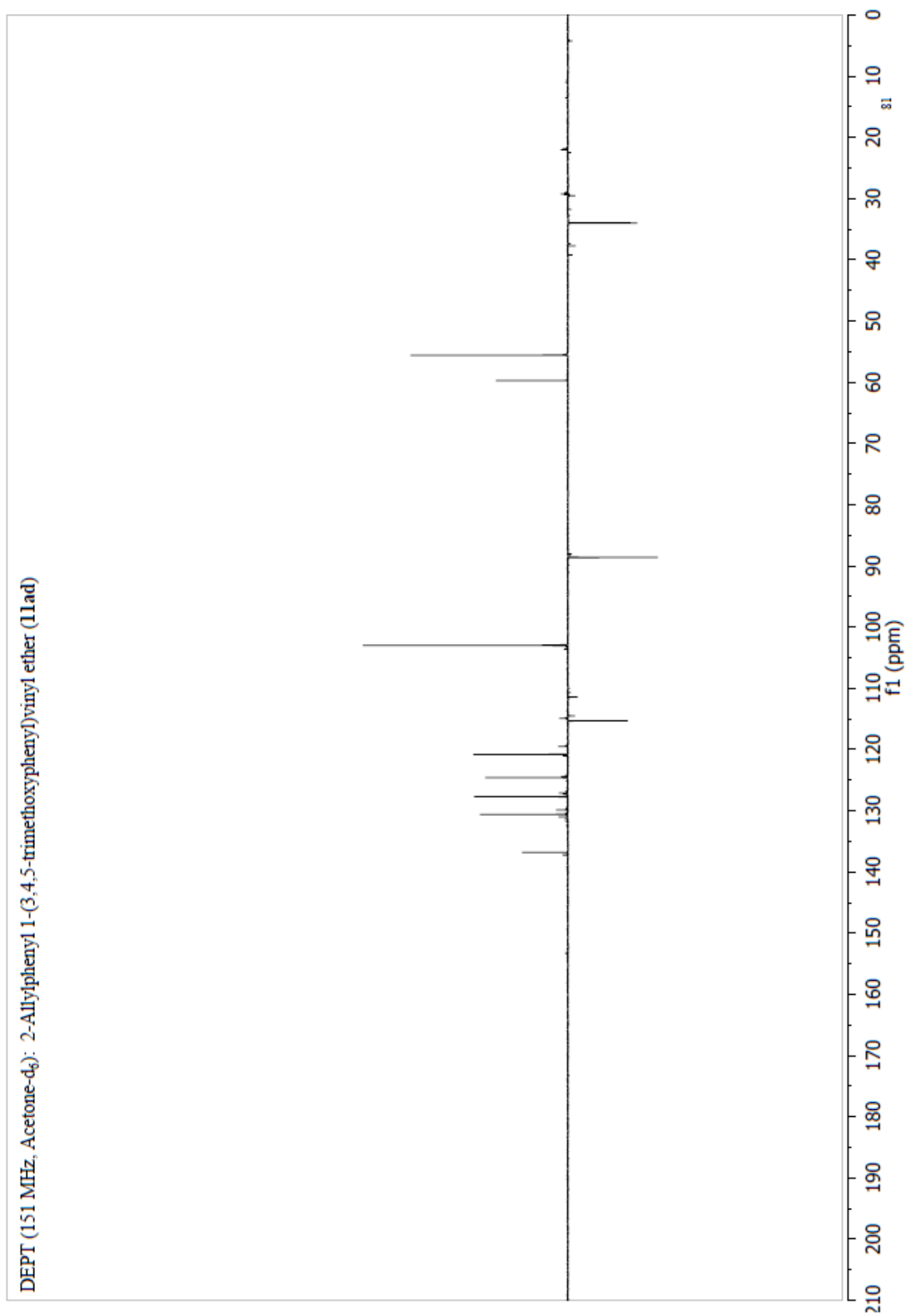
¹³C NMR (151 MHz, Acetone-d₆): 2-Allylphenyl 1-(3,4,5-trimethoxyphenyl)vinyl ether (11ad)

δ 160.28 (C-1), 154.29 (4^o-C), 154.17 (4^o-C), 140.09 (4^o-C), 137.69 (C-2^m), 132.71 (4^o-C), 131.53 (C-1^m), 131.51 (C-3^o), 128.58 (C-5^o), 125.48 (C-4^o), 121.68 (C-6^o), 116.21 (C-3^m), 103.87 (C-2^o and C-6^o), 89.49 (C-2), 60.62 (-OMe), 56.46 (-OMe), 34.87 (C-1^m)



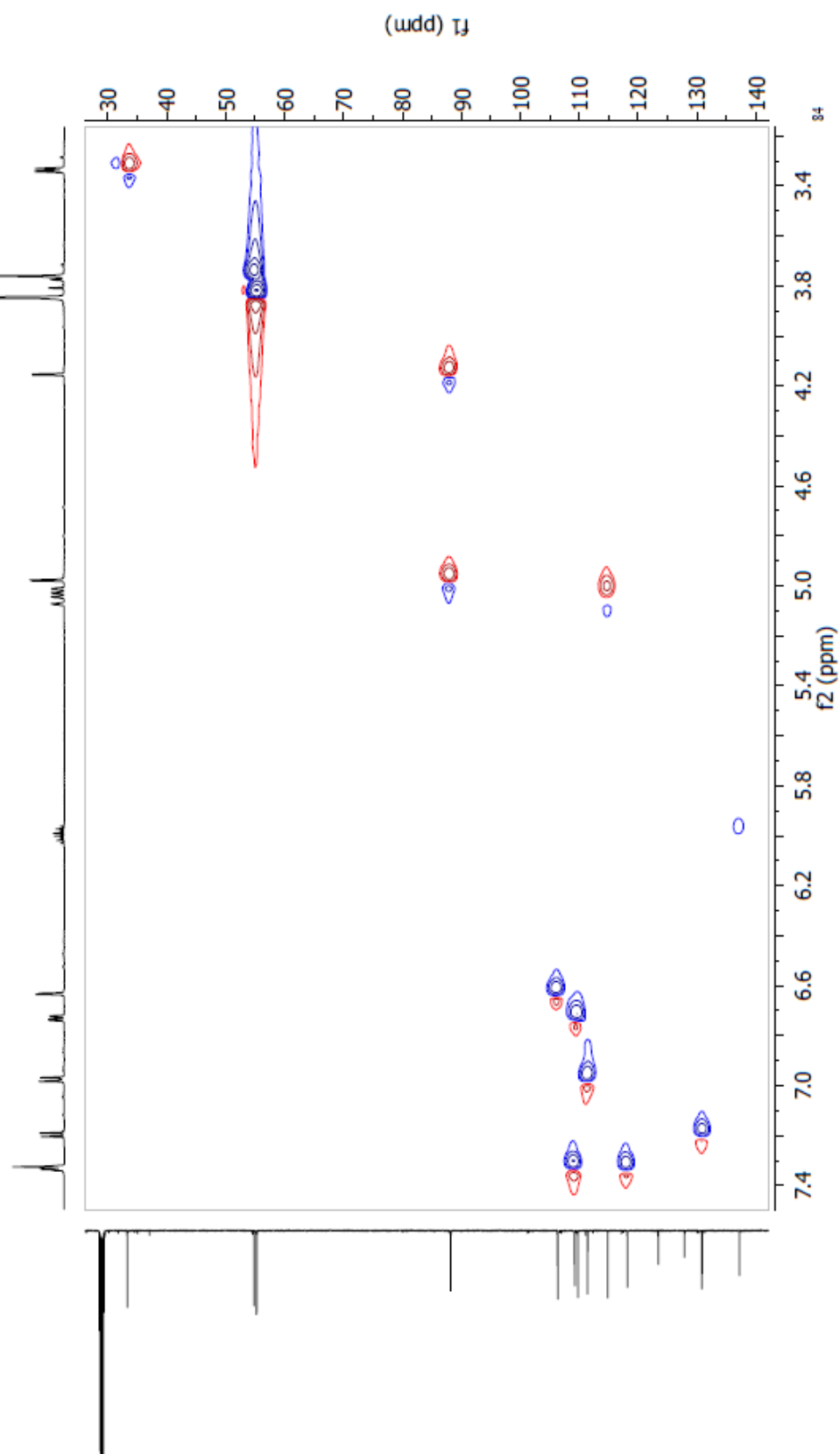
HSQC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 1-(3,4,5-trimethoxyphenyl)vinyl ether (11ad)

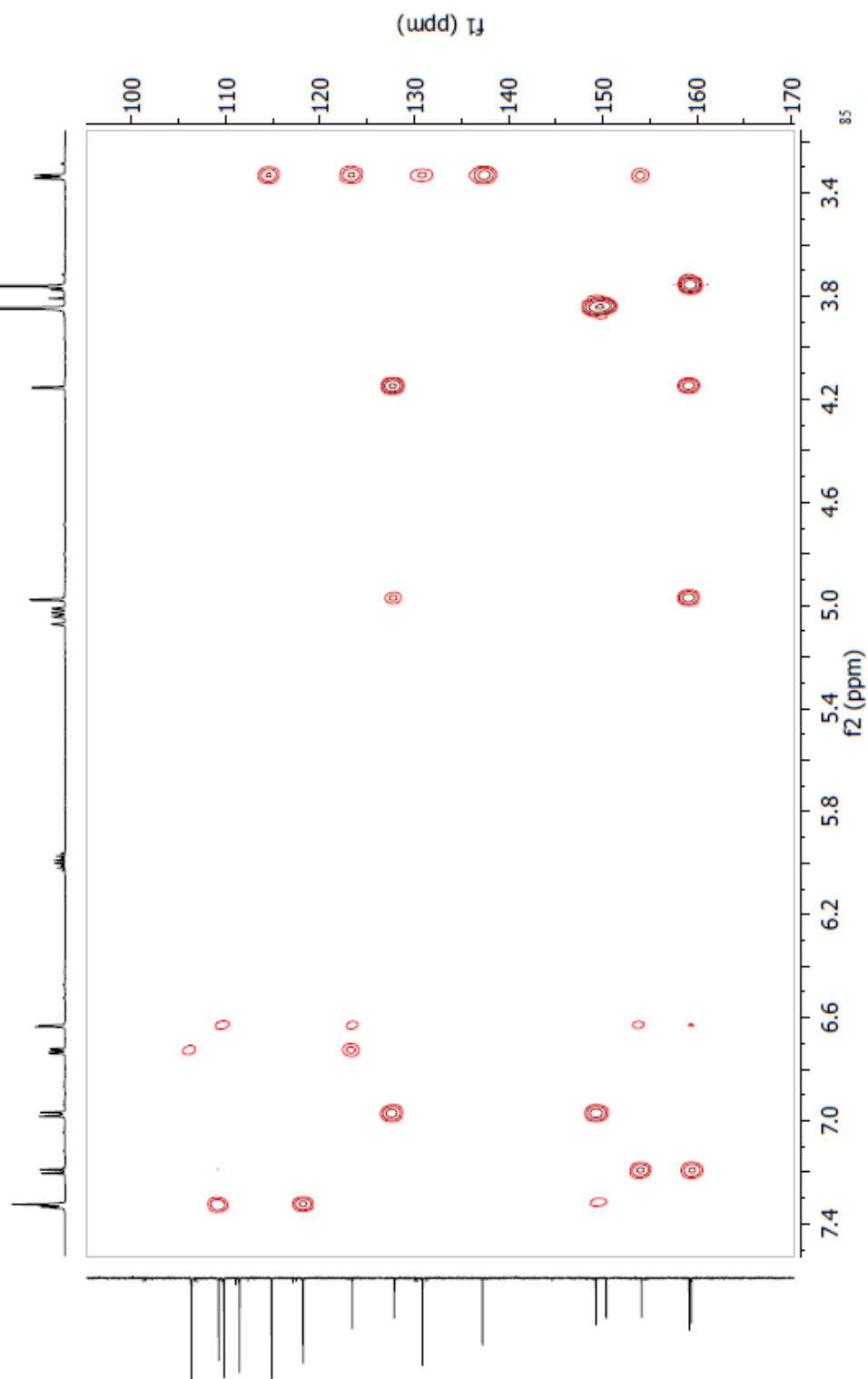
HMBC (600, 151 MHz, Acetone- d_6): 2-Allylphenyl 1-(3,4,5-trimethoxyphenyl)vinyl ether (11ad)

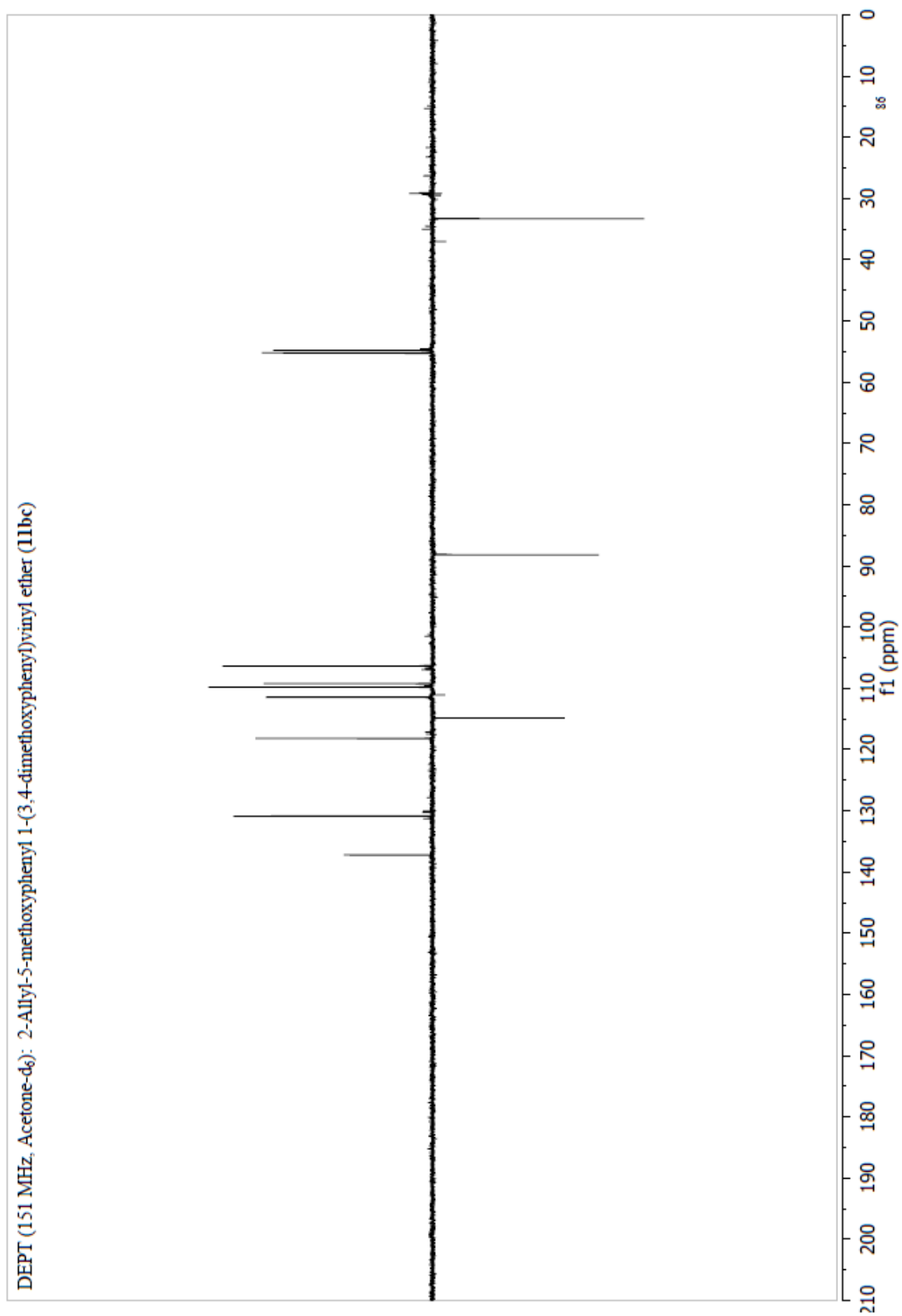






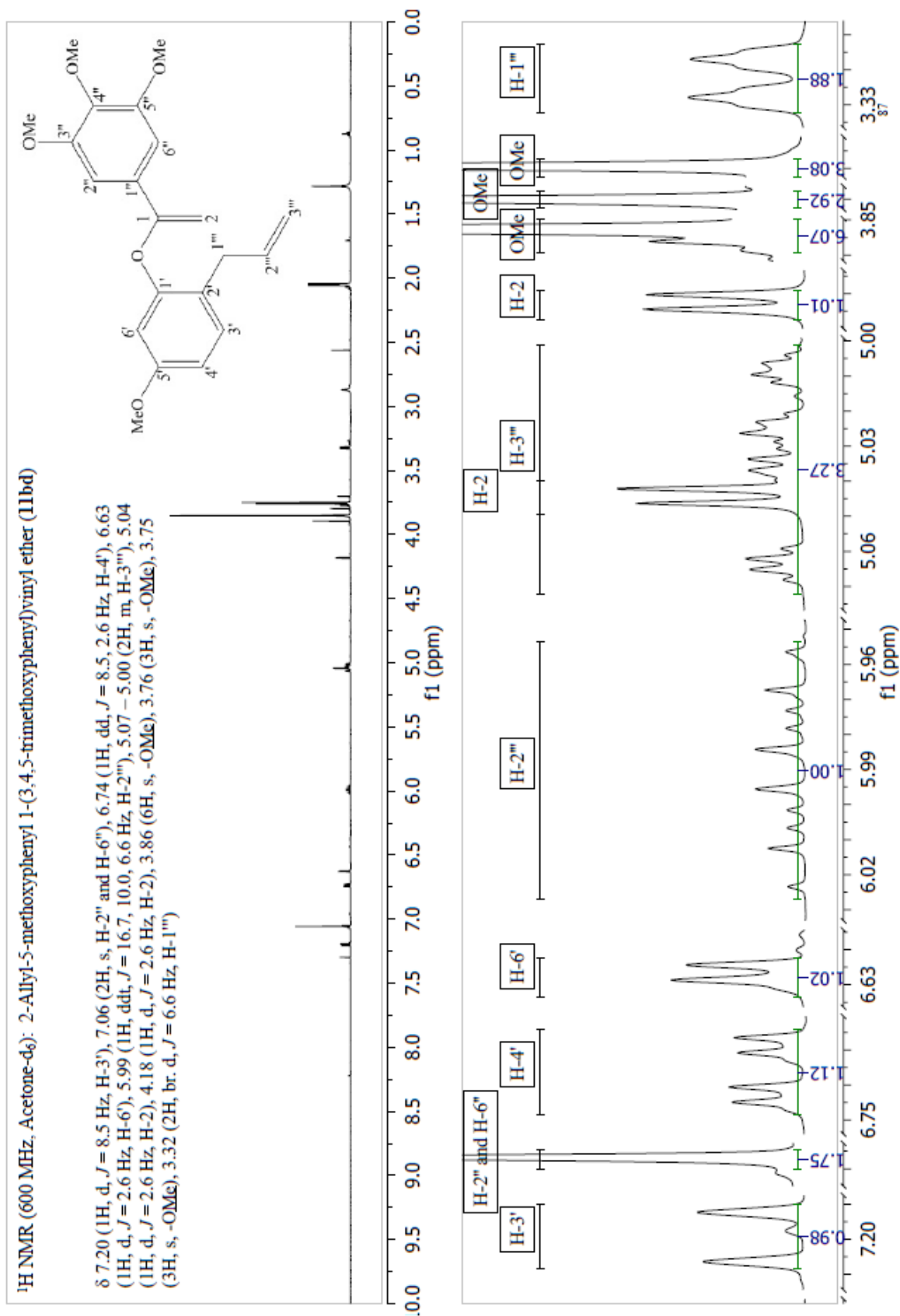
HSQC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 1-(3,4-dimethoxyphenyl)vinyl ether (11bc)

