Synthesis of β-Cyanopropan-1-one Derivates by Domino Reaction

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Supporting Information for

Experimental Section

General information:

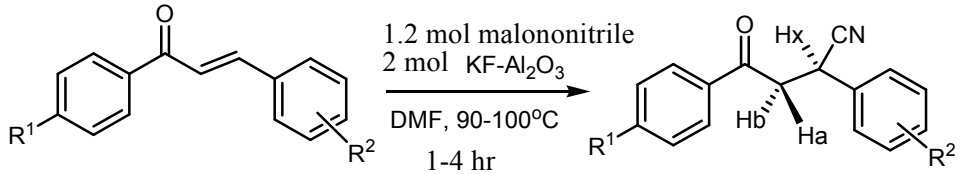
All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates. The silica gel (200−300 meshes) for column chromatography was from the Qingdao Marine Chemical Factory in China, and the distillation range of petroleum is 60−90℃. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on the Varian Mercury-plus 300BB instruments, and spectral data are reported in *ppm* relative to tetramethylsilane (TMS) as internal standard. MS were measured on a HP-5988 spectrometer by direct inlet at 70 eV, and signals were given in *m*/*z* with relative intensity (%) in brackets.

Typical procedure for the reactions

General Procedure for Preparation of KF-Al_2O_3

To a solution of KF (58 g) in water (100 mL) was added Al_2O_3 (100 g) with stirring. The mixture was stirred for 3 hr at 80℃, then the solvent was evaporated and the solid was dried for 4 hr at 120℃ to give KF- Al_2O_3.

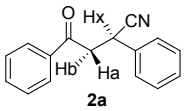
Synthesis of (2R,2S)-2,4-diphenylbutyronitrile 2a-i



1 **2**

Compound malononitrile(2.4mmol), KF-Al_2O_3(4mmol), α,β-unsaturated ketone **1a-i** (2mmol) and DMF (30mL) was added to a dry flask.. The mixture was stirred at 90-100℃ for 1-8 h, then cooled to room temperature. The solid material was filtered off and washed with DMF. The filtrate was concentrated and the residue was isolated with petroleum ether and ethyl acetate to give the target products **2a-i.**

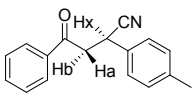
Spectroscopic data for following adducts
(2R,2S)-4-Oxo-2,4-diphenylbutanenitrile 2a



2a

Light yellow solid, yield 63%, mp 116-118℃, IR(KBr,cm^{-1}): 2237(CN), 1681(C=O); ^{1}HNMR (300MHz,$CDCl_3$):δ_H 7.905-7.876 (d, 2H, *J*=8.7Hz, Ar-H), 7.581-7.536 (m, 1H, Ar-H), 7.456-7.306 (m, 7H, Ar-H), 4.545-4.498 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.740-3.652 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.527-3.439 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.3Hz, H_b); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 194.5, 135.4, 135.1, 133.7, 129.1, 128.6, 128.2, 127.9, 127.3, 120.5, 44.3, 31.7; MS(EI, 70ev) (m/z,%): 235 (M^+,52.4), 130(33.9), 105(100), 103(23.0), 77(83.9); Anal.Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95; Found: C, 81.59; H, 5.55; N, 6.10. CA 6268-00-4.[2]

(2R,2S)-4-Oxo-4-phenyl-2-*p*-tolylbutanenitrile 2b

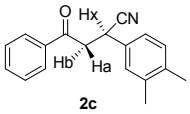


2b

Light yellow solid, yield 72%, mp 130-132℃, IR(KBr, cm^{-1}): 2239(CN), 1676(C=O); ^{1}HNMR (300MHz, $CDCl_3$): δ_H 7.909-7.882 (d, 2H, *J*=8.1Hz, Ar-H), 7.589-7.540 (m, 1H, Ar-H), 7.462-7.411 (m, 2H, Ar-H),7.313-7.285 (d, 2H, *J*=8.4Hz, Ar-H), 7.138-7.155 (d, 2H, *J*=8.4Hz, Ar-H), 4.515-4.469 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.724-3.638 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.507-3.427(dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.323(s, 3H, Ar-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 194.6, 138.1, 135.5, 133.7, 132.1, 129.8, 128.7,

127.9, 127.2, 120.7, 31.4, 20.9; MS(EI, 70ev) (m/z,%): 249 ($M^{+\cdot}$,28.3), 144(69.2), 117(40.9), 105(100), 77(88.1); Anal.Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62, 18.87; Found: C, 81.99; H, 5.95; N, 5.56. CA 95855-31-5.[3]

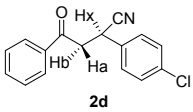
(2R,2S)-2-(3,4-Dimethylphenyl)-4-oxo-4-phenylbutanenitrile 2c



2c

Light yellow solid, yield 75%, mp 85-87℃, IR(KBr,cm^{-1}): 2237(CN), 1679(C=O); ^{1}HNMR(300MHz, $CDCl_3$):δ_H 7.910-7.882 (d, 2H, *J*=8.7Hz, Ar-H), 7.583-7.534 (m, 1H, Ar-H), 7.456-7.405 (m, 2H, Ar-H), 7.226(s, 1H, Ar-H), 7.177-7.118 (m, 2H, Ar-H), 4.474-4.428 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=5.7Hz, H_x), 3.720-3.632 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.496-3.415 (dd, 1H, $J_{b,x}$=5.7Hz, $J_{b,a}$=18.0Hz, H_b), 2.245(s, 3H, Ar-CH_3), 2.224 (s, 3H, Ar-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 194.7, 137.4, 136.7, 135.5, 133.6, 132.4, 130.2, 128.6, 128.4, 127.9, 124.6, 120.8, 44.4, 31.3, 19.6, 19.2; MS(EI, 70ev) (m/z,%): 263 ($M^{+\cdot}$,31.7), 158(42.9), 131(49.1), 105(100), 77(86.3); Anal.Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32; Found: C, 82.22; H, 6.55; N, 5.22.

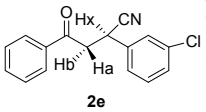
(2R,2S)-2-(4-Chlorophenyl)-4-oxo-4-phenylbutanenitrile 2d



2d

Light yellow solid, yield 55%, mp 109-110℃, IR(KBr,cm^{-1}): 2241(CN), 1675(C=O); ^{1}HNMR (300MHz, $CDCl_3$):δ_H 7.927-7.898 (d, 2H, *J*=8.7Hz, Ar-H), 7.628-7.579 (m, 1H, Ar-H), 7.497-7.472 (m, 2H, Ar-H), 7.446-7.337 (m, 4H, Ar-H), 4.584-4.537 (dd, 1H, $J_{x,a}$=7.2Hz, $J_{x,b}$=6.3Hz, H_x), 3.753-3.669 (dd, 1H, $J_{a,x}$=7.2Hz, $J_{a,b}$=17.4Hz, H_a), 3.544-3.485 (dd, 1H, $J_{b,x}$=6.3Hz, $J_{b,a}$=17.4Hz, H_b); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 194.3, 135.5, 134.4, 134.0, 133.7, 129.4, 128.9, 128.8, 128.1, 120.2, 44.3, 31.3; MS(EI, 70ev) (m/z,%): 271 (M+2,6.9), 269 ($M^{+\cdot}$,20.1), 164(45.8), 137(18.5), 105(100), 77(99.7); Anal.Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19; Found: C, 71.33; H, 4.55; N, 5.02. CA 95855-32-6.[3]

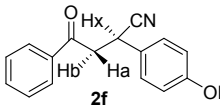
(2R,2S)-2-(3-Chlorophenyl)-4-oxo-4-phenylbutanenitrile 2e



2e

Light yellow solid, yield 72%, mp 105-106℃, IR(KBr,cm^{-1}): 2238(CN), 1689(C=O); ^{1}HNMR (300MHz, $CDCl_3$): δ_H 7.904-7.878 (d, 2H, *J*=7.8Hz, Ar-H), 7.595-7.540 (m, 1H, Ar-H), 7.460-7.411 (m, 3H, Ar-H), 7.343-7.284 (m, 3H, Ar-H), 4.529-4.482 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.750-3.652 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=17.7Hz, H_a), 3.533-3.441 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=17.7Hz, H_b); ^{13}C NMR (75.6MHz, $CDCl_3$): δ_C 194.2, 136.9, 135.2, 134.7, 133.8, 130.3, 128.6, 128.4, 127.9, 127.5, 125.6, 119.9, 43.9, 31.3; MS(EI, 70ev) (m/z,%): 271 (M+2,2.5), 269 ($M^{+\cdot}$,7.3), 164(23.1), 137(6.9), 105(100), 77(65.2); Anal.Calcd for $C_{16}H_{12}ClNO$: C, 71.25; H, 4.48; N, 5.19; N, 18.87; Found: C, 71.33; H, 4.55; N, 5.07. CA 344280-04-2.

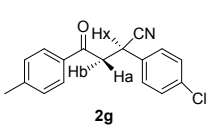
(2R,2S)-2-(4-Methoxyphenyl)-4-oxo-4-phenylbutanenitrile 2f



2f

Light yellow solid, yield 69%, mp 113-114℃, IR(KBr, cmP^{-1P}): 2235(CN), 1678(C=O); P^{1P}HNMR (300MHz,$CDClB_{3B}$):δB_{HB} 7.923-7.898 (d, 2H, *J*=7.5Hz, Ar-H), 7.605-7.556 (m, 1H, Ar-H), 7.478-7.425 (m, 2H, Ar-H), 7.351-7.321 (d, 2H, *J*=9.0Hz, Ar-H), 6.907-6.880 (d, 2H, *J*=8.1Hz, Ar-H), 4.523-4.476 (dd, 1H, $JB_{x,aB}$=7.8Hz, $JB_{x,bB}$=6.3Hz, HB_{xB}), 3.787 (s, 3H, Ar-$OCHB_{3B}$), 4.140-4.039 (dd, 1H, $JB_{a,xB}$=7.8Hz, $JB_{a,bB}$=18.3Hz, HB_{aB}), 3.732-3.648 (dd, 1H, $JB_{b,xB}$=6.3Hz, $JB_{b,aB}$=18.3Hz, HB_{bB}); P^{13P}C NMR(75.6MHz, $CDClB_{3B}$): δB_{CB}194.7, 159.4, 135.6, 133.8, 128.7, 128.6, 128.0, 127.1, 120.9, 114.5, 55.3, 44.4, 31.0; MS(EI, 70ev) (m/z,%): 265 ($MP^{+\cdot P}$,22.2), 160(25.9), 133(57.0), 105(62.8), 77(99.8), 43(100); Anal.Calcd for $CB_{17B}HB_{15B}NOB_{2B}$: C, 76.96; H, 5.70; N, 5.28; Found: C, 77.05; H, 5.55; N, 5.02. CA 3261-89-0.P[4]

(2R,2S)-2-(4-Chlorophenyl)-4-oxo-4-*p*-tolylbutanenitrile 2g

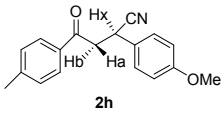


2g

Light yellow solid, yield 66%, mp 93-94℃, IR(KBr,cm^{-1}): 2247(CN), 1676(C=O); ^{1}HNMR (300MHz,$CDCl_3$):δ_H 7.816-7.778 (d, 2H, *J*=8.4Hz, Ar-H), 7.421 (s, 1H, Ar-H), 7.317-7.226 (m, 5H, Ar-H), 4.532-4.486 (dd, 1H, $J_{x,a}$=7.8Hz, $J_{x,b}$=6.0Hz, H_x), 3.724-3.638 (dd, 1H, $J_{a,x}$=7.8Hz, $J_{a,b}$=18.0Hz, H_a), 3.507-3.427 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.388 (s, 3H, Ar-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$):

δ_C 193.7, 144.9, 137.1, 134.8, 132.8, 130.3, 129.4, 128.4, 128.0, 127.6, 125.7, 120.1, 43.8, 31.4, 21.6; MS(EI, 70ev) (m/z,%): 285 (M+2,3.6), 283 ($M^{+\cdot}$,11.7), 164(8.3), 137(3.1), 119(100), 91(43.5); Anal.Calcd for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94; Found: C, 71.85; H, 5.05; N, 4.86. CA 1267378-25-5 [5]

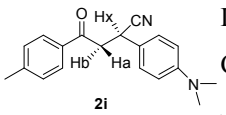
(2R,2S)-2-(4-Methoxyphenyl)-4-oxo-4-*p*-tolylbutanenitrile 2h



2h

Light yellow solid, yield 62%, mp 97-98℃, IR(KBr,cm^{-1}): 2239(CN), 1676(C=O); ^{1}HNMR (300MHz, $CDCl_3$): δ_H 7.810-7.782 (d, 2H, *J*=8.4Hz, Ar-H), 7.333-7.306 (d, 2H, *J*=8.1Hz, Ar-H), 7.239-7.212 (d, 2H, *J*=8.1Hz, Ar-H), 6.886-6.858 (d, 2H, *J*=8.4Hz, Ar-H), 4.488-4.441(dd, 1H, $J_{x,a}$=7.2Hz, $J_{x,b}$=6.0Hz, H_x), 3.798 (s, 3H, Ar-OCH_3), 3.683-3.593 (dd, 1H, $J_{a,x}$=7.2Hz, $J_{a,b}$=18.0Hz, H_a), 3.476-3.396 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b),2.376 (s, 3H, Ar-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 194.2, 159.2, 144.6, 133.1, 129.3, 128.5, 127.9, 127.0, 120.9, 114.3, 55.1, 44.1, 30.9, 21.5; MS(EI, 70ev) (m/z,%): 279 ($M^{+\cdot}$,44.6), 160(25.6), 159(43.7), 146(38.2), 133(35.4), 119(65.2), 43(100); Anal.Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01; Found: C, 77.30; H, 6.11; N, 5.27. CA 101733-90-8.[4]

(2R,2S)-2-[4-(Dimethylamino)phenyl]-4-oxo-4-*p*-tolylbutanenitrile 2i



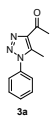
2i

Light yellow solid, yield 57%, mp 90-91℃, IR(KBr,cm^{-1}): 2242(CN), 1676(C=O); ^{1}HNMR(300MHz, $CDCl_3$):δ_H 7.806-7.778 (d, 2H, *J*=8.4Hz, Ar-H), 7.225-7.204 (m, 4H, Ar-H), 6.681-6.653 (d, 2H, *J*=8.4Hz, Ar-H), 4.434-4.388 (dd, 1H, $J_{x,a}$=7.8Hz, $J_{x,b}$=6.0Hz, H_x), 3.654-3.449 (dd, 1H, $J_{a,x}$=7.8Hz, $J_{a,b}$=18.0Hz, H_a), 3.449-3.361 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.896(s, 6H, Ar-$N(CH_3)_2$), 2.372 (s, 3H, Ar-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 194.5, 150.1, 144.4, 133.2, 129.2, 127.9, 122.2, 121.2, 112.5, 44.3, 40.2, 30.8, 21.5; MS(EI, 70ev) (m/z,%): 292 ($M^{+\cdot}$,16.9), 204(16.8), 173(7.7), 159(100), 119(24.6), 91(27.0); Anal.Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58; Found: C, 77.95; H, 6.79; N, 9.65.

Synthesis of 1-(1-aryl-5-methyl-1*H*-1,2,3-triazol-4-yl)-ethanones 3a-f

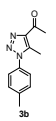
Compounds **3** were prepared by the reaction of 1-azido-4-substituted benzene[1] with pentane-2,4-dione. A cold solution of CH_3ONa(0.23mol, in 120mL absolute methanol) was added to the mixture of pentane-2,4-dione(17mL) and 1-azido-4-substituted benzene(about 0.15mol) and stirred for 1 h at 0~5℃. Then the mixture was refluxed on an oil-bath for 10 h. Finally, the mixture was acidified with concentrated hydrochloric acid. Compound **1** was separated and crystallized from methanol.

1-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)ethanone 3a


3a

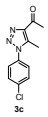
White powder, yield 58.5%, mp 99-101℃, IR(KBr,cm^{-1}): 3460, 3345, 3106, 1901, 1681, 1553, 1503, 1418, 1369, 1280, 1215, 1085, 951, 771, 690, 555, 491; ^{1}HNMR (300MHz,$CDCl_3$): δ 7.552-7.578(m, 3H, Ar-3,4,5), 7.408-7.448(m, 2H, Ar-2,6), 2.729(s, 3H, CH_3CO), 2.571(s, 3H, Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 193.9, 143.3, 137.1, 135.0, 129.7, 129.4, 125.0, 27.46, 9.79; MS(EI, 70ev) (m/z,%): 201($M^{+\cdot}$,13), 173(1), 158(18), 130(57), 118(7), 103(11), 77(97), 65(3), 43(100). CA 51118-32-2.[6]

1-(5-Methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)ethanone 3b


3b

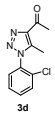
Whit powder, yield 52.6%, mp 105-107℃, IR(KBr,cm^{-1}): 3459, 3345, 3050, 1924, 1688, 1549, 1515, 1414, 1367, 1276, 1214, 1078, 949, 825, 671, 558, 499 ; ^{1}HNMR (300MHz,$CDCl_3$): δ 7.360-7.384(d, 2H, *J*=7.2Hz,Ar-2,6), 7.306-7.333(d, 2H *J*=8.1Hz,Ar-3,5), 2.757(s,3H, CH_3CO), 2.573(s, 3H, Tr-CH_3), 2.468(s, 3H, Ar-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 194.4, 143.6, 140.4, 137.4, 132.9, 130.2, 125.1, 27.81, 21.24, 10.09; MS(EI, 70ev) (m/z,%): 215($M^{+\cdot}$,19), 187(5), 172(31), 144(100), 130(16), 117(17), 91(88), 77(11), 65(76), 43(91). CA 194478-14-3.[6]

1-[1-(4-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]ethanone 3c



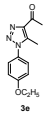
Yellow powder, yield 63.2%, mp 108-110℃, IR(KBr,cm^{-1}): 3437, 3343, 3097, 1921, 1687, 1548, 1496, 1412, 1368, 1274, 1212, 1089, 949, 839, 652, 555, 500; ^{1}HNMR (300MHz,$CDCl_3$): δ 7.546-7.585(d, 2H, *J*=11.7Hz, Ar-2,6), 7.399-7.429(d, 2H, *J*=9.0Hz, Ar-3,5), 2.757(s, 3H, CH_3CO), 2.599(s, 3H, Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 194.0, 143.5, 137.2, 136.0, 133.7, 129.8, 126.4, 27.62, 9.92; MS(EI, 70ev) (m/z,%): 235($M^{+\cdot}$,4), 207(1), 192(5), 178(1), 164(18), 130(3), 111(22), 75(38), 65(1) 43(100). CA 33821-38-4.[6]

1-[1-(2-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]ethanone 3d



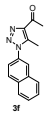
Yellow powder, yield 58.5%, mp 92-94℃, IR(KBr,cm^{-1}): 3441, 3344, 3069, 1936, 1681, 1552, 1489, 1420, 1365, 1282, 1216, 1080, 951, 764, 654, 565, 446; ^{1}HNMR (300MHz,$CDCl_3$): δ 7.374-7.606(m, 4H, *J*=6.9Hz, Ar-3,4,5,6), 2.753(s, 3H, CH_3CO), 2.428(s, 3H, Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 194.1, 143.0, 139.1, 132.9, 132.0, 131.6, 130.6, 129.0, 128.0, 27.68, 9.41; MS(EI, 70ev) (m/z,%): 235($M^{+\cdot}$,9), 207(2), 192(15), 178(2), 164(35), 130(5), 111(32), 75(49), 65(1), 43(100). CA 1017471-30-5.

1-[1-(4-Ethoxyphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]ethanone 3e



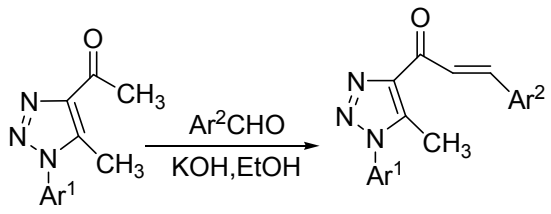
Yellow powder, yield 67.5%, mp 101-103℃, IR(KBr,cm^{-1}): 3432, 3334, 3062, 1899, 1682, 1550, 1480, 1441, 1425, 1375, 1286, 1239, 1075, 959, 869, 785, 669, 642; ^{1}HNMR (300MHz,$CDCl_3$): δ 7.351-7.321 (d, 2H, *J*=9.0Hz,Ar-2,6), 7.057-7.027(d, 2H *J*=9.0Hz,Ar-3,5), 4.144-4.121(q, 2H, J=6.9Hz, Ar-OCH_2CH_3), 2.747(s, 3H, CH_3CO), 2.552(s, 3H, Tr-CH_3), 1.452-1.429(t, 3H, *J*=6.9Hz, Ar-OCH_2CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 194.4, 160.1, 143.5, 137.5, 127.9, 126.6, 115.2, 63.97, 27.75, 14.65, 10.03; MS(EI, 70ev) (m/z,%): 245($M^{+\cdot}$,10), 217(3), 202(9), 188(15),175(20), 160(5), 146(64), 91(11), 65(40), 43(100). CA1017471-10-1.

1-[5-Methyl-1-(naphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]ethanone 3f



White powder, Yield: 73.8%; mp 146-8℃; IR(KBr,cm^{-1}): 3429, 3346, 3057, 1927, 1681, 1598, 1557, 1420, 1363, 1272, 1215, 1079, 951, 865, 826, 755, 670, 480. ^{1}H NMR(300MHz,$CDCl_3$): 7.896-8.038 (m, 4H, Ar-1,4,5,8), 7.501-7.624 (m, 3H, Ar-2,6,7), 2.778 (s, 3H, CH_3CO), 2.642 (s, 3H, TRZ-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 194.2, 143.6, 137.5, 133.2, 132.8, 132.5, 129.8, 128.2, 127.8, 127.6, 127.4, 124.2, 122.4, 27.72, 10.11; MS(EI, 70ev) (m/z,%): 251(M+., 17), 222(3), 208(9),194(3), 180(61), 153(14), 127(63), 101(12), 77(22), 63(10), 51(13), 43(100); Anal. Calcd for $C_{15}H_{13}N_2O$: C, 71.70; H, 5.21; N, 16.72; Found: C, 71.57; H, 5.45; N, 16.56. CA 1157067-74-7 [7,8]

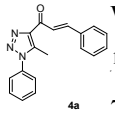
Synthesis of (*E*)-3-aryl-1-(1-aryl-5-methyl-1*H*-1,2,3-triazol-4-yl)-prop-2-en-1-ones 4a-j



3 **4**

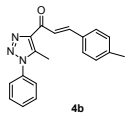
A mixture of aromatic aldehyde（0.012mol）and compound **3**(0.01mol) dissolved in ethanol(70mL) was added slowly to an aqueous solution of potassium hydroxide(0.0128mol) in water (10mL). The mixture was stirred in crushed-ice bath for 2h, stirred at 20~25 ℃ for 4 h. The mixture was filtrated and the residue was washed with cold water and cold alcohol. The product was crystallized from ethanol to give **4a-j**.

(*E*)-1-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one 4a



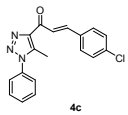
White powder, yield 92%, mp 168-170℃, IR(KBr,cm^{-1}): 1663, 1601, 1112, 1085, 1066, 1035, 979, 765, 687; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.154-8.101 (d, 1H, *J*=15.9Hz, 2-CH), 7.960-7.907 (d, 1H, *J*=15.9Hz, 3-CH), 7.757-7.726 (m, 2H, Ar-H), 7.610-7.421 (m, 8H, Ar-H), 2.691 (s, 3H, Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.0, 143.7, 143.3, 138.3, 135.2, 134.7, 130.3, 129.8, 129.4, 128.6, 128.5, 125.0, 122.8, 10.08; MS(EI, 70ev) (m/z,%): 289 ($M^{+\cdot}$,11.6), 233(24.2), 180(19.0), 131(14.4), 118(58.9), 103(36.1), 77(100), 51(43.5). Anal.Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.52; Found: C, 74.60; H, 5.01; N, 14.61. CA 1207996-14-2 [8,9]

(*E*)-1-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-*p*-tolylprop-2-en-1-one 4b



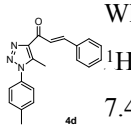
White powder, yield 86% , mp 163-165 ℃, IR(KBr,cm^{-1}): 1666, 1597, 1084, 1065, 1038, 1020, 995, 975, 923, 886, 812, 764, 738, 693; ^{1}HNMR (300MHz,$CDCl_3$): δ8.113-8.058 (d, 1H, *J*=16.5Hz, 2-CH), 7.941-7.888 (d, 1H, *J*=15.9Hz, 3-CH), 7.653-7.480 (m, 9H, Ar-H), 2.614 (s, 3H, Tr-CH_3), 2.329 (s, 3H, Ar_1-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.4, 144.0, 143.7, 141.0, 138.3, 135.4, 132.2, 129.9, 129.6, 129.5, 128.7, 125.2, 122.0, 21.47, 10.27; MS(EI, 70ev) (m/z,%): 303 ($M^{+\cdot}$,10.8), 274(1.1), 247(15.4), 194(20.6), 145(14.9), 118(72.2), 91(17.6), 77(100), 51(44.3). Anal.Calcd for $C_{19}H_{17}N_3O$: C, 75.23; H, 5.65; N, 13.85; Found: C, 75.18; H, 5.27; N, 13.97. CA 1207996-19-7 [9]

(*E*)-3-(4-Chlorophenyl)-1-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)prop-2-en-1-one 4c



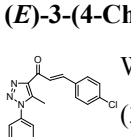
White powder, yield 90%, mp 179-181℃, IR(KBr,cm^{-1}): 1666, 1603, 1107, 1085, 1029, 988, 911, 890, 818, 788, 757, 688; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.113-8.058 (d, 1H, *J*=16.5Hz, 2-CH), 7.894-7.841 (d, 1H, *J*=15.9Hz, 3-CH), 7.667-7.589 (m,5H, Ar-H), 7.485-7.392 (m, 4H, Ar-H), 2.675 (s, 3H, Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.1, 143.9, 142.0, 138.6, 136.3, 135.4, 133.4, 130.0, 129.9, 129.7, 129.1, 125.3, 123.5, 10.30; MS(EI, 70ev) (m/z,%): 323($M^{+\cdot}$,9.6), 294(3.1), 267(27.1), 214(29.7), 165(24.0), 149(10.5), 137(13.7), 118(79.1), 101(19.3), 71(100),51(41.1). Anal.Calcd for $C_{18}H_{14}ClN_3O$: C, 66.77; H, 4.36; N, 12.98; Found: C, 66.59; H, 4.12; N, 13.07.

(*E*)-1-(5-Methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-3-phenylprop-2-en-1-one 4d



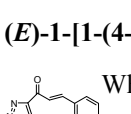
White powder, yield 90%, mp 173-175 ℃, IR(KBr,cm^{-1}): 1666, 1602, 1111, 1071, 1035, 1018, 989, 733, 693; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.150-8.097 (d, 1H, *J*=15.9Hz, 2-CH), 7.950-7.897 (d, 1H, *J*=15.9Hz, 3-CH), 7.721-7.434 (m, 2H, Ar-H), 7.434-7.417 (m,3H, Ar-H), 7.405-7.376 (d, 2H, *J*=8.7Hz, Ar-H), 7.368-7.339 (d, 2H, *J*=8.7Hz, Ar-H), 2.665 (s, 3H, Tr-CH_3), 2.475 (s, 3H, Ar_1-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.4, 143.9, 143.5, 140.3, 138.5, 135.0, 132.9, 130.4, 130.2, 128.8, 128.7, 125.1, 123.1, 21.22, 10.28; MS(EI, 70ev) (m/z,%): 303 ($M^{+\cdot}$,5.1), 274(2.8), 260(3.2), 247(30.6), 194(35.8), 144(12.9), 132(98.4), 115(34.3), 103(64.6), 91(100), 77(63.3), 65(78.6), 51(35.3). Anal.Calcd for $C_{19}H_{17}N_3O$: C, 75.23; H, 5.65; N, 13.85; Found: C, 75.42; H, 5.28; N, 13.44. CA 1207996-15-3 [10,11]

(*E*)-3-(4-Chlorophenyl)-1-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)prop-2-en-1-one 4e



White powder, yield 79%, mp 177-179℃, IR(KBr,cm^{-1}): 1664, 1605, 1032, 993, 887, 824, 786, 756; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.105-8.050 (d, 1H, *J*=16.5Hz, 2-CH), 7.888-7.833(d, 1H, *J*=16.5Hz, 3-CH), 7.671-7.644 (d, 2H, *J*=8.1Hz, Ar-H), 7.413-7.386 (d, 2H, *J*=8.1Hz, Ar-H),7.376-7.337 (m, 4H, Ar-H), 2.657(s, 3H, Tr-CH_3), 2.476(s, 3H, Ar_1-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.1, 143.8, 142.0, 140.4, 138.6, 136.4, 133.5, 132.9, 130.2, 129.9, 129.1, 125.1, 123.6, 21.24, 10.29; MS(EI, 70ev) (m/z,%): 337($M^{+\cdot}$,1.2), 308(2.7), 281(32.1), 228(28.4), 165(37.5), 137(26.2), 132(91.4), 91(100), 65(79),39(35.6). Anal.Calcd for $C_{19}H_{16}ClN_3O$: C, 67.56; H, 4.77; N, 12.44; Found: C, 67.43; H, 4.92; N, 12.72. CA 1338725-21-5 [10,11]

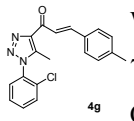
(*E*)-1-[1-(4-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-phenylprop-2-en-1-one 4f



White powder, yield 89%, mp 180-182℃, IR(KBr,cm^{-1}): 1665, 1601, 1153, 1092, 1068, 1031, 989, 843, 824, 775, 732, 689; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.128-8.074 (d, 1H, *J*=16.2Hz, 2-CH), 7.956-7.904 (d, 1H, *J*=15.9Hz, 3-CH), 7.737-7.718 (m, 2H, Ar-H), 7.595-7.565 (dd, 2H, *J*=9.0Hz, 1.8Hz ,Ar-H), 7.558-7.419 (m,5H, Ar-H), 2.687 (s, 3H,

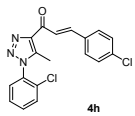
Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 183.9, 143.9, 143.6, 138.3, 135.9, 134.7, 133.7, 130.4, 129.7, 128.7, 128.6, 126.3, 122.7, 10.13; MS(EI, 70ev) (m/z,%):323 ($M^{+\cdot}$,21.0), 294(3.5), 267(70.1), 214(47.3), 152(65.6), 131(100), 111(62.1), 103(59.1), 77(58.4), 51(27.9). Anal.Calcd for $C_{18}H_{14}ClN_3O$: C, 66.77; H, 4.36; N, 10.95; Found: C, 66.42; H, 4.53; N, 10.72. CA 1207996-16-4 [7,9]

(*E*)-1-[1-(2-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-*p*-tolylprop-2-en-1-one 4g


4g

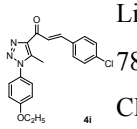
White powder, yield 92%, mp 150-152℃, IR(KBr,cm^{-1}): 1665, 1598, 1073, 1024, 997, 880, 875, 816, 771, 746, 725, 690; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.113-8.060(d, 1H, *J*=15.9Hz, 2-CH), 7.952-7.900 (d, 1H, *J*=15.6Hz, 3-CH), 7.653-7.442(m, 6H, Ar-H), 7.255-7.227 (d, 2H, *J*=8.4Hz, Ar-H), 2.542 (s, 3H, Tr-CH_3), 2.401 (s, 3H, Ar_2-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.4, 143.9, 143.5, 141.1, 140.2, 133.2, 132.3, 132.0, 131.9, 130.7, 129.7, 129.2, 128.8, 128.0, 122.0, 21.54, 9.73; MS(EI, 70ev) (m/z,%): 337 ($M^{+\cdot}$,7.7), 281(10.5), 228(20.1), 152(100), 145(22.9), 115(37.8), 111(47.9), 91(24.4), 75(35.8), 44(34.5). Anal.Calcd for $C_{19}H_{16}ClN_3O$: C, 67.56; H, 4.77; N, 12.44; Found: C, 67.49; H, 4.82; N, 12.27. CA 1207996-22-2 [9]

(*E*)-3-(4-Chlorophenyl)-1-[1-(2-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one 4h


4h

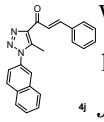
White powder, yield 95%, mp 156-158℃, IR(KBr, cm^{-1}): 1664, 1608, 1087, 1066, 1025, 989, 890, 870, 825, 789, 756, 693; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.118-8.066 (d, 1H, *J*=15.6Hz, 2-CH), 7.909-7.855 (d, 1H, *J*=16.2Hz, 3-CH), 7.683-7.394 (m, 8H, Ar-H), 2.548 (s, 3H, Tr-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.0, 143.4, 142.2, 140.4, 136.4, 133.5, 133.0, 132.1, 131.8, 130.7, 129.9, 129.2, 129.1, 128.0, 123.4, 9.72; MS(EI, 70ev) (m/z,%): 357 ($M^{+\cdot}$,7.6), 301(19.7), 248(27.2), 165(25.1), 152(100), 111(66.9), 102(34.4), 75(69.8), 51(18.5). Anal.Calcd for $C_{18}H_{13}Cl_2N_3O$: C, 60.38; H, 3.66; N, 11.73; Found: C, 60.18; H, 3.82; N, 11.66. CA 1207996-22-2 [9]

(*E*)-3-(4-Chlorophenyl)-1-[1-(4-ethoxyphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]prop-2-en-1-one 4i


4i

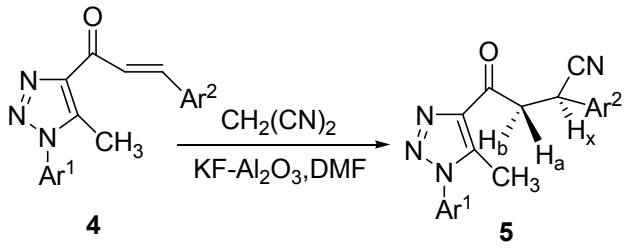
Light yellow solid, yield 95%, mp 172-173℃, IR(KBr,cm^{-1}): 1663, 1602, 1172, 1093, 1039, 1007, 989, 841, 812, 784, 723, 698; ^{1}HNMR (300MHz,$CDCl_3$): δ 8.101-8.046 (d, 1H, *J*=16Hz, 2-CH), 7.884-7.831 (d, 1H, *J*=16Hz, 3-CH), 7.669-7.640 (d, 2H, *J*=8.7Hz, Ar-H), 7.411-7.343 (m, 4H, Ar-H), 7.571-7.541 (d, 2H, *J*=9.0Hz, Ar-H), 4.152-4.082 (q, 2H, *J*=6.9Hz, Ar_1-OCH_2CH_3), 2.638 (s, 3H, Tr-CH_3), 1.495-1.448 (t, 3H, *J*=6.9Hz, Ar_1-OCH_2CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.1, 160.1, 143.7, 141.9, 138.7, 136.3, 133.5, 129.9, 129.1, 128.0, 126.6, 123.5, 115.2, 63.97, 14.66, 10.24; MS(EI, 70ev) (m/z,%): 367($M^{+\cdot}$,0.2), 339(5), 311(25.5), 258(21.3), 175(15.2), 165(83.9), 137(40.9), 102(50.9), 77(34.6), 65(100). Anal.Calcd for $C_{20}H_{18}ClN_3O_2$: C, 65.31; H, 4.93; N, 11.42; Found: C, 65.18; H, 4.82; N, 11.66.