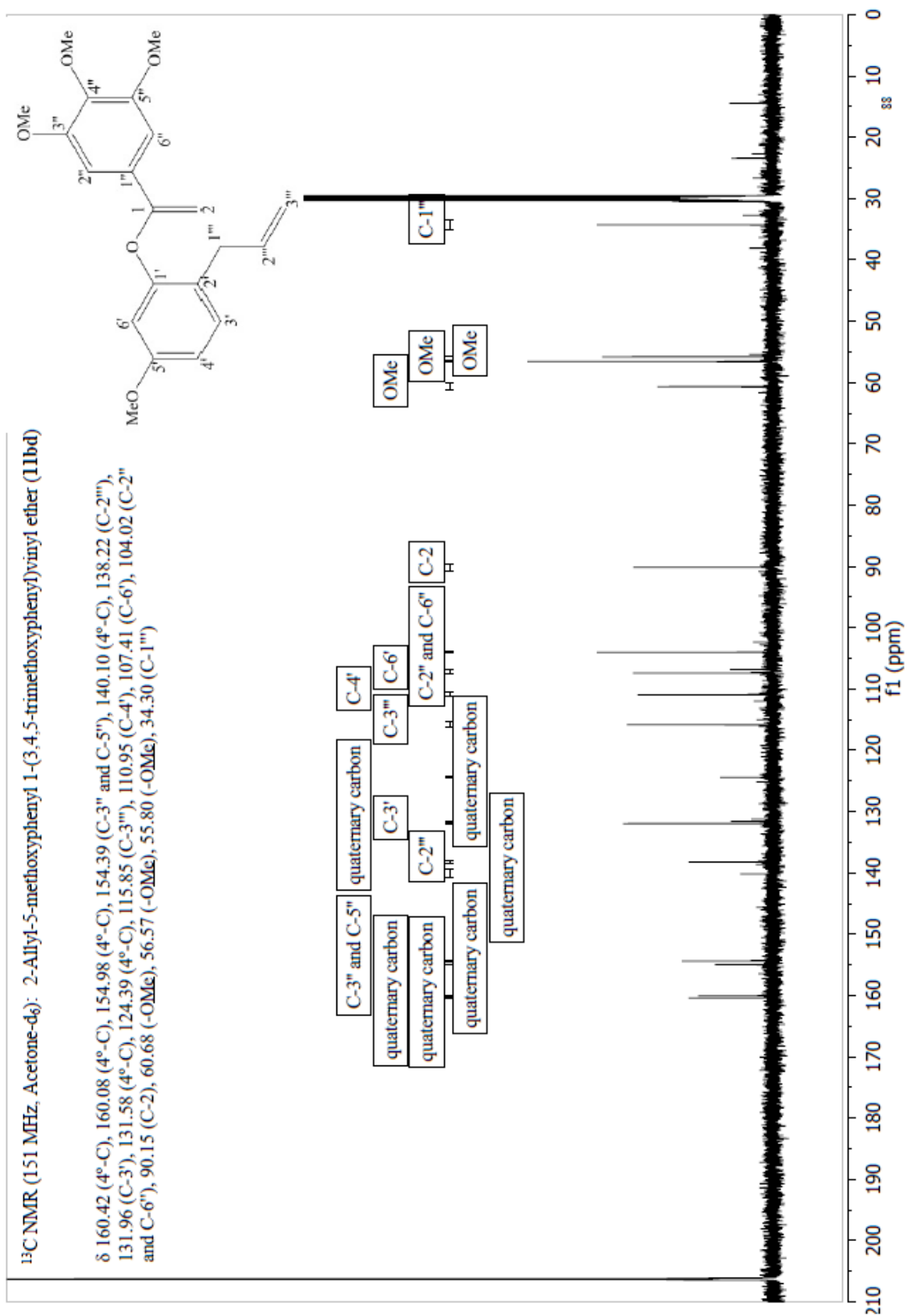
HMBC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 1-(3,4-dimethoxyphenyl)vinyl ether (11bc)

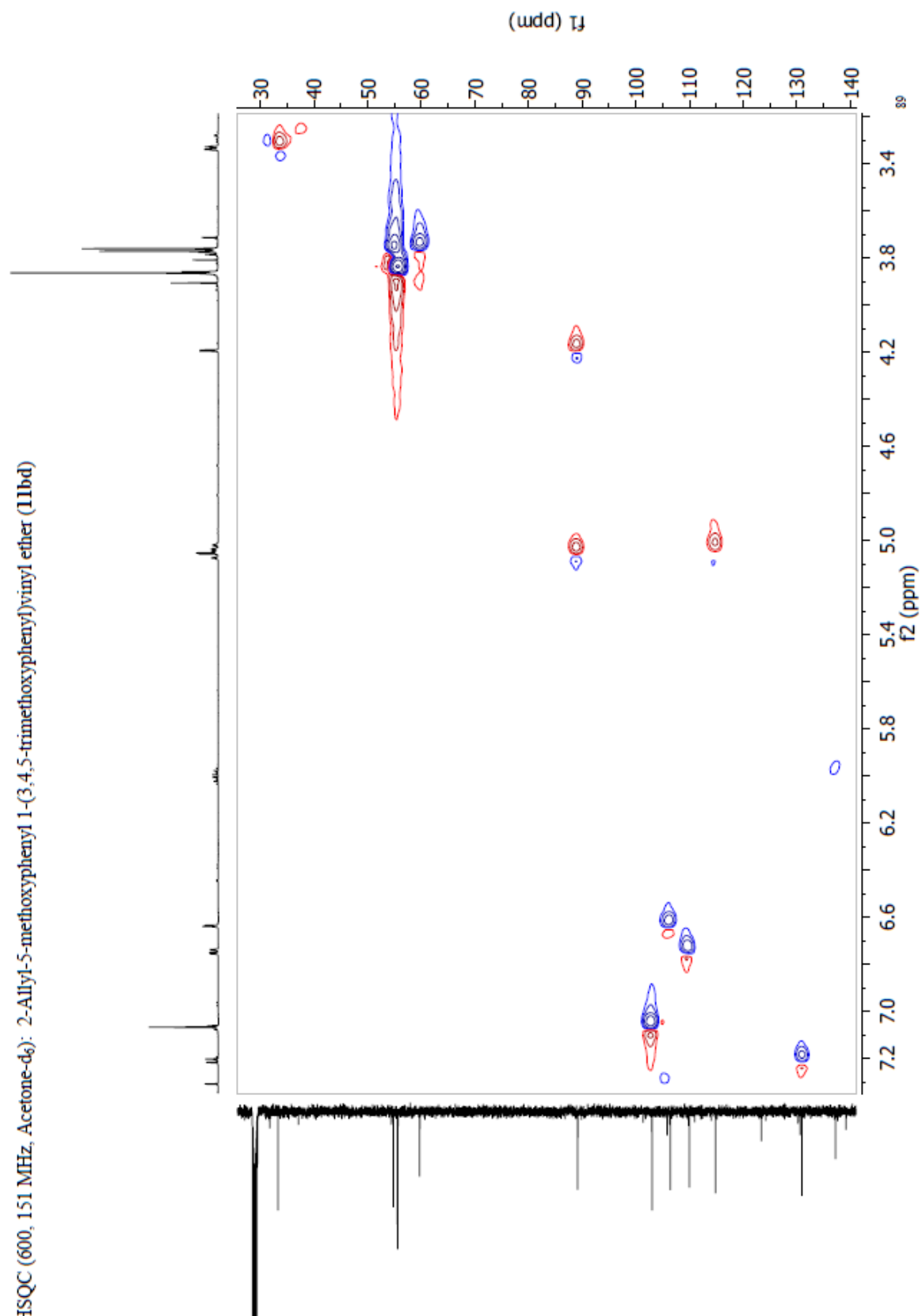


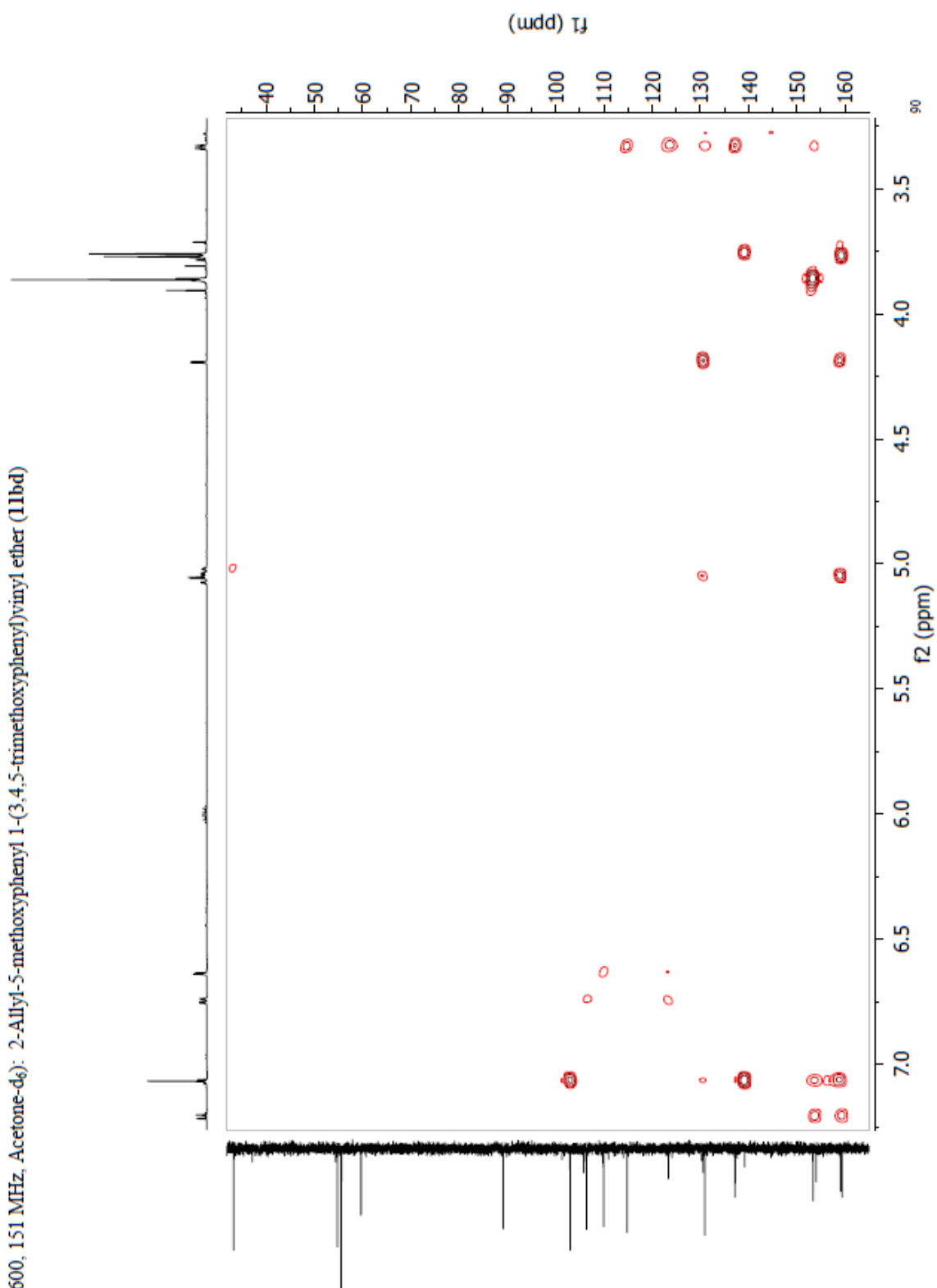
¹H NMR (600 MHz, Acetone-d₆): 2-Allyl-5-methoxyphenyl 1-(3,4,5-trimethoxyphenyl)vinyl ether (11bd)

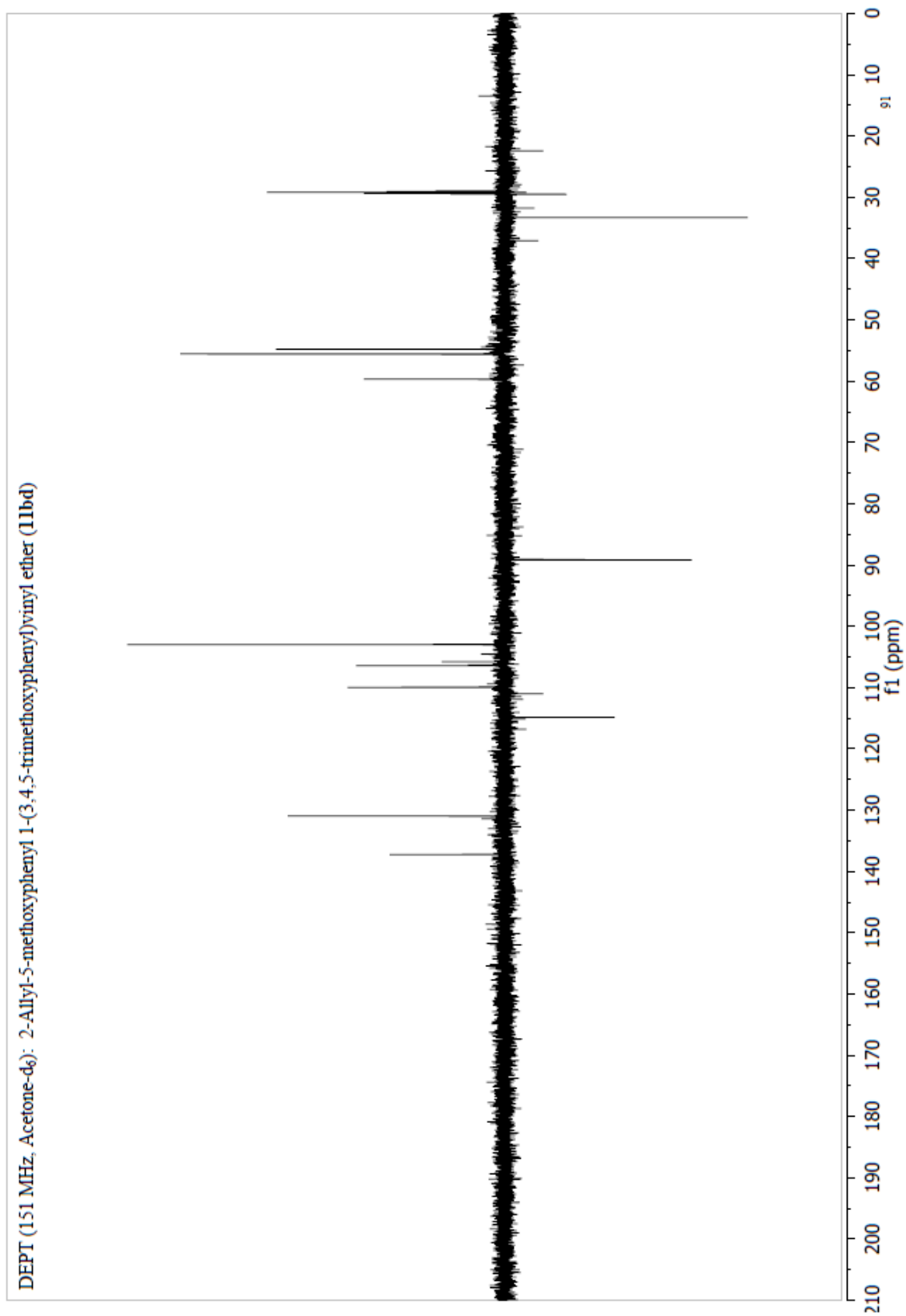
δ 7.20 (1H, d, *J* = 8.5 Hz, H-3'), 7.06 (2H, s, H-2'' and H-6''), 6.74 (1H, dd, *J* = 8.5, 2.6 Hz, H-4'), 6.63 (1H, d, *J* = 2.6 Hz, H-6'), 5.99 (1H, ddt, *J* = 16.7, 10.0, 6.6 Hz, H-2'''), 5.07 – 5.00 (2H, m, H-3'''), 5.04 (1H, d, *J* = 2.6 Hz, H-2), 4.18 (1H, d, *J* = 2.6 Hz, H-2), 3.86 (6H, s, -OMe), 3.76 (3H, s, -OMe), 3.75 (3H, s, -OMe), 3.32 (2H, br. d, *J* = 6.6 Hz, H-1''')

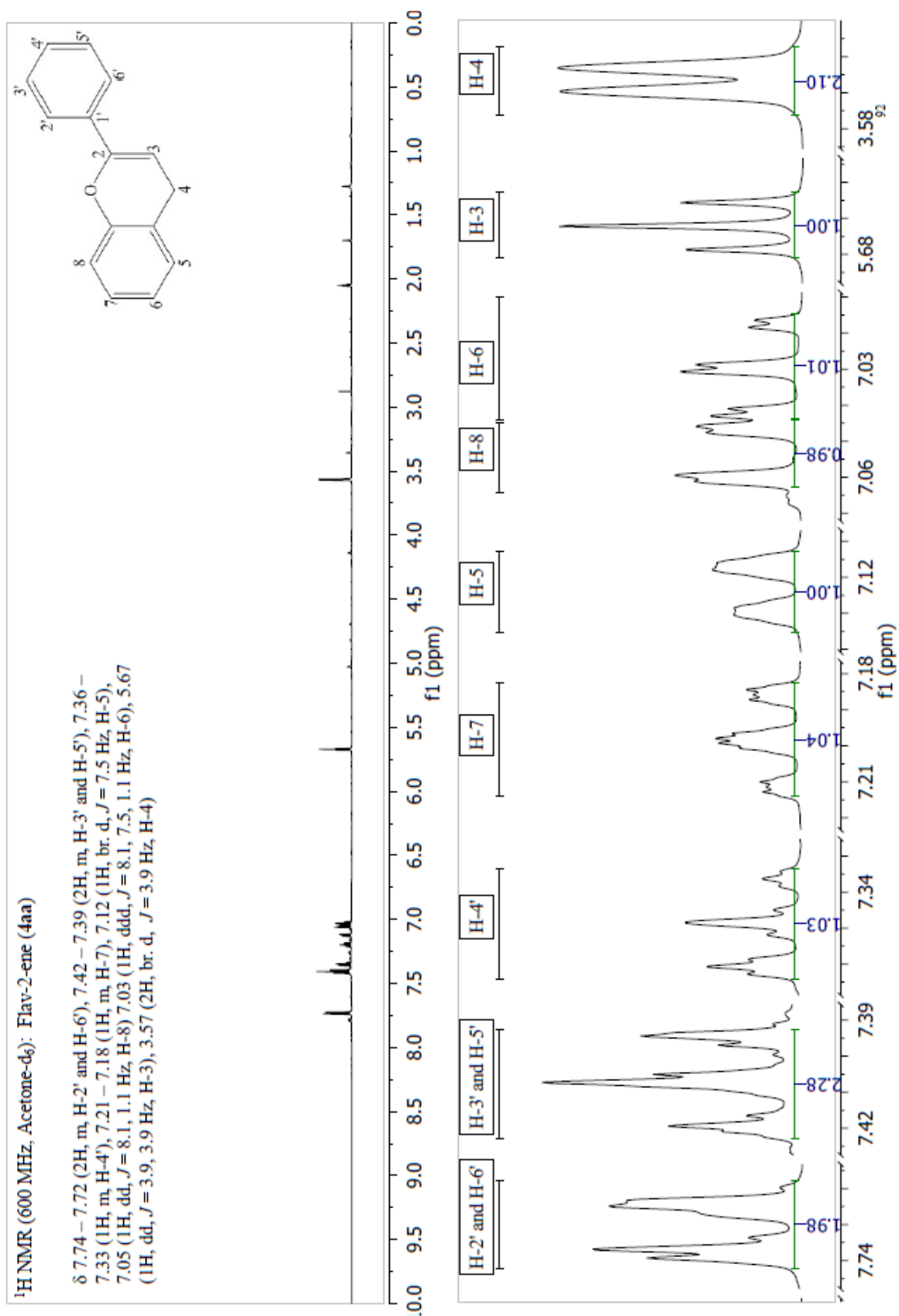


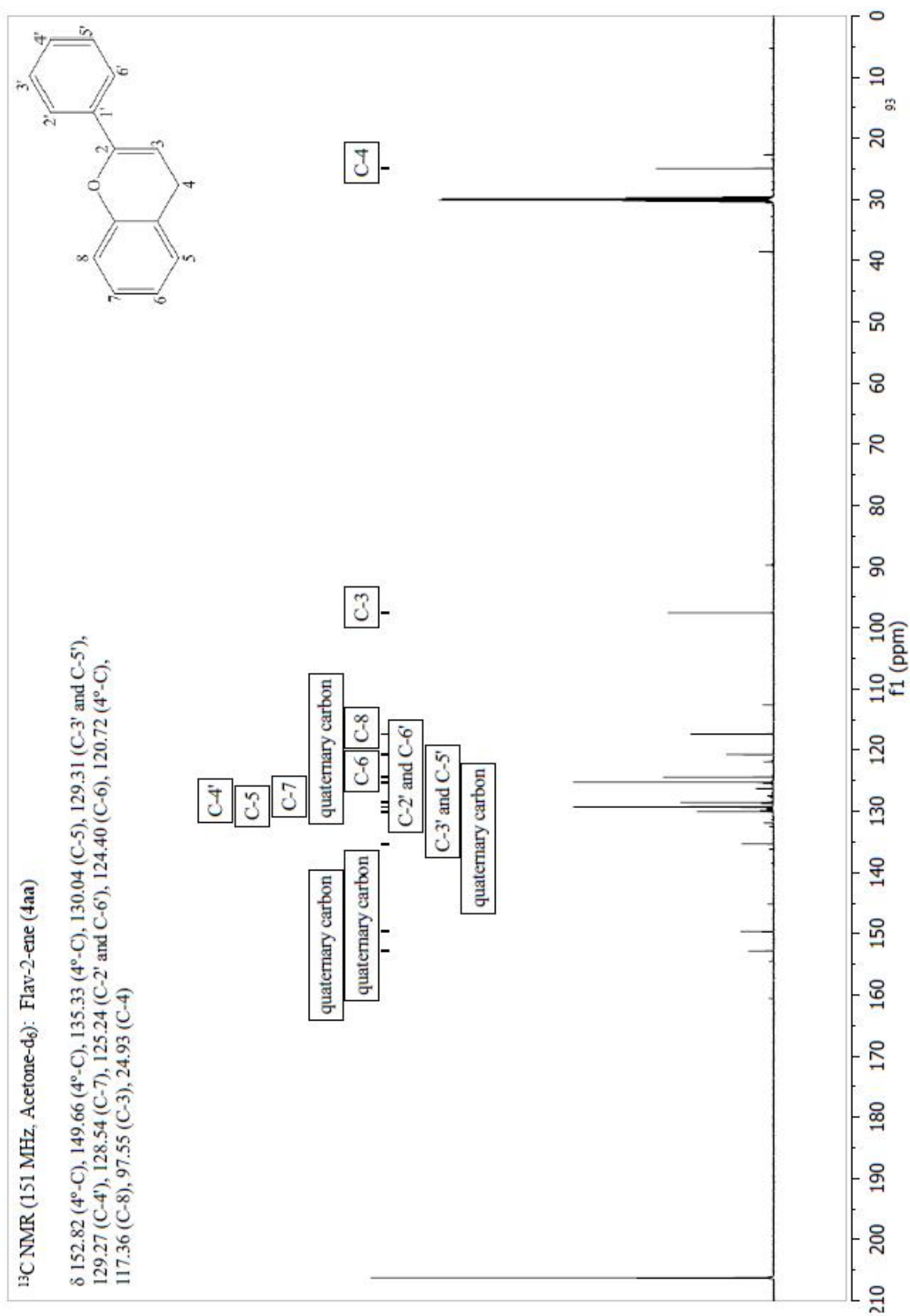


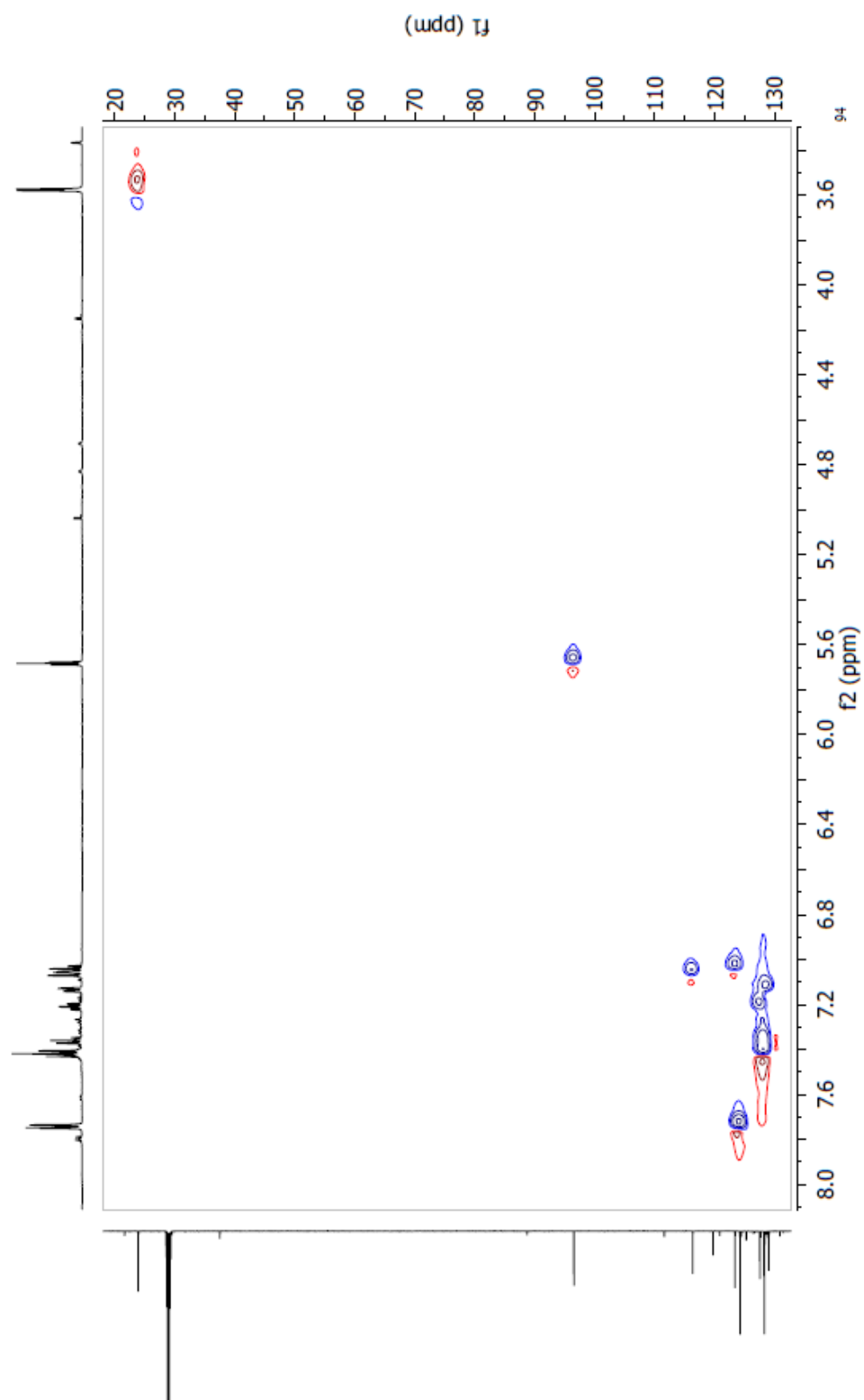
HSQC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 1-(3,4,5-trimethoxyphenyl)vinyl ether (11bd)

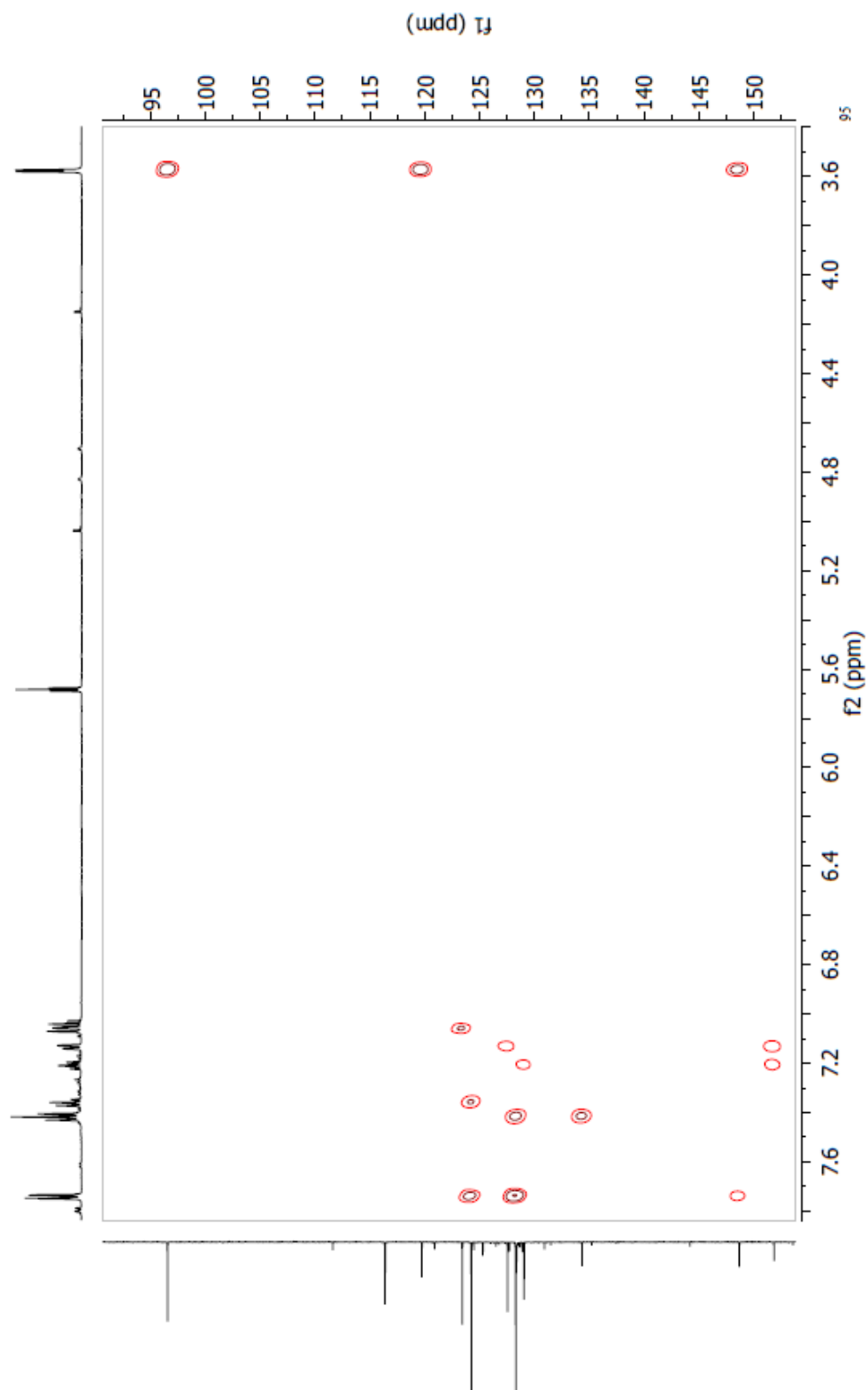
HMBC (600, 151 MHz, Acetone- d_6): 2-Allyl-5-methoxyphenyl 1-(3,4,5-trimethoxyphenyl)vinyl ether (11bd)