(*E*)-1-[5-Methyl-1-(naphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]-3-phenylprop-2-en-1-one 4j


4j

White solid, Yield: 97.7%; mp 178-180℃; IR(KBr,cm^{-1}): 1664, 1600, 1556, 1488, 1446, 1421, 1302, 1269, 1206, 1074, 1033, 989, 826, 689. ^{1}H NMR(300MHz,$CDCl_3$): 8.120-8.173(d, 1H, *J*=15.9Hz, CH=C-CO), 8.023-8.052(d, 1H, *J*=8.7Hz, C=CH-CO), 7.919-7.972(m, 4H, Ar-1,4,5,8), 7.718-7.747(m, 2H, *J*=8.7Hz, Ph-2,6), 7.544-7.632(m, 3H, Ar-3,6,7), 7.409-7.438(m, 3H, *J*=8.7Hz, Ph-3,4,5), 2.732(s, 3H, TRZ-CH_3); ^{13}C NMR(100.6MHz, $CDCl_3$): δ_C 184.4, 144.1, 143.7, 138.7, 135.0, 133.4, 133.0, 132.7, 130.5, 130.0, 128.9, 128.8, 128.5, 128.4, 128.0, 127.7, 124.4, 123.1, 122.6, 10.40; MS(EI, 70ev) (m/z,%): 339(M^+,1), 310(3), 283(23), 268(3), 251(7), 230(22), 180(27), 168(42), 127(100), 115(20), 103(51), 77(61), 51(24), 39(11). Anal. Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38; Found: C, 77.65; H, 5.27; N, 12.46. CA 1207996-22-2 [7]

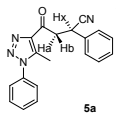
Synthesis of (2R,2S)-2-aryl-4-(1-aryl-5-methyl-1*H*-1,2,3-triazol- 4-yl)-4-oxo-butanenitriles 5a-j



4 5

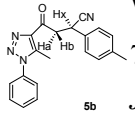
Compound malononitrile(2.4mmol), KF-Al_2O_3(4mmol), α,β-unsaturated ketone **4a-j** (2mmol) and DMF (30mL) was added to a dry flask. The mixture was stirred at 90-100℃ for 1-8 h, then cooled to room temperature. The solid material was filtered off and the residue was washed with DMF. The filtrate was concentrated and the residue was isolated with petroleum ether and ethyl acetate to give the target products **5a-j**.

(2R,2S)-4-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-oxo-2-phenylbutyronitrile (5a)



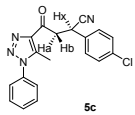
White solid, yield 62%, mp 79-81℃, IR(KBr,cm^{-1}): 2243(CN), 1685(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.620-7.558 (m, 3H, Ar-H), 7.476-7.306 (m, 7H, Ar-H), 4.592-4.544 (dd, 1H, $J_{x,a}$=8.4Hz, $J_{x,b}$=6.0Hz, H_x), 4.007-3.918 (dd, 1H, $J_{a,x}$=8.4Hz, $J_{a,b}$=18.0Hz, H_a), 3.820-3.740 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.603(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.8, 142.4, 138.2, 135.0, 130.2, 129.7, 129.2, 128.3, 127.5, 125.2, 120.5, 45.1, 31.6, 10.1; MS(EI, 70ev) (m/z,%): 316 ($M^{+\cdot}$,8.6), 299(0.3), 235(4.1), 172(5.66), 158(23.5), 149(18.1), 131(21.8), 118(43.5), 103(10.6), 77(100), 39(8.8); Anal.Calcd for $C_{19}H_{16}N_4O$: C, 72.13; H, 5.10; N, 17.71; Found: C, 72.00; H, 5.15; N, 17.66.

(2R,2S)-4-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-oxo-2-*p*-tolylbutyronitrile (5b)



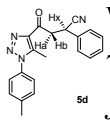
White solid, yield 63%, mp 65-67℃, IR(KBr,cm^{-1}): 2242(CN), 1685(C=O); ^{1}HNMR(300MHz,$CDCl_3$): 7.581-7.544 (m, 3H, Ar-H), 7.438-7.407 (m, 2H, Ar-H), 7.351-7.323 (d, 2H, *J*=8.4Hz, Ar-H), 7.190-7.163 (d, 2H, *J*=8.1Hz, Ar-H), 4.547-4.500 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.966-3.878 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.787-3.707 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.575(s, 3H, Tr-CH_3), 2.325 (s, 3H, Ar_2-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.7, 142.3, 137.9, 137.8, 134.8, 131.9, 129.9, 129.6, 129.5, 127.2, 125.0, 120.5, 44.9, 30.9, 20.8, 9.9; MS(EI, 70ev) (m/z,%): 330 ($M^{+\cdot}$,14.8), 301(1.2), 273(1.4), 172(2.7), 159(24.1), 144(1.7), 130(29.3), 118(34.9), 84(100), 77(77.4), 39(10.6); Anal.Calcd for $C_{20}H_{18}N_4O$: C, 72.71; H, 5.49; N, 16.96; Found: C, 72.86; H, 5.55; N, 16.80.

(2R,2S)-2-(4-Chlorophenyl)-4-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-4-oxobutyronitrile (5c)



Light yellow solid, yield 70%, mp 71-73℃, IR(KBr,cm^{-1}): 2244(CN), 1685(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.857(s, 3H, Ar-H), 7.560-7.329 (m, 6H, Ar-H), 4.586-4.539 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.966-3.879 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.816-3.735 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.575(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.2, 142.1, 138.1, 134.7, 134.0, 133.5, 130.0, 129.5, 129.1, 128.8, 124.9, 119.9, 44.6, 30.8, 9.9; MS(EI, 70ev) (m/z,%): 352 (M+2,6.2), 350 ($M^{+\cdot}$,16.1), 321(1.4), 293(2.5), 269(2.6), 159(38.1), 130(100), 118(29.8), 77(73.5), 51(93.5), 39(11.8); Anal.Calcd for $C_{19}H_{15}ClN_4O$: C, 65.05; H, 4.31; N, 15.97; Found: C, 65.15; H, 4.55; N, 15.88.

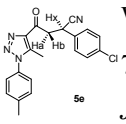
(2R,2S)-4-(5-Methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4-oxo-2-phenylbutyronitrile (5d)



White solid, yield 74%, mp 84-86℃, IR(KBr,cm^{-1}): 2243(CN), 1685(C=O); ^{1}HNMR(300MHz, $CDCl_3$):δ_H 7.470-7.448 (d, 2H, *J*=6.6Hz, Ar-H), 7.413-7.354 (m, 5H, Ar-H), 7.315-7.286 (d, 2H, *J*=8.7Hz, Ar-H), 4.588-4.539 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.996-3.908 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.814-3.734 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.577(s, 3H, Tr-CH_3), 2.456 (s, 3H, Ar_1-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.8, 142.4, 140.5, 138.1, 135.1, 132.5, 130.2, 129.1, 128.2, 127.5, 125.0, 120.5, 45.1, 31.6, 21.2, 10.0; MS(EI, 70ev) (m/z,%): 330 ($M^{+\cdot}$,17.4),

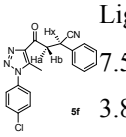
301(0.7), 273(2.5), 198(6.9), 186(9.9), 172(41.4), 158(20.9), 132(75.4), 91(100), 39(36.3); Anal.Calcd for $C_{20}H_{18}N_4O$: C, 72.71; H, 5.49; N, 16.96; Found: C, 72.68; H, 5.54; N, 16.87.

(2R,2S)-2-(4-Chlorophenyl)-4-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-4-oxobutyronitrile (5e)



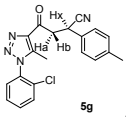
White solid, yield 65%, mp 81-83℃, IR(KBr,cm^{-1}): 2244(CN), 1685(C=O); ^{1}HNMR(300MHz, $CDCl_3$):δ_H 7.429-7.290 (m, 8H, Ar-H), 4.580-4.553 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.0Hz, H_x), 3.955-3.867 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.810-3.730 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.558(s, 3H, Tr-CH_3), 2.444 (s, 3H, Ar_1-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.3, 142.1, 140.4, 138.1, 134.0, 133.5, 132.3, 130.1, 129.1, 128.8, 124.8, 119.9, 44.6, 30.8, 21.0, 9.9; MS(EI, 70ev) (m/z,%): 366 (M+2,5.7), 364 ($M^{+\cdot}$,16.0), 335(1.8), 307(2.3), 225(2.5), 172(43.9), 150(35.8), 145(58.4), 132(71.3), 91(100), 39(21.1); Anal.Calcd for $C_{20}H_{17}ClN_4O$: C, 65.84; H, 4.70; N, 15.36; Found: C, 65.79; H, 4.55; N, 15.60.

(2R,2S)-4-[1-(4-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-4-oxo-2-phenylbutyronitrile (5f)



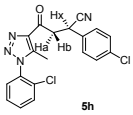
Light yellow solid, yield 74%, mp 98-100℃, IR(KBr,cm^{-1}): 2243(CN), 1686(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.564-7.517 (m, 2H, Ar-H), 7.460-7.296 (m, 7H, Ar-H), 4.571-4.523 (dd, 1H, $J_{x,a}$=8.4Hz, $J_{x,b}$=6.0Hz, H_x), 3.980-3.892 (dd, 1H, $J_{a,x}$=8.4Hz, $J_{a,b}$=18.0Hz, H_a), 3.787-3.707 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.589(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.6, 142.4, 138.1, 136.2, 134.9, 133.4, 129.9, 129.1, 128.2, 127.4, 126.3, 120.4, 44.9, 31.4, 9.9; MS(EI, 70ev) (m/z,%): 352 (M+2,7.3), 350 ($M^{+\cdot}$,21.6), 321(2.9), 293(3.7), 279(4.0), 192(47.2), 165(60.1), 152(83.7), 116(88.8), 111(100), 39(16.9); Anal.Calcd for $C_{19}H_{15}ClN_4O$: C, 65.05; H, 4.31; N, 15.97; Found: C, 64.95; H, 4.45; N, 15.69.

(2R,2S)-4-[1-(2-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-4-oxo-2-*p*-tolylbutyronitrile (5g)



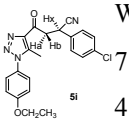
White solid, yield 69%, mp 75-77℃, IR(KBr,cm^{-1}): 2243(CN), 1686(C=O); ^{1}HNMR(300MHz, $CDCl_3$):δ_H 7.626-7.550 (m, 2H, Ar-H), 7.528-7.333 (m, 4H, Ar-H), 7.200-7.175 (d, 2H, *J*=7.5Hz, Ar-H), 4.560-4.512 (dd, 1H, $J_{x,a}$=9.0Hz, $J_{x,b}$=6.0Hz, H_x), 4.000-3.909 (dd, 1H, $J_{a,x}$=9.0Hz, $J_{a,b}$=18.0Hz, H_a), 3.808-3.728 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.453(s, 3H, Tr-CH_3), 2.333 (s, 3H, Ar_2-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.5, 141.7, 139.8, 137.8, 132.4, 132.1, 131.8, 131.2, 130.4, 129.6, 128.8, 127.9, 127.1, 120.5, 44.9, 30.9, 20.8, 9.2; MS(EI, 70ev) (m/z,%): 366 ($M^{+\cdot}$,6.5), 364 ($M^{+\cdot}$,17.3), 335(1.6), 293(3.9), 283(4.3), 221(4.5), 206(5.6), 193(52.7), 152(83.5), 130(73.1), 111(100), 39(28.7); Anal.Calcd for $C_{20}H_{17}ClN_4O$: C, 65.84; H, 4.70; N, 15.36; Found: C, 65.90; H, 4.39; N, 15.44.

(2R,2S)-2-(4-Chlorophenyl)-4-[1-(2-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-4-oxobutyronitrile (5h)



Light yellow solid, yield 77%, mp 113-115℃, IR(KBr,cm^{-1}): 2244(CN), 1683(C=O); ^{1}HNMR (300MHz, $CDCl_3$): δ_H 7.655-7.478 (m, 3H, Ar-H), 7.435-7.337 (m, 5H, Ar-H), 4.584-4.535 (dd, 1H, $J_{x,a}$=8.1Hz, $J_{x,b}$=6.3Hz, H_x), 3.994-3.906 (dd, 1H, $J_{a,x}$=8.1Hz, $J_{a,b}$=18.0Hz, H_a), 3.841-3.759 (dd, 1H, $J_{b,x}$=6.3Hz, $J_{b,a}$=18.0Hz, H_b), 2.464(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.3, 141.8, 140.1, 134.3, 133.5, 132.6, 132.3, 131.6, 130.7, 129.3, 128.9, 128.1, 120.1, 44.9, 30.9, 9.5; MS(EI, 70ev) (m/z,%): 386 (M+2,4.6), 384 ($M^{+\cdot}$,7.5), 355(0.6), 303(1.8), 221(2.8), 206(4.2), 192(29.4), 165(33.9), 152(100), 111(86.7), 75(66.3), 39(10.8); Anal.Calcd for $C_{19}H_{14}Cl_2N_4O$: C, 59.24; H, 3.66; N, 14.54; Found: C, 59.17; H, 3.55; N, 14.45.

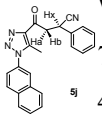
(2R,2S)-2-(4-Chlorophenyl)-4-[1-(4-ethoxyphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-4-oxobutyronitrile (5i)



White solid, yield 64%, mp 76-78℃, IR(KBr,cm^{-1}): 2244(CN), 1685(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.454-7.278 (m, 6H, Ar-H), 7.054-7.024 (d, 2H, *J*=9.0Hz, Ar-H), 4.599-4.553 (dd, 1H, $J_{x,a}$=7.8Hz, $J_{x,b}$=6.0Hz, H_x), 4.162-4.090 (q, 2H, *J*=6.9Hz, Ar_1-OCH_2CH_3), 3.951-3.865 (dd, 1H, $J_{a,x}$=7.8Hz, $J_{a,b}$=17.7Hz, H_a), 3.812-3.732 (dd, 1H, $J_{b,x}$=6.3Hz, $J_{b,a}$=17.7Hz, H_b), 2.548(s, 3H, Tr-CH_3), 1.481-1.434 (t,3H, *J*=6.9Hz, Ar_1-OCH_2CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.4, 160.1, 142.1, 138.3, 134.2, 133.6, 129.3, 128.9, 127.5, 126.5, 120.1, 115.2, 63.9, 44.7, 30.9, 14.5, 9.9; MS(EI, 70ev) (m/z,%): 396 (M+2,4.4), 394 ($M^{+\cdot}$,12.2), 366(1.2), 337(4.7), 216(23.1), 202(39.2), 175(100),

150(52.8), 146(80.4), 65(70.9), 39(29.7); Anal.Calcd for $C_{21}H_{19}ClN_4O_2$: C, 63.88; H, 4.85; N, 14.19; Found: C, 63.96; H, 5.01; N, 14.00.

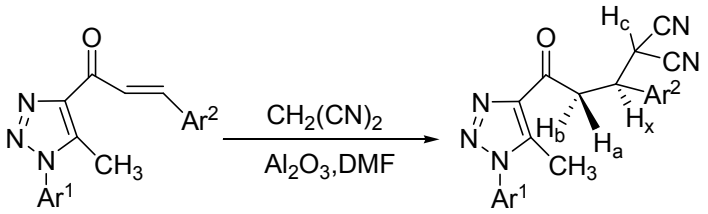
(2R,2S)-4-[5-Methyl-1-(naphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]-4-oxo-2-phenylbutyronitrile (5j)



5j

White solid, yield 77%, mp 118-120℃, IR(KBr,cm^{-1}): 2239(CN), 1690(C=O); ^{1}HNMR(300MHz, $CDCl_3$):δ_H 8.029-7.999 (d, 1H, *J*=9.0Hz, Ar-H), 7.921--7.898 (m, 3H, Ar-H), 7.634-7.587 (m, 2H, Ar-H), 7.511-7.247 (m, 6H, Ar-H), 4.599-4.551 (dd, 1H, $J_{x,a}$=8.7Hz, $J_{x,b}$=6.0Hz, H_x), 4.021-3.931 (dd, 1H, $J_{a,x}$=8.7Hz, $J_{a,b}$=18.0Hz, H_a), 3.834-3.753 (dd, 1H, $J_{b,x}$=6.0Hz, $J_{b,a}$=18.0Hz, H_b), 2.632(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 190.7, 142.4, 138.4, 134.9, 133.3, 132.7, 132.2, 129.9, 129.1, 128.4, 128.2, 127.9, 127.8, 127.5, 127.4, 124.2, 122.2, 120.5, 45.0, 31.5, 10.1; MS(EI, 70ev) (m/z,%): 366 ($M^{+\cdot}$,8.8), 337(1.1), 309(0.6), 222(7.2), 208(11.9), 181(66.8), 168(26.4), 127(100), 116(36.2), 77(27.4), 39(8.4); Anal.Calcd for $C_{23}H_{18}N_4O$: C, 75.39; H, 4.95; N, 15.29; Found: C, 75.29; H, 5.05; N, 15.02.

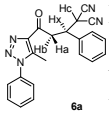
Synthesis of (1'R,1'S)-2-(3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-oxo-1-phenylpropyl)malononitrile 6a-j



4 **6**

Compound malononitrile(2.4mmol), Al_2O_3(4mmol), α,β-unsaturated ketone **4a-j** (2mmol) and DMF (30mL) was added to a dry flask. The mixture was stirred at 90-100℃ for 7 h, then cooled to room temperature. The solid material was filtered off and the residue was washed with DMF. The filtrate was concentrated and the residue was isolated with petroleum ether and ethyl acetate to give the target products **6a-j.**

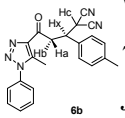
(1'R,1'S)-2-[3-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-oxo-1-phenylpropyl]malononitrile (6a)



6a

Light yellow solid, yield 72%, mp 50-52℃, IR(KBr,cm^{-1}): 2255(CN), 1682(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.603-7.554 (m, 3H, Ar-H) 7.497-7.390 (m, 7H, Ar-H), 4.590-4.572 (d, 1H, *J*=5.4Hz, H_c), 4.113-3.988 (m, 2H, H_b, H_x), 3.906-3.836 (m, 1H, H_a), 2.588(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 192.4, 142.5, 138.2, 136.3, 134.9, 130.2, 129.7, 129.1, 128.9, 128.0, 125.1, 111.9, 111.6, 41.2, 41.0, 29.1, 10.0; MS(EI, 70ev) (m/z,%): 355 ($M^{+\cdot}$,0.8), 290(1.4), 266(4.7), 235(4.7), 202(6.3), 180(7.2), 158(14.5), 130(25.3), 118(33.1), 105(23.0), 77(100), 39(15.9); Anal.Calcd for $C_{21}H_{17}N_5O$: C, 70.97; H, 4.82; N, 19.71; Found: C, 70.88; H, 4.69; N, 19.66.

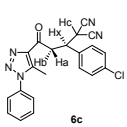
(1'R,1'S)-2-[3-(5-Methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-oxo-1-*p*-tolylpropyl)malononitrile (6b)



6b

White solid, yield 62%, mp 53-54℃, IR(KBr,cm^{-1}): 2255(CN), 1682(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.581-7.544 (m,3H, Ar-H), 7.435-7.347 (m, 4H, Ar-H), 7.206-7.181 (d, 2H, *J*=7.5Hz, Ar-H), 4.564-4.545 (d, 1H, *J*=5.7Hz, H_c), 4.095-3.974 (m, 2H, H_b, H_x), 3.849-3.777 (m, 1H, H_a), 2.536(s, 3H, Tr-CH_3), 2.323 (s, 3H, Ar_2-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 192.3, 142.5, 138.6, 138.1, 134.8, 133.3, 130.1, 129.6, 129.5, 127.8, 124.9, 111.9, 111.6, 41.2, 40.6, 29.2, 20.9, 9.9; MS(EI, 70ev) (m/z,%): 369 ($M^{+\cdot}$,1.9), 323(1.2), 303(0.6), 249(1.8), 220(9.2), 158(11.2), 131(17.1), 118(49.1), 105(8.6), 91(17.0),77(100) , 39(26.0); Anal.Calcd for $C_{22}H_{19}N_5O$: C, 71.53; H, 5.18; N, 18.96; Found: C, 70.48; H, 5.05; N, 19.00.

(1'R,1'S)-2-[1-(4-Chlorophenyl)-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)-3-oxopropyl]malononitrile (6c)

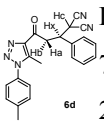


6c

Light yellow solid, yield 73%, mp 63-65℃, IR(KBr,cm^{-1}): 2255(CN), 1681(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.872-7.630 (m, 3H, Ar-H), 7.575-7.364 (m, 6H, Ar-H), 4.603-4.586 (d, 1H, *J*=5.1Hz, H_c), 4.095-4.027 (m, 2H,

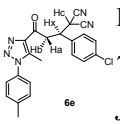
H_b, H_x), 3.863-3.763 (dd, 1H, $J_{a,x}$=9.9Hz, $J_{a,b}$=20.1Hz, H_a), 2.552(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 191.9, 142.4, 138.3, 134.9, 134.7, 130.2, 129.7, 129.5, 129.0, 125.1, 125.0, 111.7, 111.4, 41.0, 40.4, 28.9, 10.0; MS(EI, 70ev) (m/z,%): 391 (M+2,0.3), 389 ($M^{+\cdot}$,1.4), 323(3.1), 294(1.1), 267(8.8), 214(12.2), 158(14.3), 130(16.0), 118(68.1), 77(100), 39(10.2); Anal.Calcd for $C_{21}H_{16}ClN_5O$: C, 64.70; H, 4.14; N, 17.96; Found: C, 64.63; H, 4.09; N, 17.90.

(1'R,1'S)-2-[3-(5-Methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-3-oxo-1-phenylpropyl]malononitrile (6d)


6d

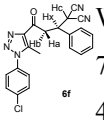
Light yellow solid, yield 72%, mp 54-56℃, IR(KBr,cm^{-1}): 2255(CN), 1682(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.485-7.460 (d, 2H, *J*=7.5Hz, Ar-H), 7.403-7.300 (m, 7H, Ar-H), 4.625-4.607 (d, 1H, *J*=5.4Hz, H_c), 4.125-4.015 (m, 2H, H_b, H_x), 3.875-3.773 (dd, 1H, $J_{a,x}$=9.9Hz, $J_{a,b}$=20.7Hz, H_a), 2.501(s, 3H, Tr-CH_3), 2.423 (s, 3H, Ar_1-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 192.0, 142.3, 140.3, 138.0, 136.3, 132.1, 129.9, 128.8, 128.6, 127.8, 124.7, 111.9, 111.6, 41.0, 40.7, 28.9, 20.9, 9.8; MS(EI, 70ev) (m/z,%): 369 ($M^{+\cdot}$,7.4), 304(4.6), 276(3.7), 202(11.9), 172(50.0), 145(69.7), 132(82.6), 103(34.5), 91(100), 77(14.1), 39(30.5); Anal.Calcd for $C_{22}H_{19}N_5O$: C, 71.53; H, 5.18; N, 18.96; Found: C, 71.49; H, 5.05; N, 19.02.

(1'R,1'S)-2-[1-(4-Chlorophenyl)-3-(5-methyl-1-*p*-tolyl-1*H*-1,2,3-triazol-4-yl)-3-oxopropyl]malononitrile (6e)


6e

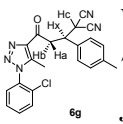
Light yellow solid, yield 62%, mp 56-57℃, IR(KBr,cm^{-1}): 2255(CN), 1682(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.446-7.284 (m, 8H, Ar-H), 4.607-4.590 (d, 1H, *J*=5.1Hz, H_c), 4.091-4.004 (m, 2H, H_b, H_x), 3.847-3.750 (dd, 1H, $J_{a,x}$=9.3Hz, $J_{a,b}$=19.8Hz, H_a), 2.522(s, 3H, Tr-CH_3), 2.448 (s, 3H, Ar_1-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 191.9, 142.3, 140.5, 138.2, 134.8, 134.7, 132.2, 130.2, 129.4, 129.2, 124.8, 111.7, 111.4, 41.0, 40.5, 28.9, 21.1, 9.9; MS(EI, 70ev) (m/z,%): 405 (M+2,0.4), 403 ($M^{+\cdot}$,1.3), 338(0.3), 310(0.2), 215(1.8), 188(4.7), 172(12.6), 145(20.4), 132(26.5), 84(100), 39(20.2); Anal.Calcd for $C_{22}H_{18}ClN_5O$: C, 65.43; H, 4.49; N, 17.34; Found: C, 65.38; H, 4.40; N, 17.55.

(1'R,1'S)-2-{3-[1-(4-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-oxo-1-phenylpropyl}malononitrile (6f)


6f

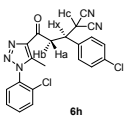
White solid, yield 79%, mp 55-57℃, IR(KBr,cm^{-1}): 2256(CN), 1684(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.575-7.528 (m, 2H, Ar-H), 7.483-7.452 (m, 2H, Ar-H), 7.429-7.353 (m, 5H, Ar-H), 4.566-4.547 (d, 1H, *J*=5.7Hz, H_c), 4.095-3.994 (m, 2H, H_b, H_x), 3.877-3.773 (dd, 1H, $J_{a,x}$=10.8Hz, $J_{a,b}$=21.0Hz, H_a), 2.544(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 192.1, 142.6, 138.2, 136.3, 133.3, 129.9, 129.1, 128.8, 127.9, 126.3, 111.8, 111.6, 41.2, 40.9, 29.1, 9.9; MS(EI, 70ev) (m/z,%): 391 (M+2,2.1), 389 ($M^{+\cdot}$,5.9), 324(5.3), 296(2.8), 257(6.8), 207(6.7), 192(39.5), 165(65.6), 152(95.9), 111(100), 39(22.3); Anal.Calcd for $C_{21}H_{16}ClN_5O$: C, 64.70; H, 4.14; N, 17.96; Found: C, 64.77; H, 4.03; N, 17.85.

(1'R,1'S)-2-{3-[1-(2-Chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-oxo-1-*p*-tolylpropyl}malononitrile (6g)


6g

White solid, yield 70%, mp 57-58℃, IR(KBr,cm^{-1}): 2255(CN), 1684(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.630-7.454 (m, 3H, Ar-H), 7.415-7.353 (m, 3H, Ar-H), 7.218-7.192 (d, 2H, *J*=7.8Hz, Ar-H), 4.572-4.555 (d, 1H, *J*=5.1Hz, H_c), 4.105-3.972 (m, 2H, H_b, H_x), 3.892-3.796 (m, 1H, H_a), 2.413(s, 3H, Tr-CH_3), 2.335 (s, 3H, Ar_2-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 192.2, 141.9, 139.9, 138.6, 133.2, 132.4, 132.2, 131.3, 130.5, 129.7, 128.8, 128.0, 127.7, 111.9, 111.7, 41.2, 40.6, 29.2, 20.9, 9.3; MS(EI, 70ev) (m/z,%): 405 (M+2,1.9), 403 ($M^{+\cdot}$,4.7), 338(1.5), 310(1.5), 257(2.7), 221(6.6), 193(32.1), 152(100), 111(58.2), 91(21.9), 39(27.6); Anal.Calcd for $C_{22}H_{18}ClN_5O$: C, 65.43; H, 4.49; N, 17.34; Found: C, 65.55; H, 4.44; N, 17.29.

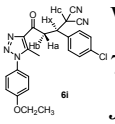
(1'R,1'S)-2-{1-(4-Chlorophenyl)-3-[1-(2-chlorophenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-oxopropyl}malononitrile (6h)


6h

Light yellow solid, yield 78%, mp 64-66℃, IR(KBr,cm^{-1}): 2255(CN), 1683(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.651-7.571 (m, 2H, Ar-H), 7.550-7.454 (m, 2H, Ar-H), 7.425-7.376 (m, 4H, Ar-H), 4.584-4.566 (d, 1H, *J*=5.4Hz, H_c), 4.095-3.978(m, 2H, H_b, H_x), 3.882-3.814 (m, 1H, H_a), 2.425(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 191.9, 141.9, 140.1, 134.9, 134.7, 132.5, 132.2, 131.5, 130.7, 129.4, 129.3, 128.9, 128.1, 111.7, 111.4, 41.1, 40.6, 29.0,

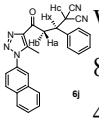
9.5; MS(EI, 70ev) (m/z,%): 425 (M+2,2.4), 423 ($M^{+\cdot}$,2.6), 358(2.3), 330(1.9), 257(3.5), 192(29.2), 165(43.3), 152(100), 111(24.7), 39(28.3); Anal.Calcd for $C_{21}H_{15}Cl_2N_5O$: C, 59.45; H, 3.56; N, 16.51; Found: C, 59.55; H, 3.45; N, 16.55.

(1'R,1'S)-2-{1-(4-Chlorophenyl)-3-[1-(4-ethoxyphenyl)-5-methyl-1*H*-1,2,3-triazol-4-yl]-3-oxopropyl}malononitrile (6i)



White solid, yield 77%, mp 58-60℃, IR(KBr,cm^{-1}): 2256(CN), 1681(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 7.448-7.427 (d, 2H, *J*=6.3Hz, Ar-H), 7.419-7.282 (m, 4H, Ar-H), 7.036-7.013 (d, 2H, *J*=6.9Hz, Ar-H), 4.623-4.605 (d, 1H, *J*=5.4Hz, H_c), 4.129-4.002 (m, 4H, H_b, H_x, Ar_1-OCH_2CH_3), 3.841-3.744 (dd, 1H, $J_{a,x}$=9.3Hz, $J_{a,b}$=19.8Hz, H_a), 2.503(s, 3H, Tr-CH_3), 1.467-1.421 (t, 3H, *J*=6.9Hz, Ar_1-OCH_2CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 191.8, 160.0, 142.2, 138.3, 134.8, 134.7, 129.4, 129.1, 127.2, 126.3, 115.1, 111.7, 111.4, 63.8, 40.9, 40.4, 28.9, 14.4, 9.8; MS(EI, 70ev), (m/z,%): 435 (M+2,1.4), 433 ($M^{+\cdot}$,4.9), 405(1.3), 340(1.1), 202(48.0), 188(36.4), 175(98.2), 162(54.4), 146(89.1), 65(100), 39(51.4); Anal.Calcd for $C_{23}H_{20}ClN_5O_2$: C, 63.67; H, 4.65; N, 16.14; Found: C, 63.77; H, 4.72; N, 16.03.

(1'R,1'S)-2-{3-[5-Methyl-1-(naphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]-3-oxo-1-phenylpropyl}malononitrile (6j)



White solid, yield 82%, mp 59-61℃, IR(KBr,cm^{-1}): 2254(CN), 1681(C=O); ^{1}HNMR(300MHz, $CDCl_3$): δ_H 8.044-8.017 (d, 1H, *J*=8.1Hz, Ar-H), 7.966-7.911 (m, 3H, Ar-H), 7.653-7.587 (m, 2H, Ar-H), 7.517-7.366 (m, 6H, Ar-H), 4.586-4.566 (d, 1H, *J*=6.0Hz, H_c), 4.131-4.000 (m, 2H, H_b, H_x), 3.918-3.839 (m, 1H, H_a), 2.608(s, 3H, Tr-CH_3); ^{13}C NMR(75.6MHz, $CDCl_3$): δ_C 192.4, 142.7, 138.5, 136.4, 133.4, 132.8, 132.2, 129.9, 129.2, 128.9, 128.3, 128.0, 127.9, 127.8, 127.6, 124.3, 122.2, 111.8, 111.6, 41.3, 41.2, 29.2, 10.2; MS(EI, 70ev) (m/z,%): 405 ($M^{+\cdot}$,2.5), 340(0.2), 312(1.1), 251(7.5), 208(14.2), 181(67.2), 168(26.6), 127(100), 103(25.7), 39(22.2); Anal.Calcd for $C_{25}H_{19}N_5O$: C, 74.06; H, 4.72; N, 17.27; Found: C, 74.00; H, 4.86; N, 17.15.

Refenance:

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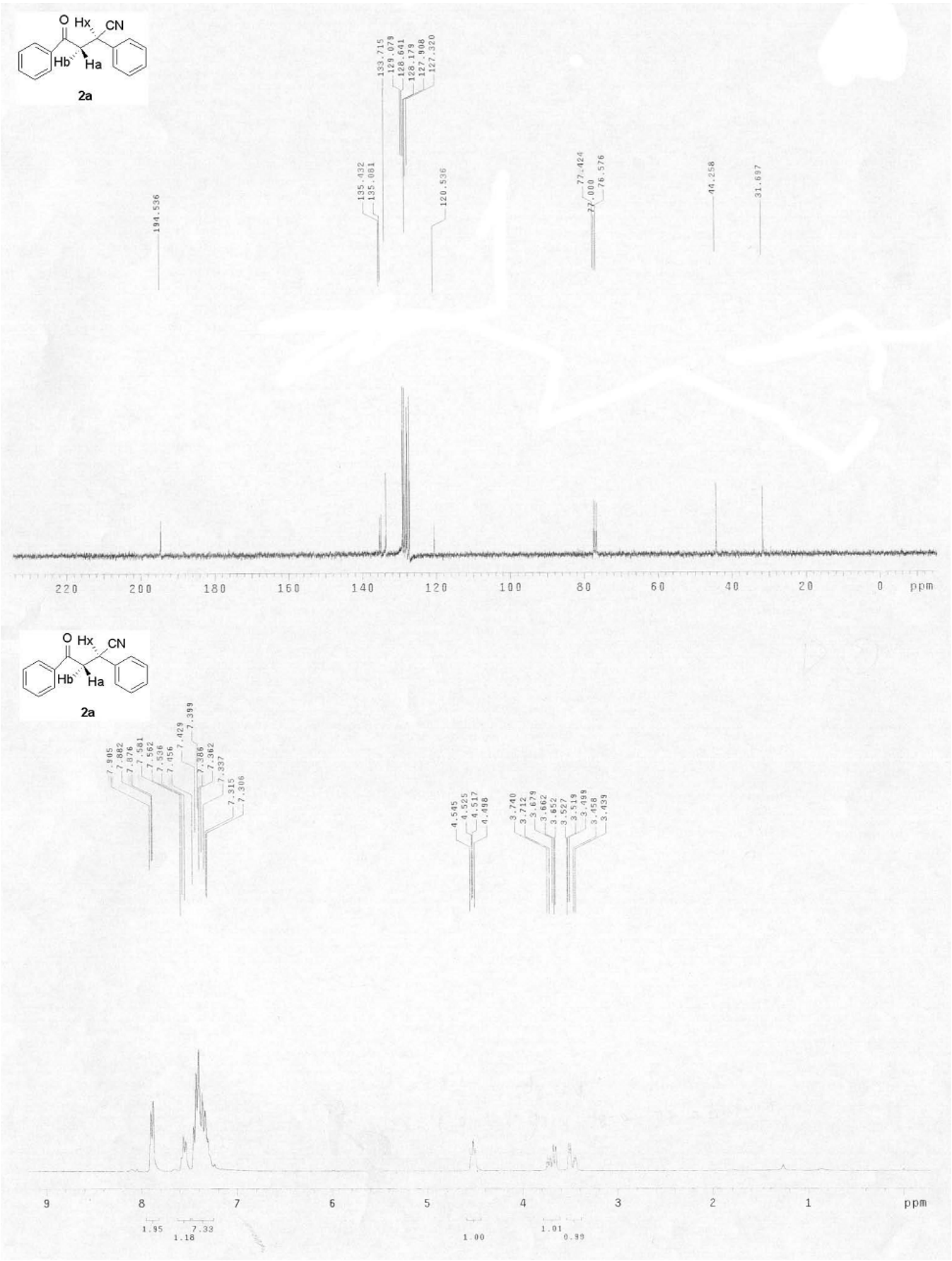
12.

Copies of ^{1}H NMR/^{13}C NMR

Figure of compounds 2a-i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77.000
76.576
44.258
31.697
220 200 180 160 140 120 100 80 60 40 20 0 ppm
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Hb Ha
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7.876
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7.562
7.536
7.456
7.429
7.399
7.386
7.362
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3.679
3.662
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3.527
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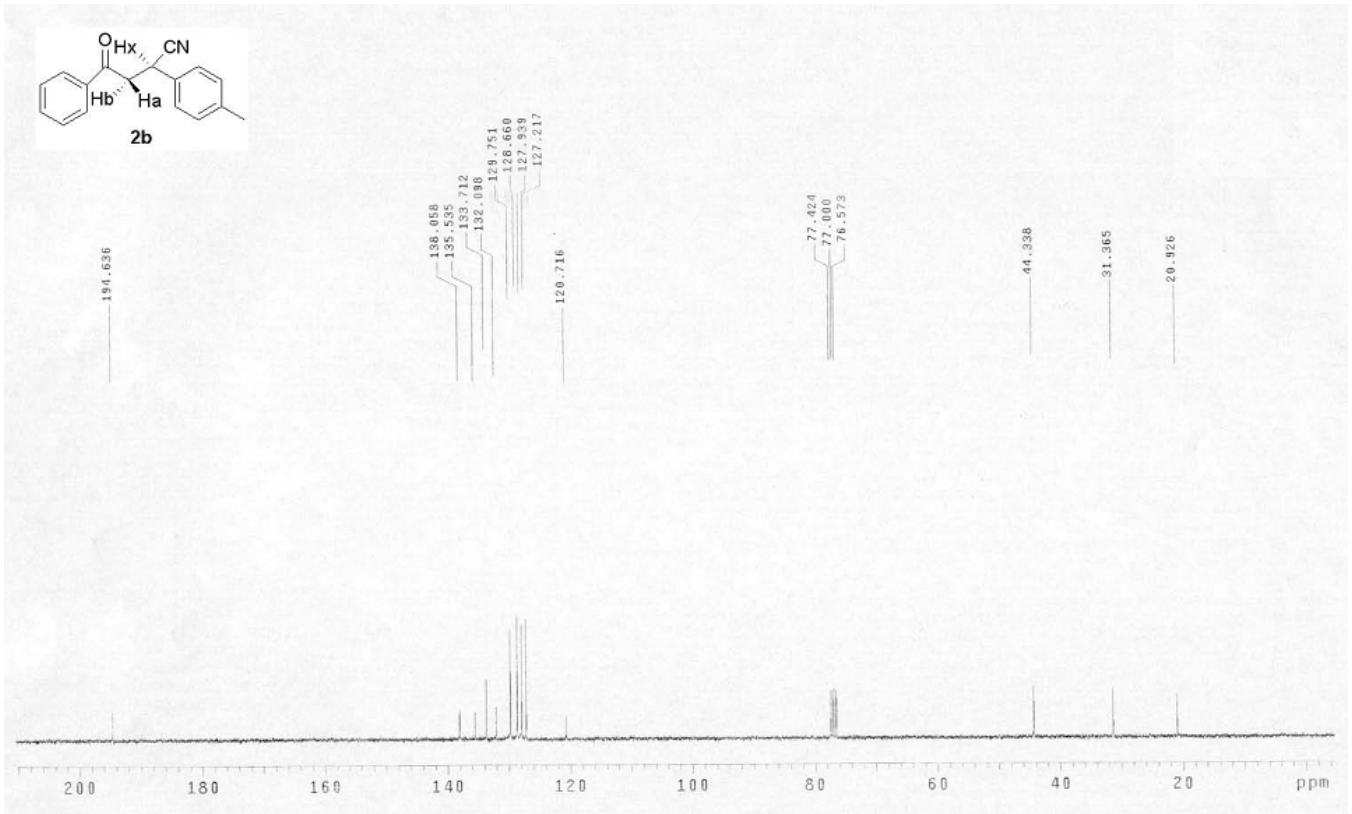
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140
120
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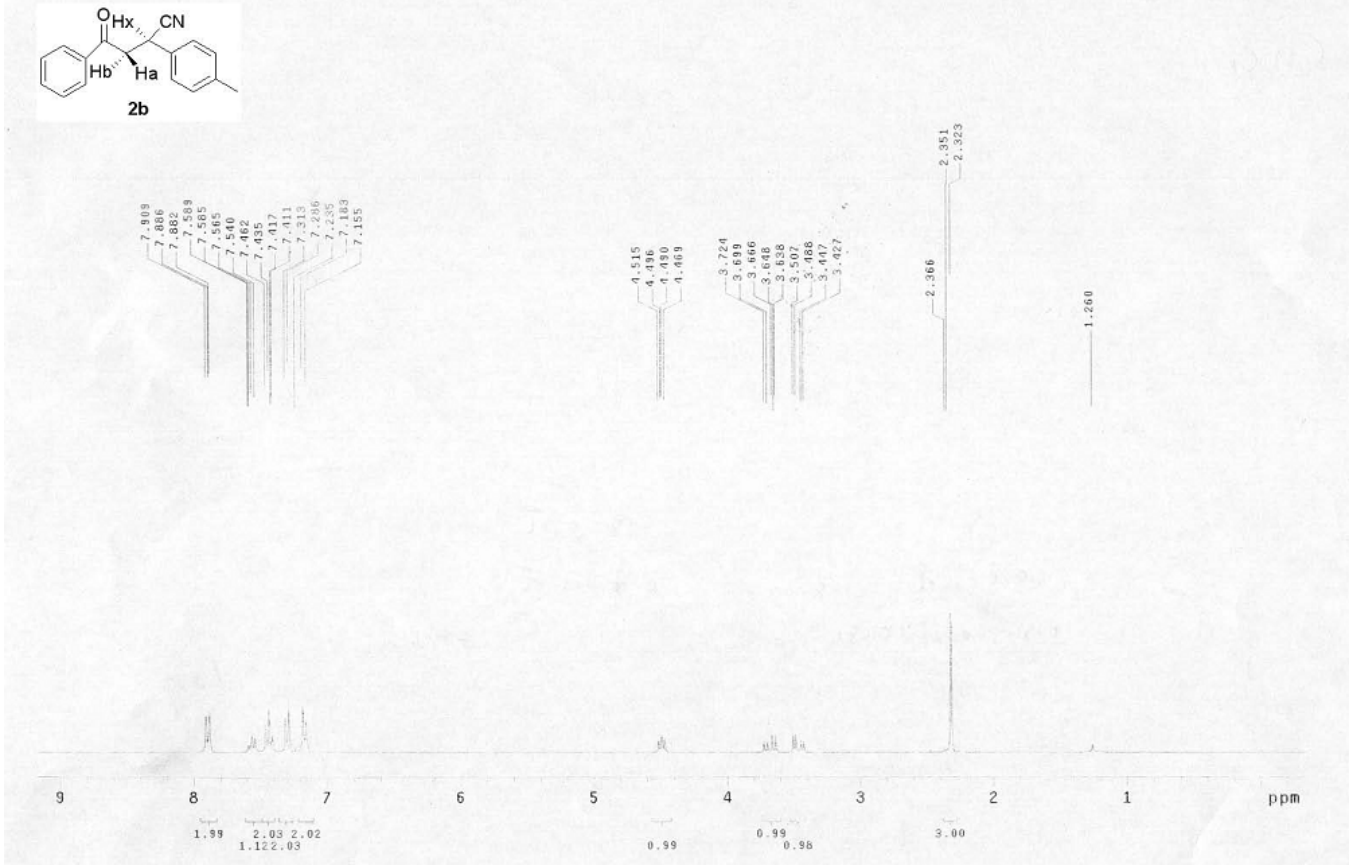
80
60
40
20
ppm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7.540
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7.155
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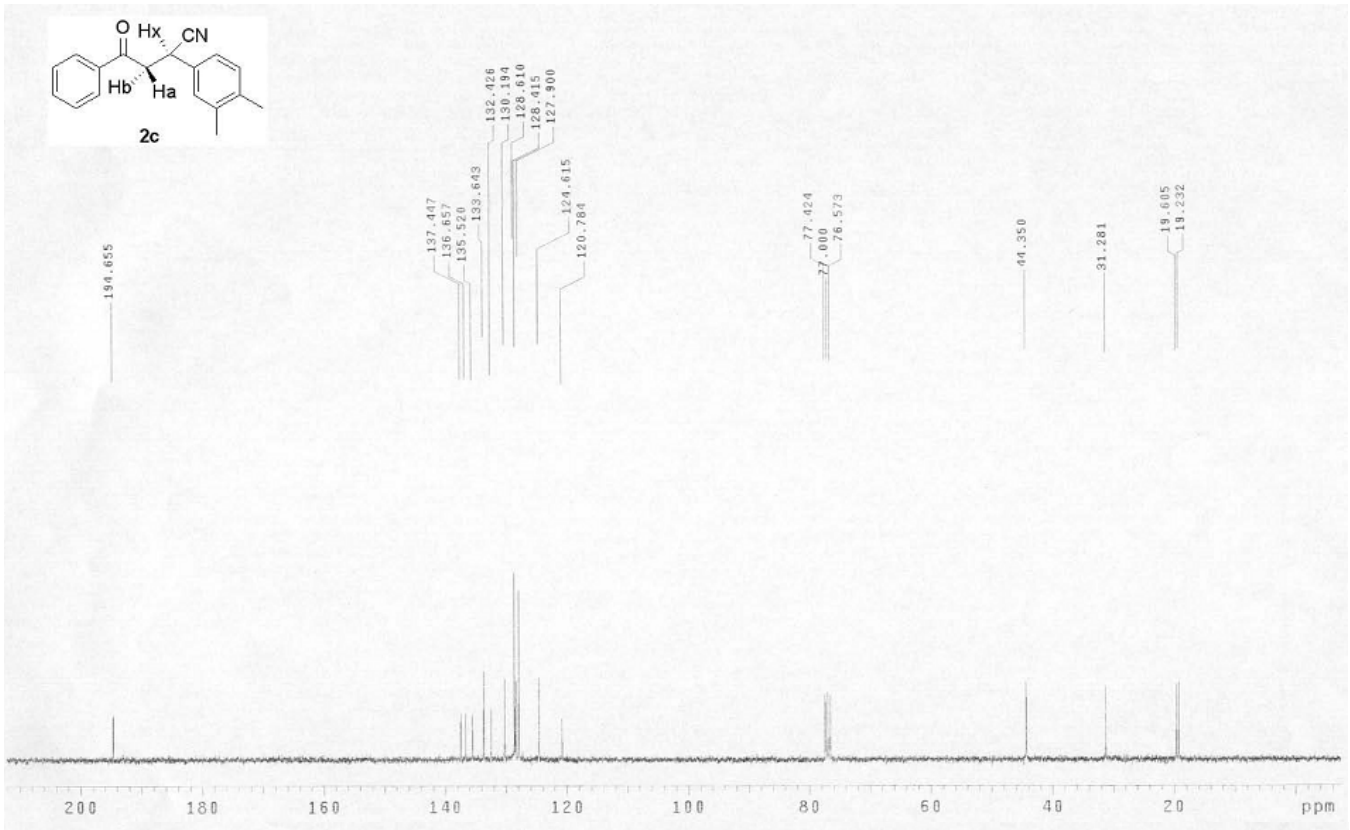
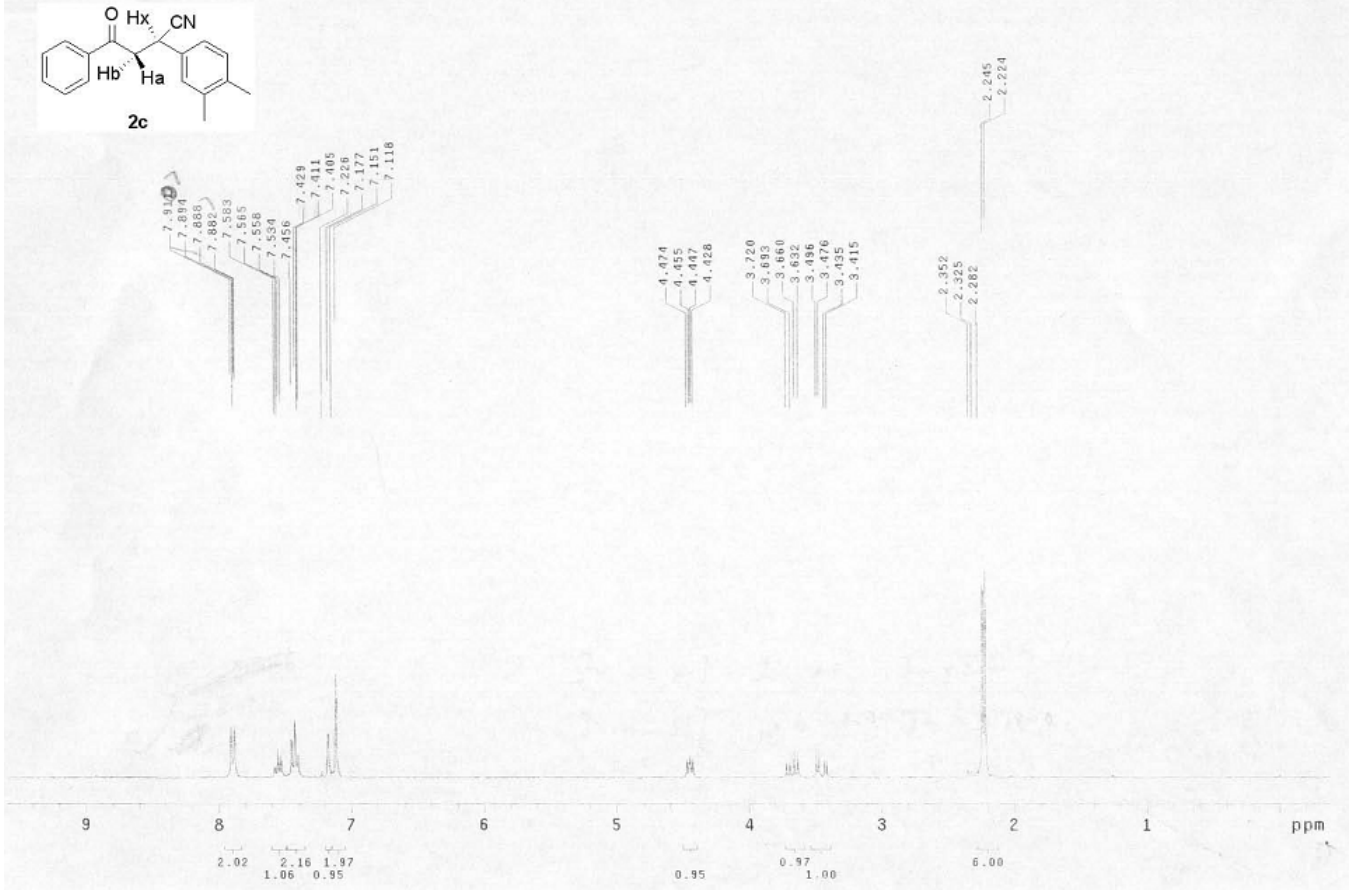
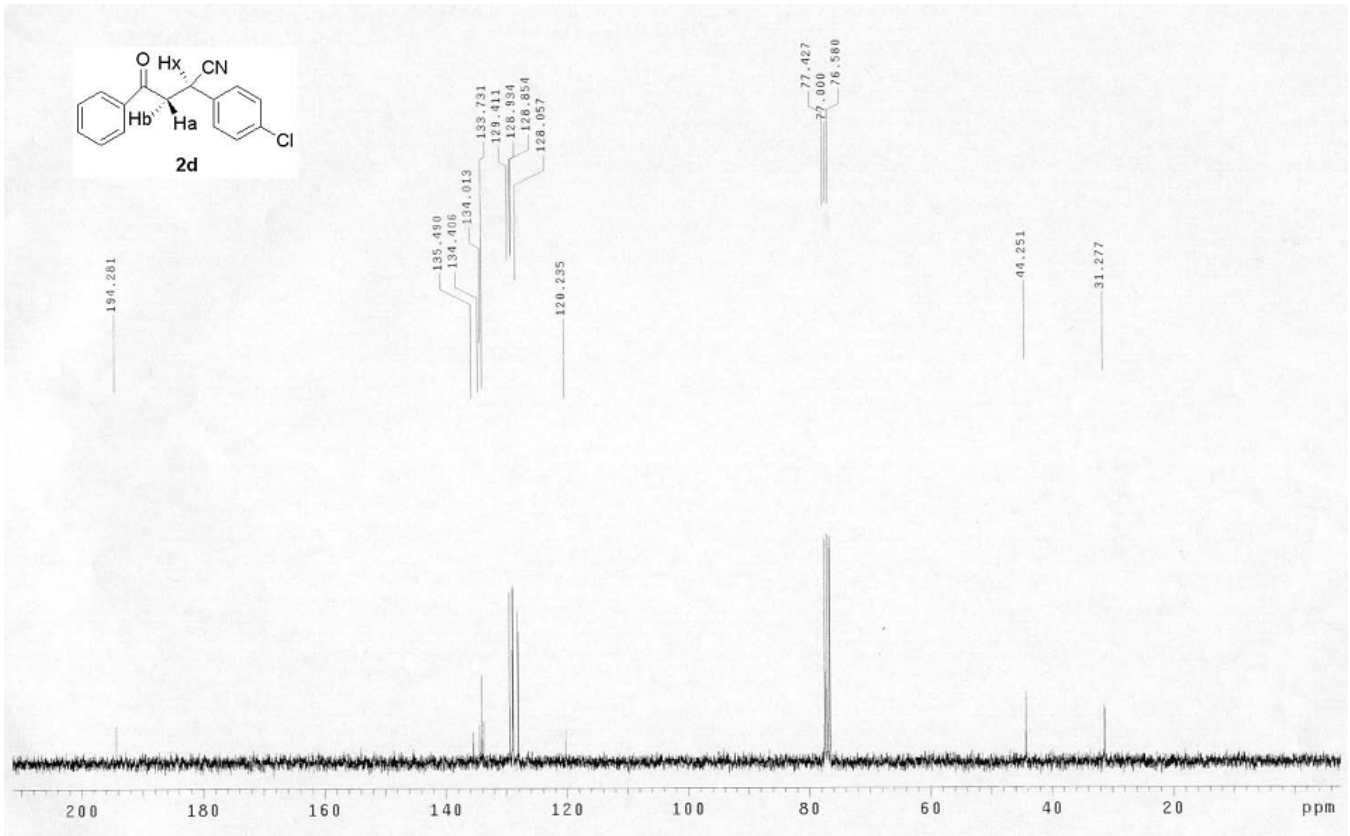
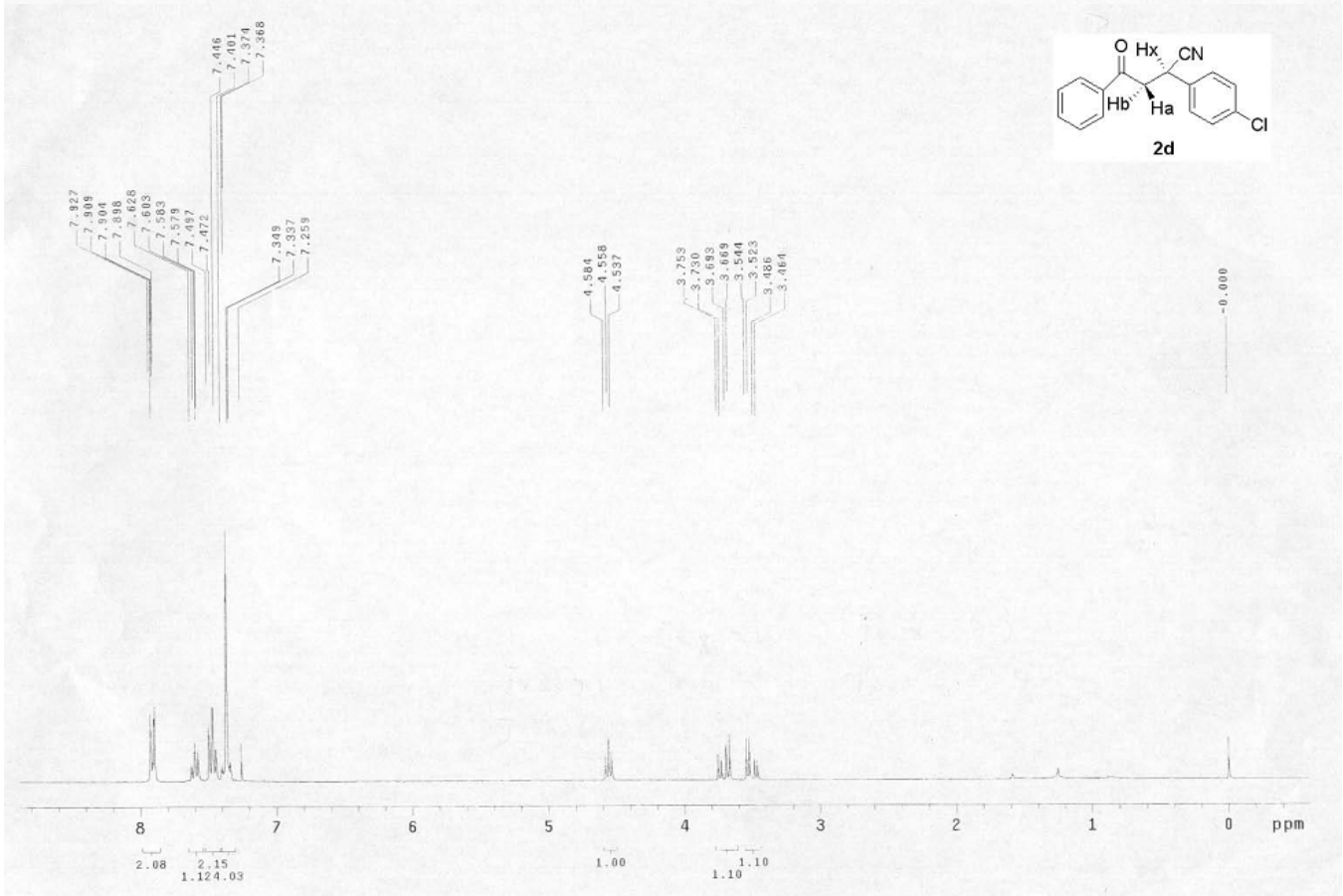
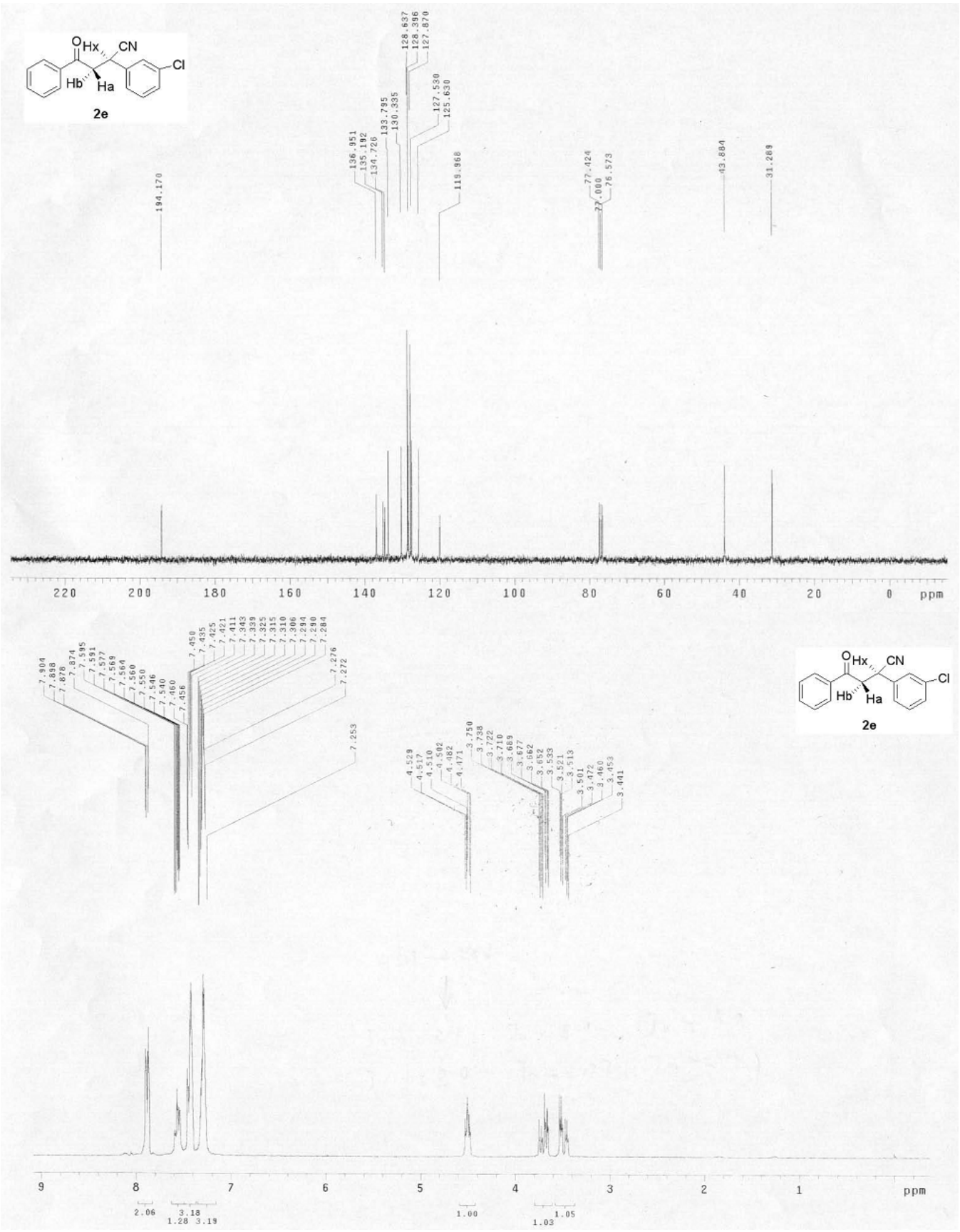
3.638
3.507
3.488
3.447
3.427
2.351
2.323
2.366
1.260
9
8
7
6
5
4
3
2
1
ppm
1.99
2.03
2.02
1.12
2.03
0.99
0.99
0.98
3.00

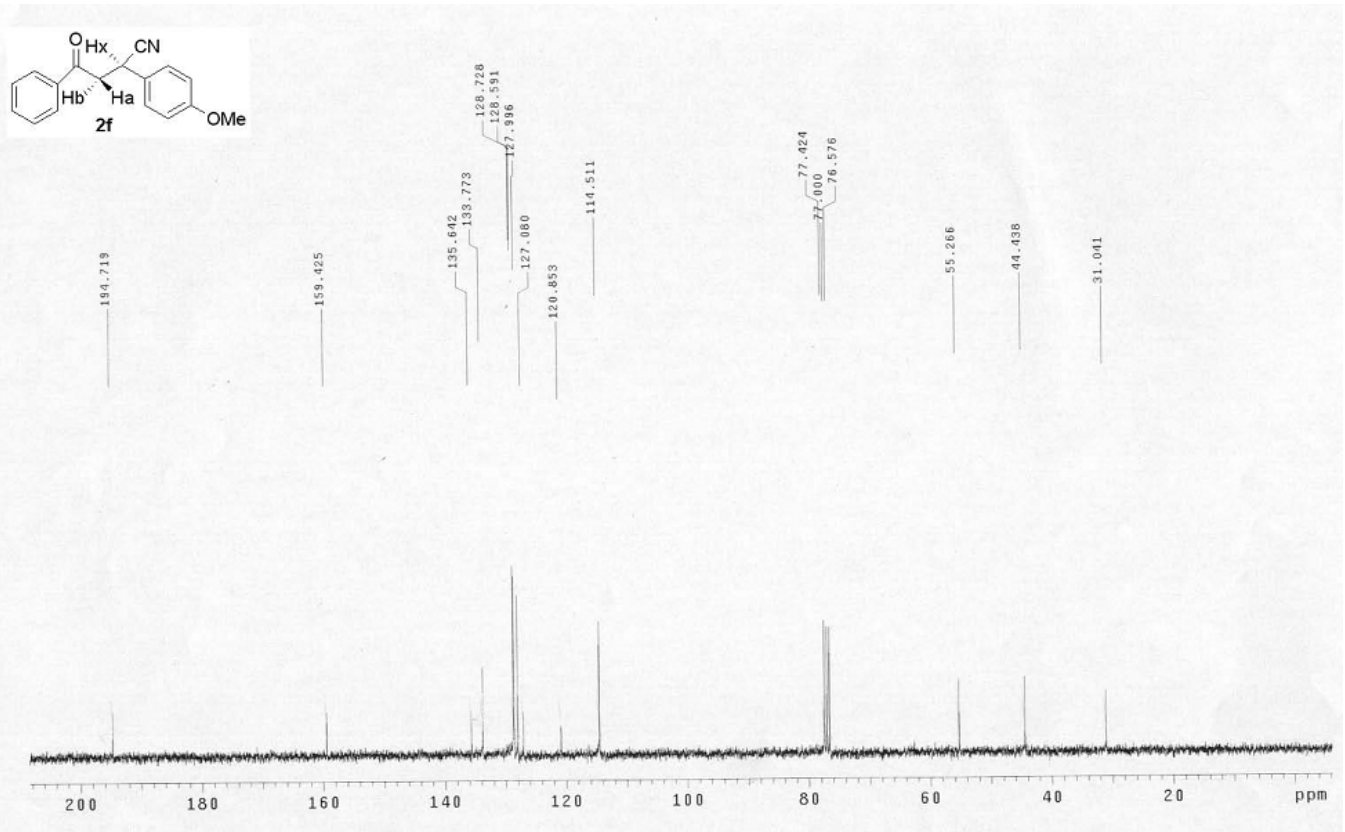

O Hx CN
Hb Ha
2c
194.655
137.447
136.657
135.520
133.643
132.426
130.194
128.610
128.415
127.900
124.615
120.784
77.424
77.000
76.573
44.350
31.281
19.605
19.232
200
180
160
140
120
100
80
60
40
20
ppm

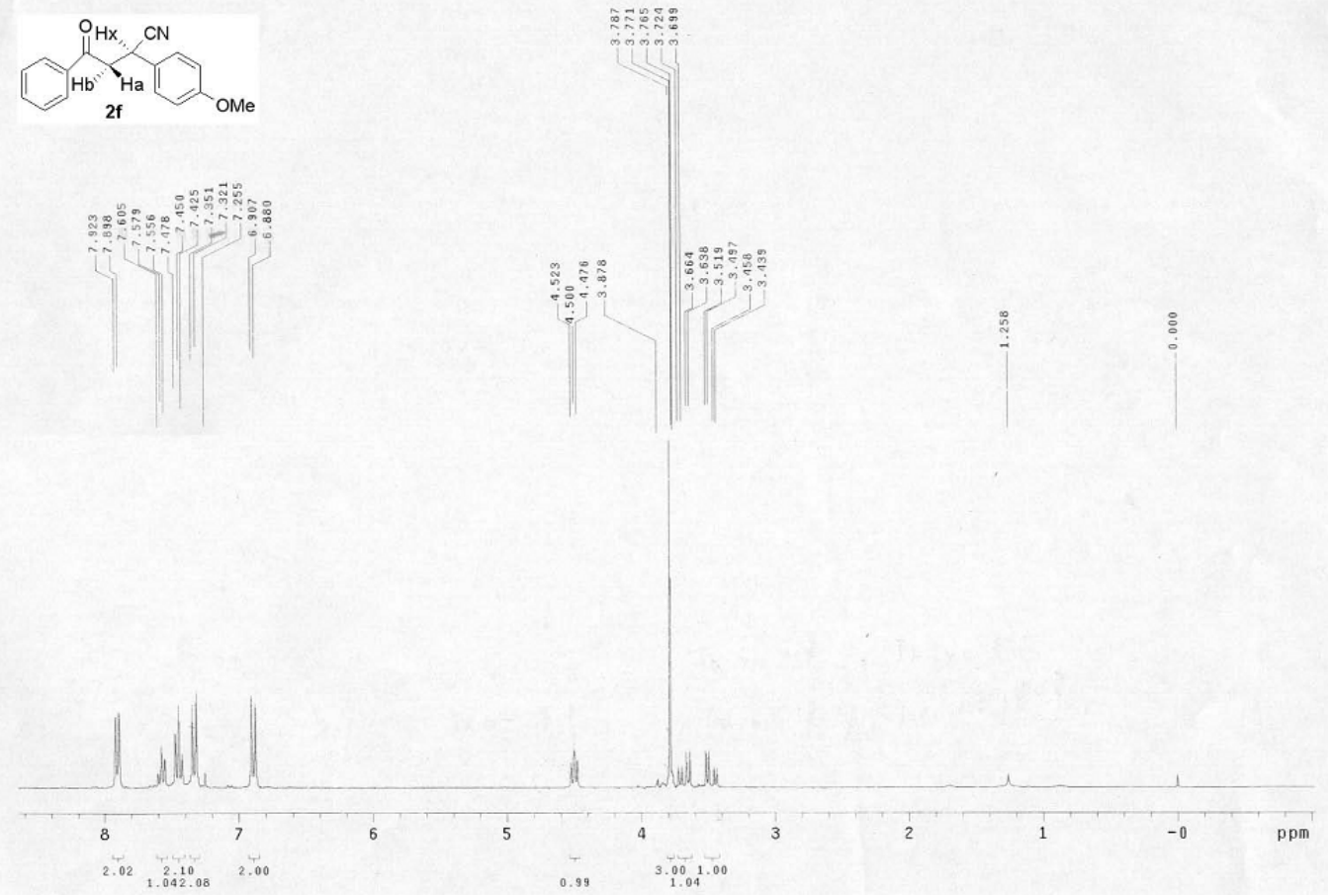

O Hx CN
Hb Ha
2c
7.918
7.894
7.888
7.882
7.583
7.565
7.556
7.534
7.456
7.429
7.411
7.405
7.226
7.177
7.151
7.118
4.474
4.455
4.447
4.428
3.720
3.693
3.660
3.632
3.496
3.476
3.435
3.415
2.352
2.325
2.282
2.245
2.224
9
8
7
6
5
4
3
2
1
ppm
2.02
2.16
1.97
1.06
0.95
0.95
0.97
1.00
6.00