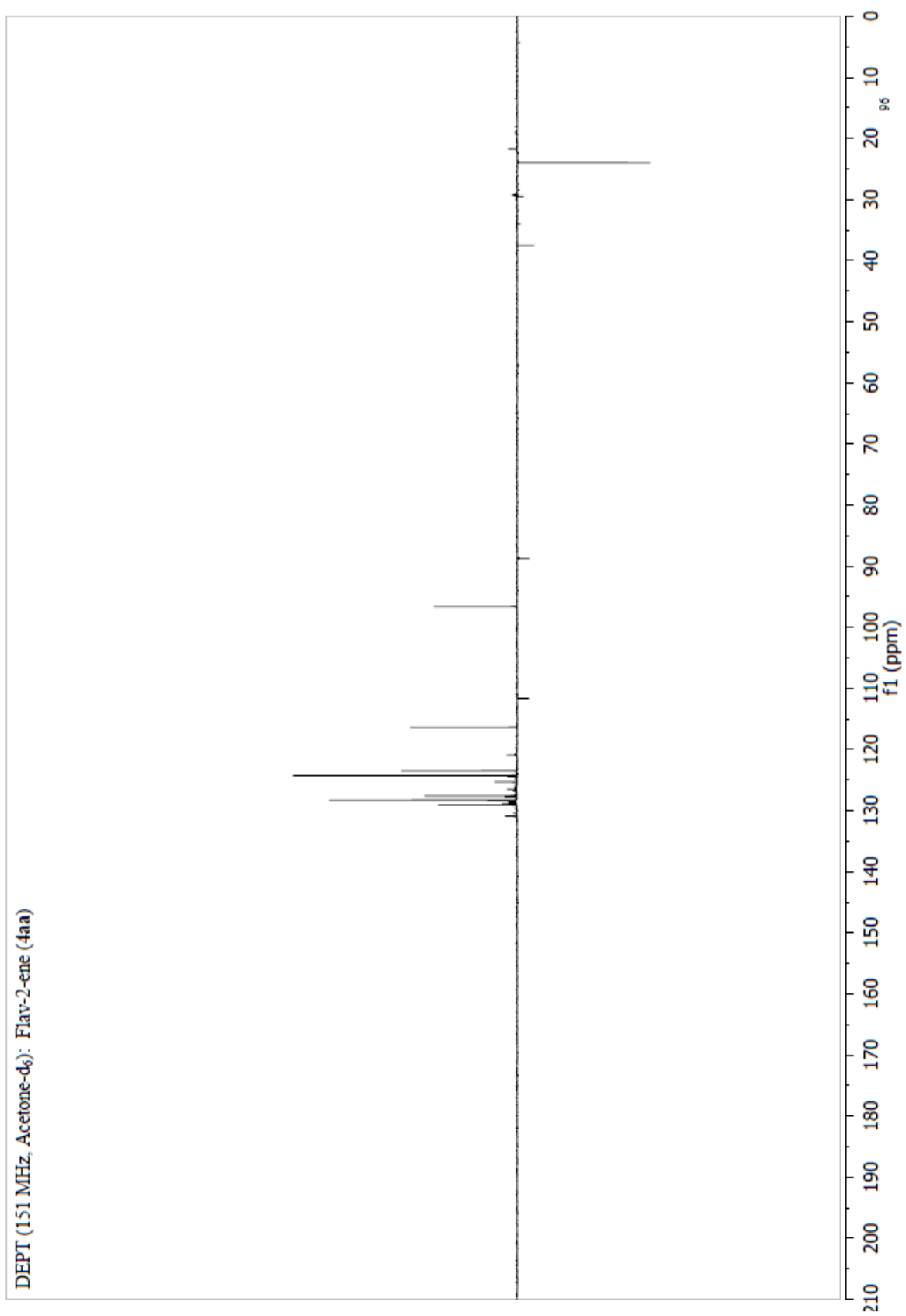






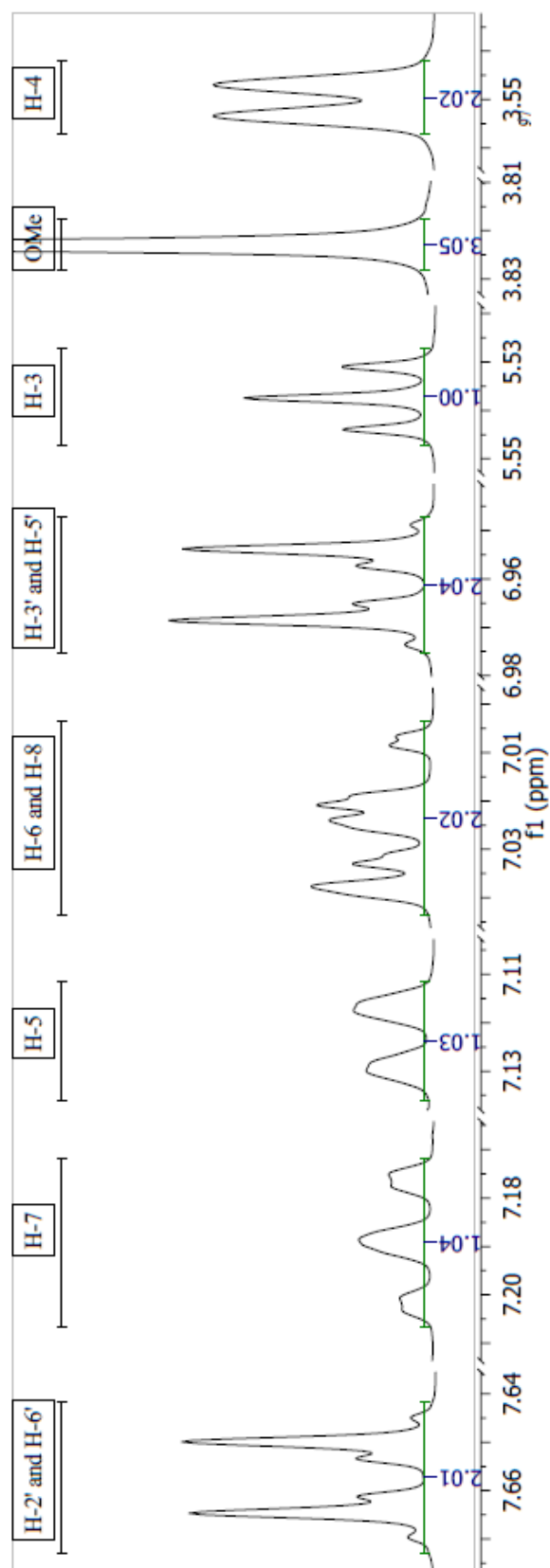
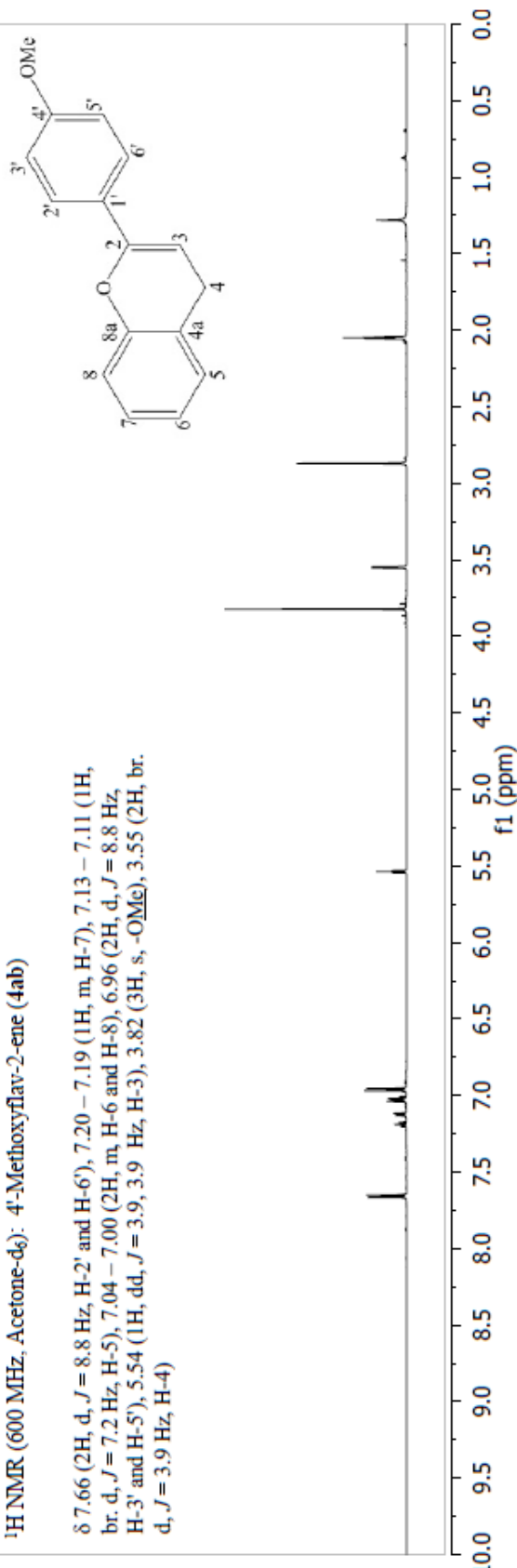
HSQC (600, 151 MHz, Acetone- d_6): Flav-2-ene (4aa)

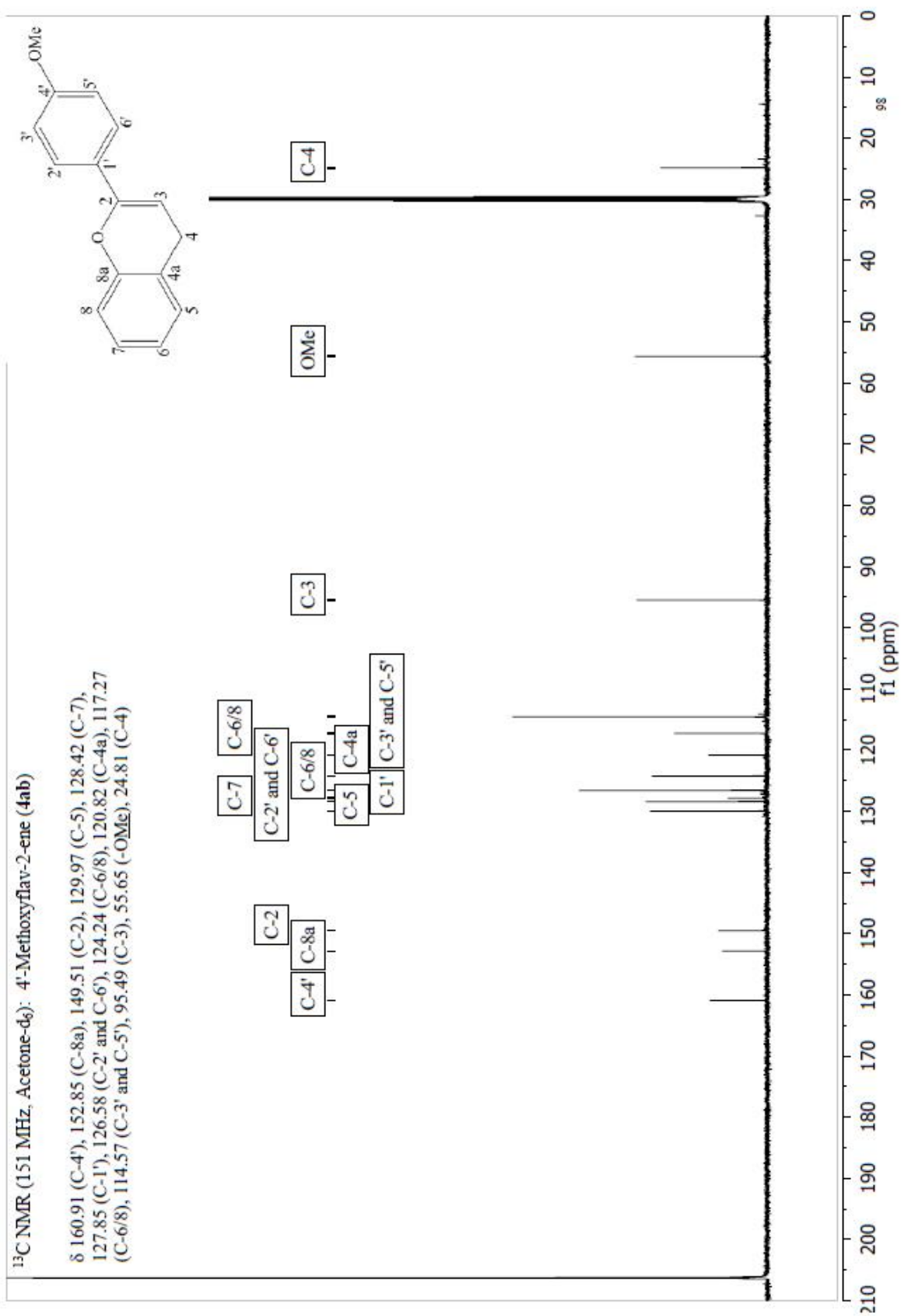
HMBC (600, 151 MHz, Acetone- d_6): Flav-2-ene (4aa)



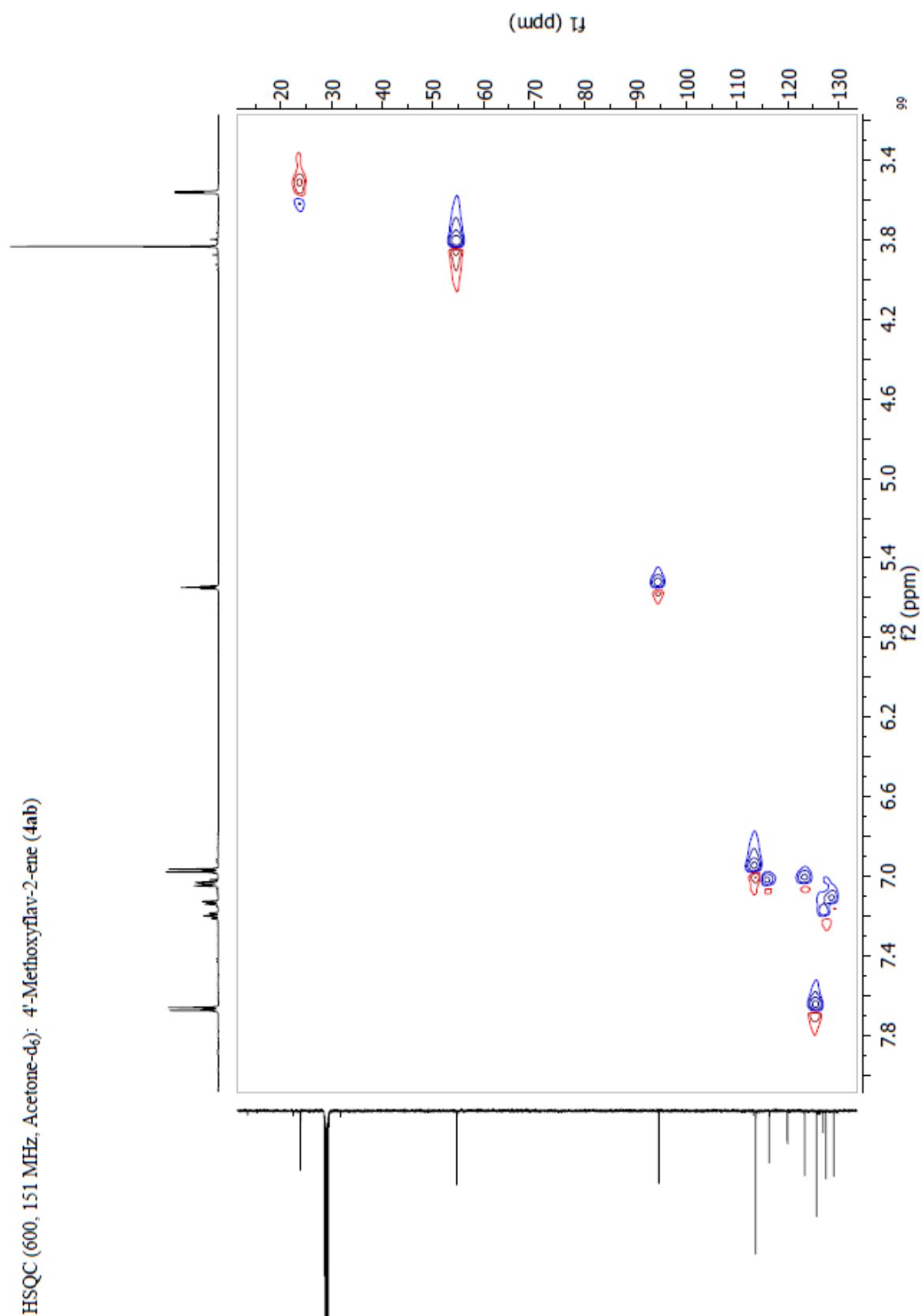
¹H NMR (600 MHz, Acetone-d₆): 4'-Methoxyflav-2-ene (4ab)

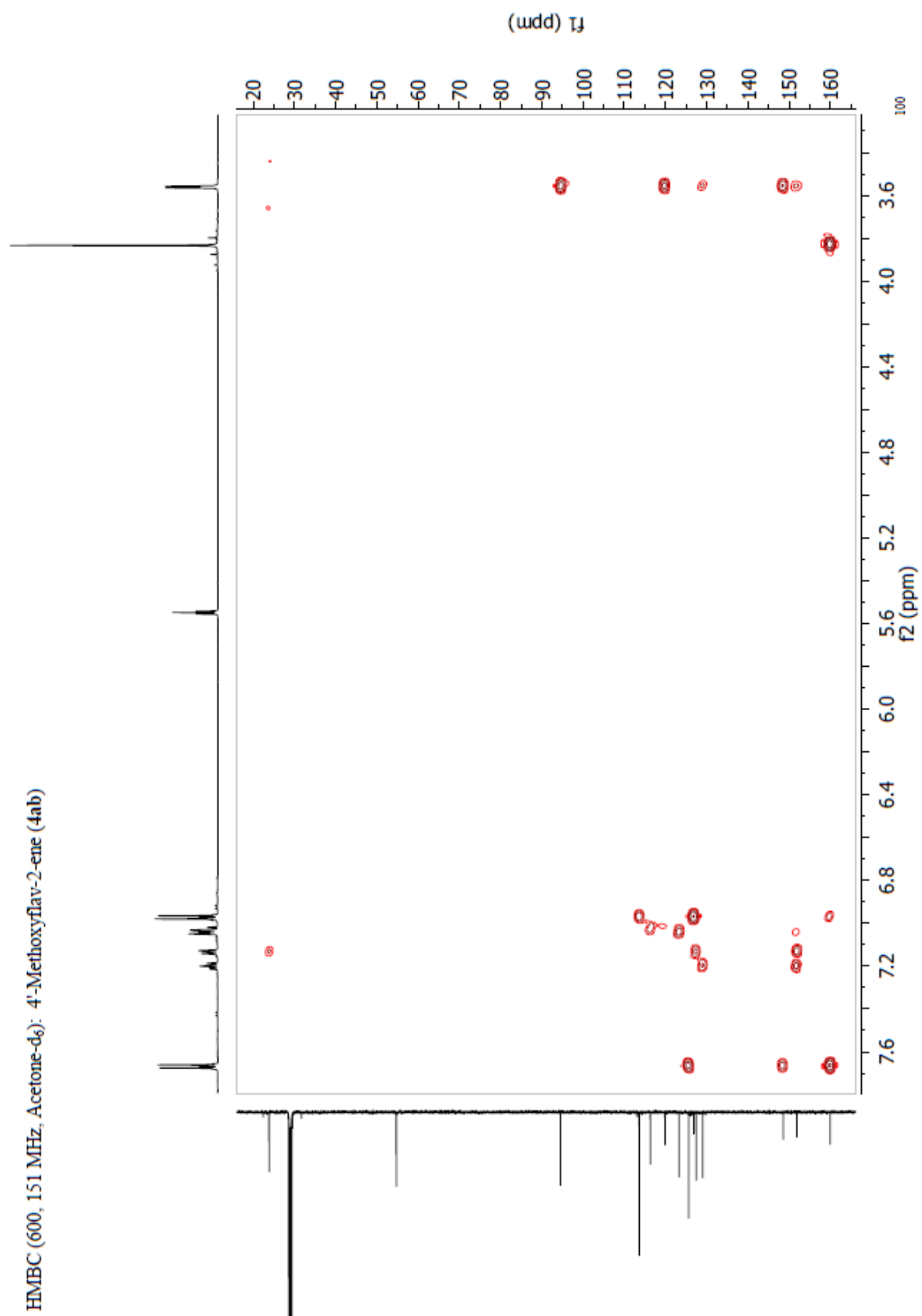
δ 7.66 (2H, d, $J = 8.8$ Hz, H-2' and H-6'), 7.20 – 7.19 (1H, m, H-7), 7.13 – 7.11 (1H, br. d, $J = 7.2$ Hz, H-5), 7.04 – 7.00 (2H, m, H-6 and H-8), 6.96 (2H, d, $J = 8.8$ Hz, H-3' and H-5'), 5.54 (1H, dd, $J = 3.9$, 3.9 Hz, H-3), 3.82 (3H, s, -OMe), 3.55 (2H, br. d, $J = 3.9$ Hz, H-4)