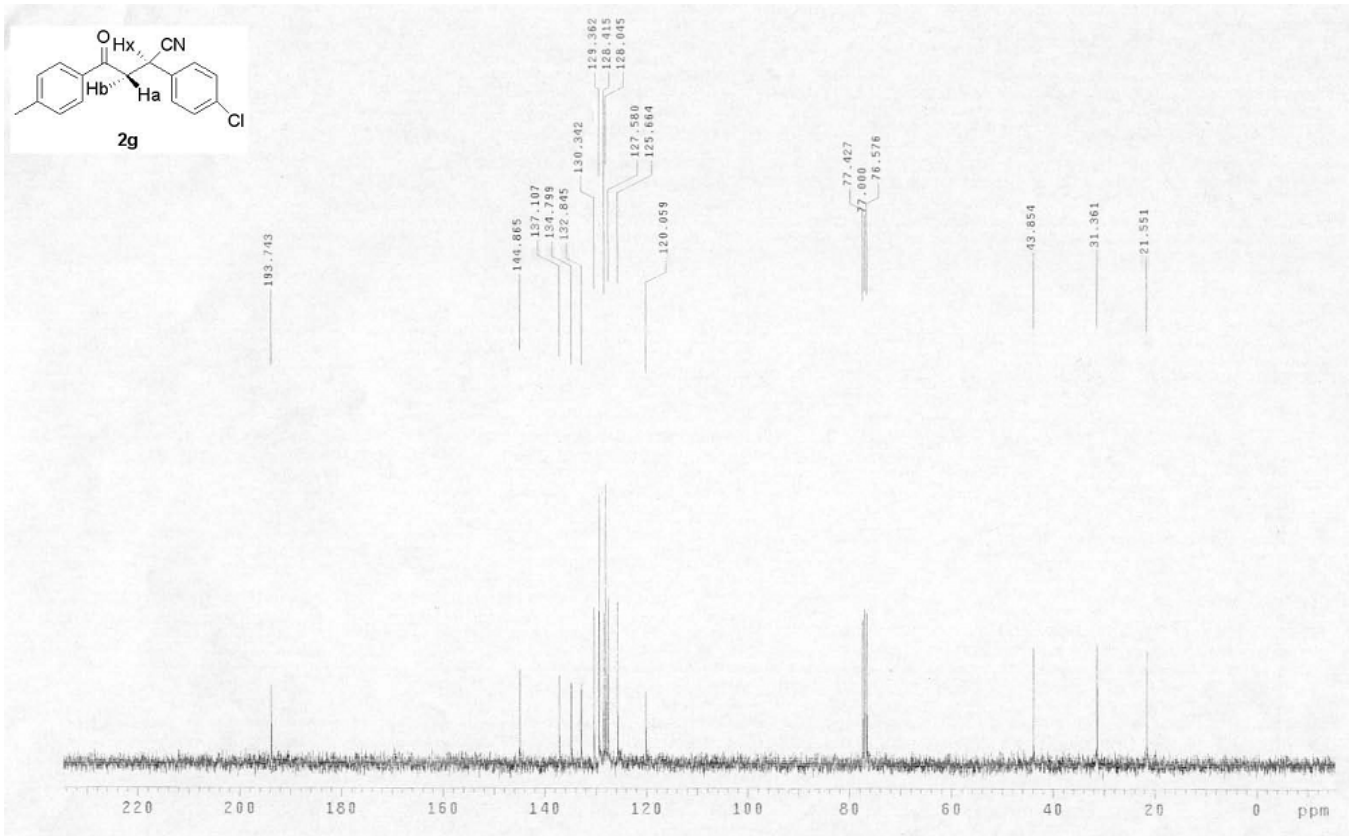

O Hx CN
Hb Ha
Cl
2d
194.281
135.490
134.406
134.013
133.731
129.411
128.934
126.854
128.057
120.235
77.427
77.000
76.580
44.251
31.277
200
180
160
140
120
100
80
60
40
20
ppm

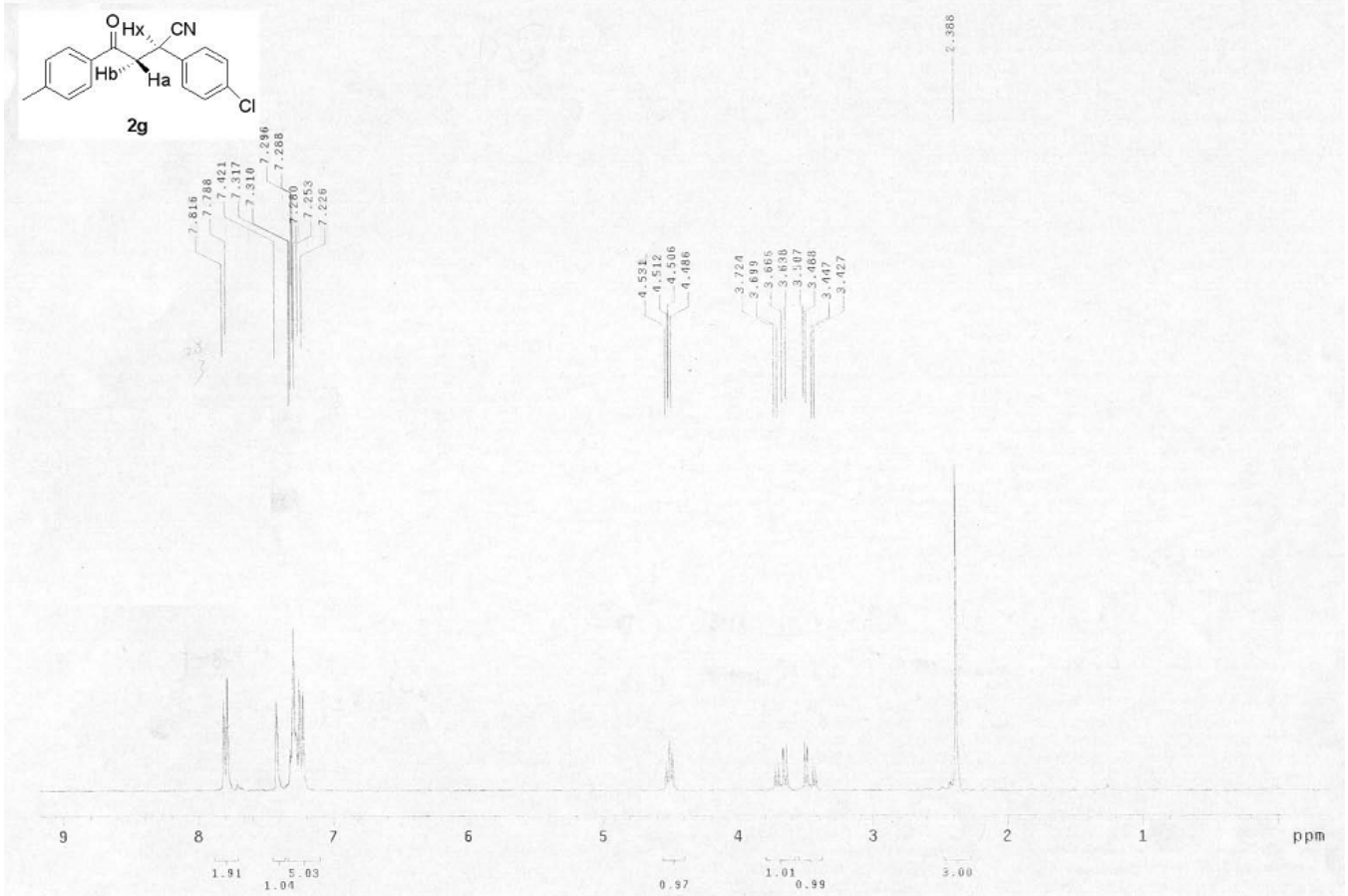

O Hx CN
Hb Ha
Cl
2d
7.927
7.909
7.904
7.898
7.628
7.603
7.583
7.579
7.497
7.472
7.446
7.401
7.374
7.368
7.349
7.337
7.259
4.584
4.558
4.537
3.753
3.730
3.693
3.669
3.544
3.523
3.486
3.464
0.000
8
7
6
5
4
3
2
1
0
ppm
2.08
2.15
1.12
4.03
1.00
1.10
1.10

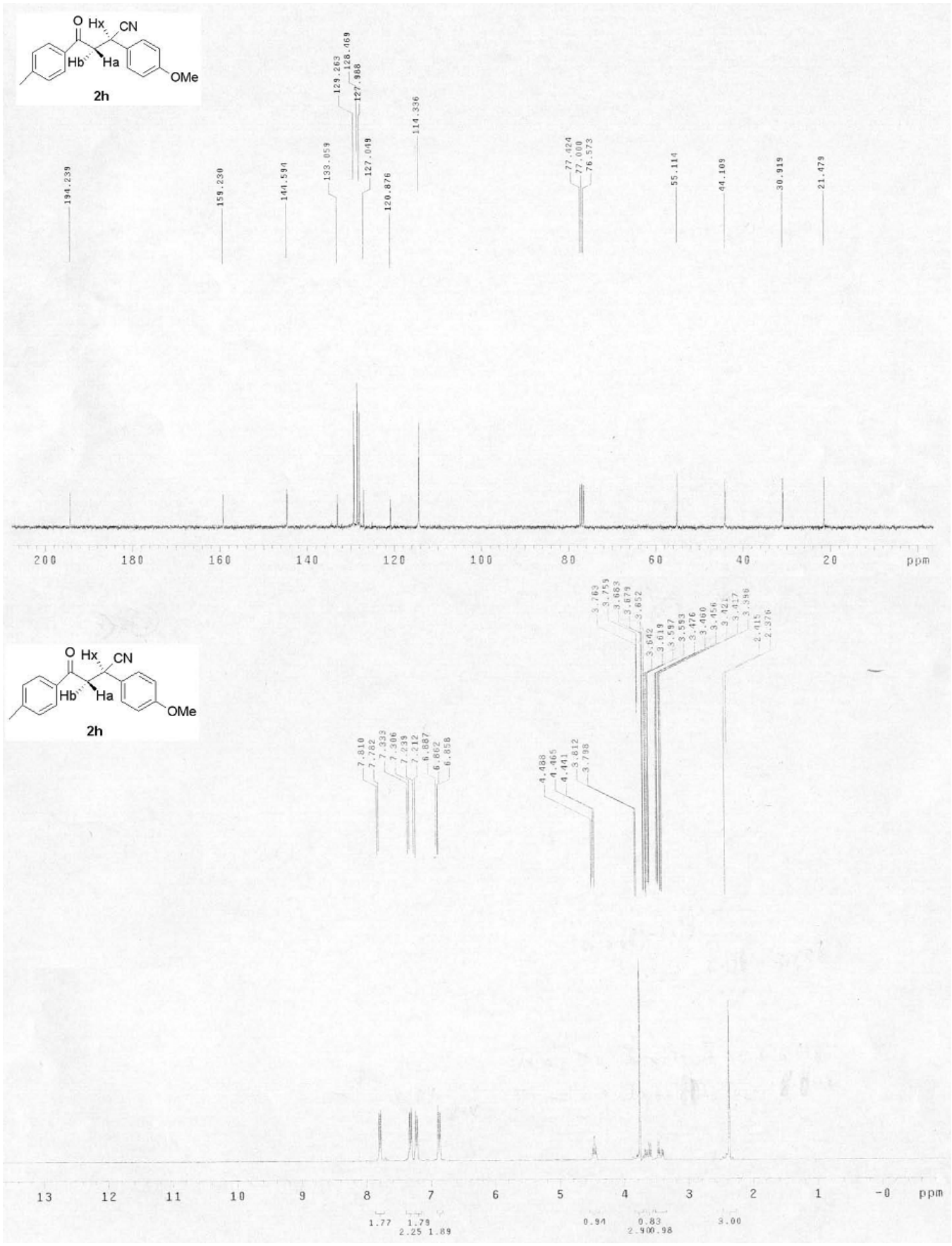

O
Hx
CN
Cl
Hb
Ha
2e
194.170
136.951
135.192
134.726
133.795
130.335
128.637
128.396
127.870
127.530
125.630
119.966
77.424
77.000
76.573
43.884
31.289
220
200
180
160
140
120
100
80
60
40
20
0
ppm
7.904
7.898
7.878
7.874
7.595
7.591
7.577
7.569
7.564
7.560
7.550
7.546
7.540
7.460
7.456
7.450
7.435
7.425
7.421
7.411
7.343
7.339
7.325
7.315
7.310
7.306
7.294
7.290
7.284
7.276
7.272
7.253
4.529
4.517
4.510
4.502
4.482
4.471
3.750
3.738
3.722
3.710
3.669
3.677
3.662
3.652
3.533
3.521
3.513
3.501
3.472
3.460
3.453
3.441
9
8
7
6
5
4
3
2
1
ppm
2.06
3.18
1.28
3.19
1.00
1.03
1.05


O
Hx
CN
Hb
Ha
OMe
2f
194.719
159.425
135.642
133.773
128.728
128.591
127.996
127.080
120.853
114.511
77.424
77.000
76.576
55.266
44.438
31.041
200
180
160
140
120
100
80
60
40
20
ppm


O
Hx
CN
Hb
Ha
OMe
2f
7.923
7.898
7.605
7.579
7.556
7.478
7.450
7.425
7.351
7.321
7.255
6.907
6.880
4.523
4.500
4.476
3.878
3.787
3.771
3.765
3.724
3.699
3.664
3.638
3.519
3.497
3.458
3.439
1.258
0.000
8
7
6
5
4
3
2
1
-0
ppm
2.02
2.10
1.04
2.08
2.00
0.99
3.00
1.00
1.04


O
Hx
CN
Hb
Ha
Cl
2g
193.743
144.865
137.107
134.798
132.845
130.342
129.362
128.415
128.045
127.580
125.664
120.059
77.427
77.000
76.576
43.854
31.361
21.551
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
Hx
CN
Hb
Ha
Cl
2g
2.388
7.816
7.788
7.421
7.317
7.310
7.296
7.288
7.260
7.253
7.226
4.531
4.512
4.506
4.486
3.724
3.699
3.665
3.638
3.507
3.488
3.447
3.427
9
8
7
6
5
4
3
2
1
ppm
1.91
5.03
1.04
0.97
1.01
0.99
3.00


O
Hx
CN
Hb
Ha
OMe
2h
194.239
159.230
144.594
133.059
129.263
128.469
127.988
127.049
120.876
114.336
77.424
77.000
76.573
55.114
44.109
30.919
21.479
200
180
160
140
120
100
80
60
40
20
ppm
7.810
7.782
7.333
7.306
7.239
7.212
6.887
6.862
6.858
4.488
4.465
4.141
3.812
3.798
3.763
3.759
3.663
3.679
3.652
3.642
3.619
3.597
3.583
3.476
3.460
3.456
3.421
3.417
3.396
2.415
2.376
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.77
1.79
2.25
1.89
0.94
0.83
2.90
0.98
3.00

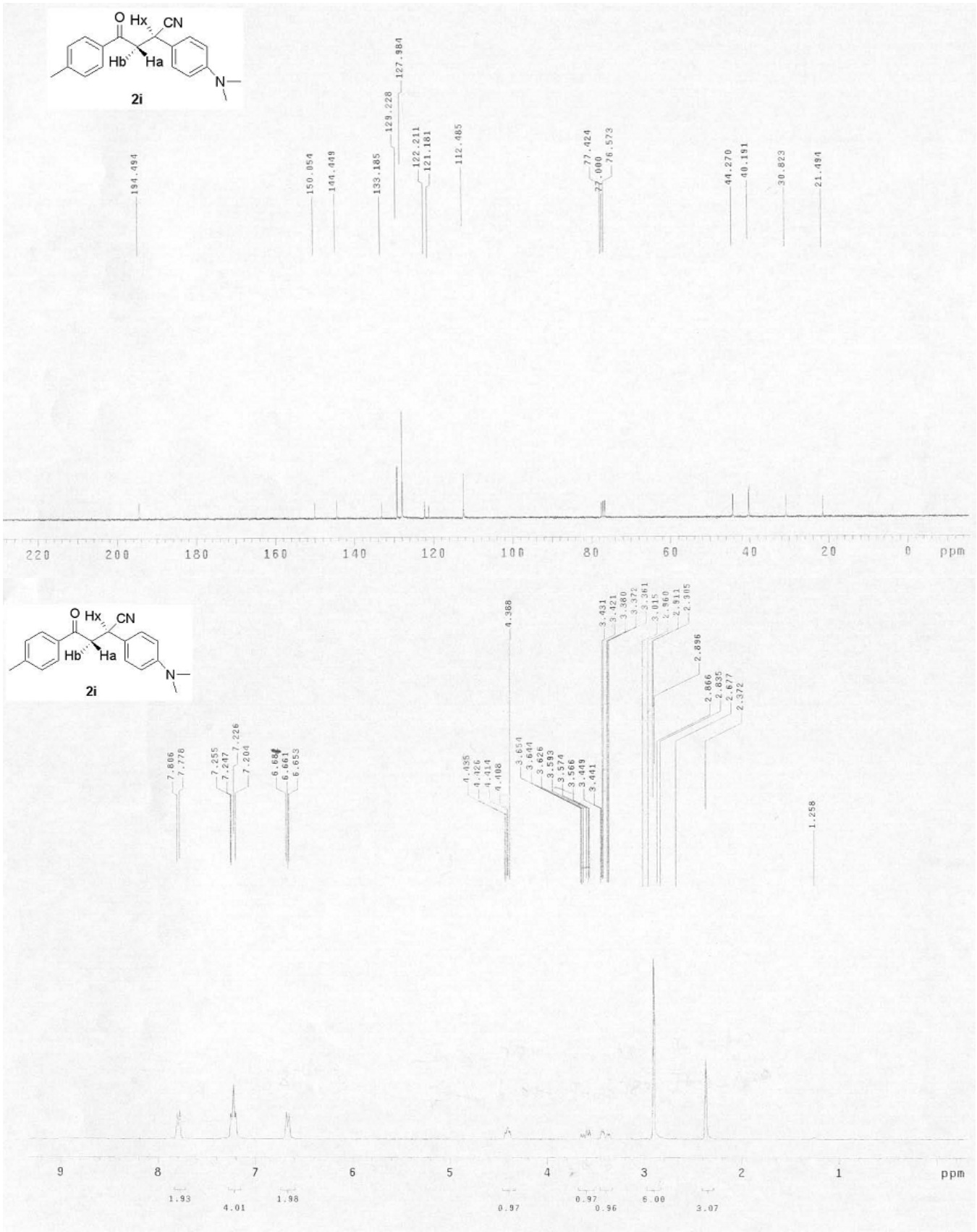
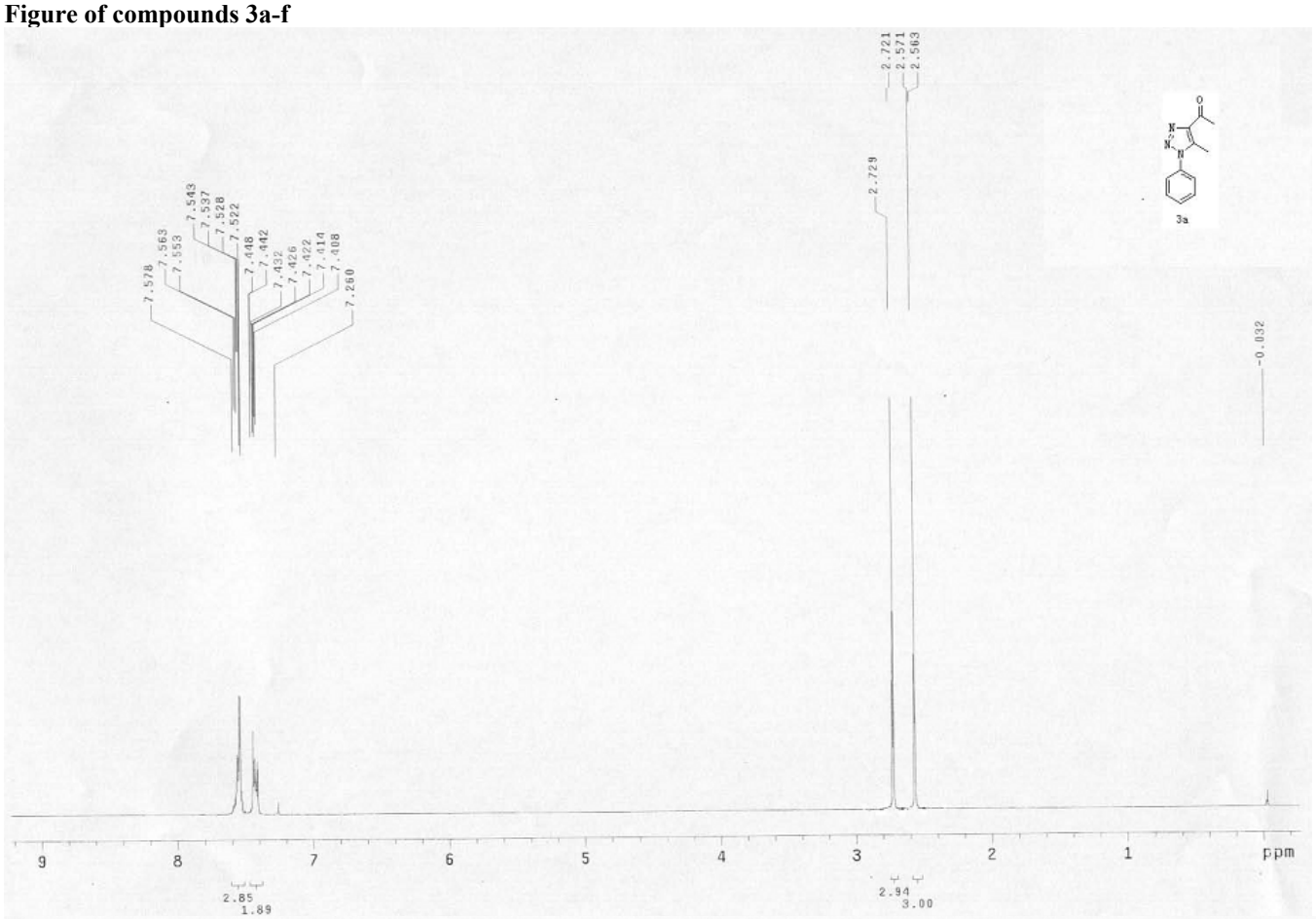
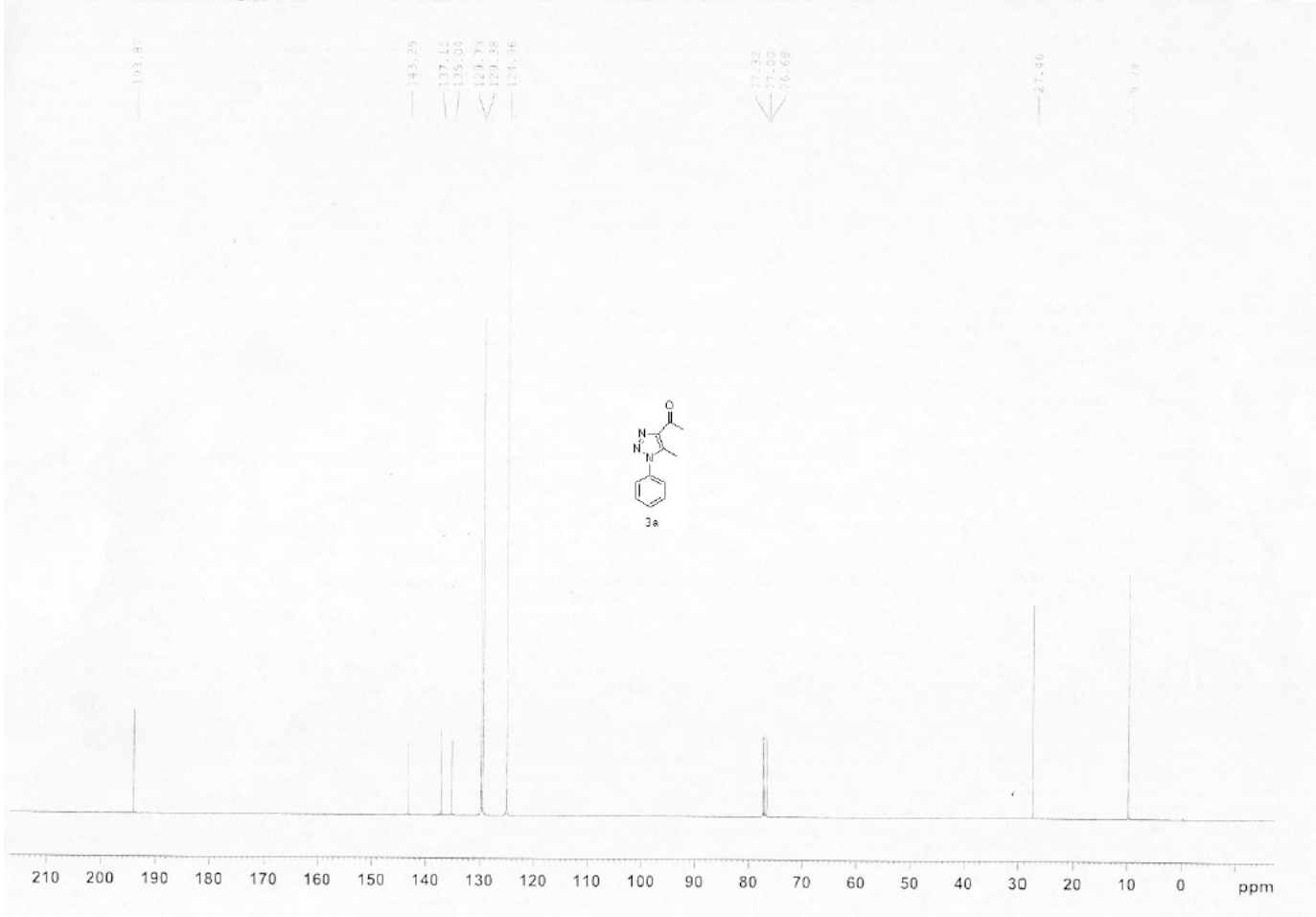
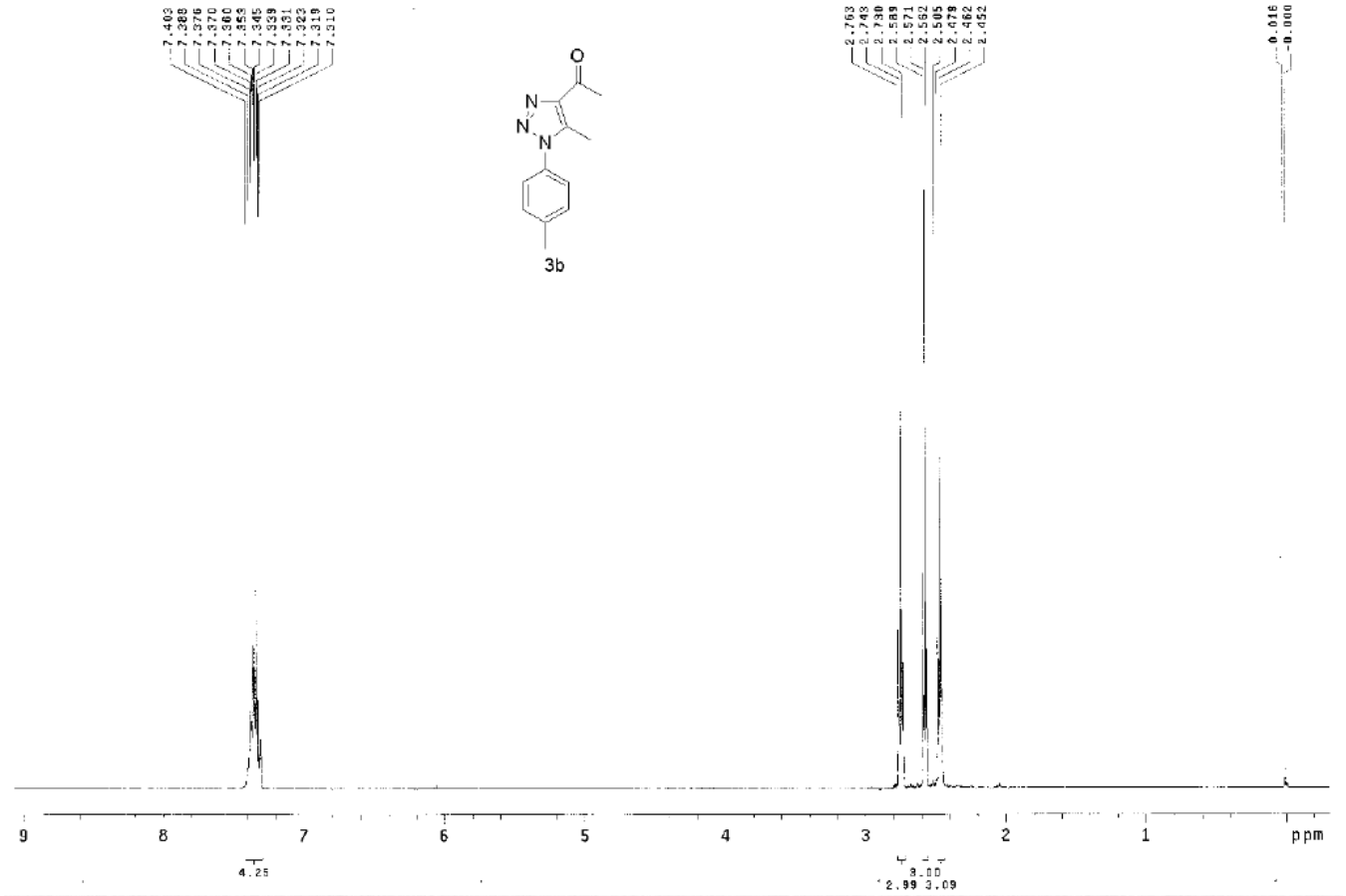
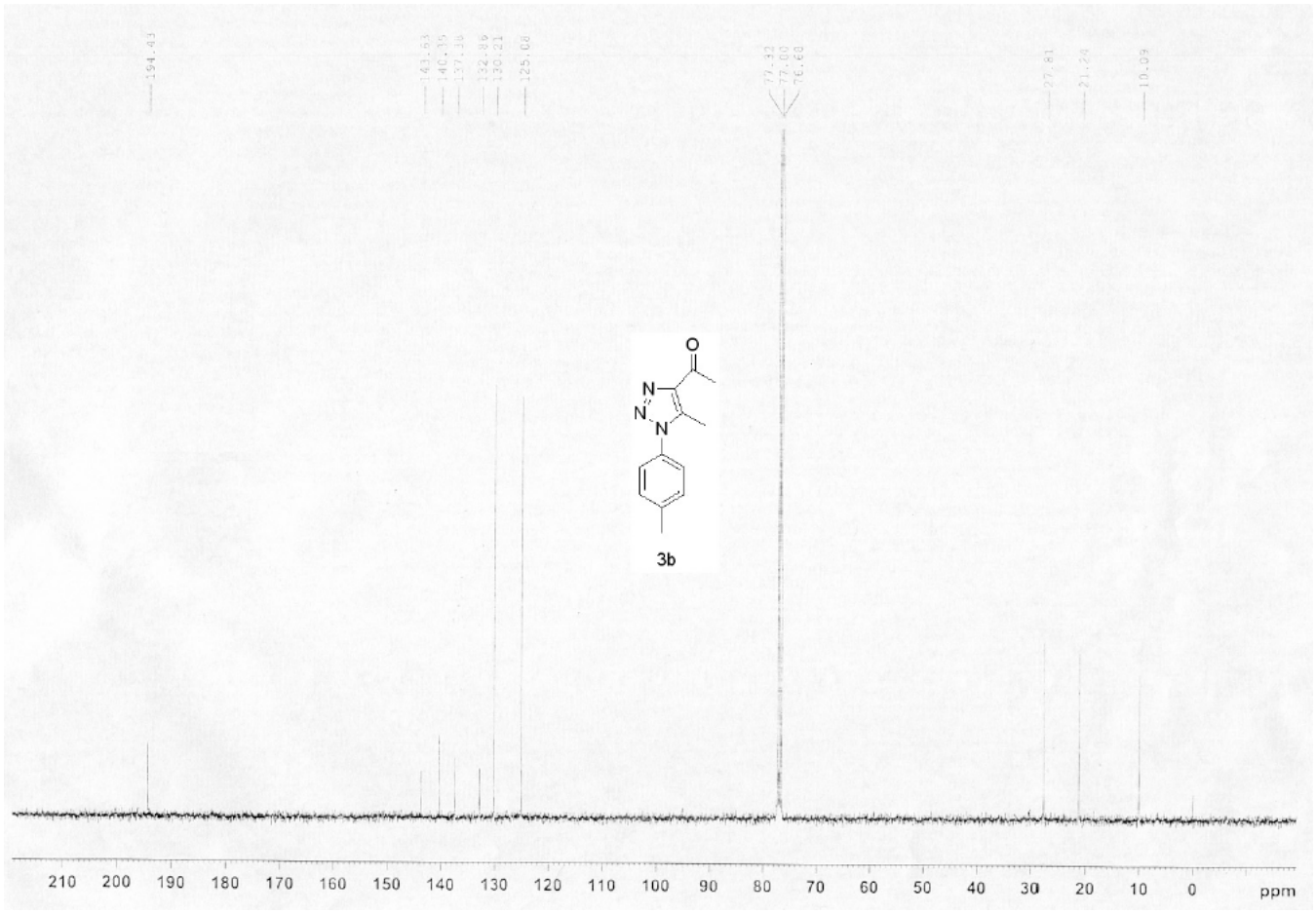

O Hx CN
Hb Ha
N
2i
194.494
150.054
144.449
133.185
129.228
127.984
122.211
121.181
112.485
77.424
77.000
76.573
44.270
40.191
30.823
21.494
220 200 180 160 140 120 100 80 60 40 20 0 ppm
O Hx CN
Hb Ha
N
2i
7.806
7.776
7.255
7.247
7.226
7.204
6.684
6.661
6.653
4.435
4.426
4.414
4.408
4.388
3.654
3.644
3.626
3.593
3.574
3.566
3.449
3.441
3.431
3.421
3.380
3.372
3.361
3.015
2.960
2.911
2.905
2.896
2.866
2.835
2.677
2.372
1.258
9 8 7 6 5 4 3 2 1 ppm
1.93
4.01
1.98
0.97
0.97
0.96
6.00
3.07

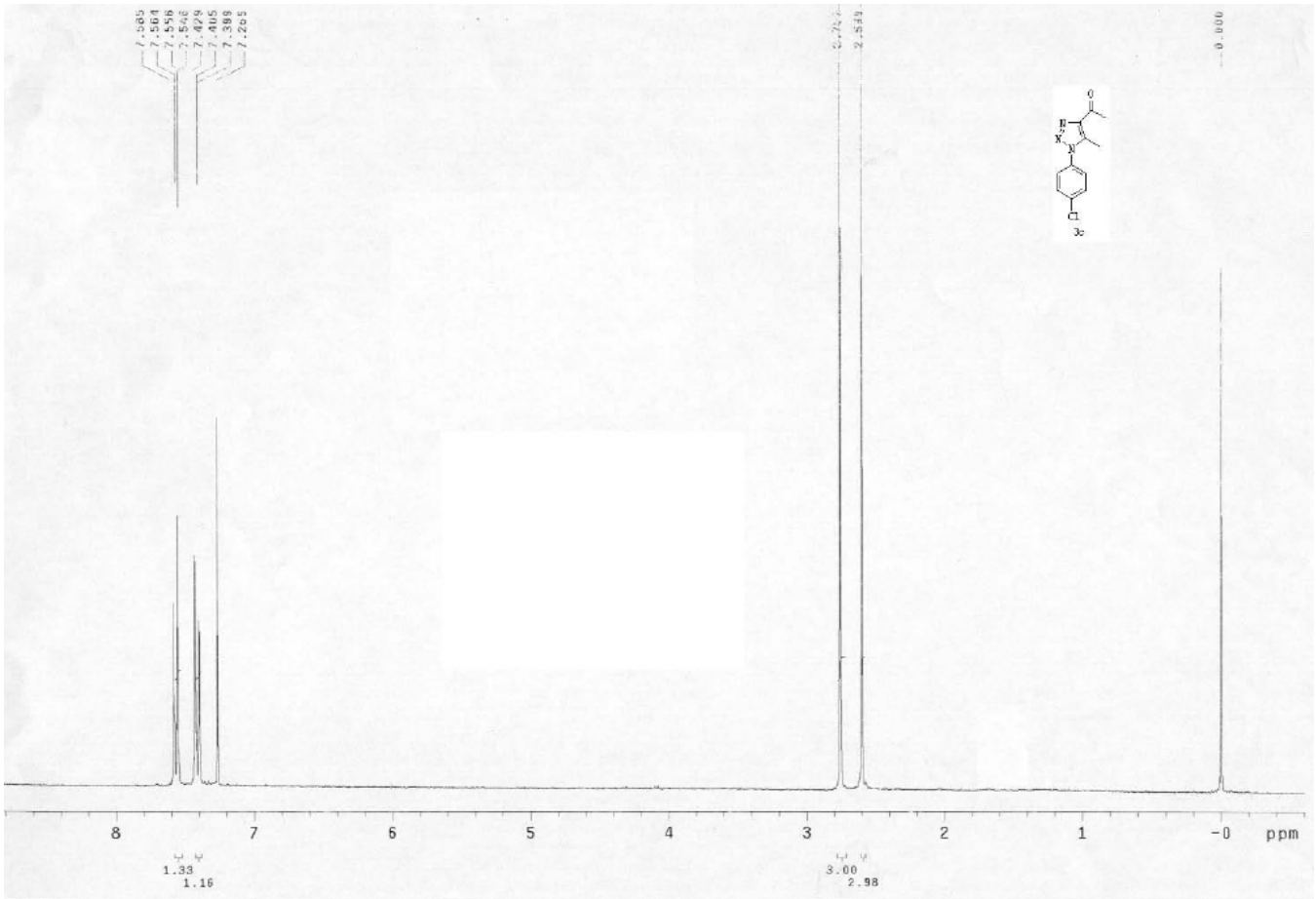
Figure of compounds 3a-f

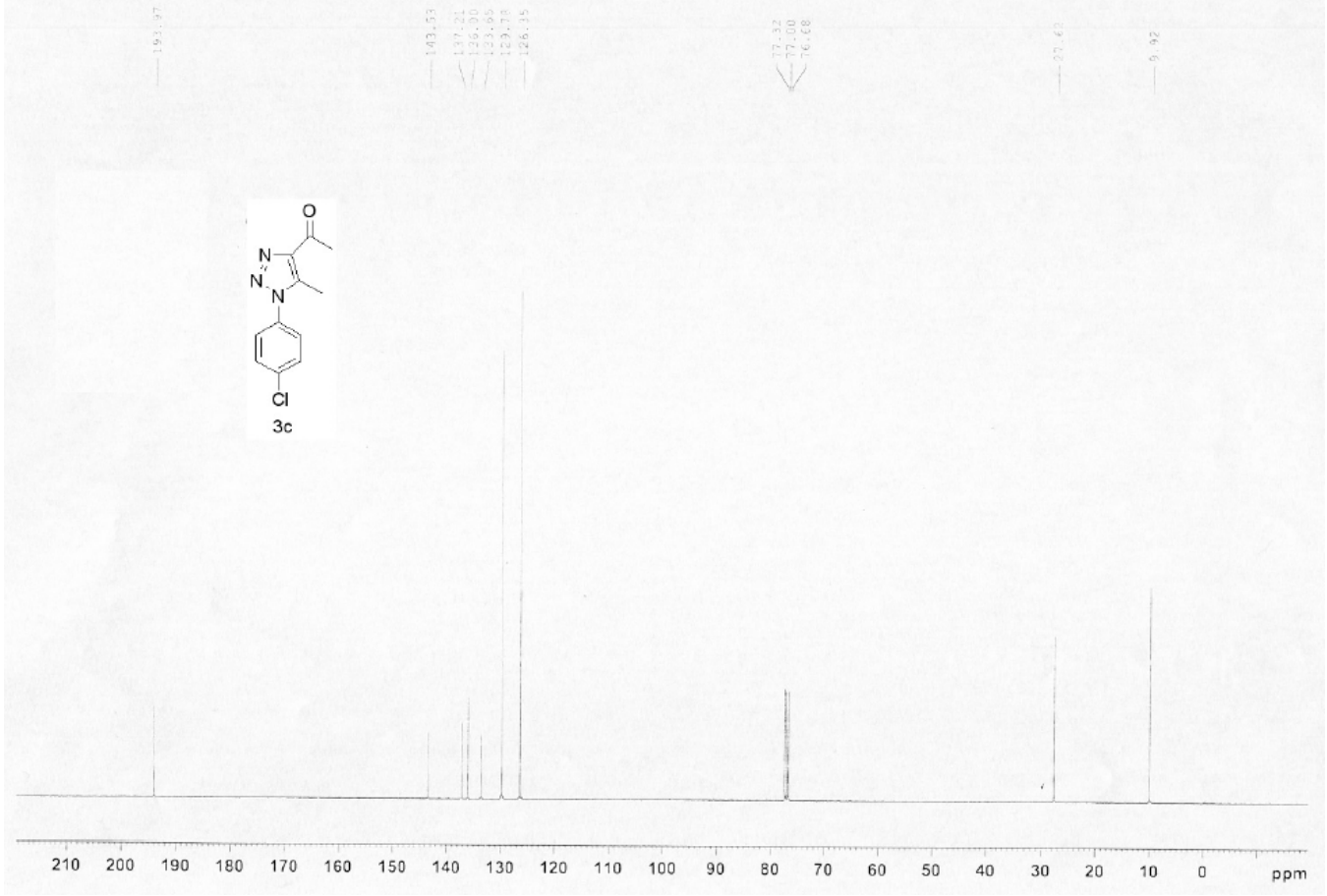


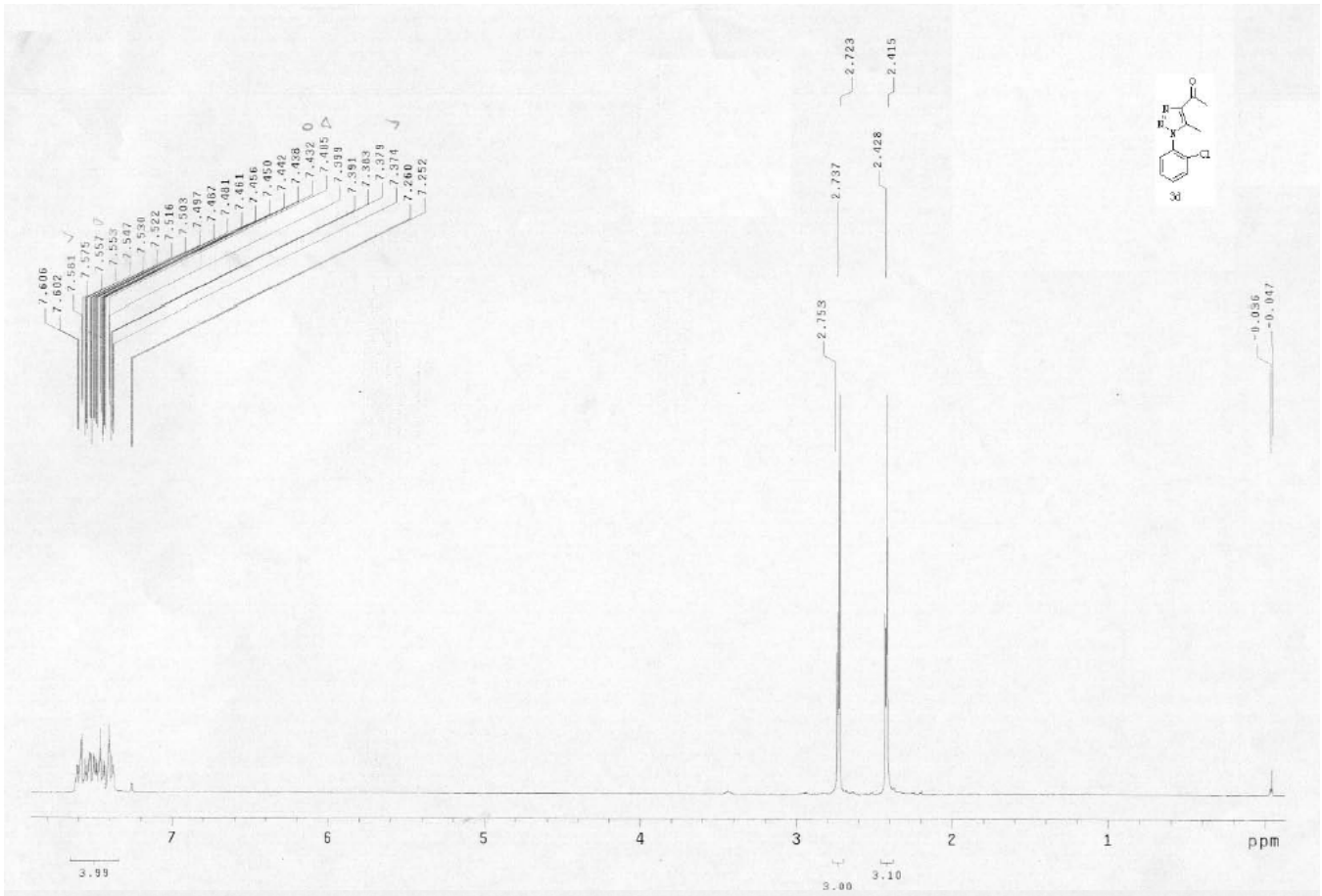


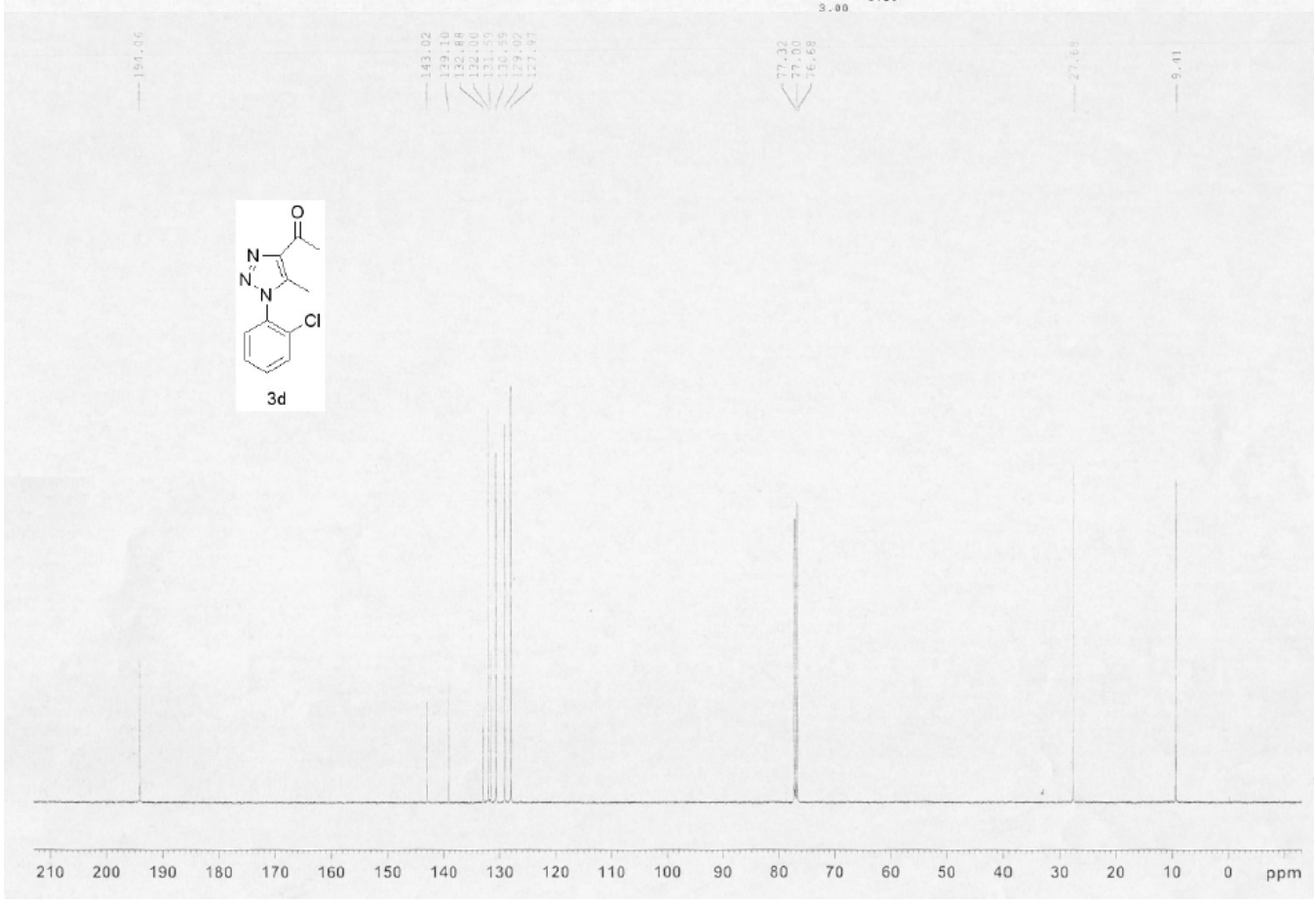

7.403
7.388
7.376
7.370
7.360
7.358
7.345
7.339
7.331
7.323
7.319
7.310
2.763
2.743
2.730
2.589
2.571
2.562
2.505
2.478
2.462
2.452
0.016
0.000
3b
9
8
7
6
5
4
3
2
1
ppm
4.25
3.00
2.99
3.09

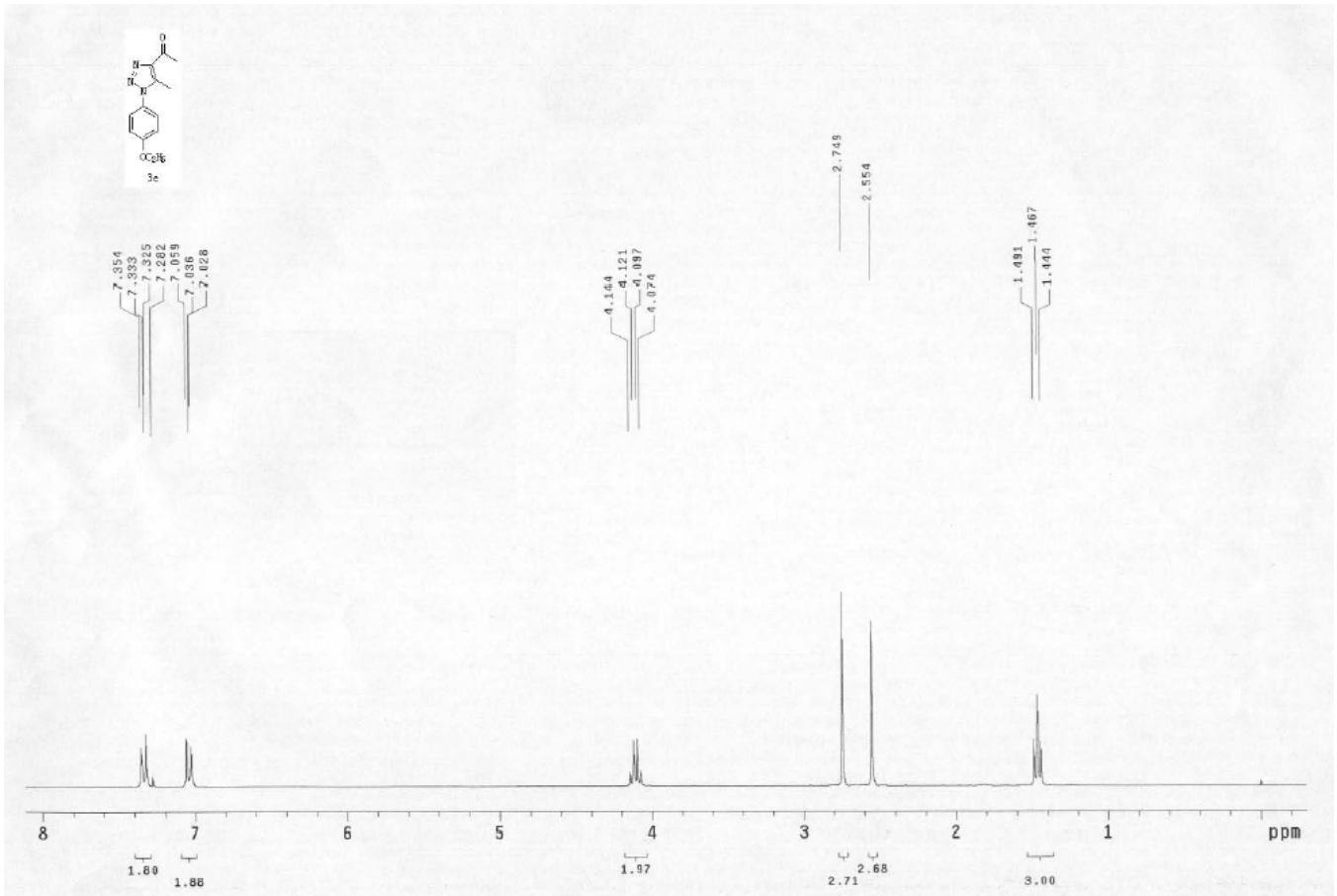

194.43
143.63
140.35
137.30
132.89
130.21
125.08
77.32
77.00
76.68
27.81
21.29
10.09
3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

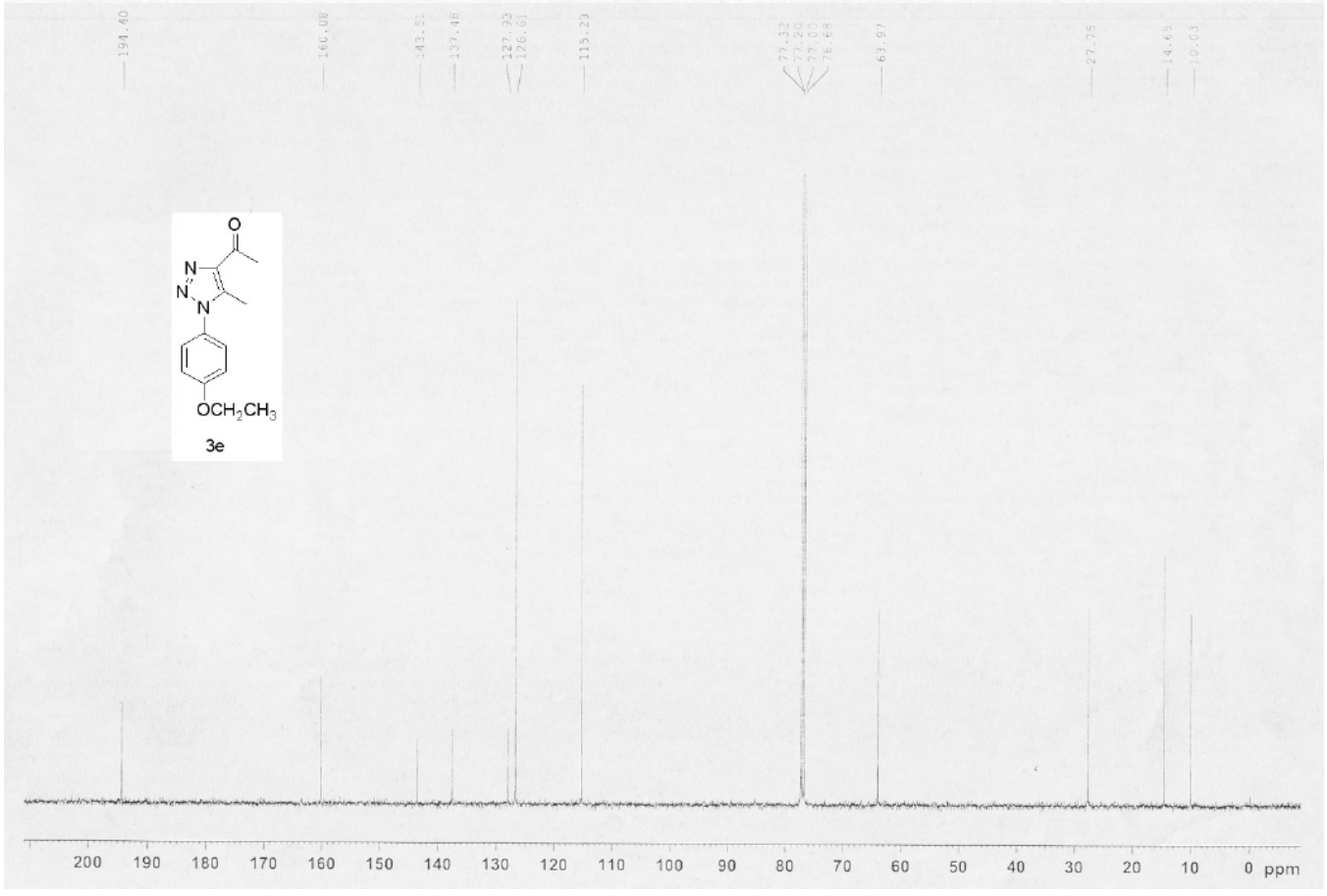

7.585
7.564
7.556
7.548
7.429
7.405
7.399
7.265
2.724
2.539
0.000
3c
8
7
6
5
4
3
2
1
-0
ppm
1.33
1.16
3.00
2.98

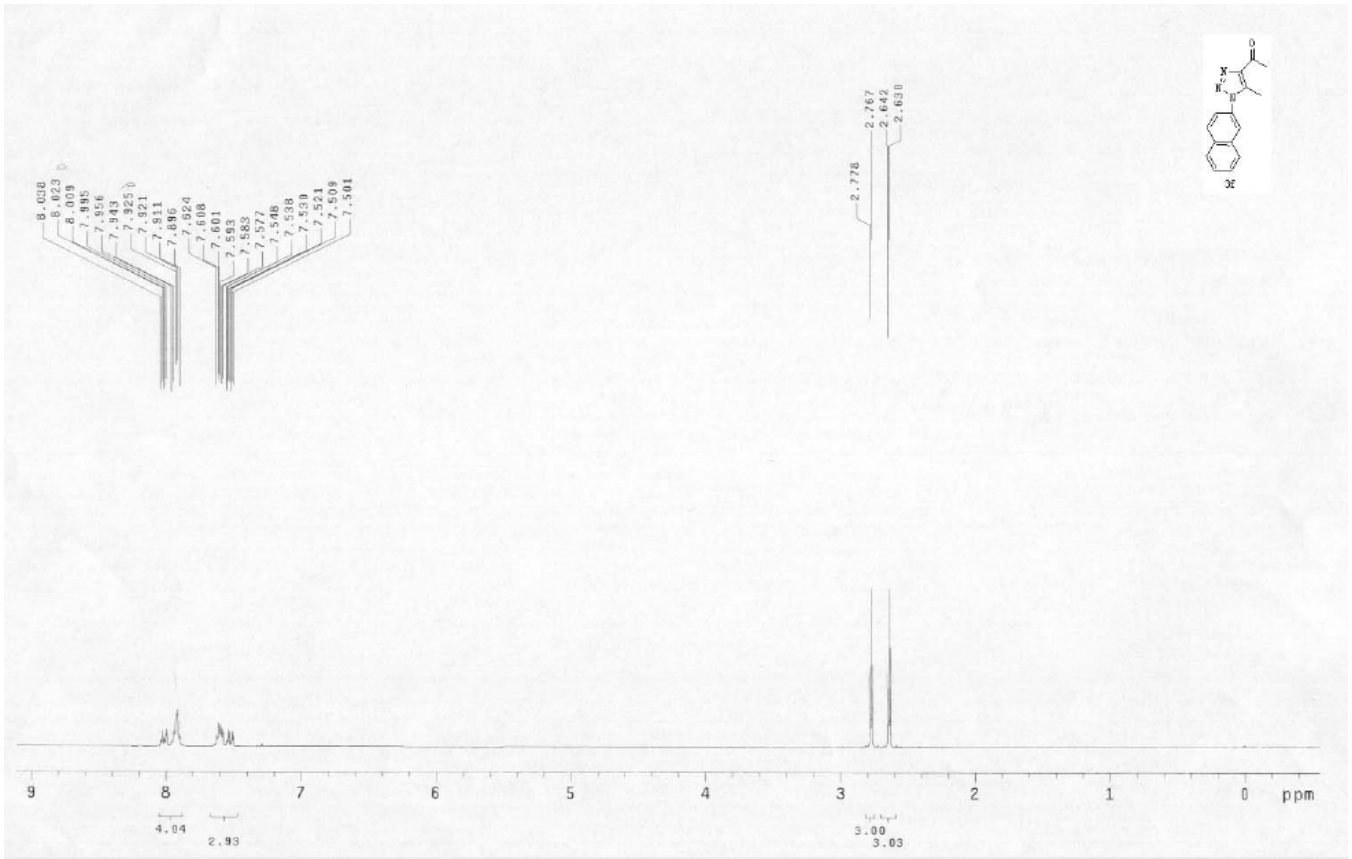

193.97
143.53
137.21
129.90
123.95
119.78
106.15
77.32
77.00
76.68
32.43
9.92
O
N
N
N
Cl
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.606
7.602
7.581
7.575
7.557
7.555
7.547
7.530
7.522
7.516
7.503
7.497
7.467
7.461
7.456
7.450
7.442
7.438
7.432
7.405
7.399
7.391
7.383
7.379
7.374
7.260
7.252
2.723
2.415
2.737
2.428
2.753
-0.036
-0.047
3d
7
6
5
4
3
2
1
ppm
3.99
3.00
3.10


191.06
143.02
139.10
132.88
132.00
131.55
130.69
129.02
127.97
77.32
77.00
76.68
27.69
9.41
O
N
N
N
Cl
3d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


3e
7.354
7.333
7.325
7.282
7.059
7.036
7.028
4.164
4.121
4.097
4.074
2.749
2.554
1.491
1.467
1.443
8
7
6
5
4
3
2
1
ppm
1.80
1.88
1.97
2.71
2.68
3.00


194.40
160.08
143.51
137.48
127.33
126.61
115.23
77.32
77.00
76.68
63.97
27.75
14.65
10.03
O
N
N
N
OCH2CH3
3e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


8.038
8.023
8.009
7.995
7.956
7.943
7.925
7.921
7.911
7.896
7.624
7.608
7.601
7.593
7.583
7.577
7.548
7.538
7.530
7.521
7.509
7.501
2.778
2.767
2.642
2.630
9
8
7
6
5
4
3
2
1
0
ppm
4.04
2.93
3.00
3.03