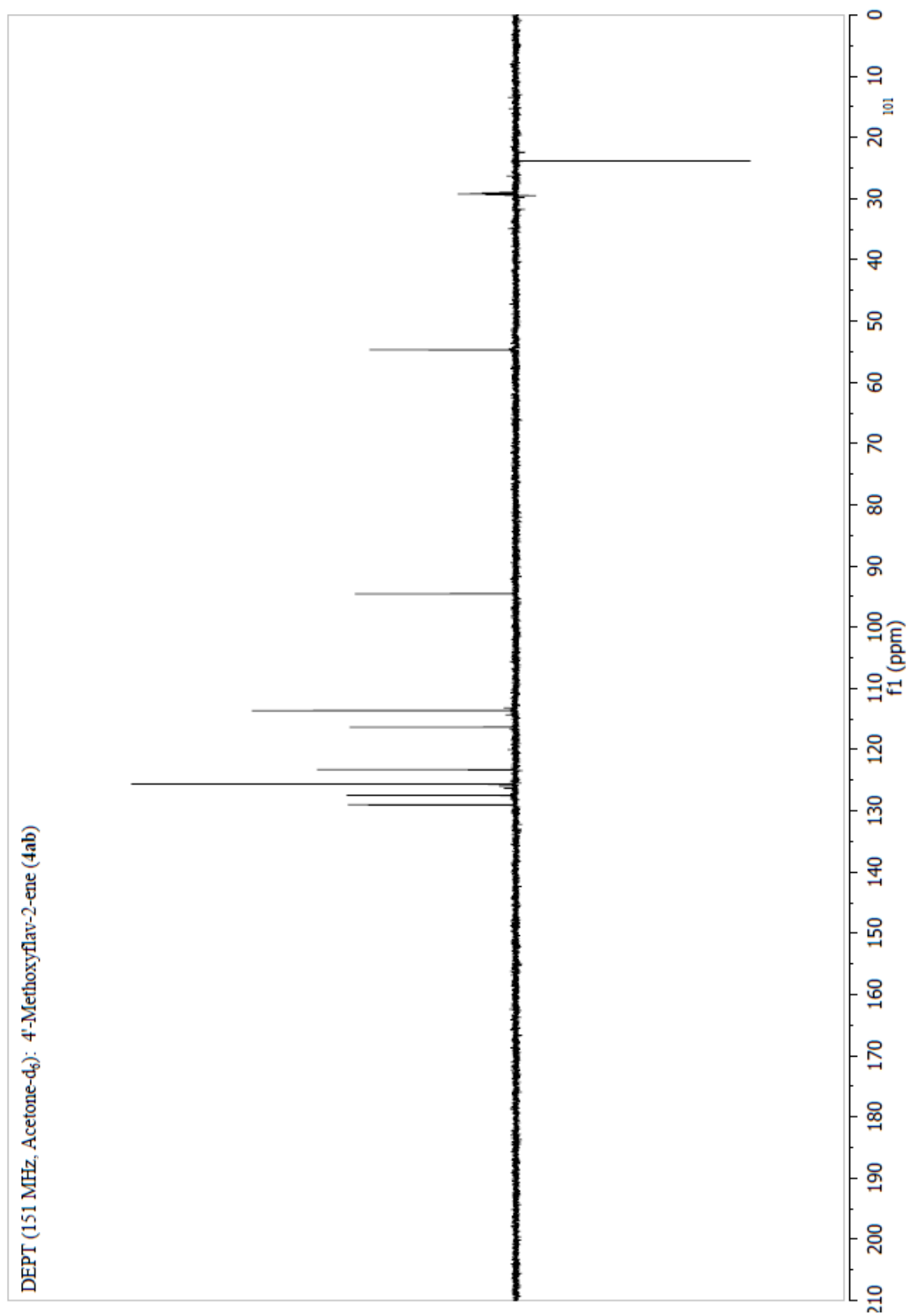


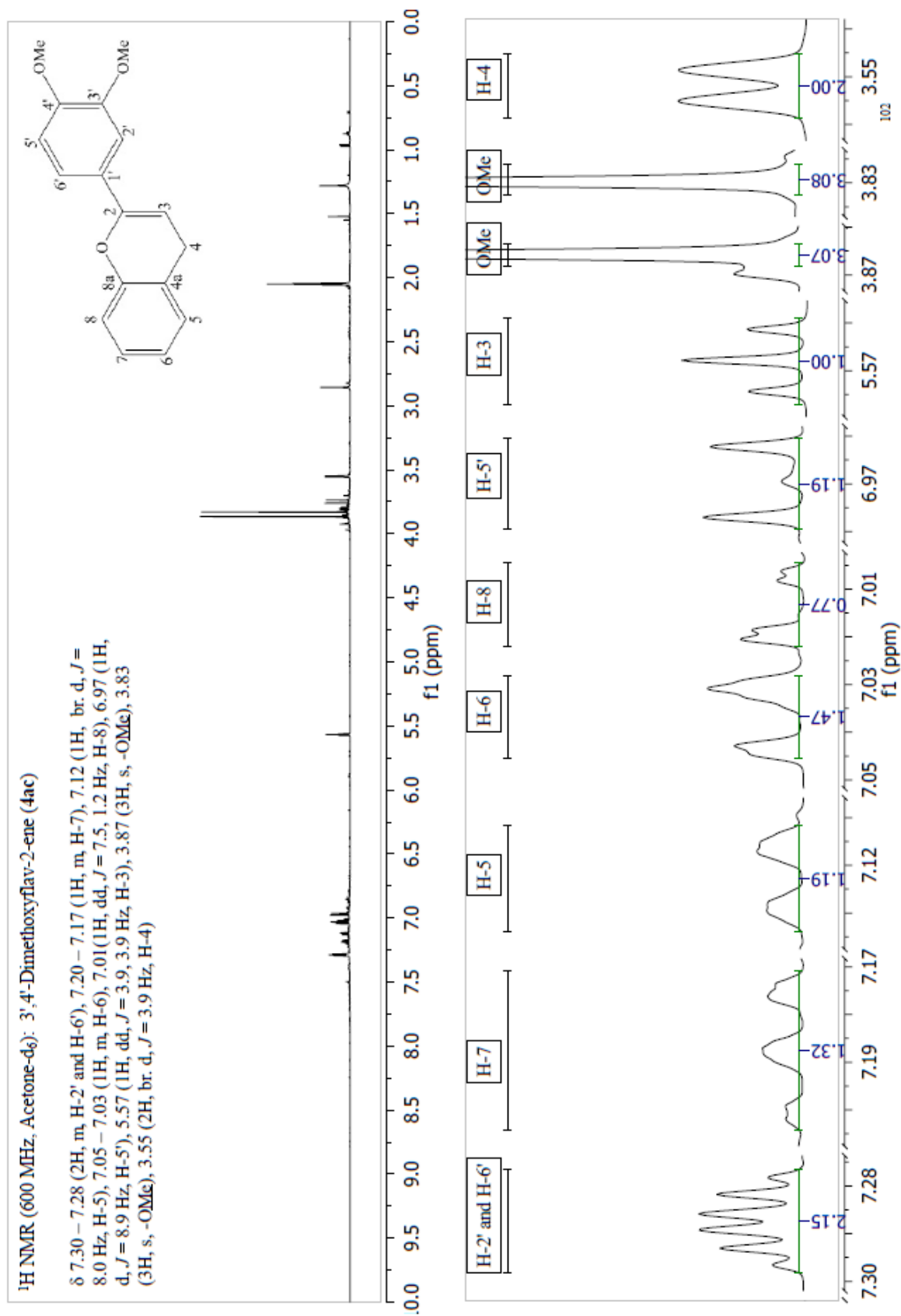


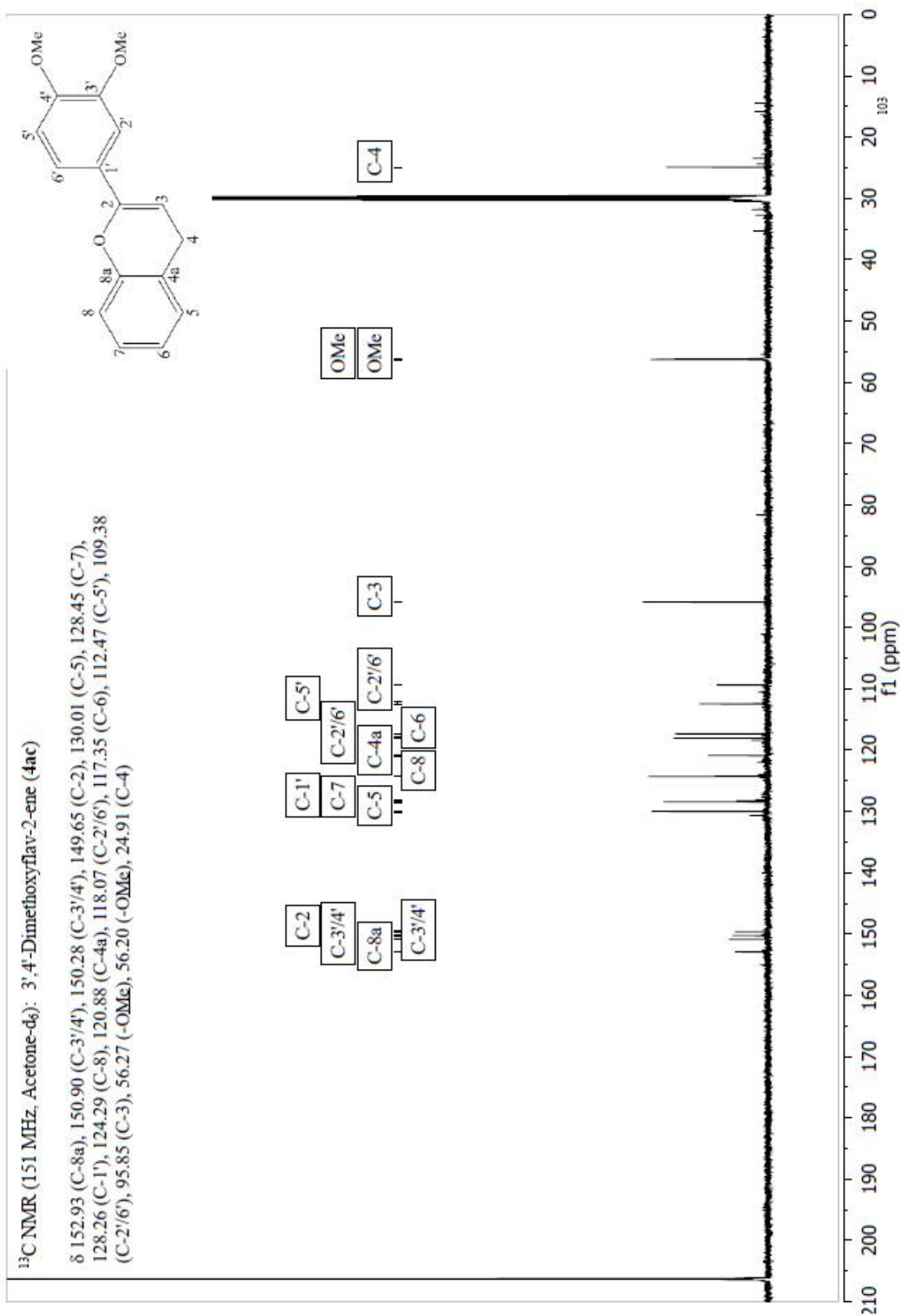
HSQC (600, 151 MHz, Acetone- d_6): 4'-Methoxyflav-2-ene (4ab)



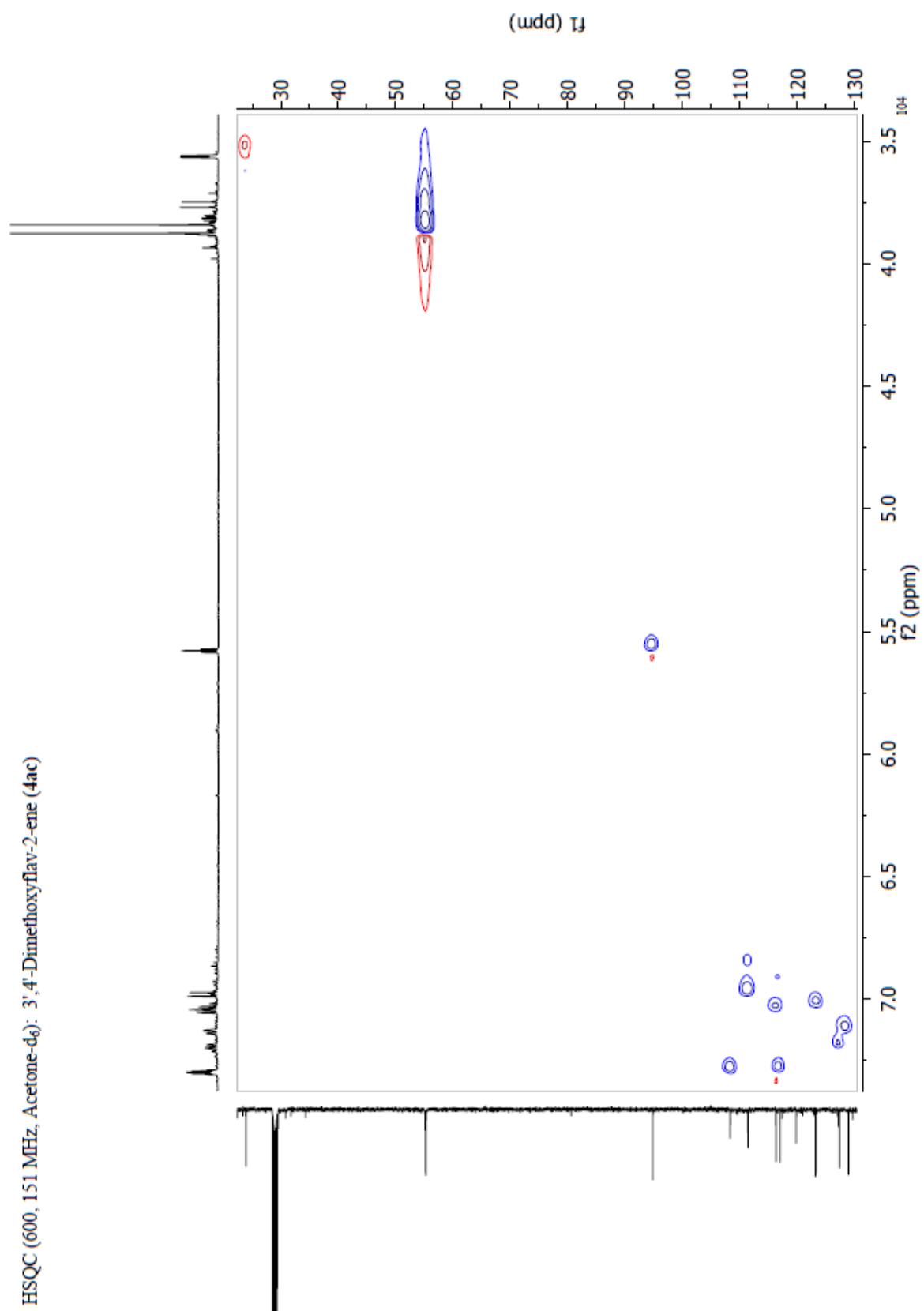
HMBC (600, 151 MHz, Acetone- d_6): 4'-Methoxyflav-2-ene (4ab)