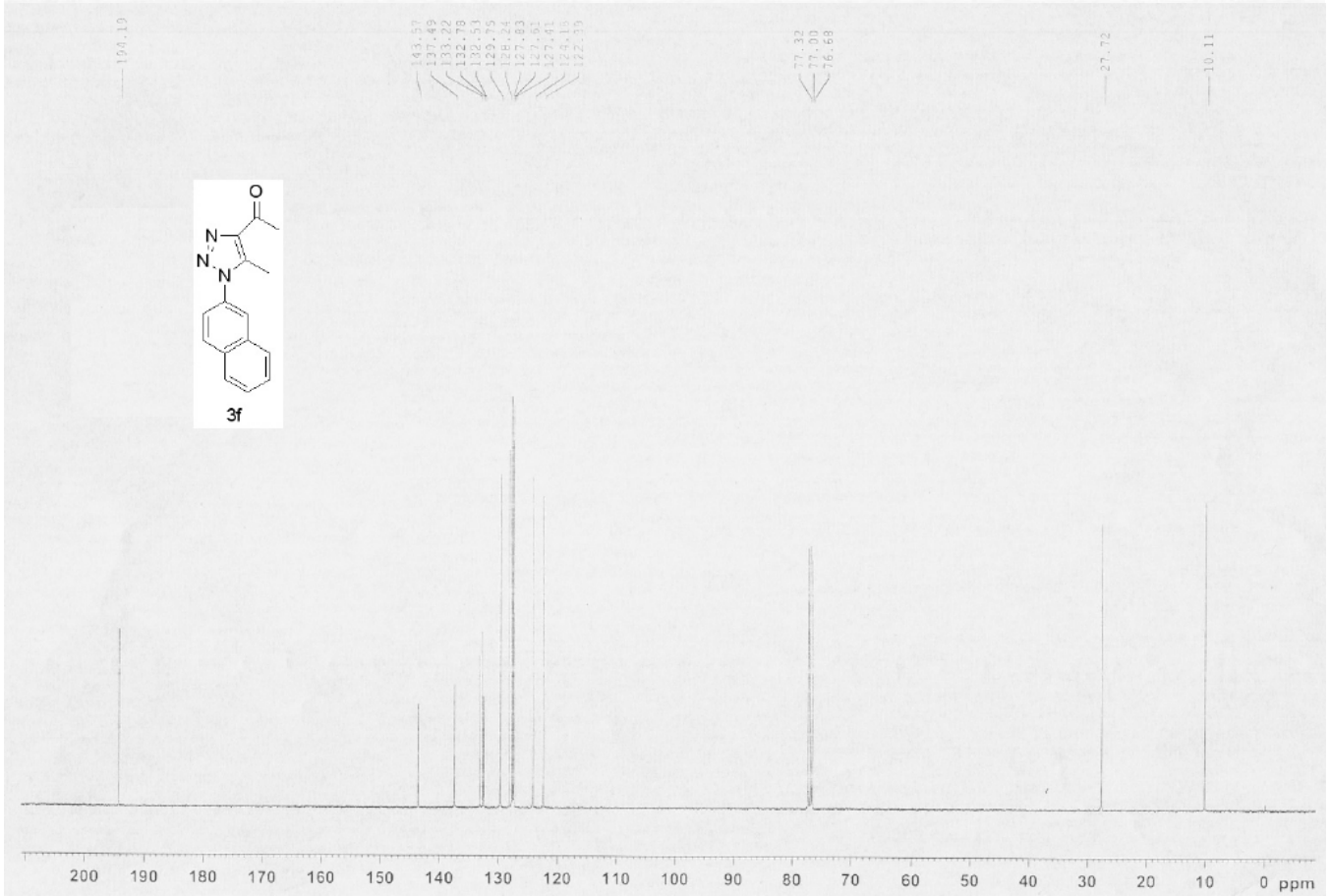
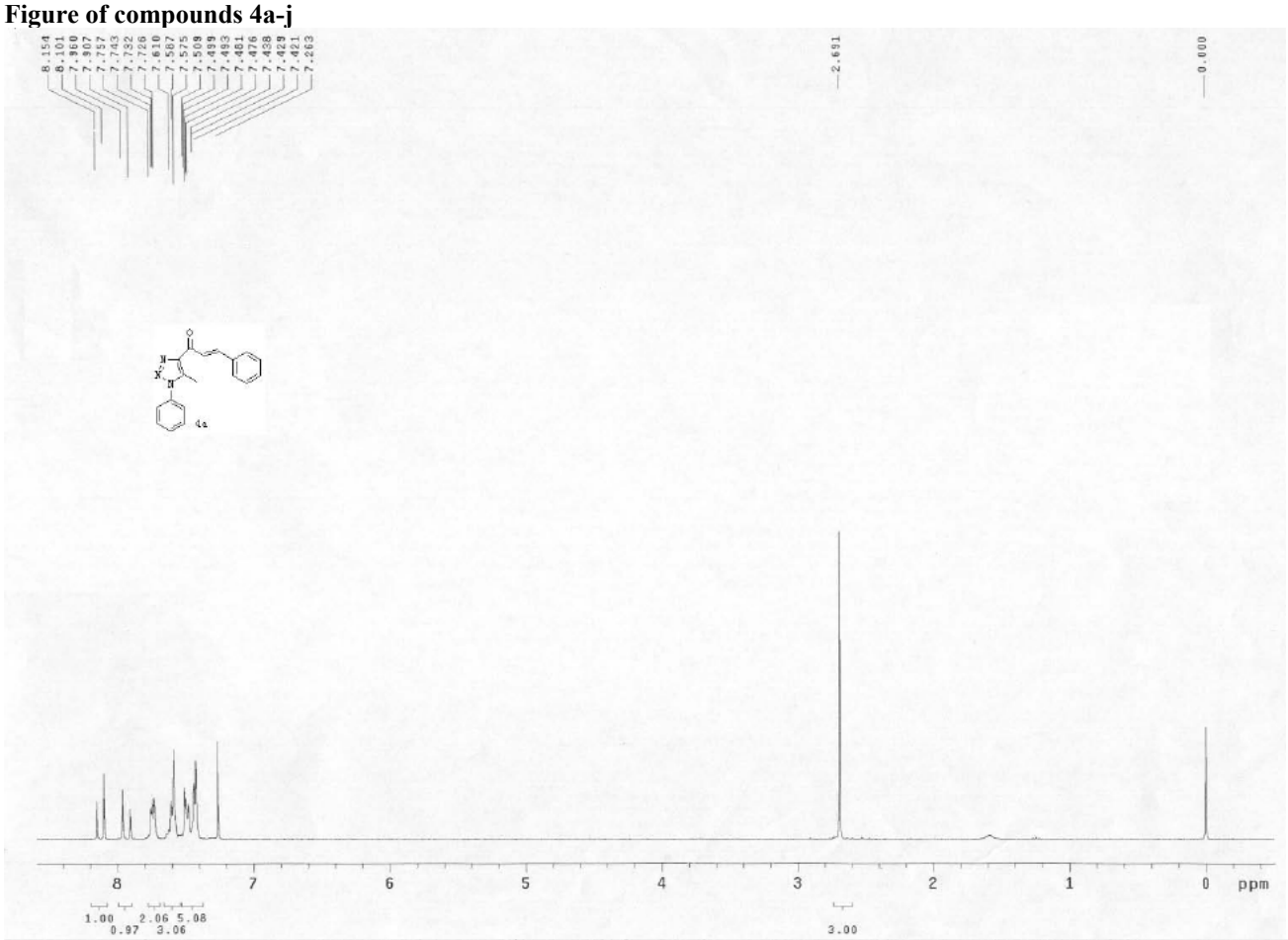
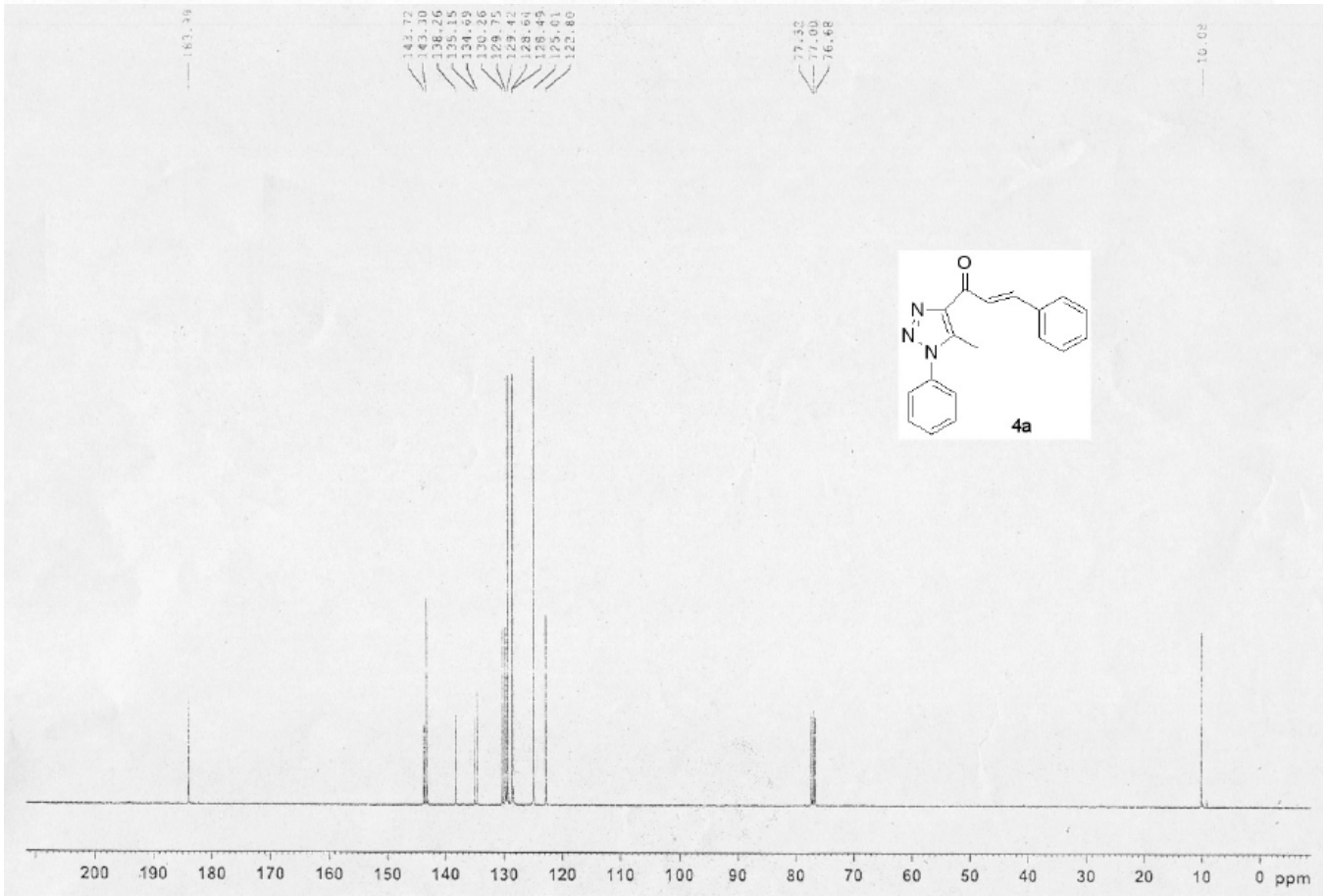
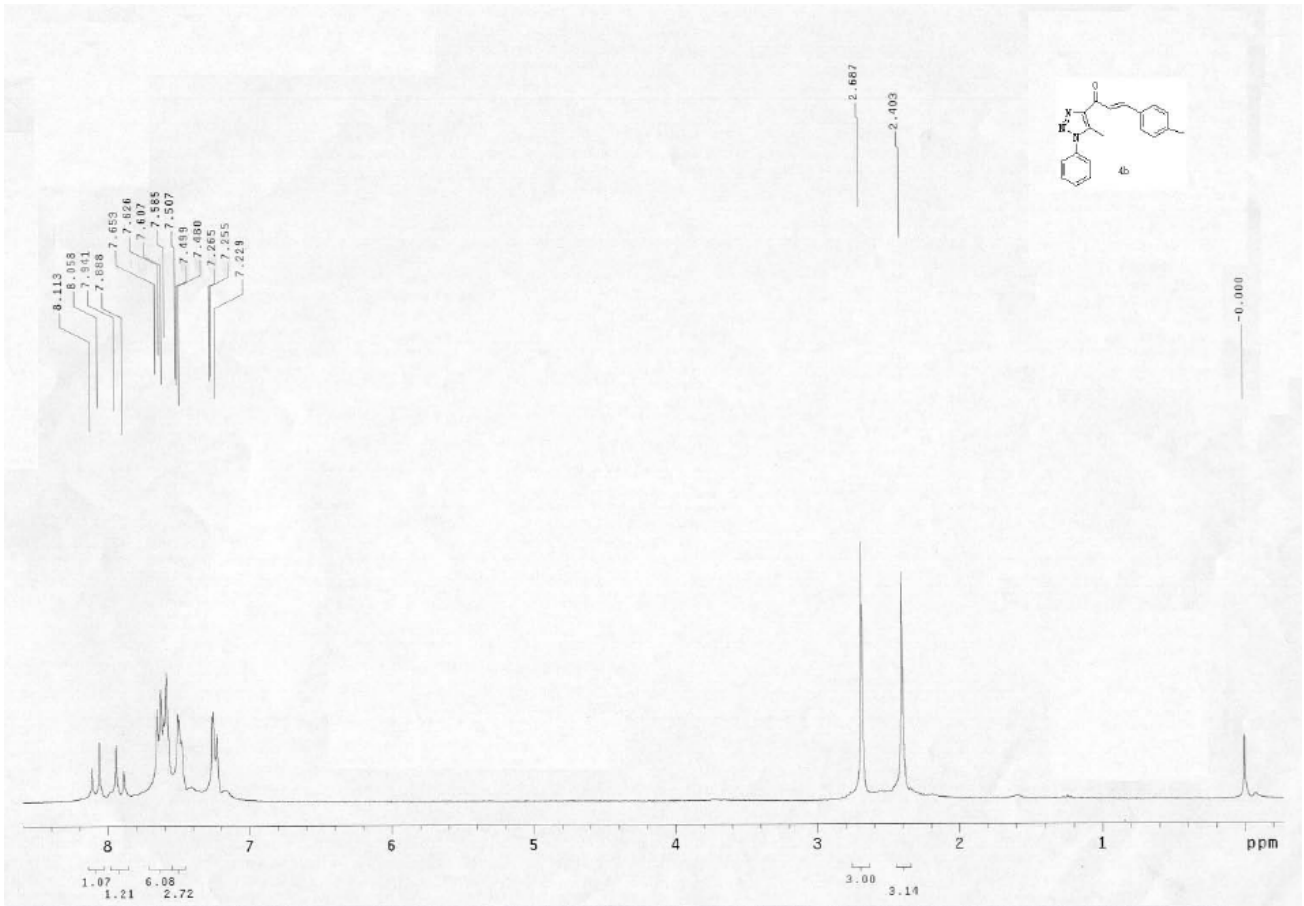
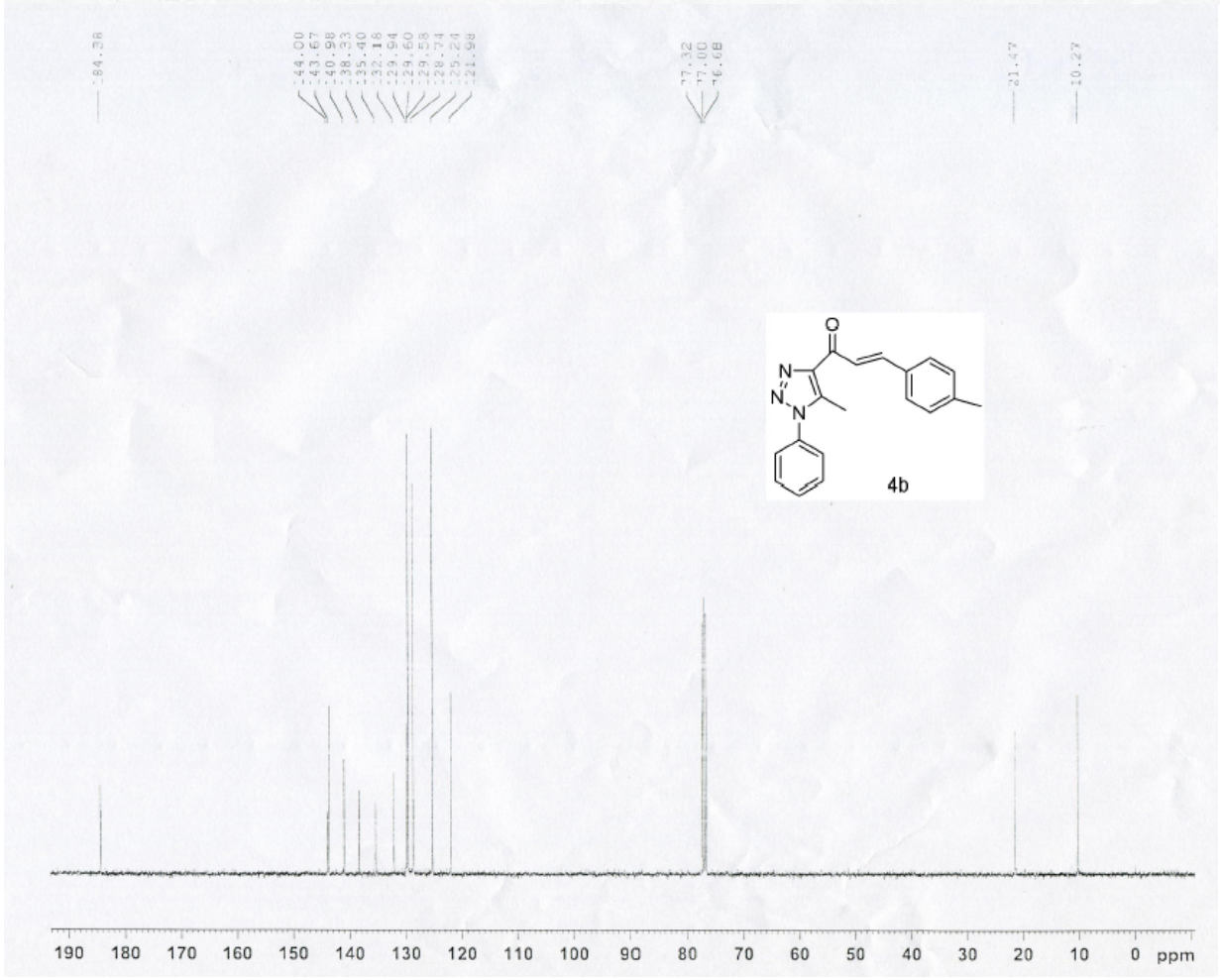

194.19
143.53
137.49
133.22
132.78
132.53
129.75
128.24
127.83
127.61
127.41
124.15
122.39
77.32
77.00
76.68
27.72
10.11
O
N
N
N
3f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

Figure of compounds 4a-j






8.113
8.058
7.941
7.868
7.653
7.626
7.607
7.585
7.507
7.499
7.480
7.265
7.255
7.229
2.687
2.403
0.000
4b
8
7
6
5
4
3
2
1
ppm
1.07
1.21
6.08
2.72
3.00
3.14


184.26
144.00
143.67
140.98
138.33
135.40
132.16
129.94
129.60
129.58
128.74
125.24
121.98
77.32
77.00
76.68
21.47
10.27
4b
190
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140
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80
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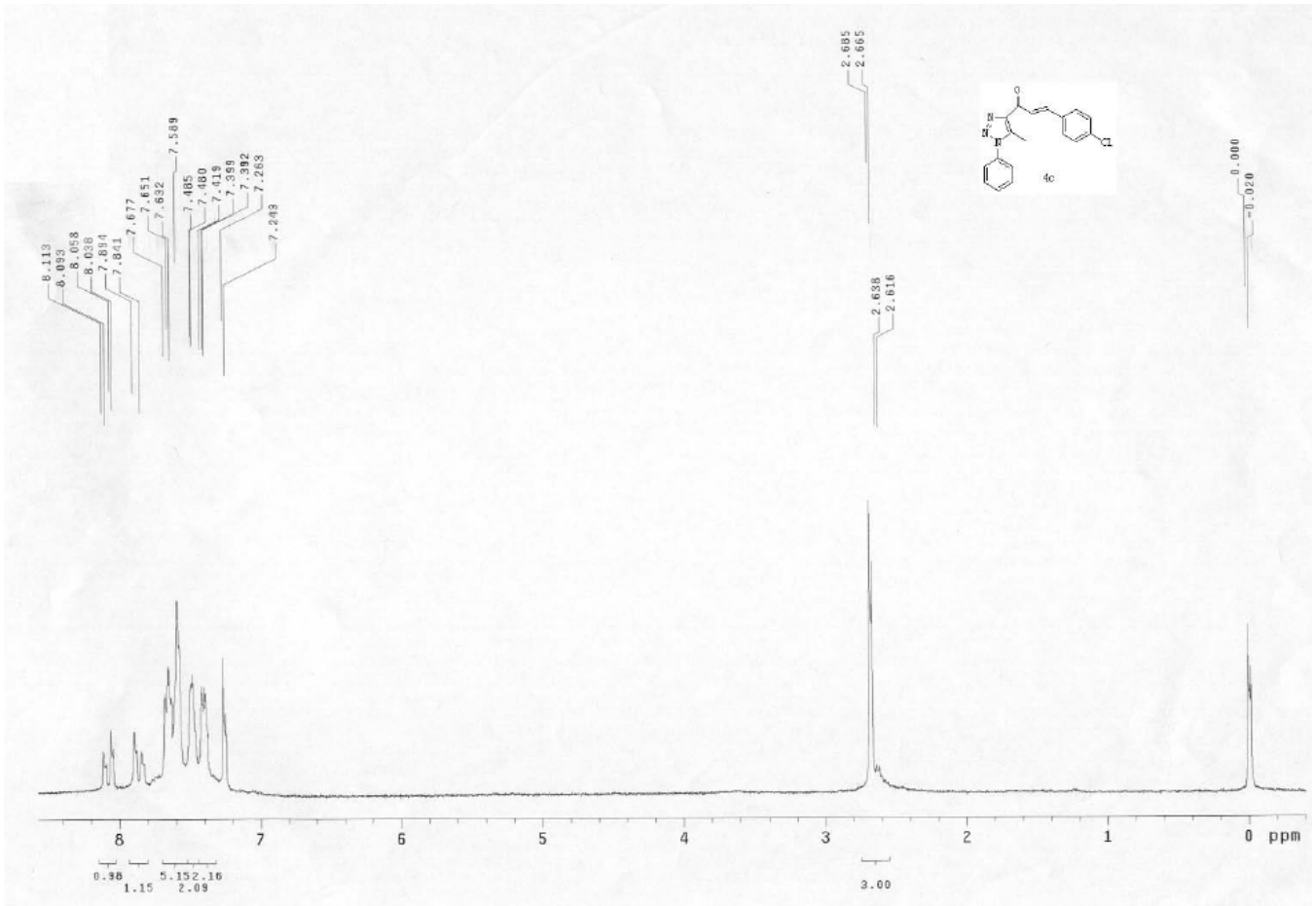
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8.093
8.058
8.038
7.884
7.841
7.677
7.651
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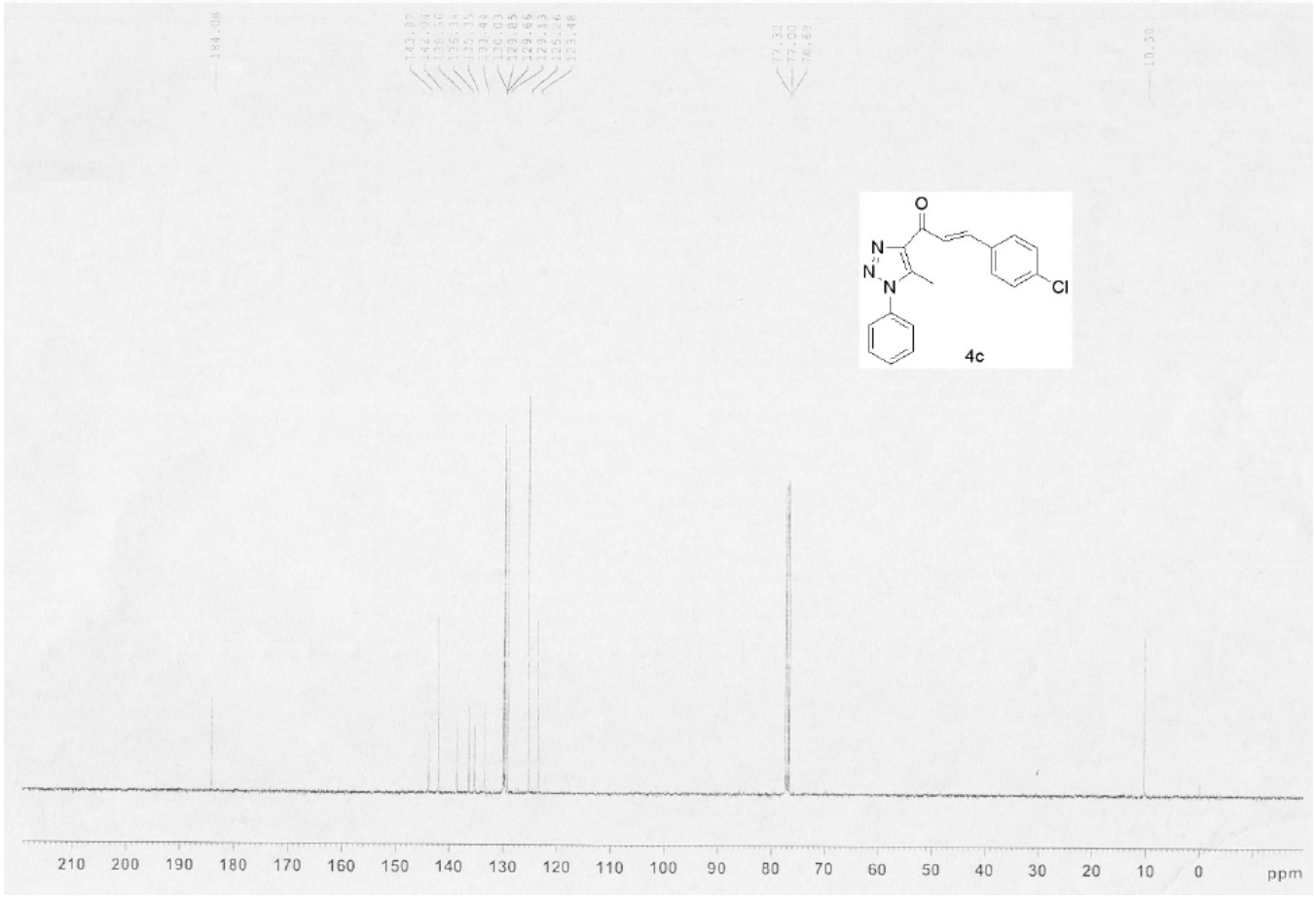
7.589
7.485
7.480
7.419
7.399
7.392
7.263
7.243
2.685
2.665
2.638
2.616
0.000
-0.020
4c
8
7
6
5
4
3
2
1
0 ppm
0.98
1.15
5.15
2.09
2.16
3.00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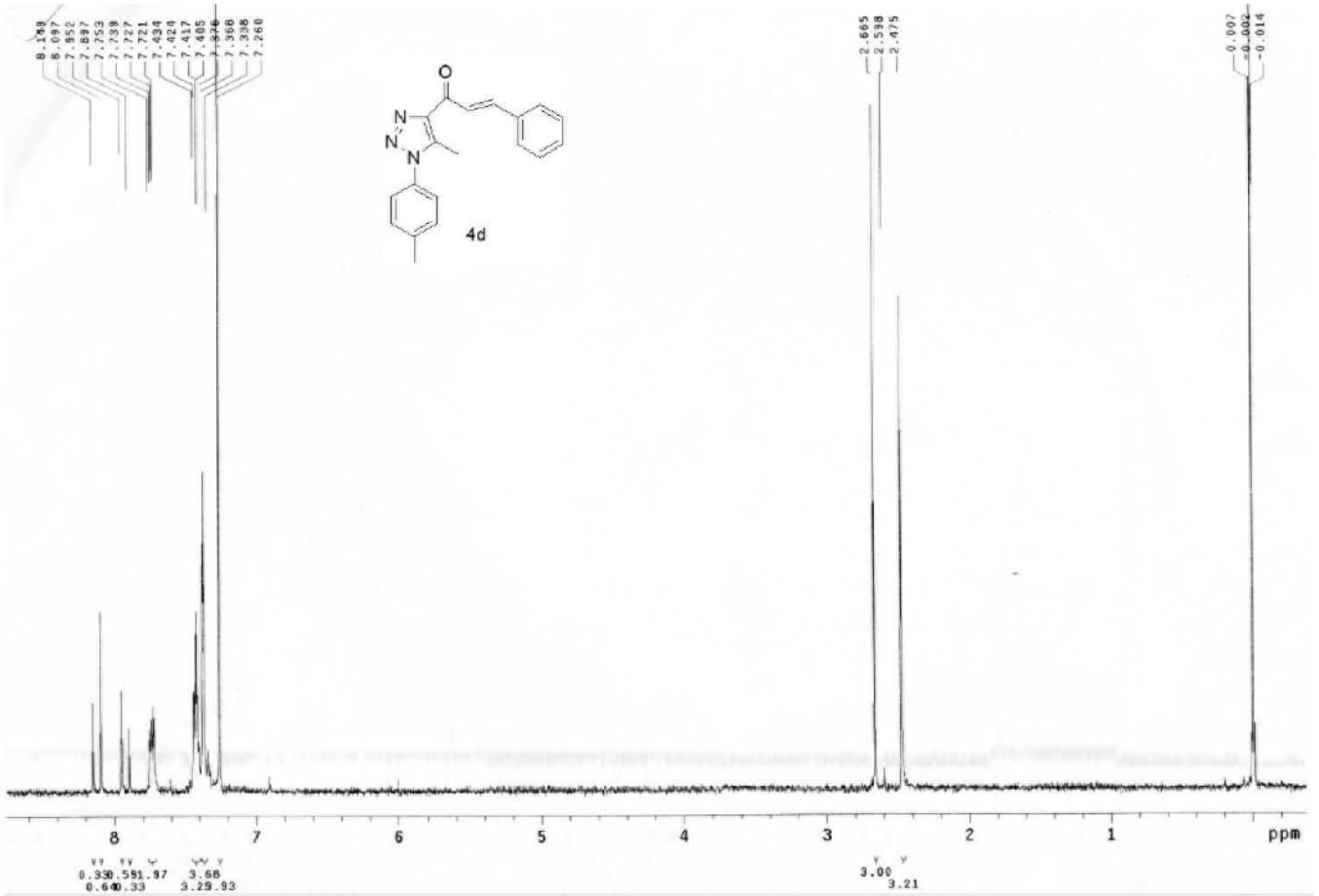
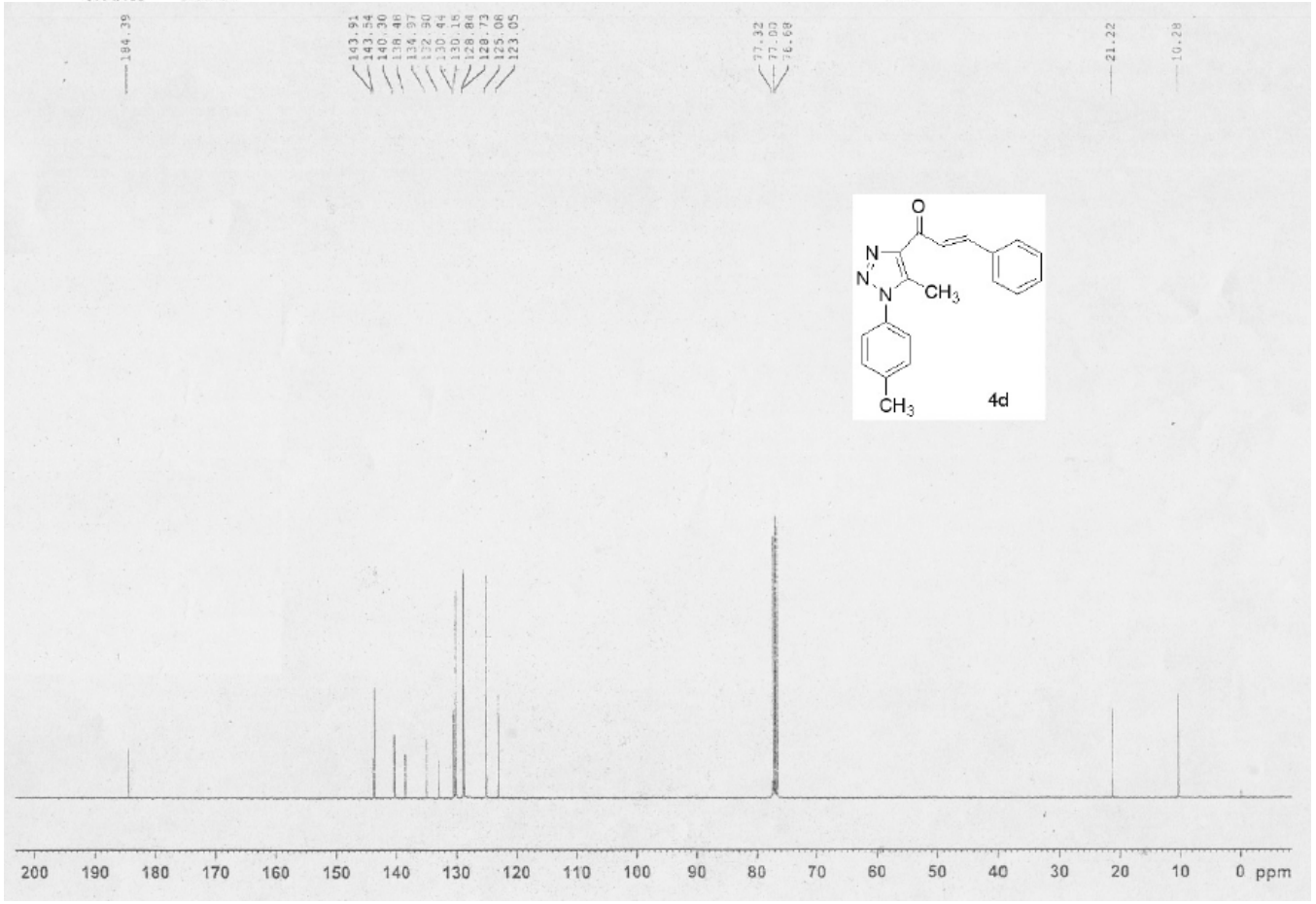
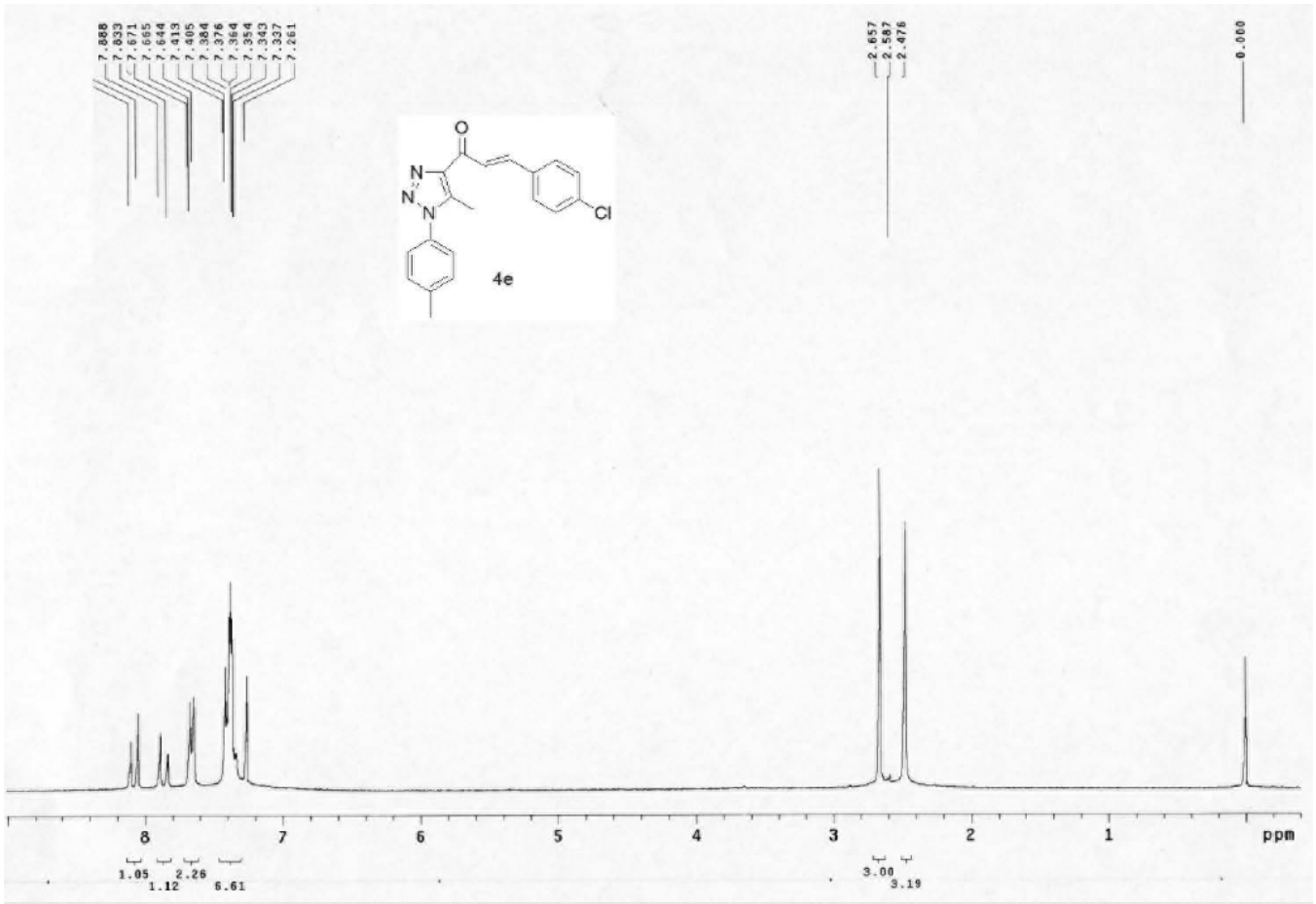
142.24
136.36
135.14
133.44
130.03
129.85
129.66
129.13
125.26
123.48
77.32
77.00
76.68
19.30
O
N
N
N
Cl
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


4d
ppm


4d
ppm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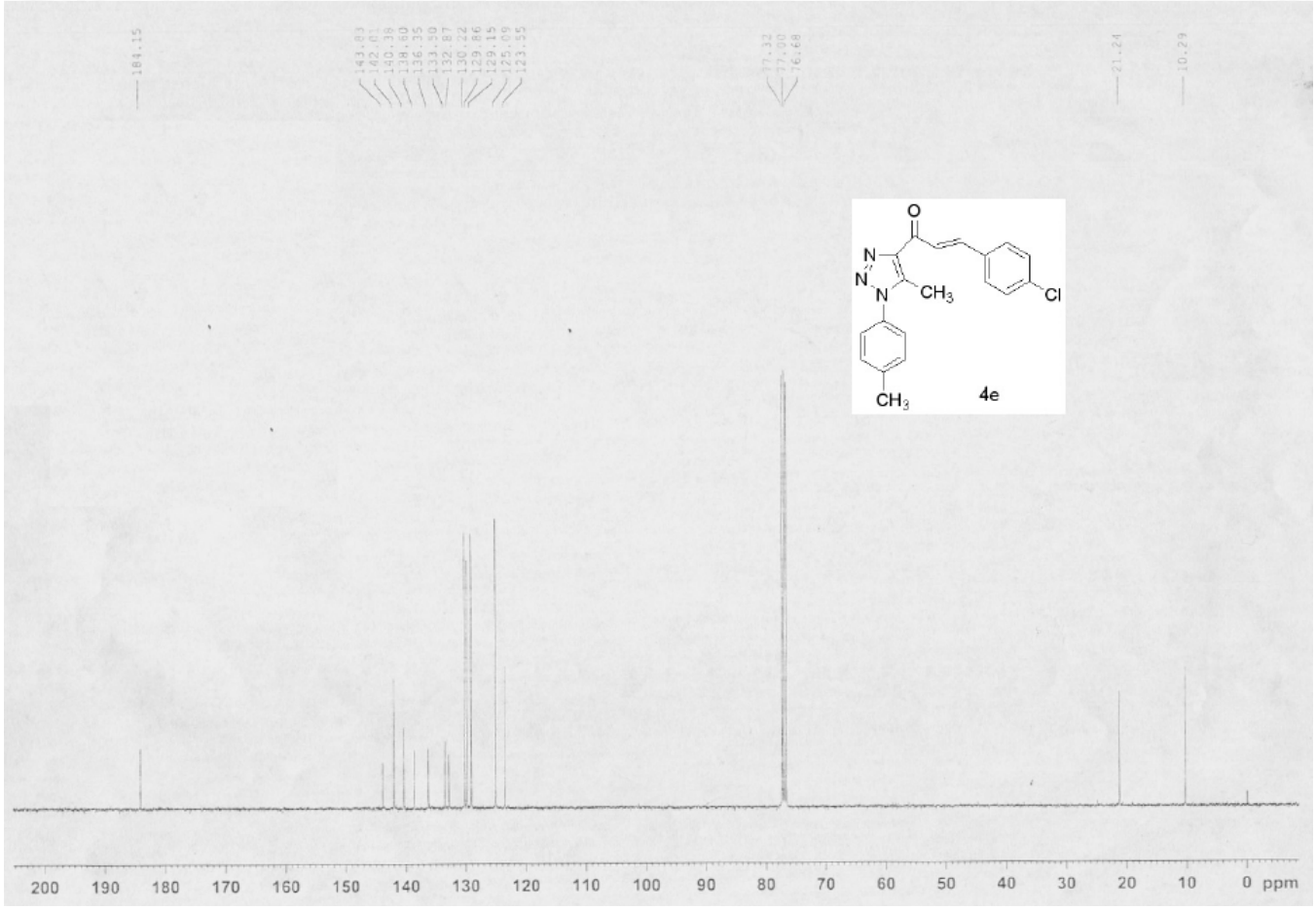
7.665
7.644
7.413
7.405
7.384
7.376
7.364
7.354
7.343
7.337
7.261
2.657
2.587
2.476
0.000
O
N
N
N
Cl
4e
8
7
6
5
4
3
2
1
ppm
1.05
1.12
2.26
6.61
3.00
3.19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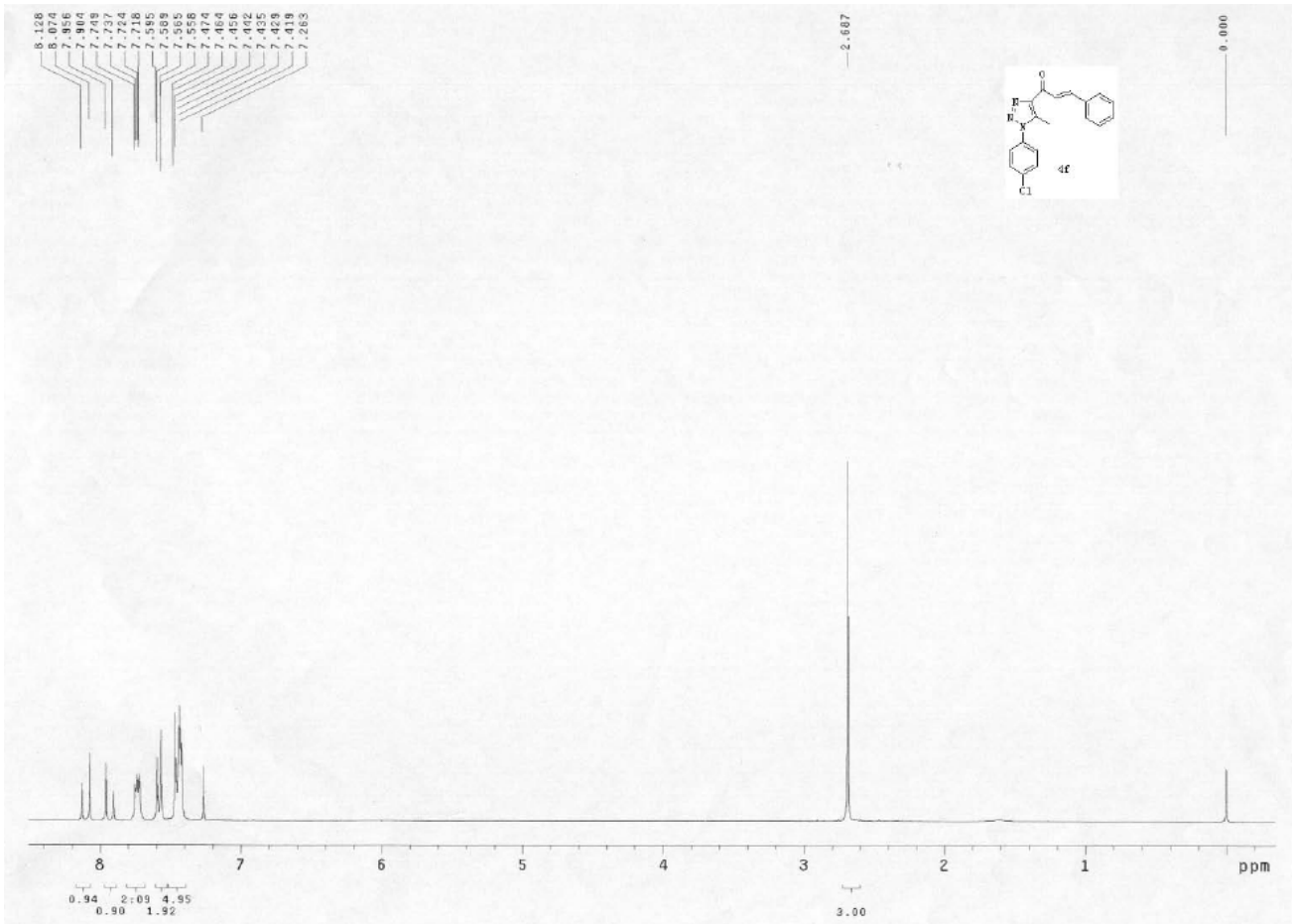
136.35
133.50
132.87
130.42
129.86
129.15
125.09
123.55
77.32
77.00
76.68
21.24
10.29
O
N
N
N
CH3
Cl
CH3
4e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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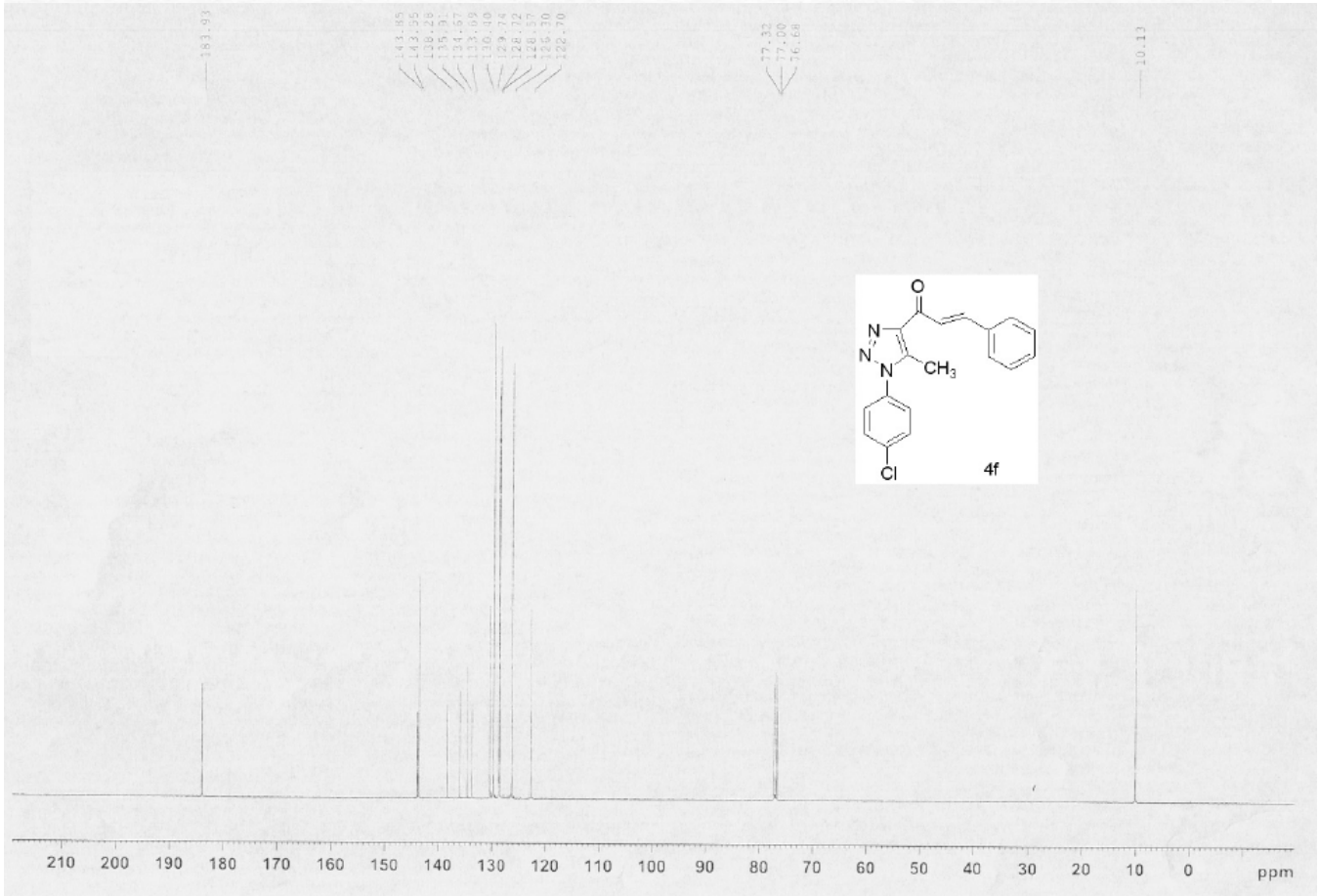
8.074
7.956
7.904
7.749
7.737
7.724
7.718
7.595
7.589
7.565
7.558
7.474
7.464
7.456
7.442
7.435
7.429
7.419
7.263
2.687
0.000
4f
Cl
8
7
6
5
4
3
2
1
ppm
0.94
2.09
4.95
0.90
1.92
3.00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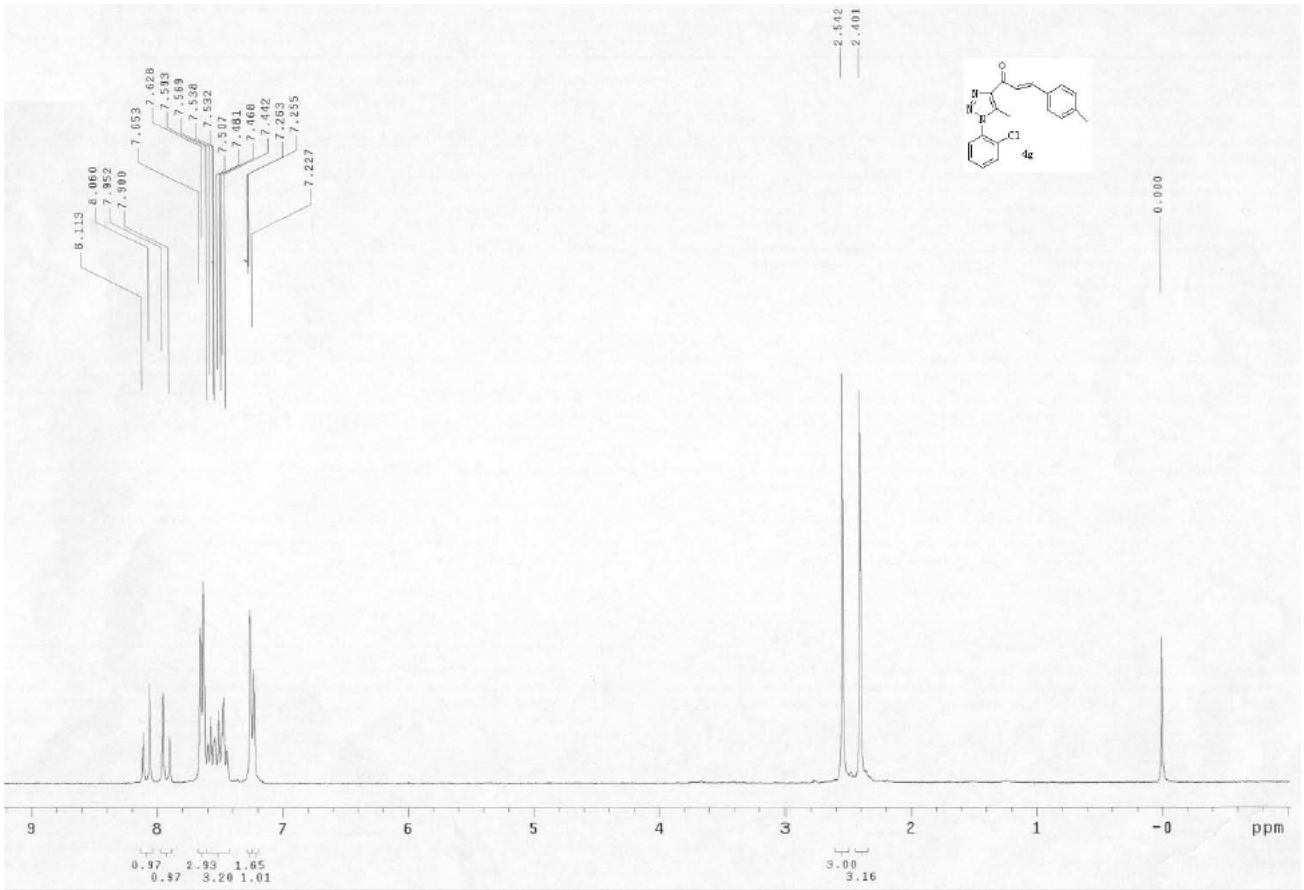
143.55
138.28
135.91
134.67
133.09
130.40
129.74
128.72
126.57
125.30
122.70
77.32
77.00
76.68
10.13
O
N
N
CH3
Cl
4f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


2.542
2.401
8.113
8.060
7.952
7.900
7.653
7.628
7.593
7.569
7.538
7.532
7.507
7.481
7.468
7.442
7.263
7.255
7.227
0.000
4g
9
8
7
6
5
4
3
2
1
-0
ppm
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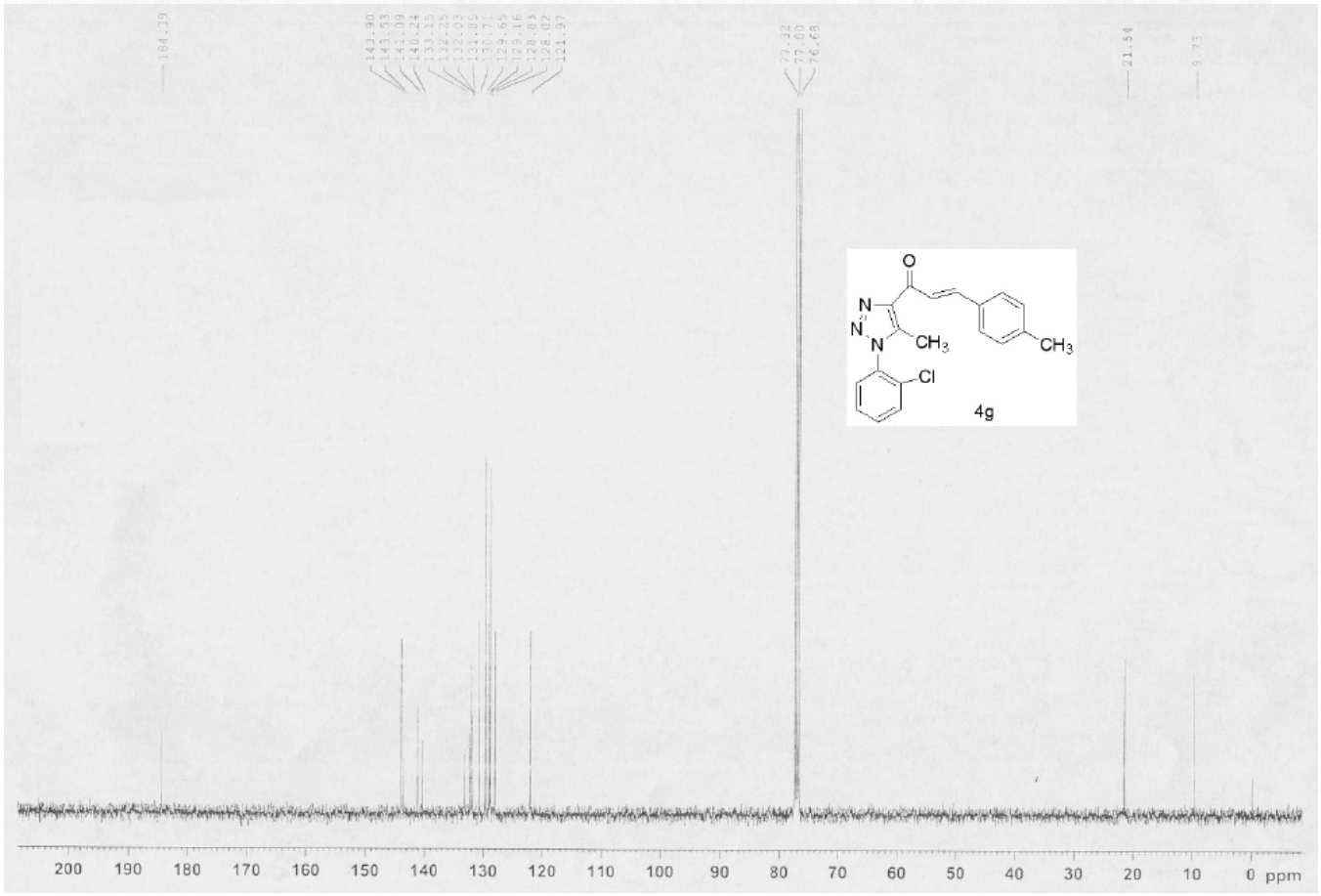
0.97
2.93
3.20
1.65
1.01
3.00
3.16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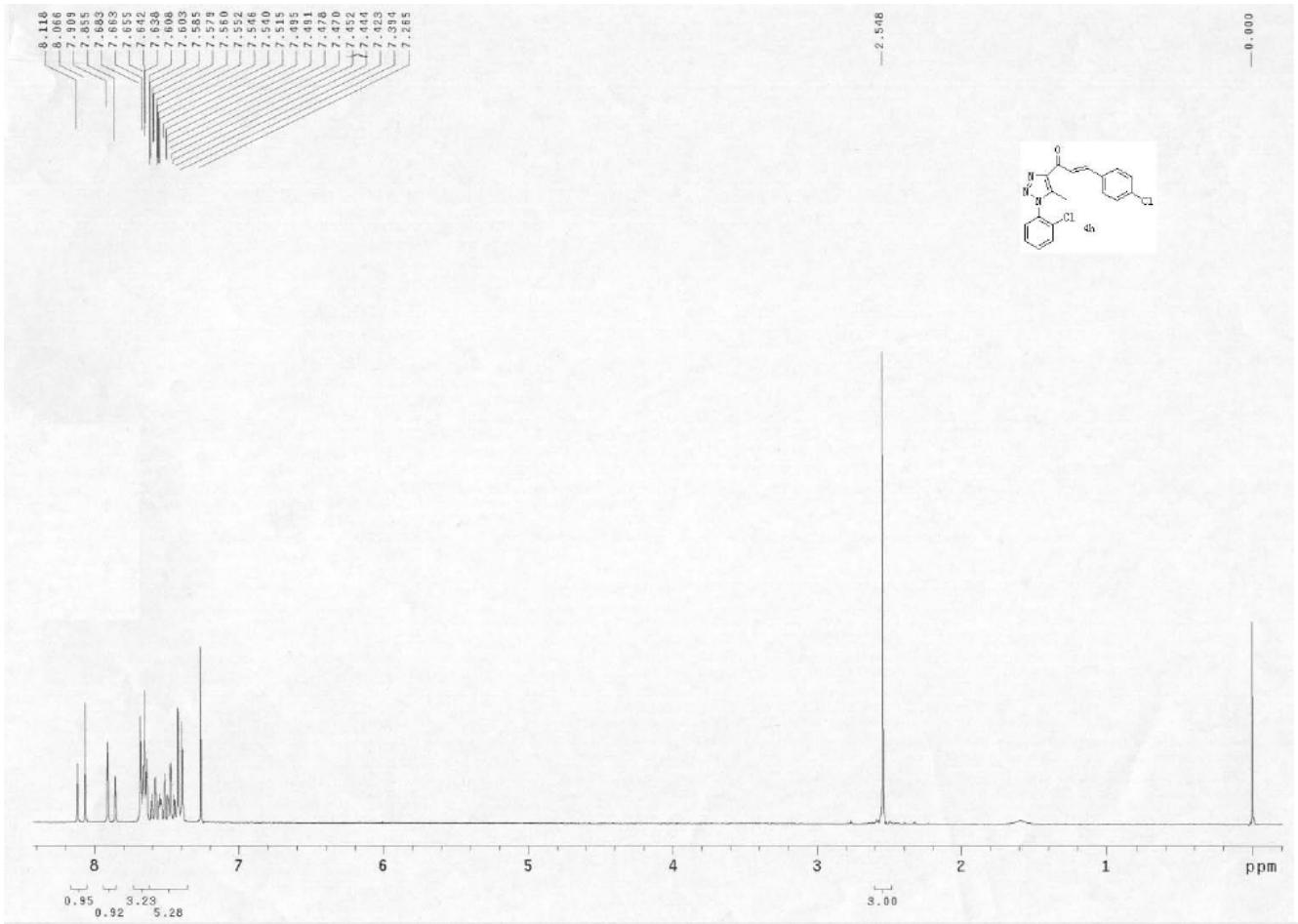
143.90
143.53
141.09
140.24
133.15
132.25
132.03
131.05
130.71
129.65
129.16
128.83
128.02
121.97
77.32
77.00
76.68
21.54
9.73
O
N
N
CH3
CH3
Cl
4g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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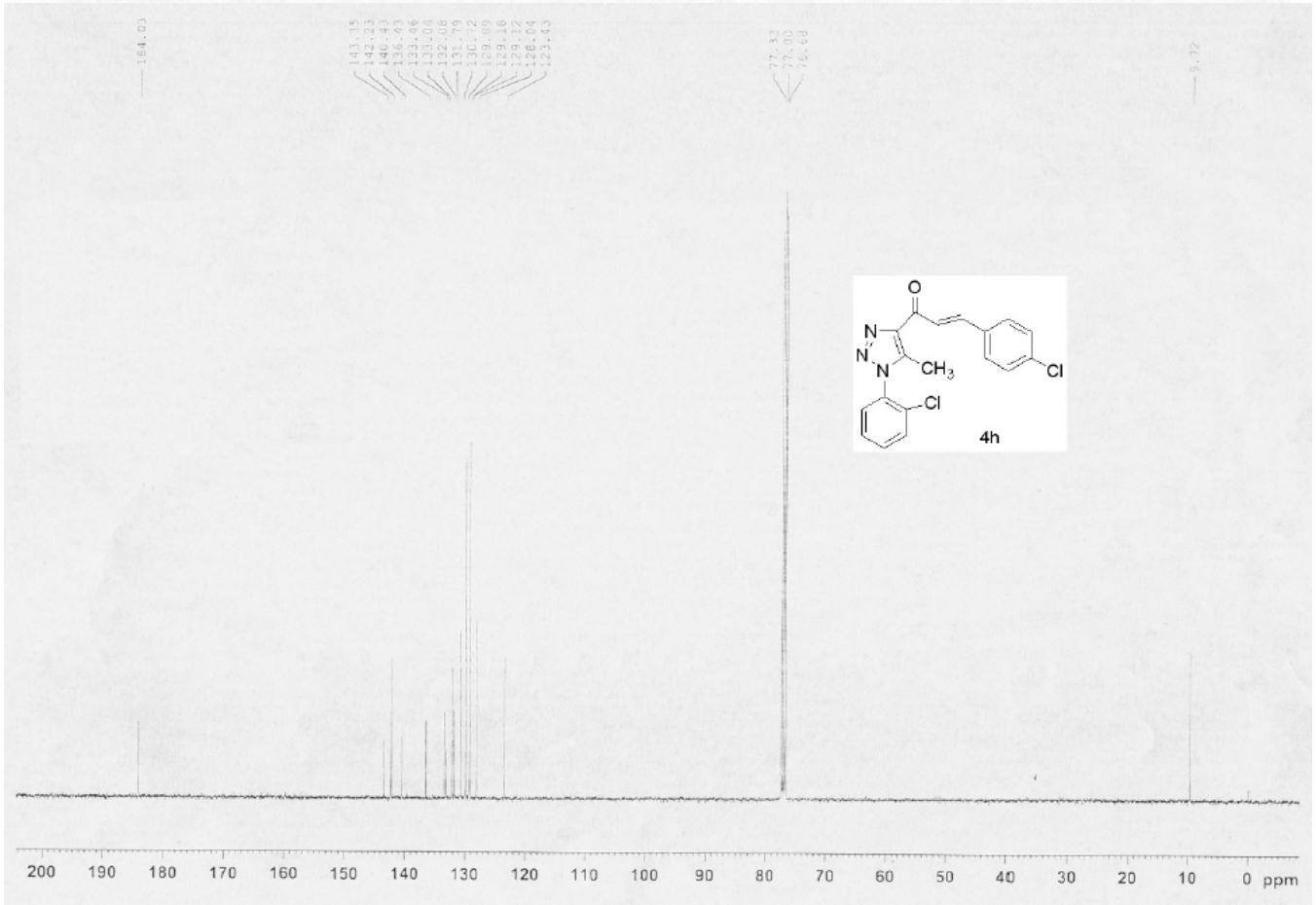
8.066
7.909
7.855
7.683
7.663
7.655
7.642
7.638
7.606
7.603
7.585
7.579
7.560
7.552
7.546
7.540
7.515
7.495
7.491
7.478
7.470
7.452
7.444
7.423
7.394
7.265
2.548
0.000
4h
8
7
6
5
4
3
2
1
ppm
0.95
0.92
3.23
5.28
3.00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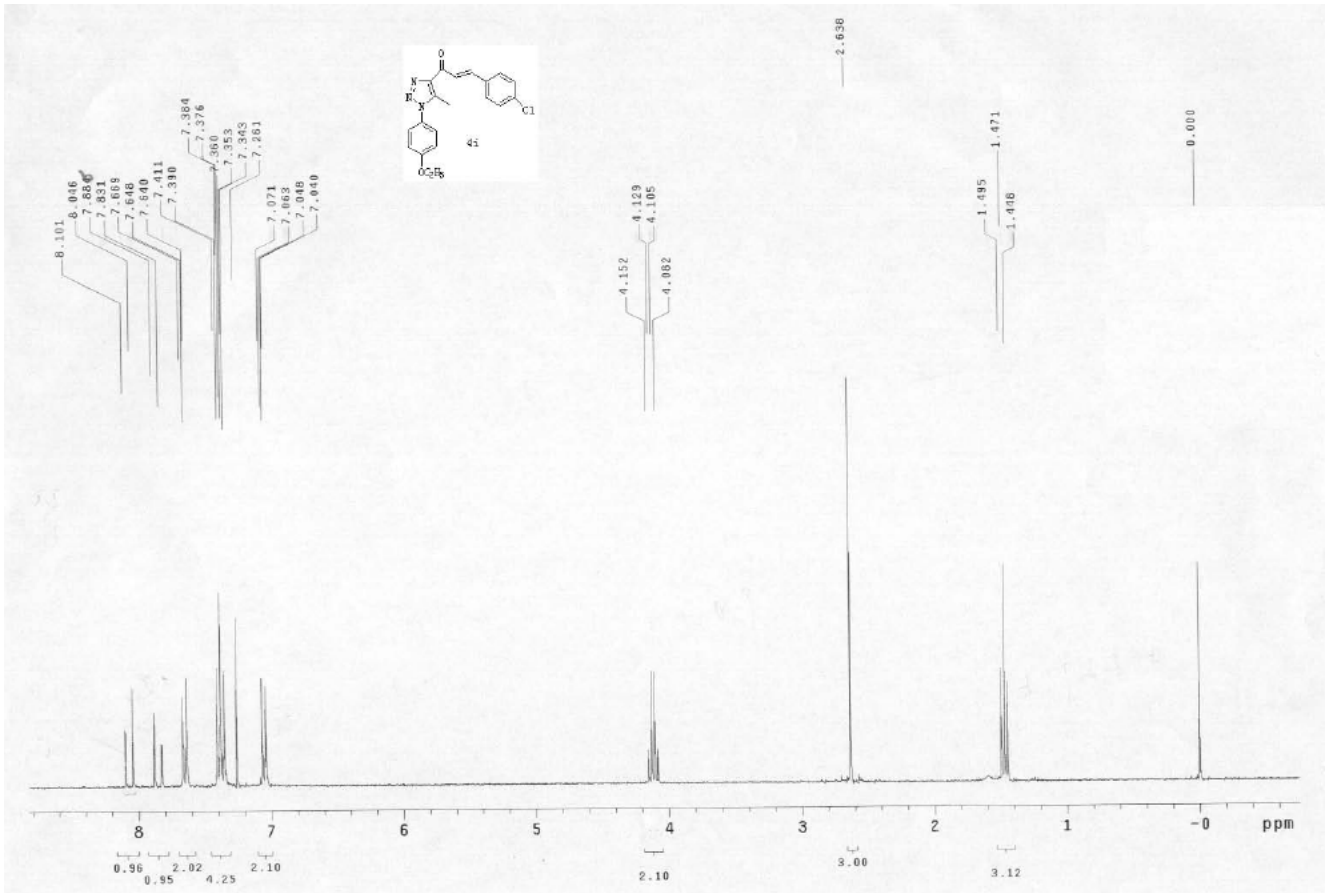
142.23
140.43
136.43
133.46
133.04
132.08
131.79
130.12
129.89
129.18
129.12
126.04
123.43
77.32
77.00
76.68
9.72
4h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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8.046
7.884
7.831
7.669
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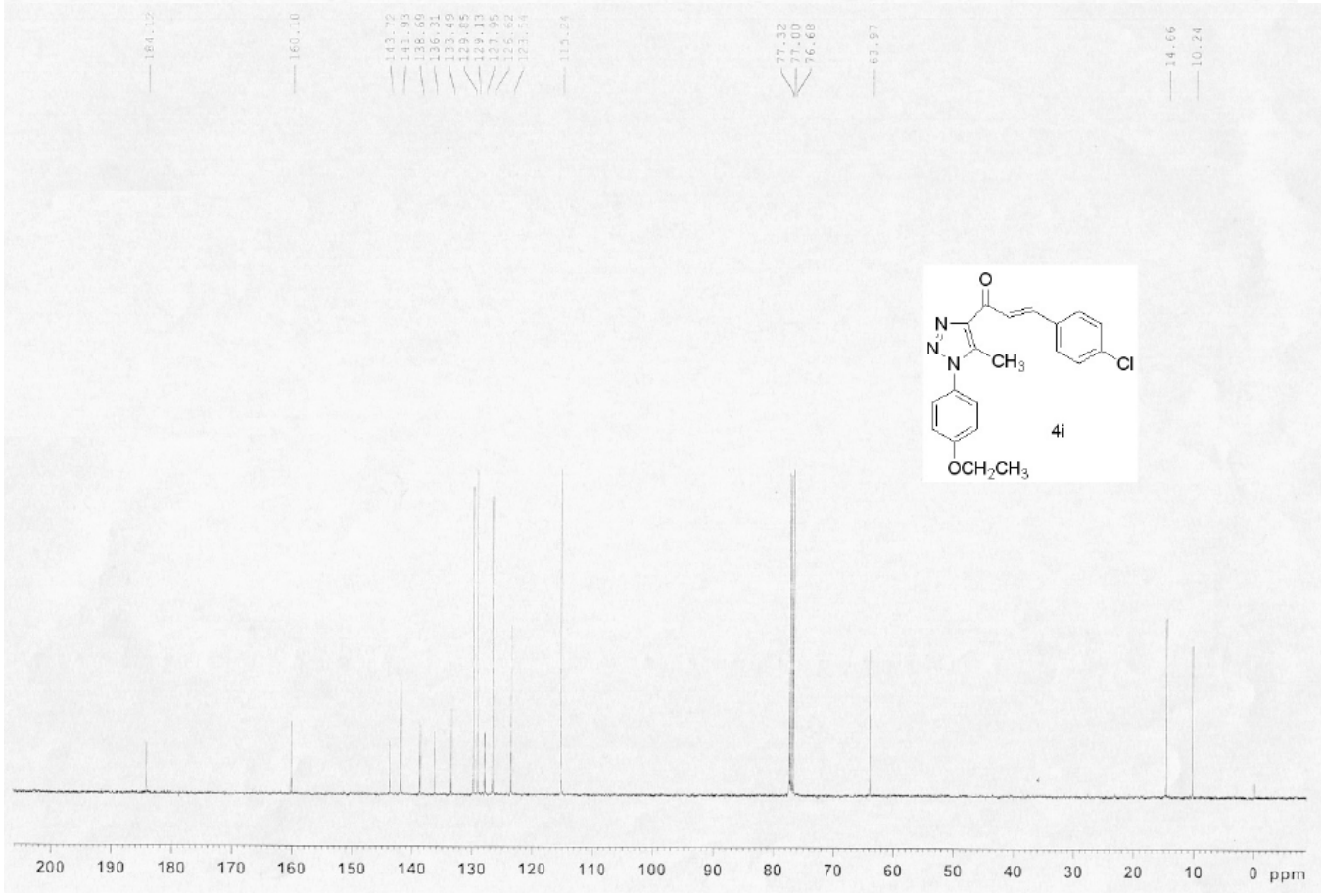
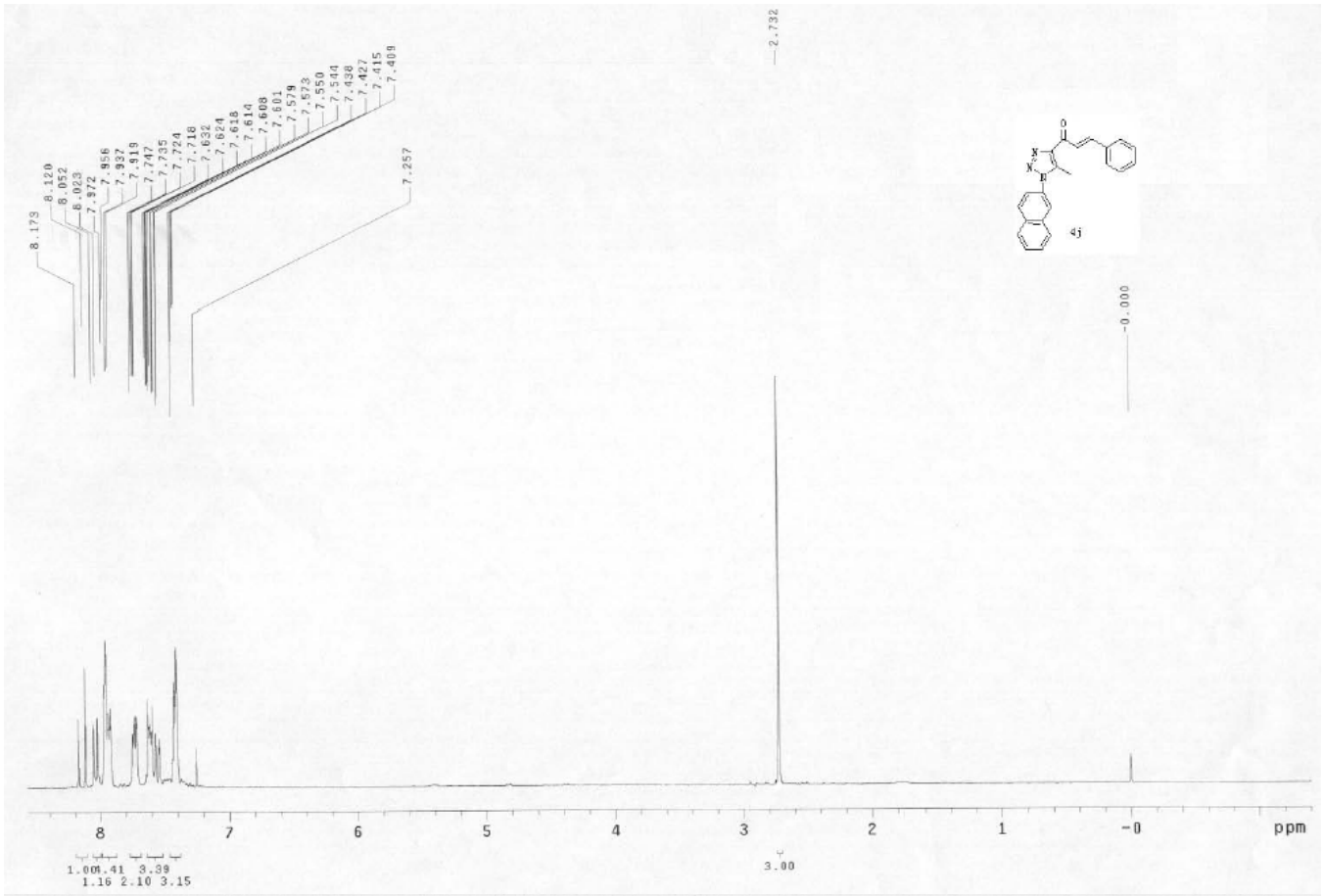
7.640
7.411
7.390
7.384
7.376
7.360
7.353
7.343
7.261
7.071
7.063
7.048
7.040
4.152
4.129
4.105
4.082
2.638
1.495
1.471
1.446
0.000
8
7
6
5
4
3
2
1
-0
ppm
0.96
2.02
4.25
2.10
0.95
2.10
3.00
3.12