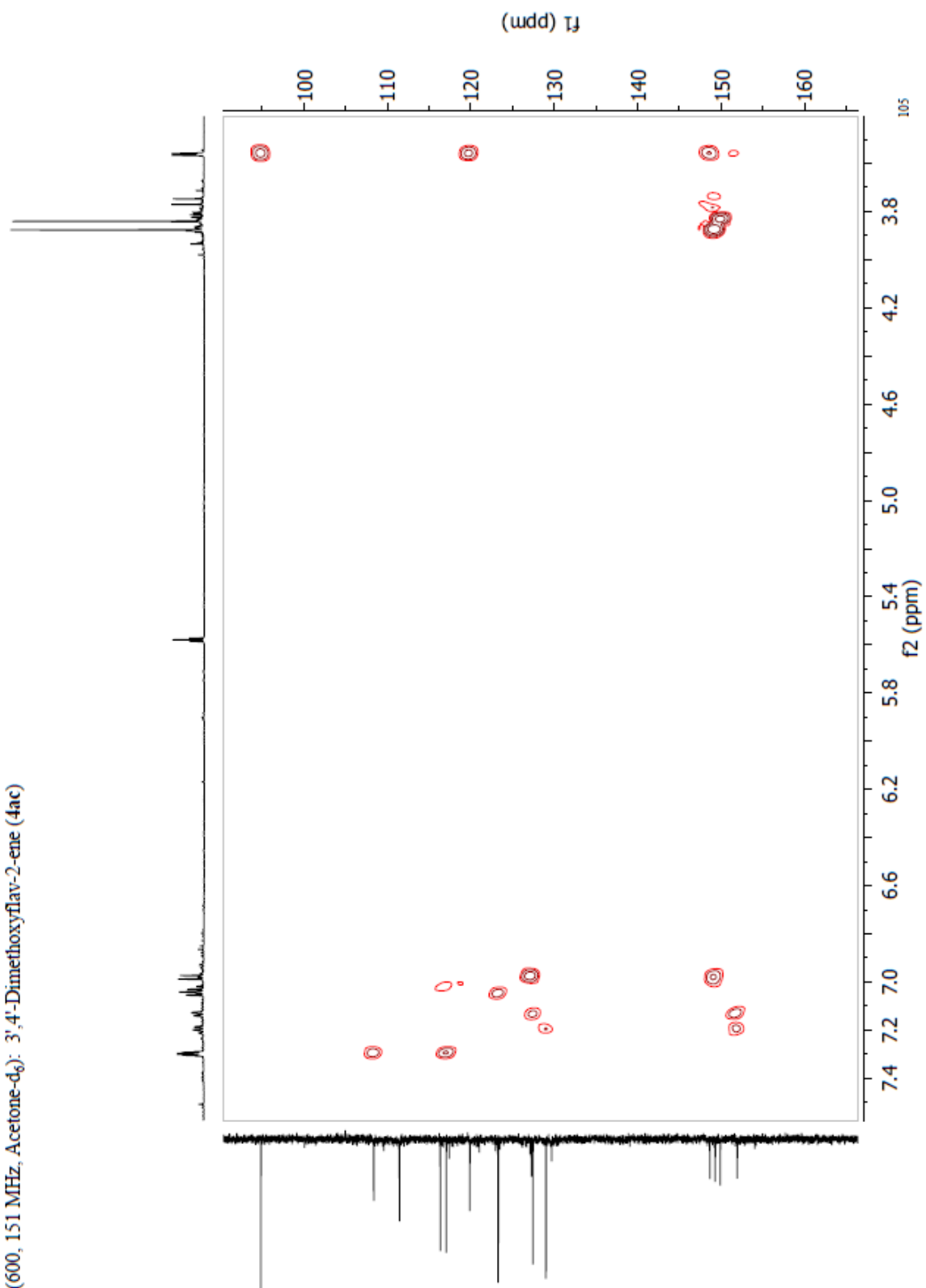


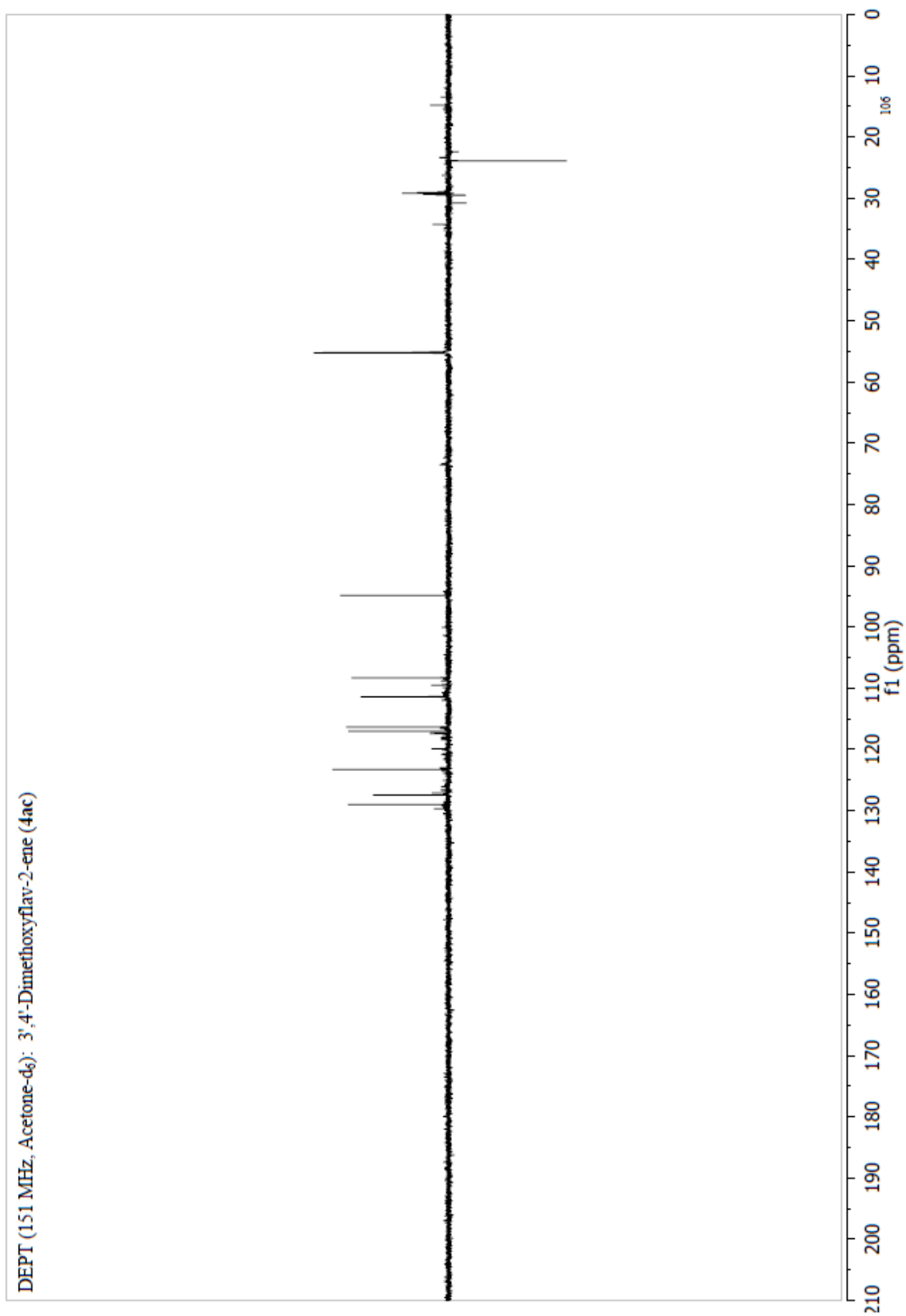


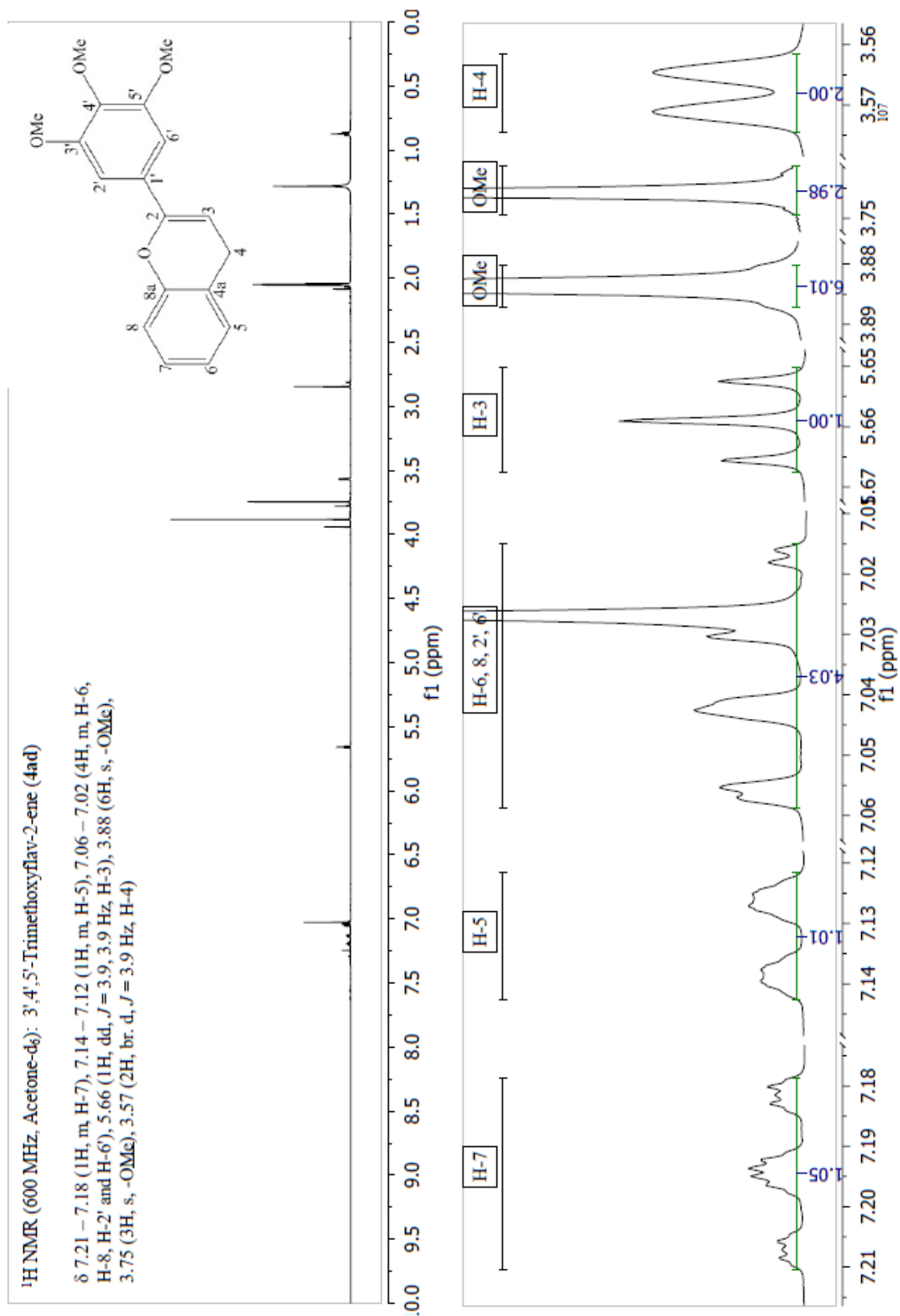


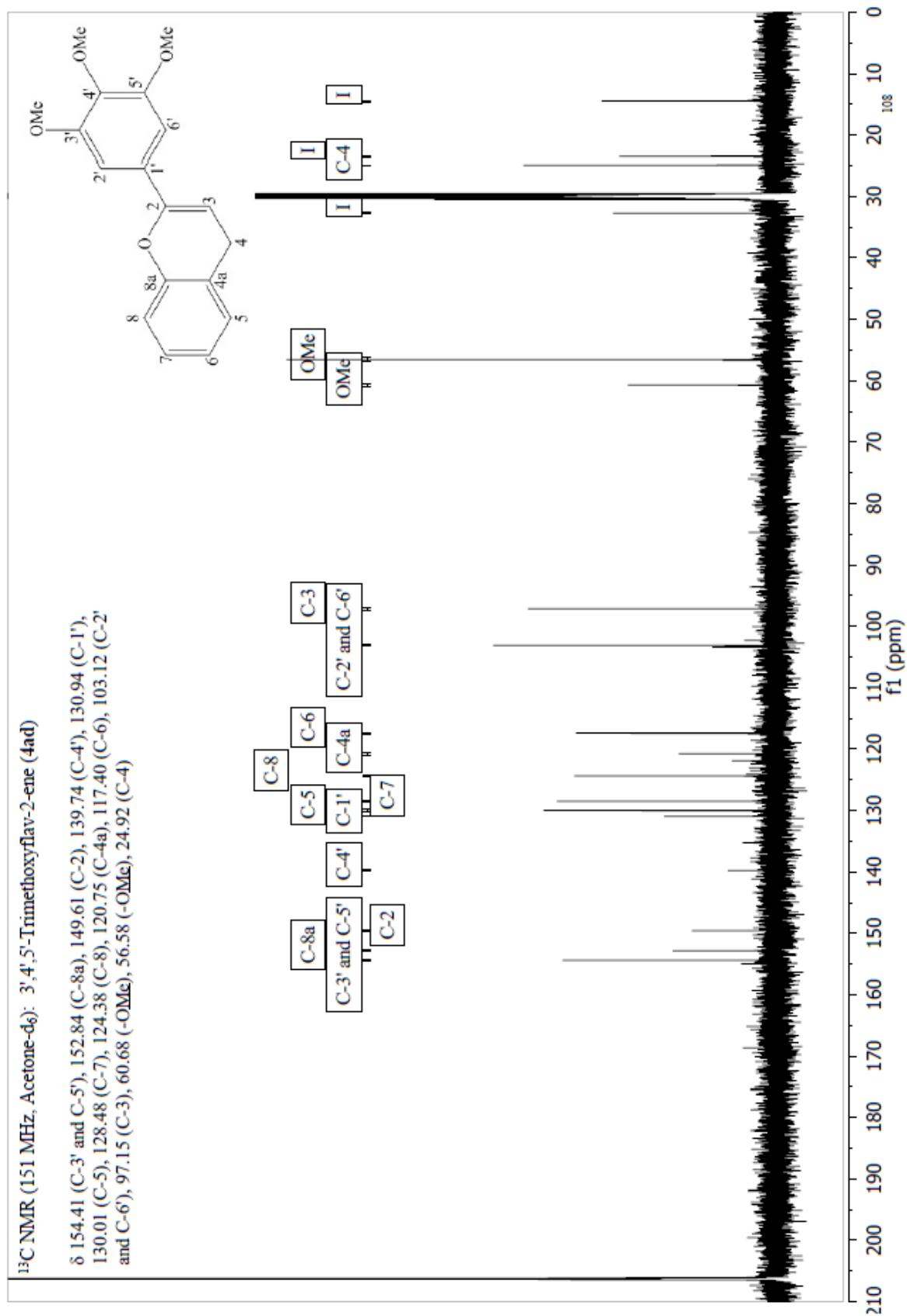
HSQC (600, 151 MHz, Acetone- d_6): 3',4'-Dimethoxyflav-2-ene (4ac)



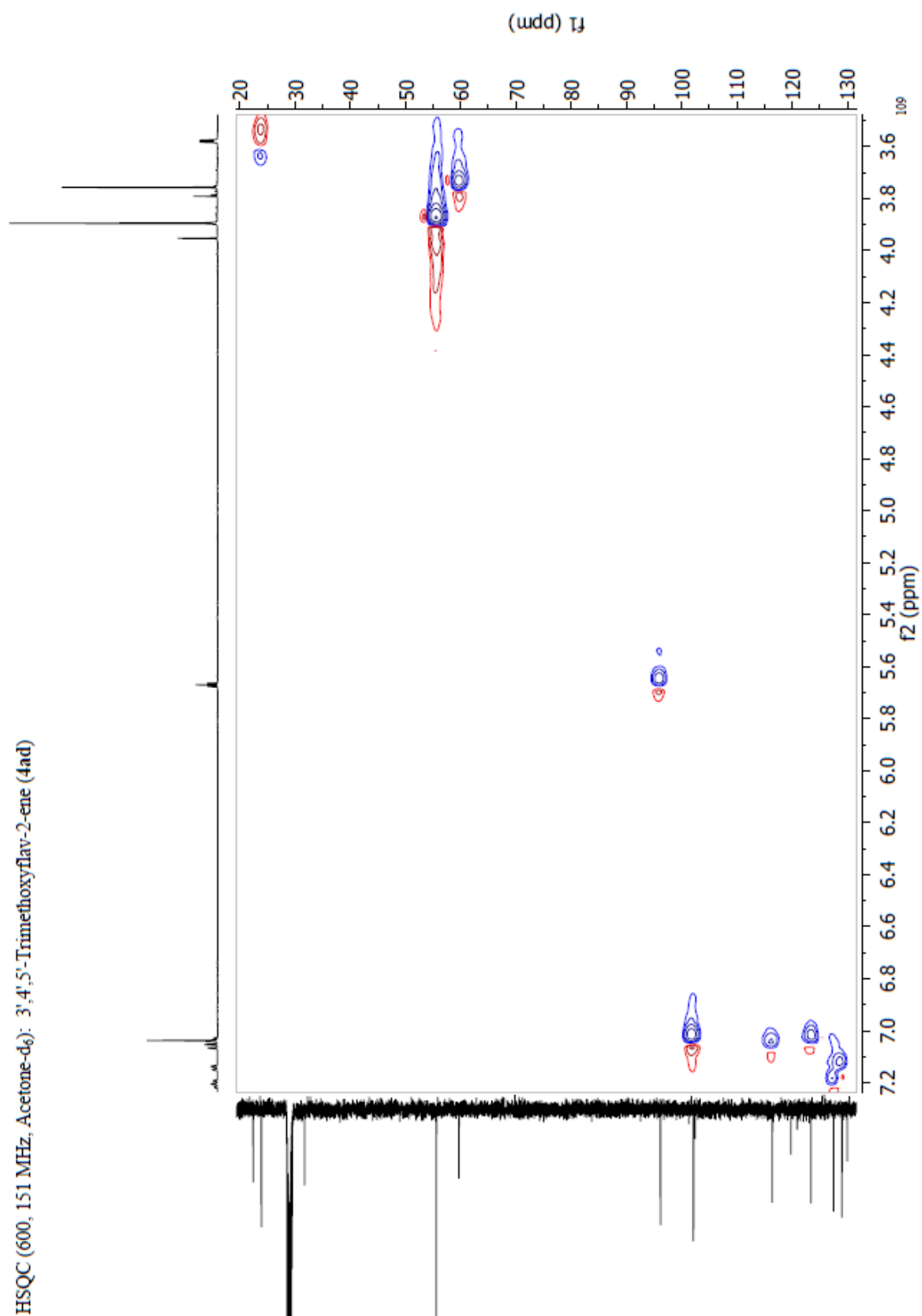
HMBC (600, 151 MHz, Acetone- d_6): 3',4'-Dimethoxyflav-2-ene (4ac)

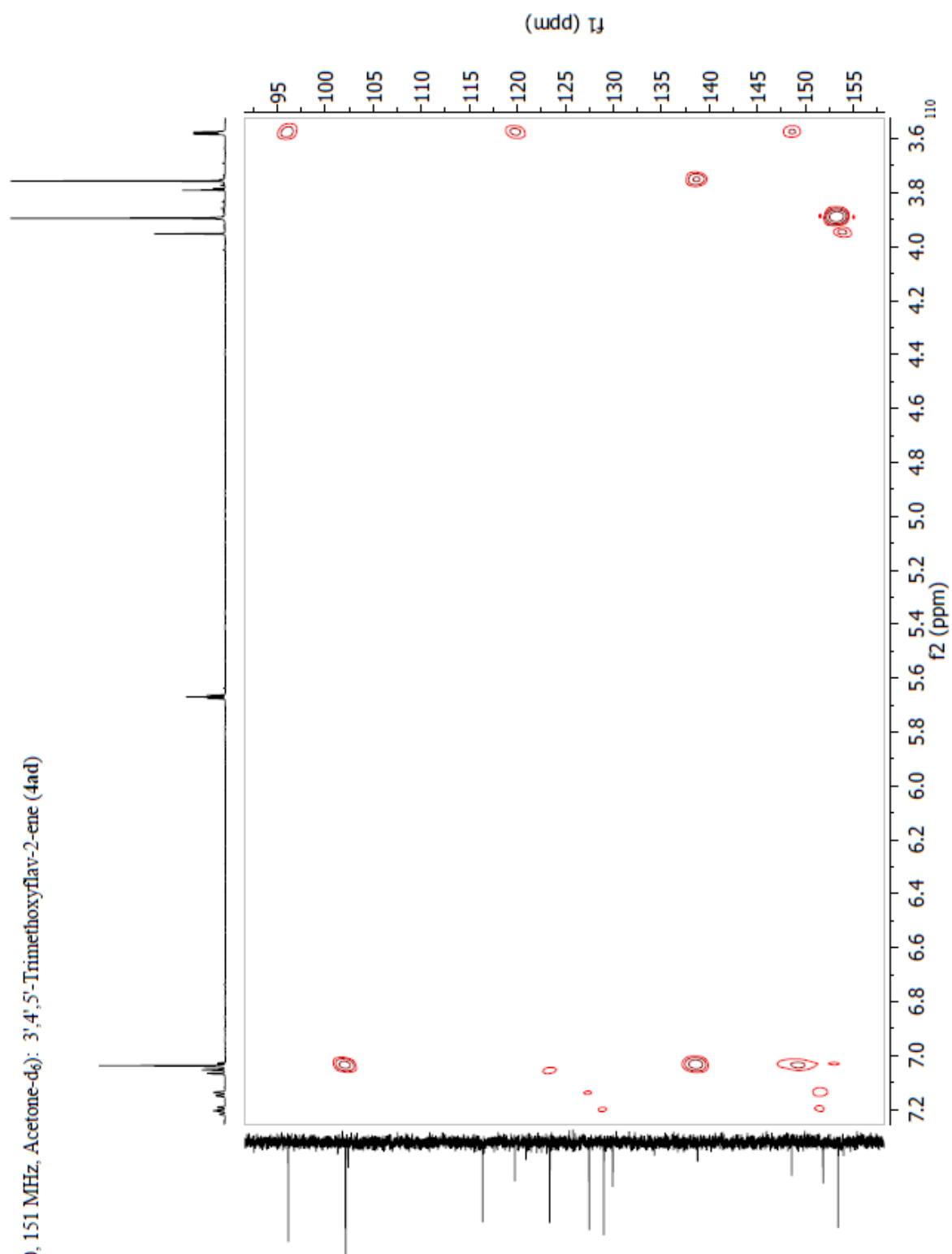


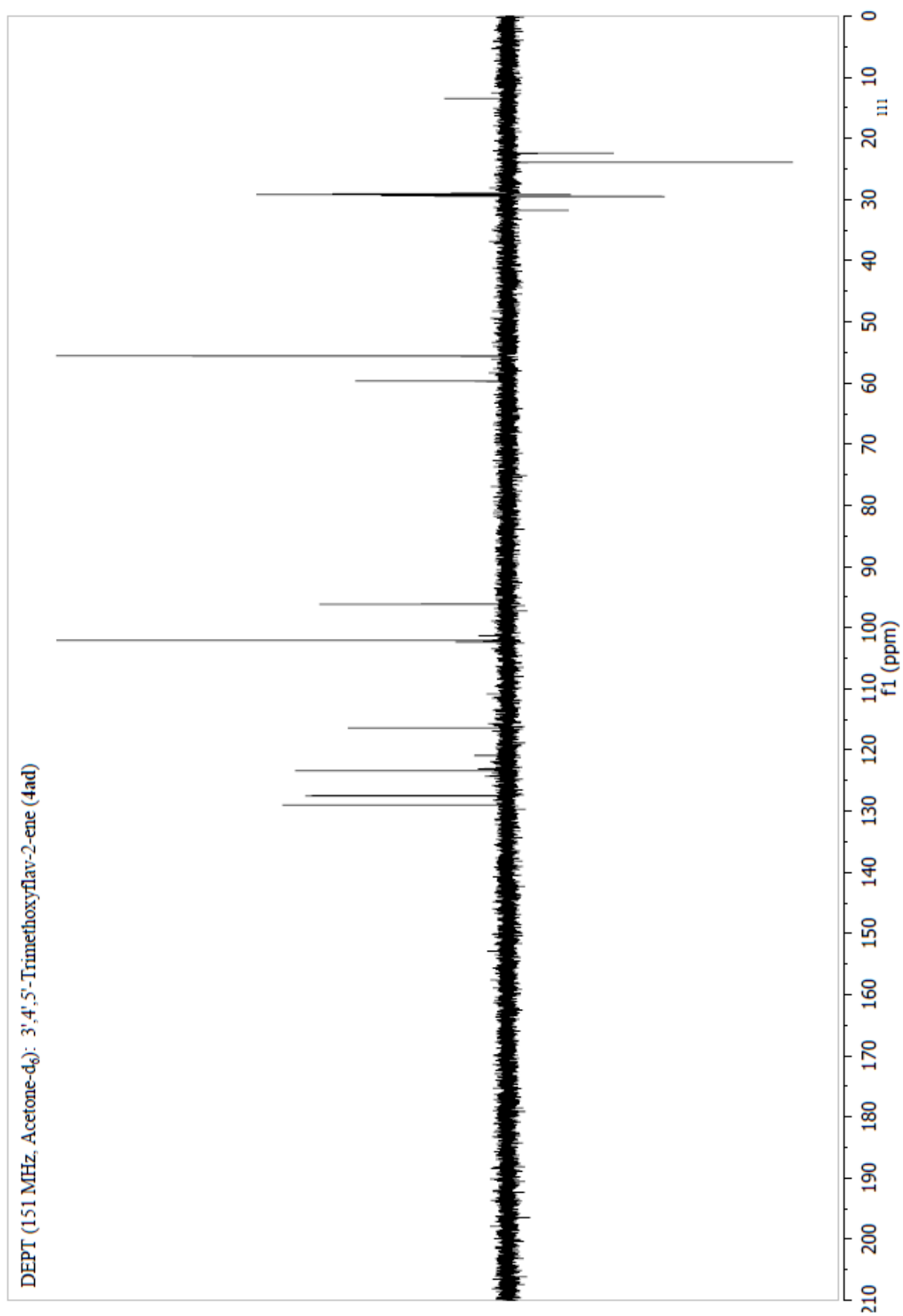


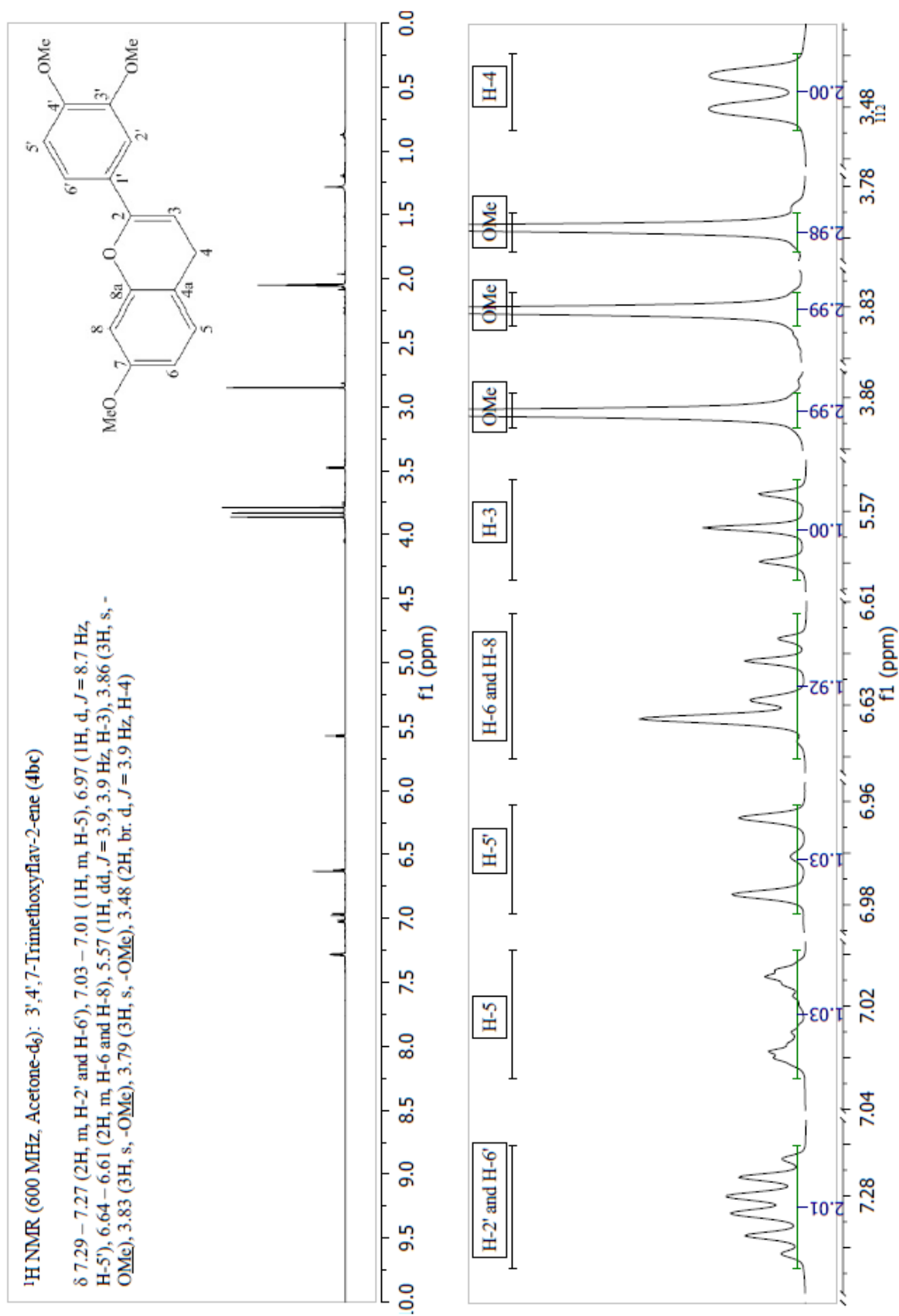


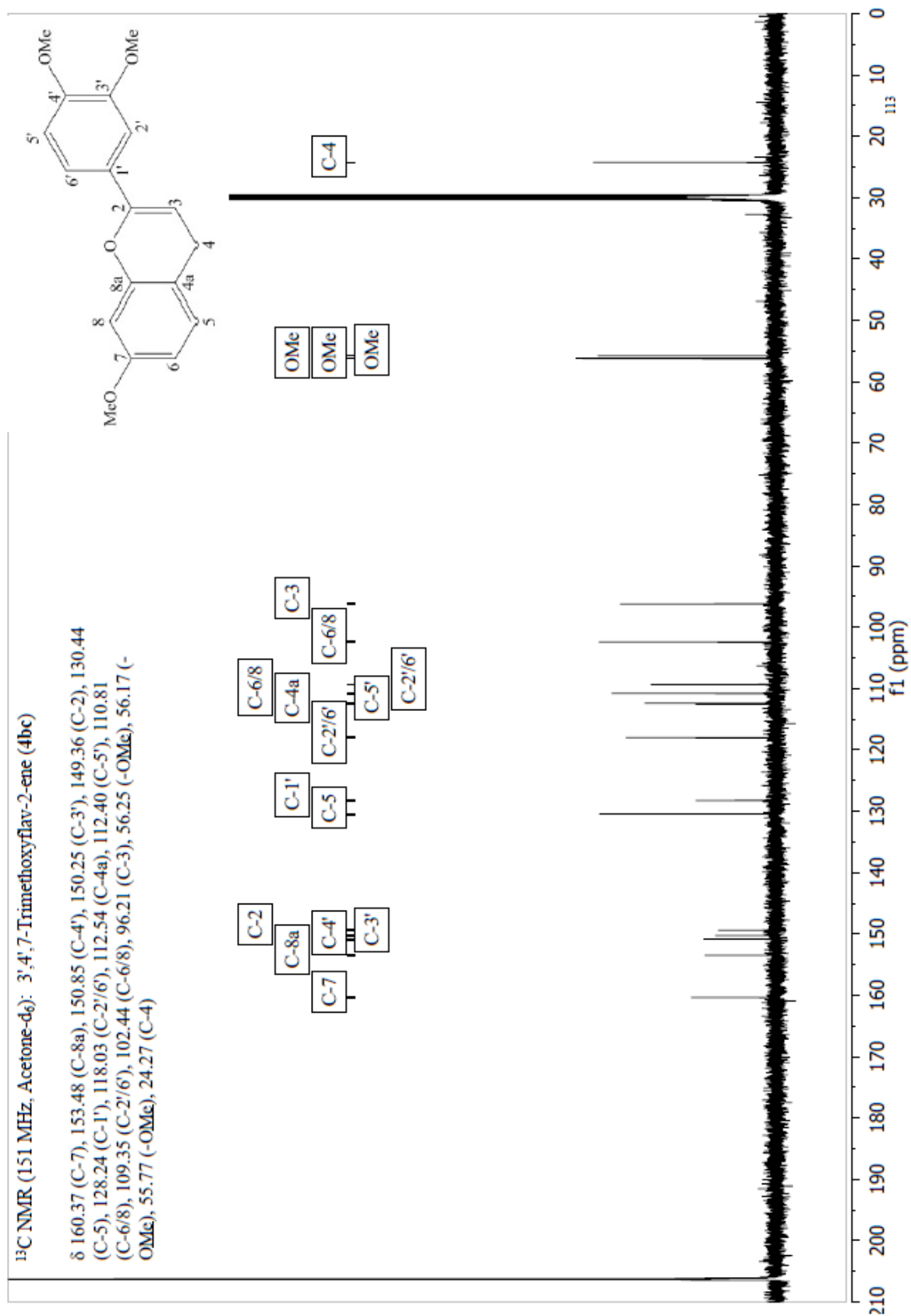
HSQC (600, 151 MHz, Acetone- d_6): 3',4',5'-Trimethoxyflav-2-ene (4ad)



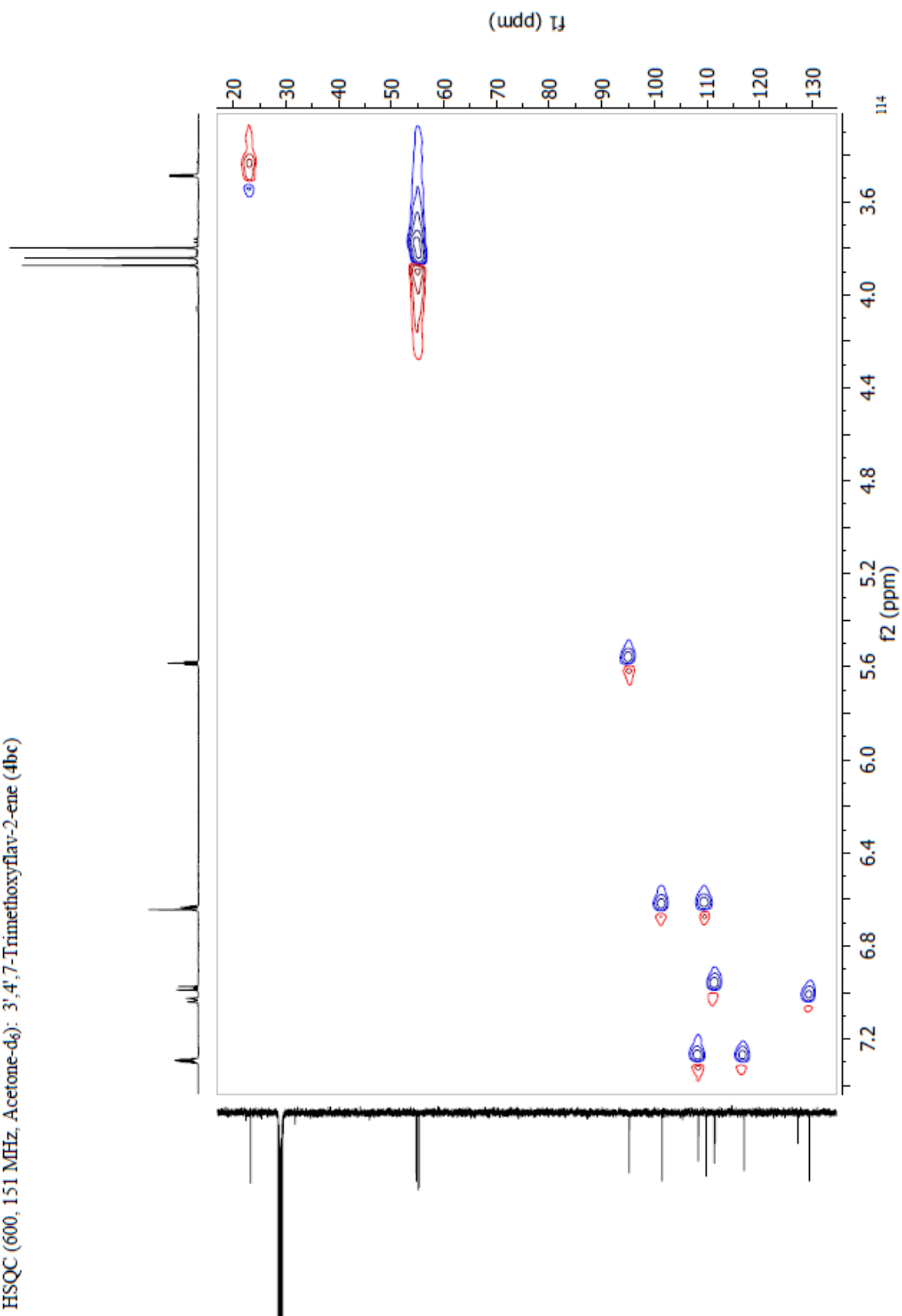
HMBC (600, 151 MHz, Acetone- d_6): 3',4',5'-Trimethoxyflav-2-ene (4ad)

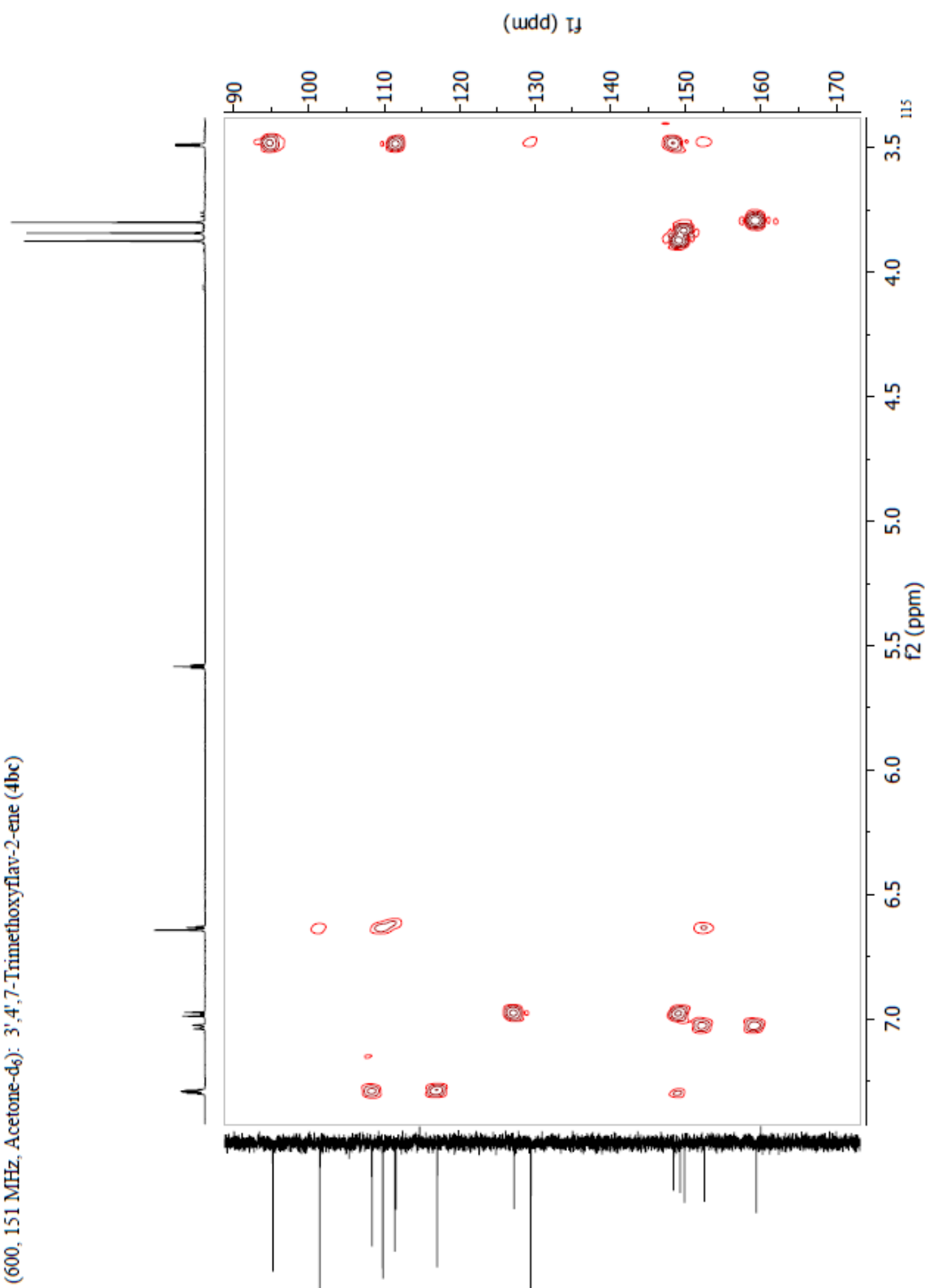


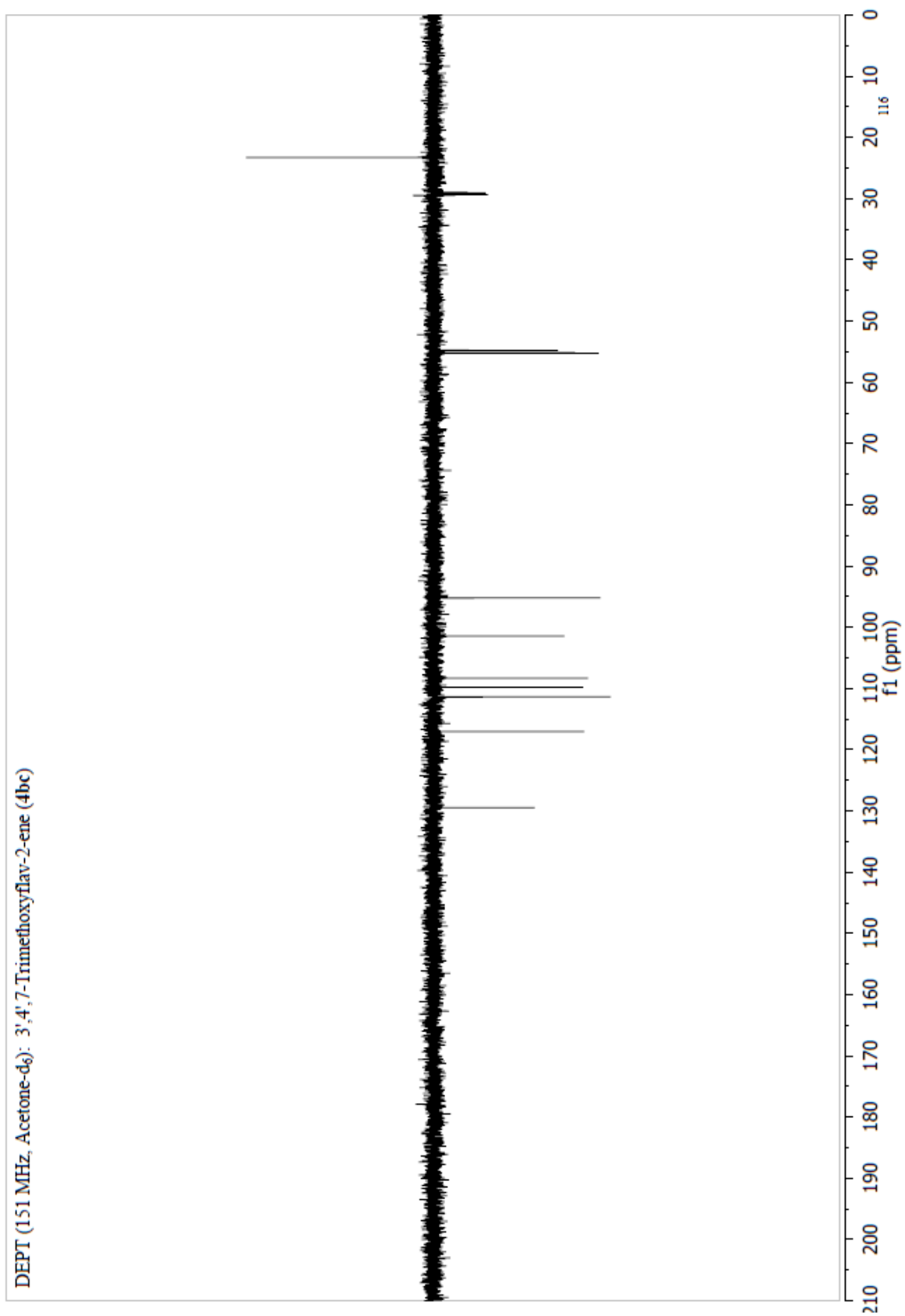


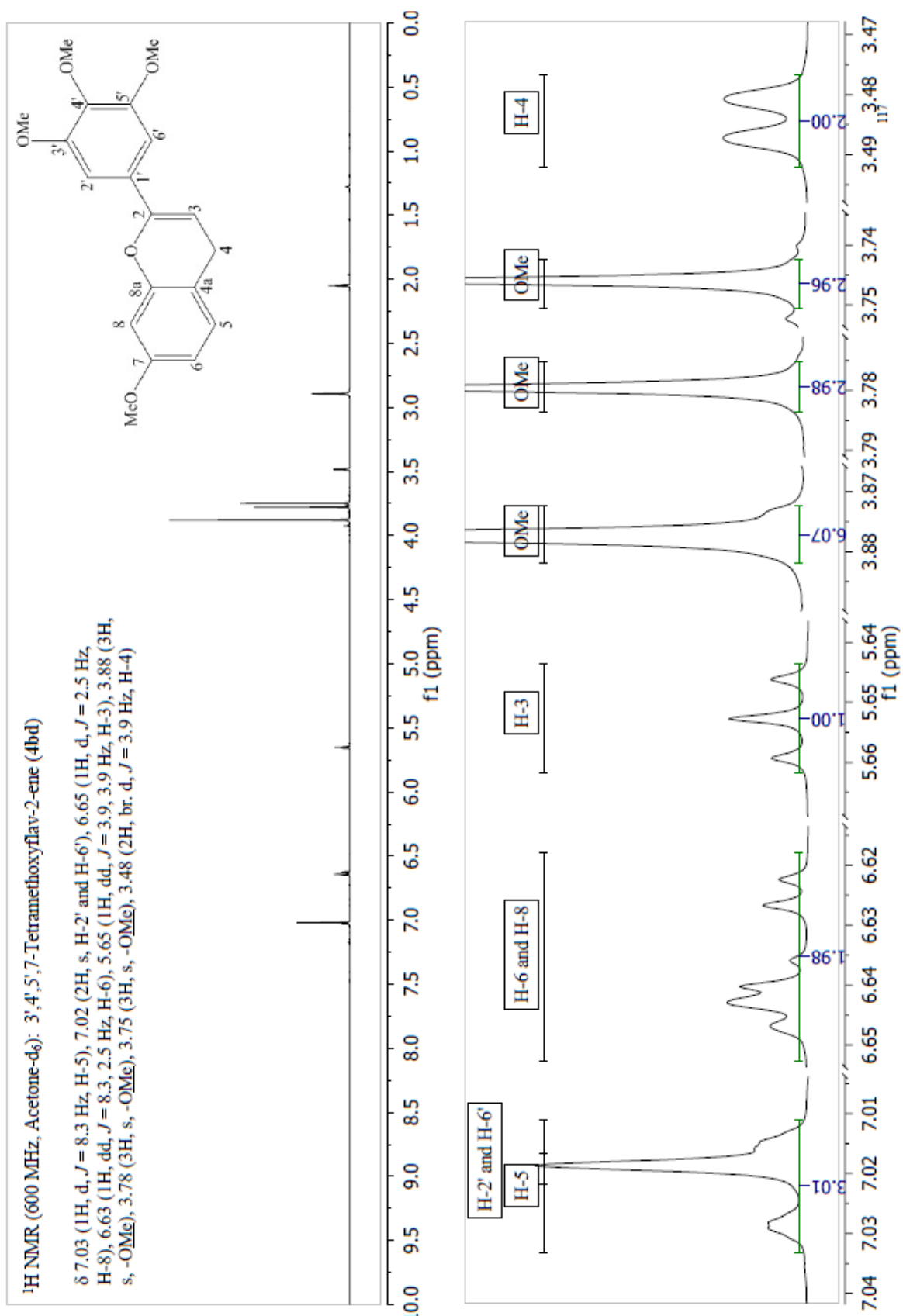


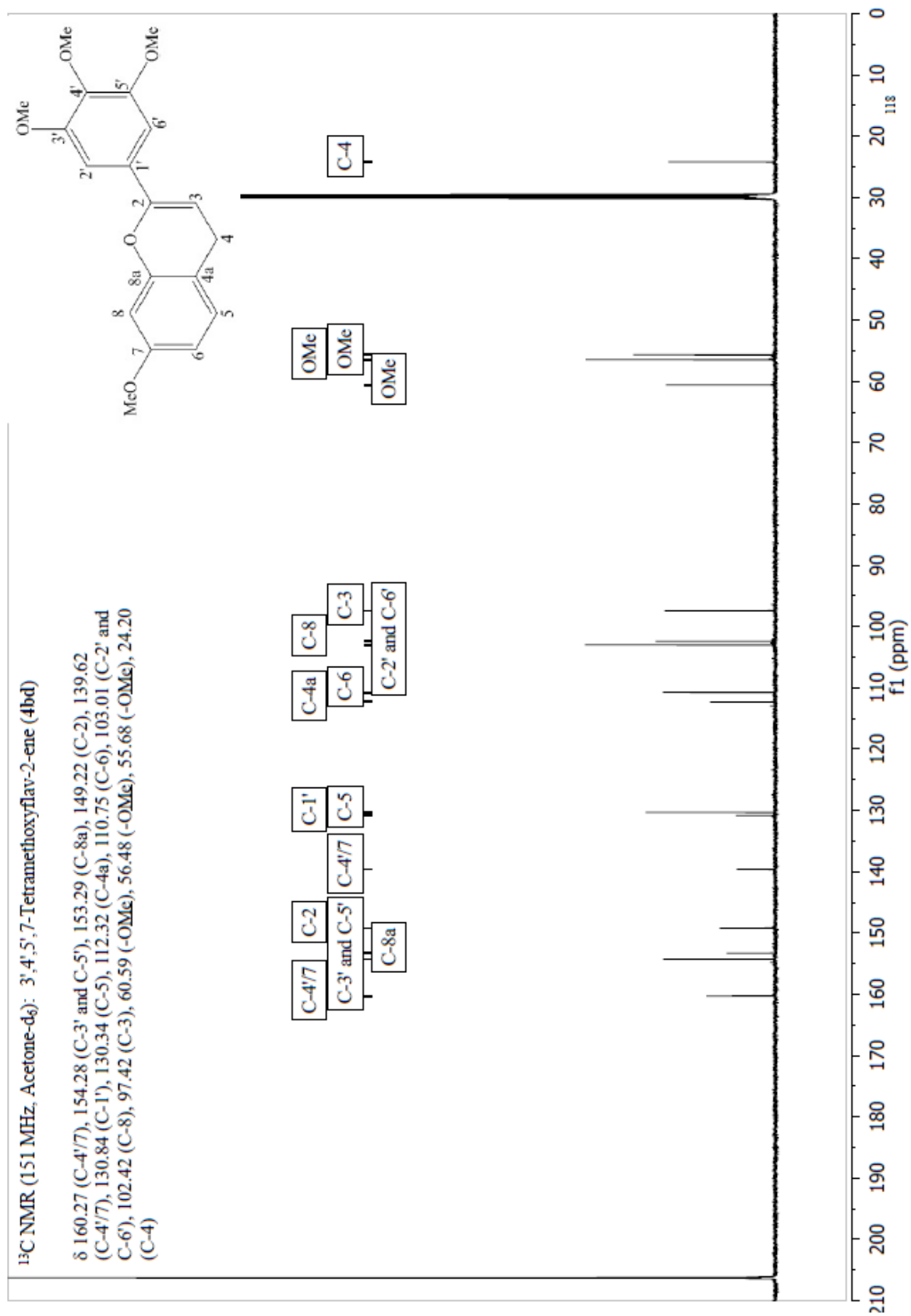
HSQC (600, 151 MHz, Acetone- d_6): 3',4',7-Trimethoxyflav-2-ene (4bc)

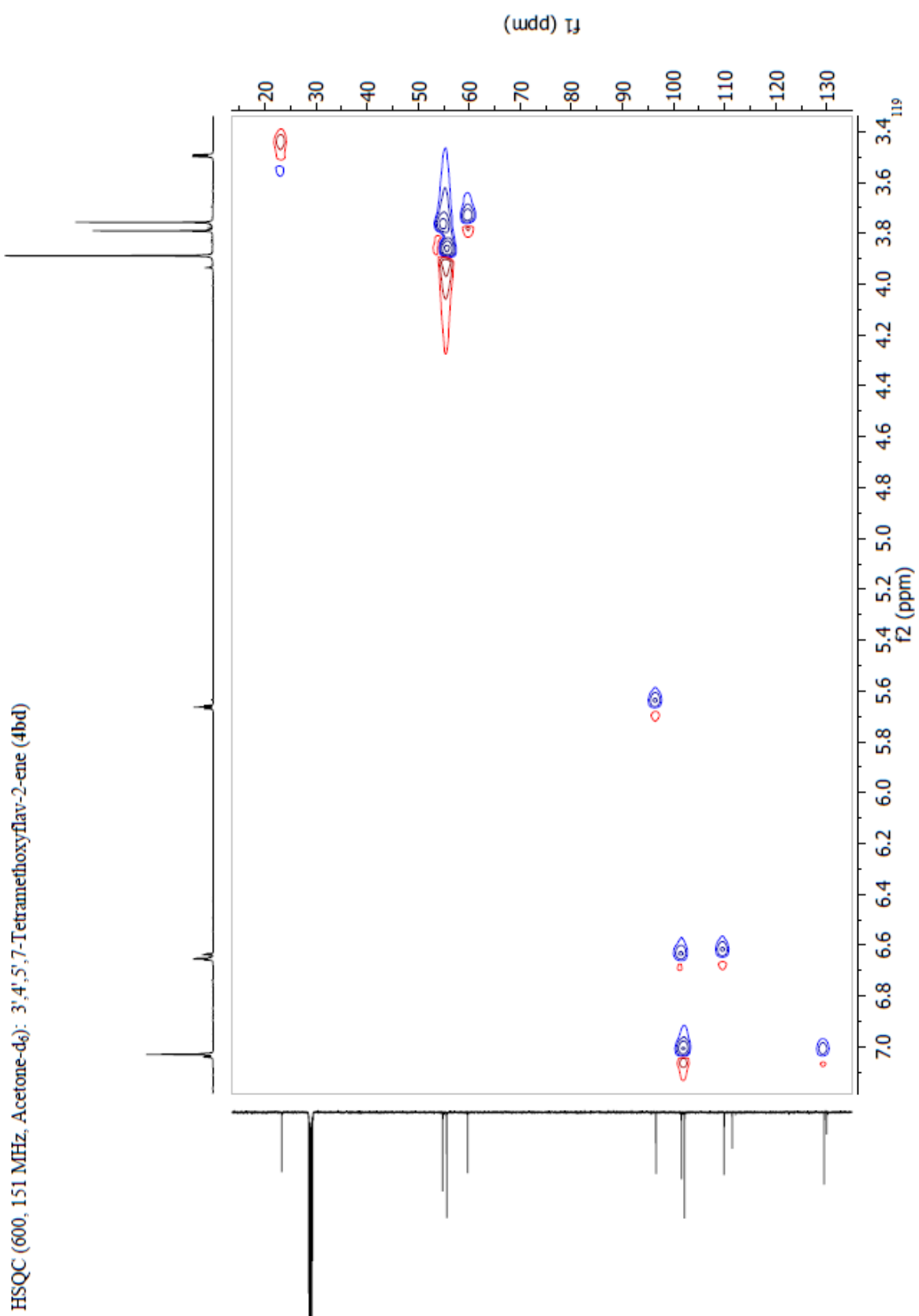


HMBC (600, 151 MHz, Acetone- d_6): 3',4',7'-Trimethoxyflav-2-ene (4bc)









HMBC (600, 151 MHz, Acetone- d_6): 3',4',5',7'-Tetramethoxyflav-2-ene (4bd)