184.12
160.10
143.72
141.93
138.69
136.31
133.49
129.85
129.13
127.95
126.62
123.54
115.24
77.32
77.00
76.68
63.97
14.66
10.24
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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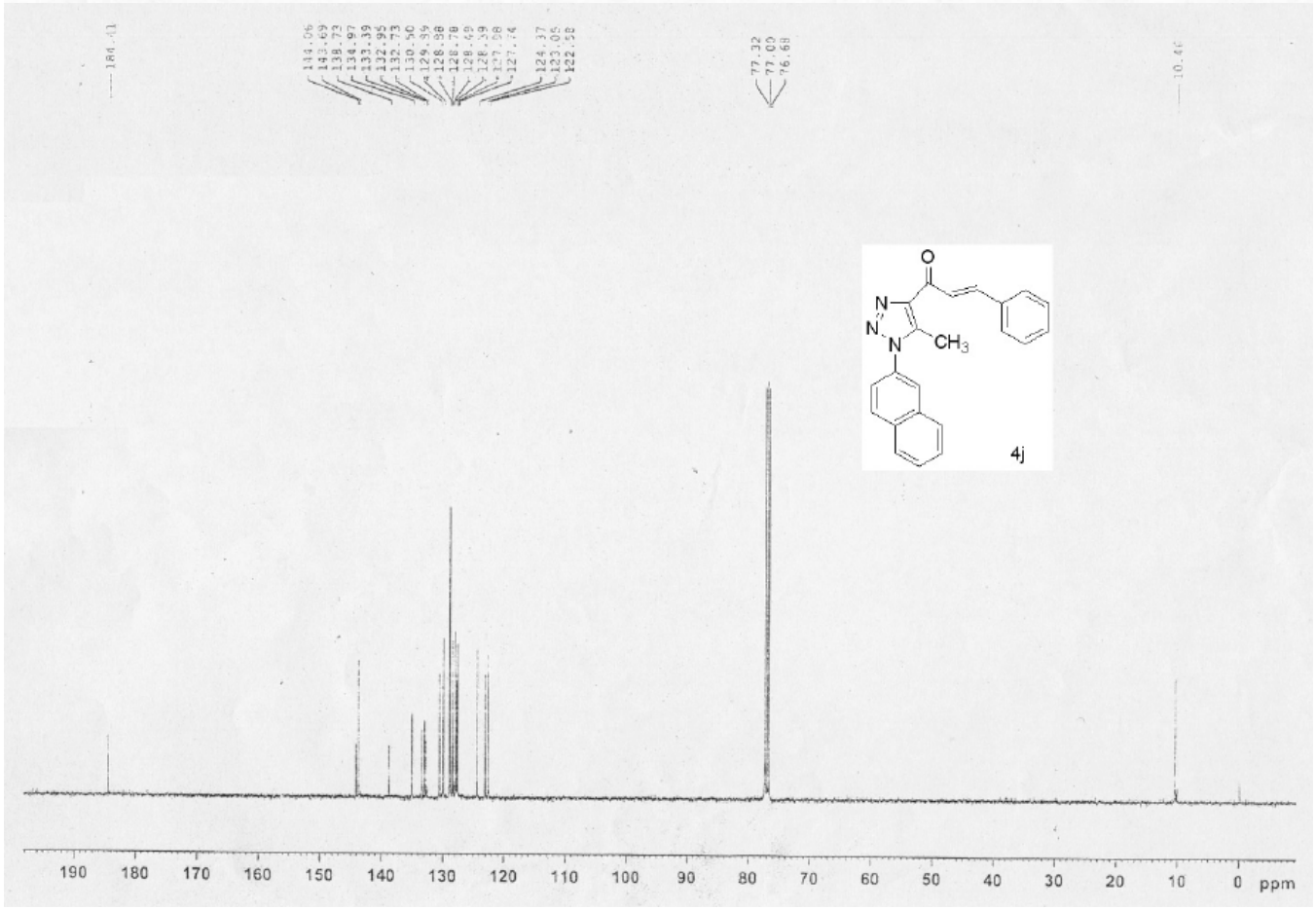
8.120
8.052
8.023
7.972
7.956
7.937
7.919
7.747
7.735
7.724
7.718
7.632
7.624
7.618
7.614
7.608
7.601
7.579
7.573
7.550
7.544
7.438
7.427
7.415
7.409
7.257
2.732
-0.000
4j
1.00 1.41 3.39
1.16 2.10 3.15
3.00
8
7
6
5
4
3
2
1
-0
ppm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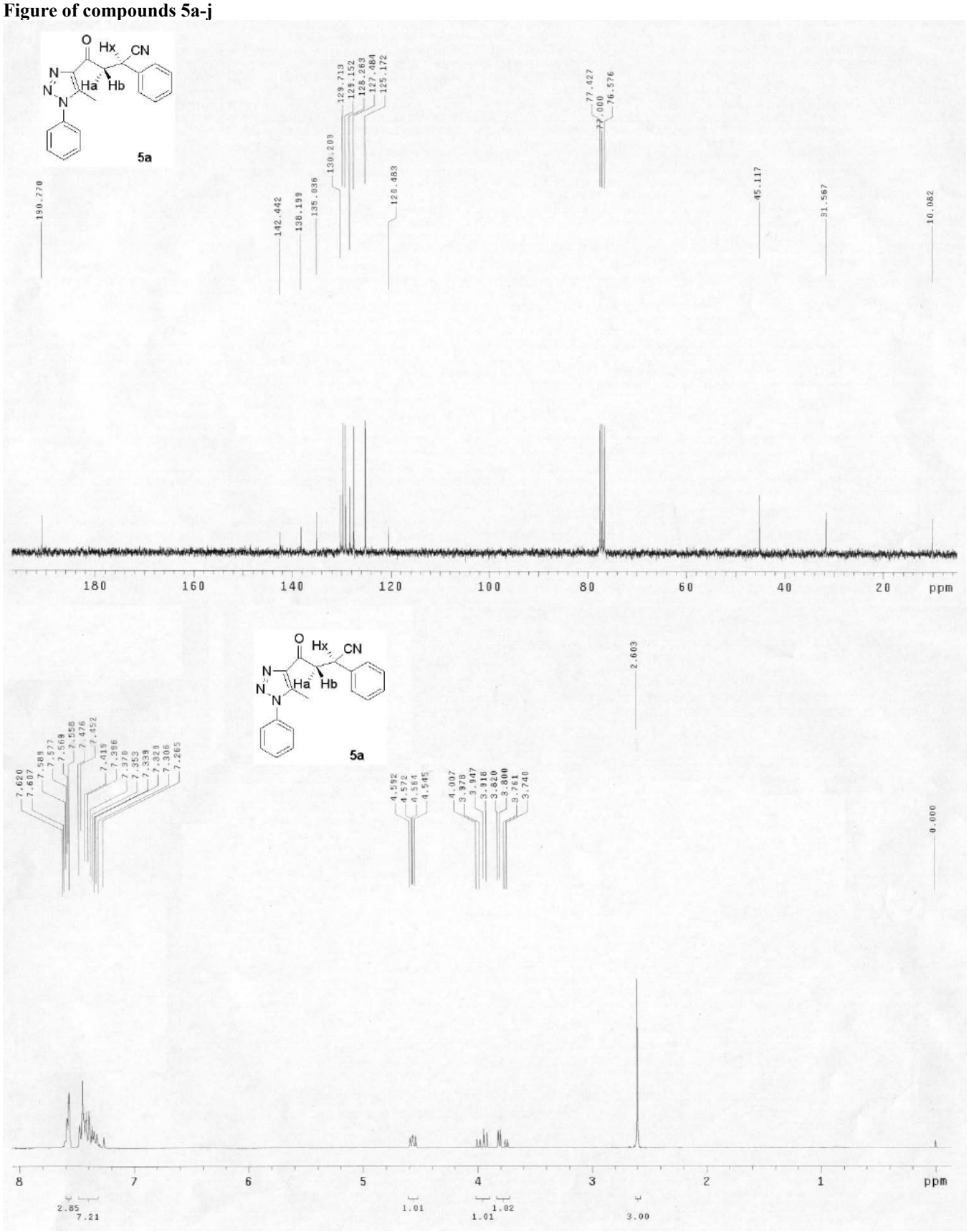
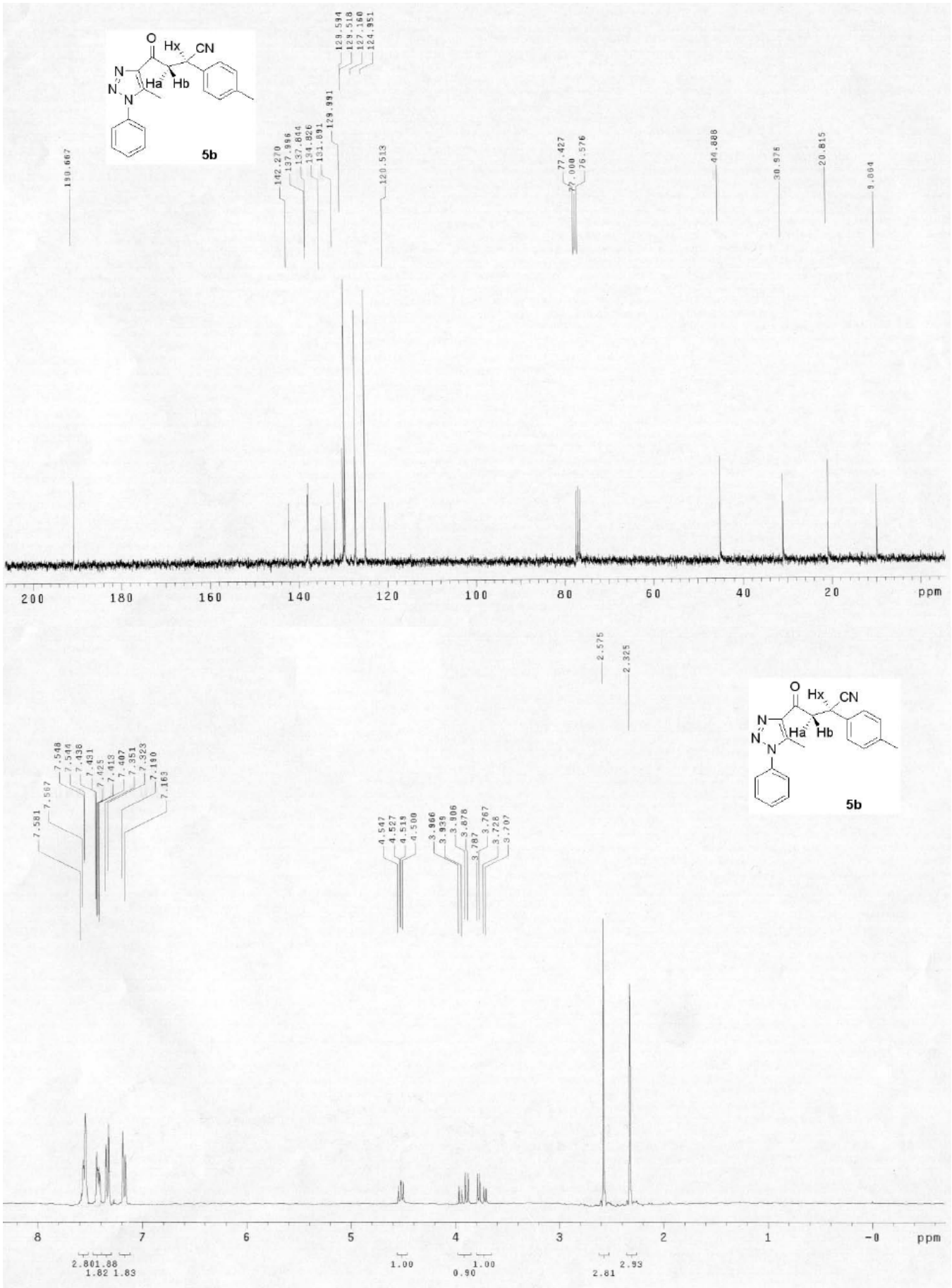
144.06
143.69
138.73
134.97
133.39
132.95
132.73
130.50
129.39
128.98
128.78
128.69
128.39
127.58
127.24
124.37
123.05
122.58
77.32
77.05
76.68
10.46
O
N
N
N
CH3
4j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Figure of compounds 5a-j




O
Hx
CN
N
N
Ha
Hb
5b
190.667
142.270
137.996
137.844
134.826
131.891
129.991
129.594
129.518
127.160
124.951
120.513
77.427
77.000
76.576
46.888
30.976
20.815
9.864
200
180
160
140
120
100
80
60
40
20
ppm
2.575
2.325
7.581
7.567
7.548
7.544
7.438
7.431
7.425
7.418
7.407
7.351
7.323
7.190
7.163
4.547
4.527
4.519
4.500
3.966
3.939
3.806
3.878
3.787
3.767
3.728
3.707
8
7
6
5
4
3
2
1
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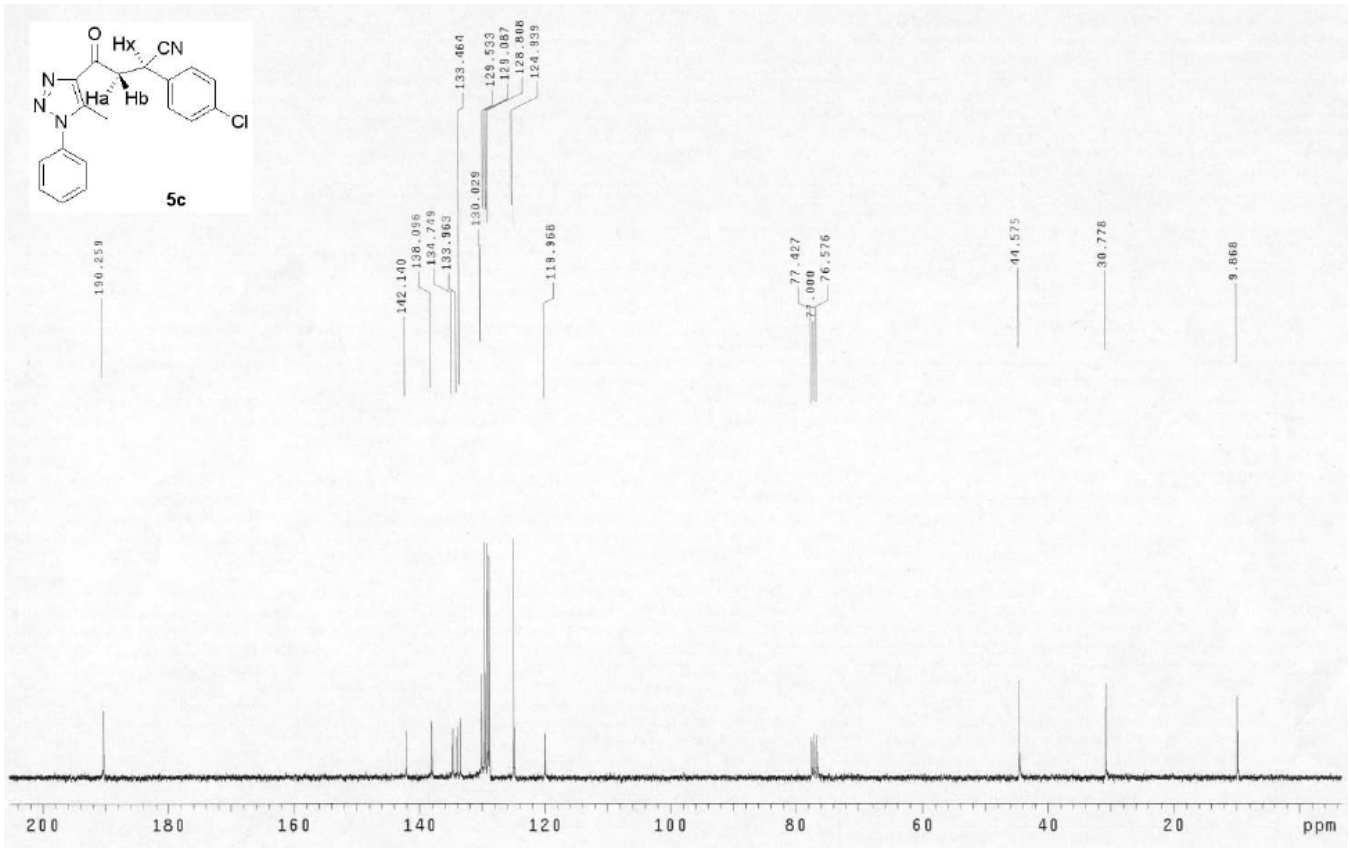
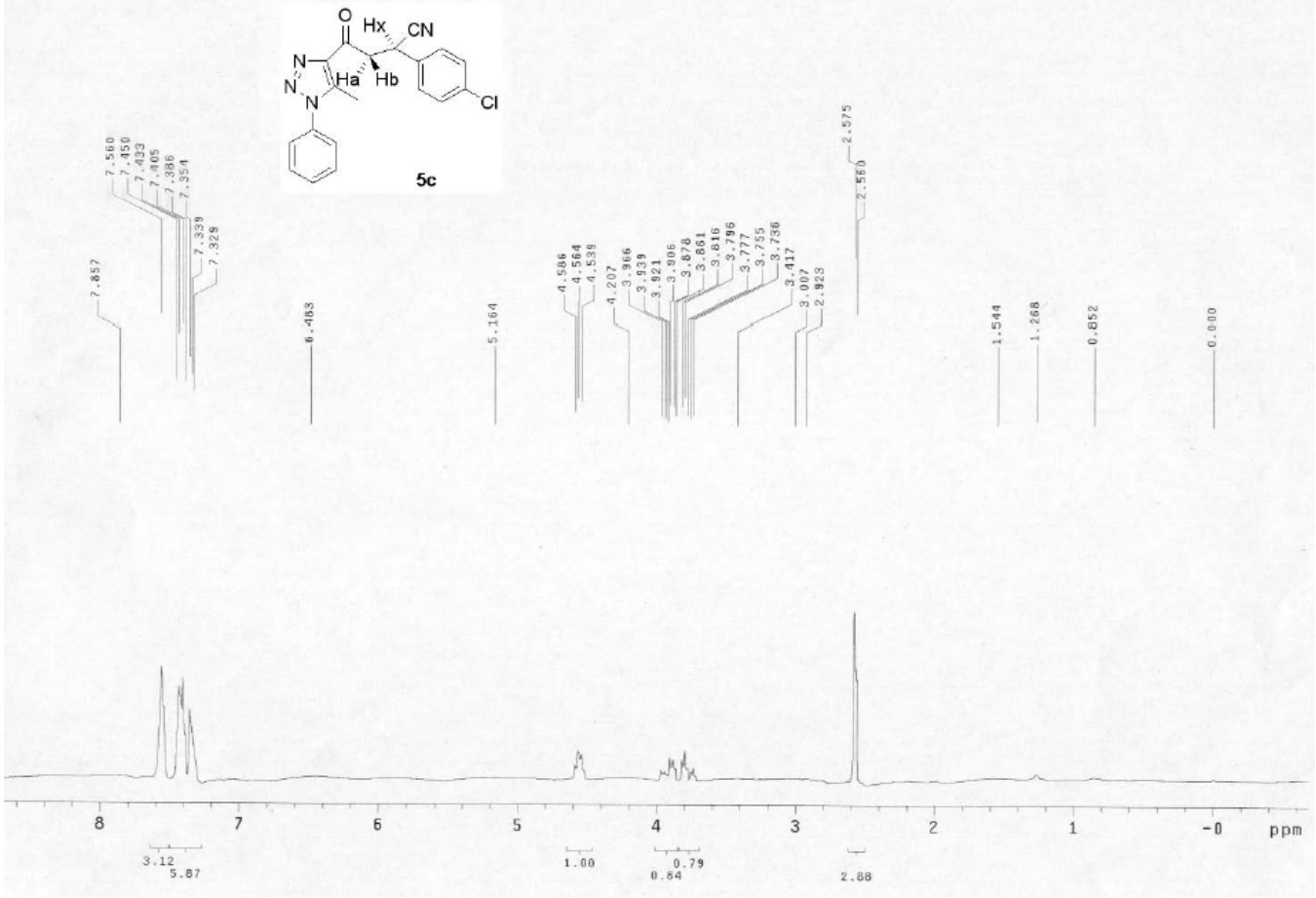
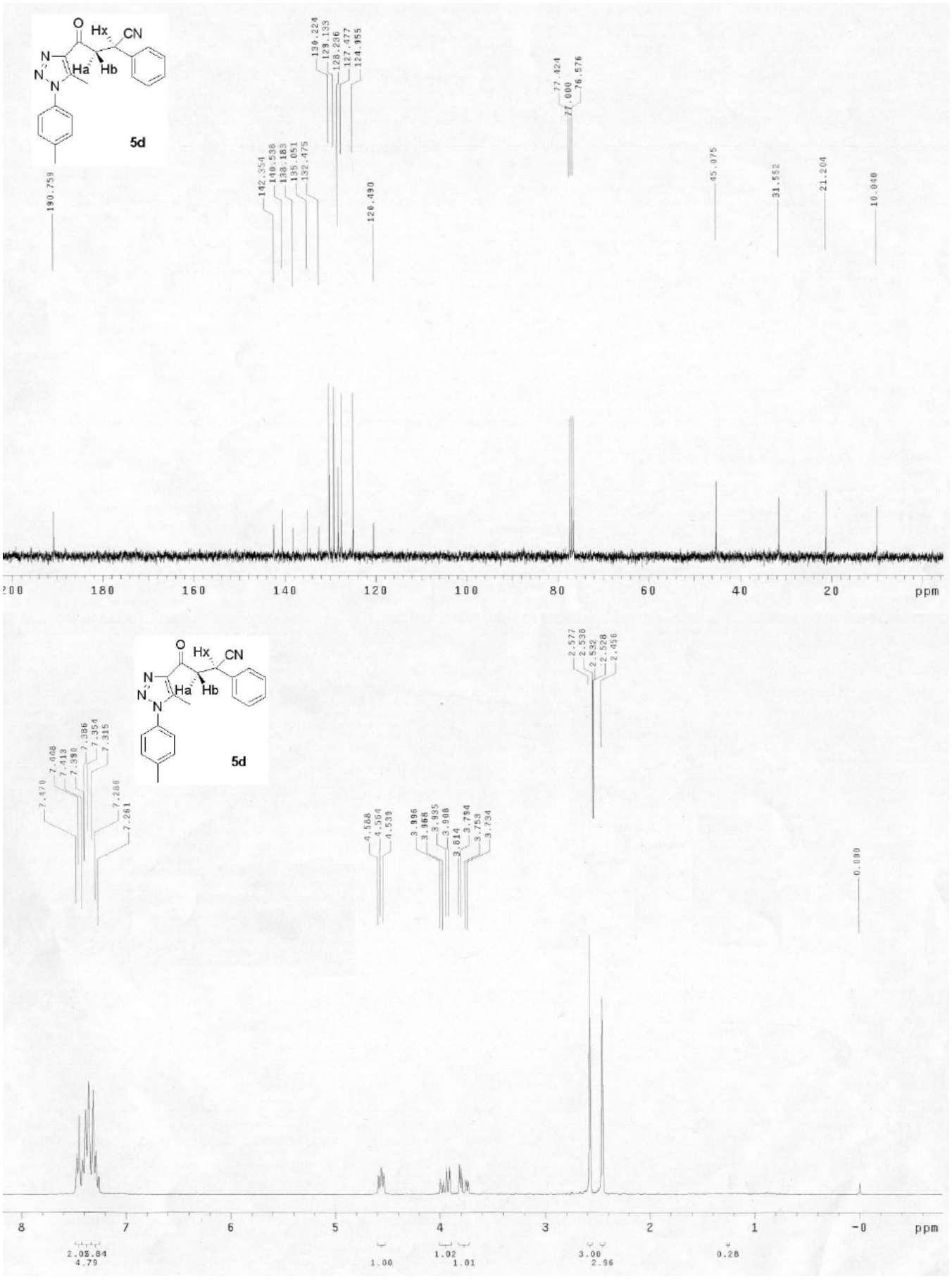
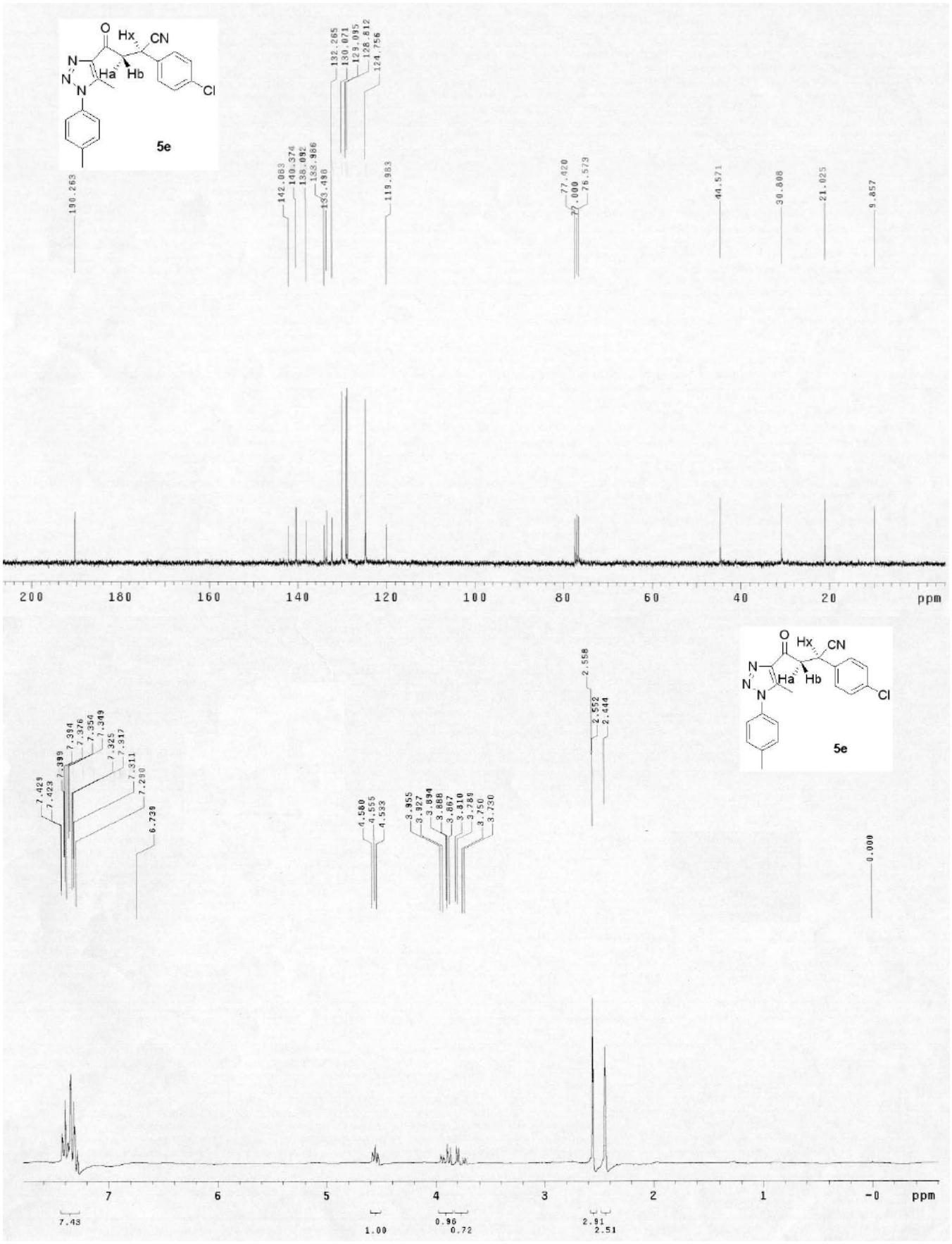
ppm
2.80
1.88
1.82
1.83
1.00
1.00
0.90
2.81
2.93


O
Hx
CN
N
N
Ha
Hb
Cl
5c
190.259
142.140
138.096
134.749
133.963
133.464
130.029
129.533
129.087
128.808
124.939
119.968
77.427
77.000
76.576
44.575
30.778
9.868
200
180
160
140
120
100
80
60
40
20
ppm


O
Hx
CN
N
N
Ha
Hb
Cl
5c
7.857
7.560
7.450
7.433
7.405
7.386
7.354
7.339
7.329
6.483
5.164
4.586
4.564
4.539
4.207
3.966
3.939
3.921
3.906
3.878
3.861
3.816
3.796
3.777
3.755
3.736
3.417
3.007
2.923
2.575
2.560
1.544
1.268
0.852
0.000
8
7
6
5
4
3
2
1
-0
ppm
3.12
5.87
1.00
0.79
0.84
2.88


O
Hx
CN
N
N
N
Ha
Hb
5d
190.759
142.354
140.538
138.183
135.051
132.475
130.224
129.133
128.236
127.477
124.955
120.490
77.424
77.000
76.576
45.075
31.552
21.204
10.040
200
180
160
140
120
100
80
60
40
20
ppm
7.470
7.408
7.413
7.390
7.386
7.354
7.315
7.286
7.261
4.588
4.564
4.539
3.996
3.968
3.835
3.808
3.814
3.794
3.753
3.734
2.577
2.538
2.532
2.528
2.456
0.000
8
7
6
5
4
3
2
1
-0
ppm
2.00
3.84
4.79
1.00
1.02
1.01
3.00
2.96
0.28


O
Hx
CN
N
N
Ha
Hb
Cl
5e
190.263
142.083
140.374
138.092
133.986
133.496
132.265
130.071
129.095
128.812
124.756
119.983
77.420
77.000
76.573
44.571
30.808
21.025
9.857
200
180
160
140
120
100
80
60
40
20
ppm
7.429
7.423
7.399
7.394
7.376
7.356
7.349
7.325
7.317
7.311
7.290
6.739
4.580
4.555
4.533
3.955
3.927
3.894
3.888
3.867
3.810
3.789
3.750
3.730
2.558
2.552
2.444
0.000
7
6
5
4
3
2
1
-0
ppm
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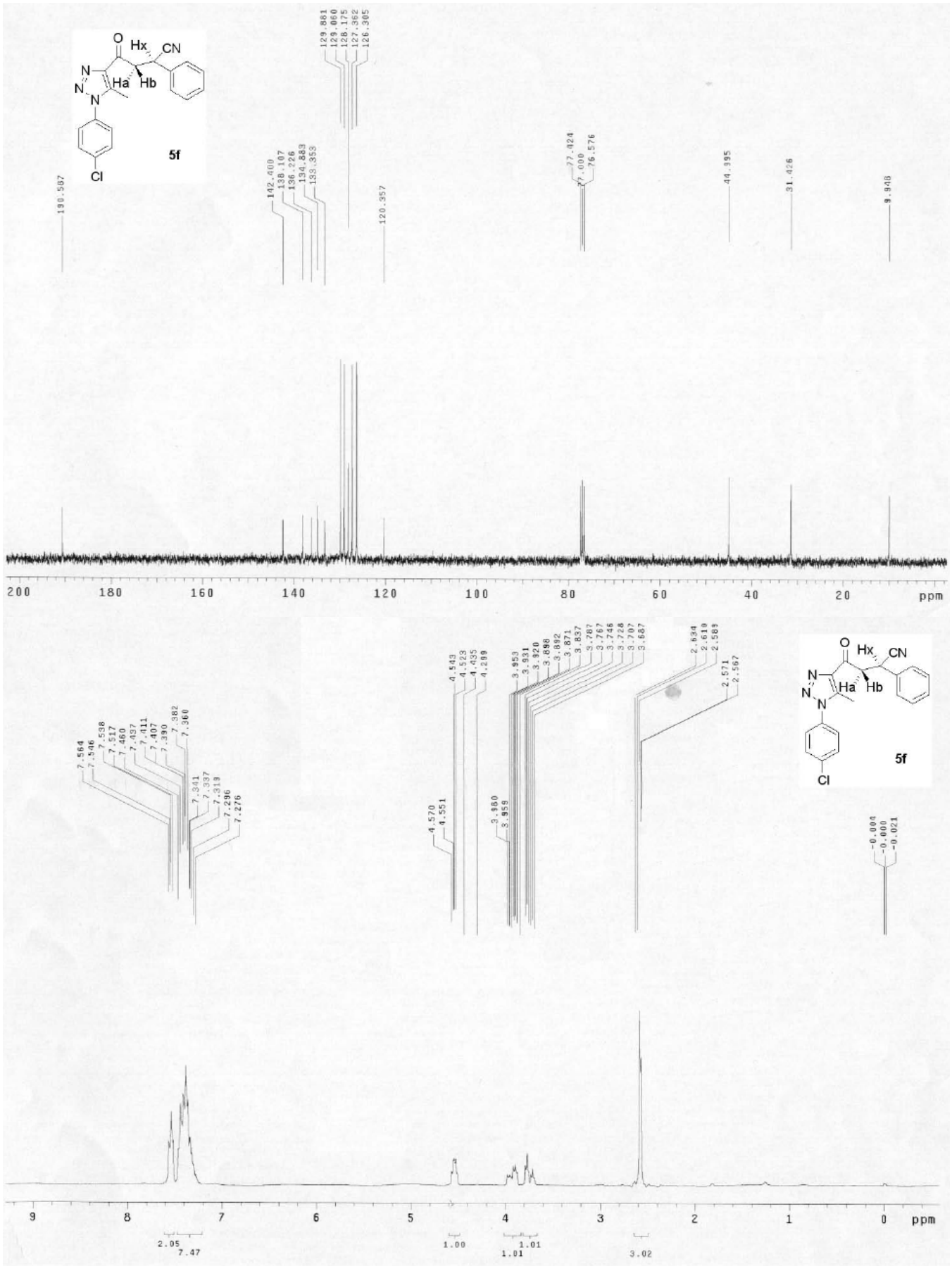
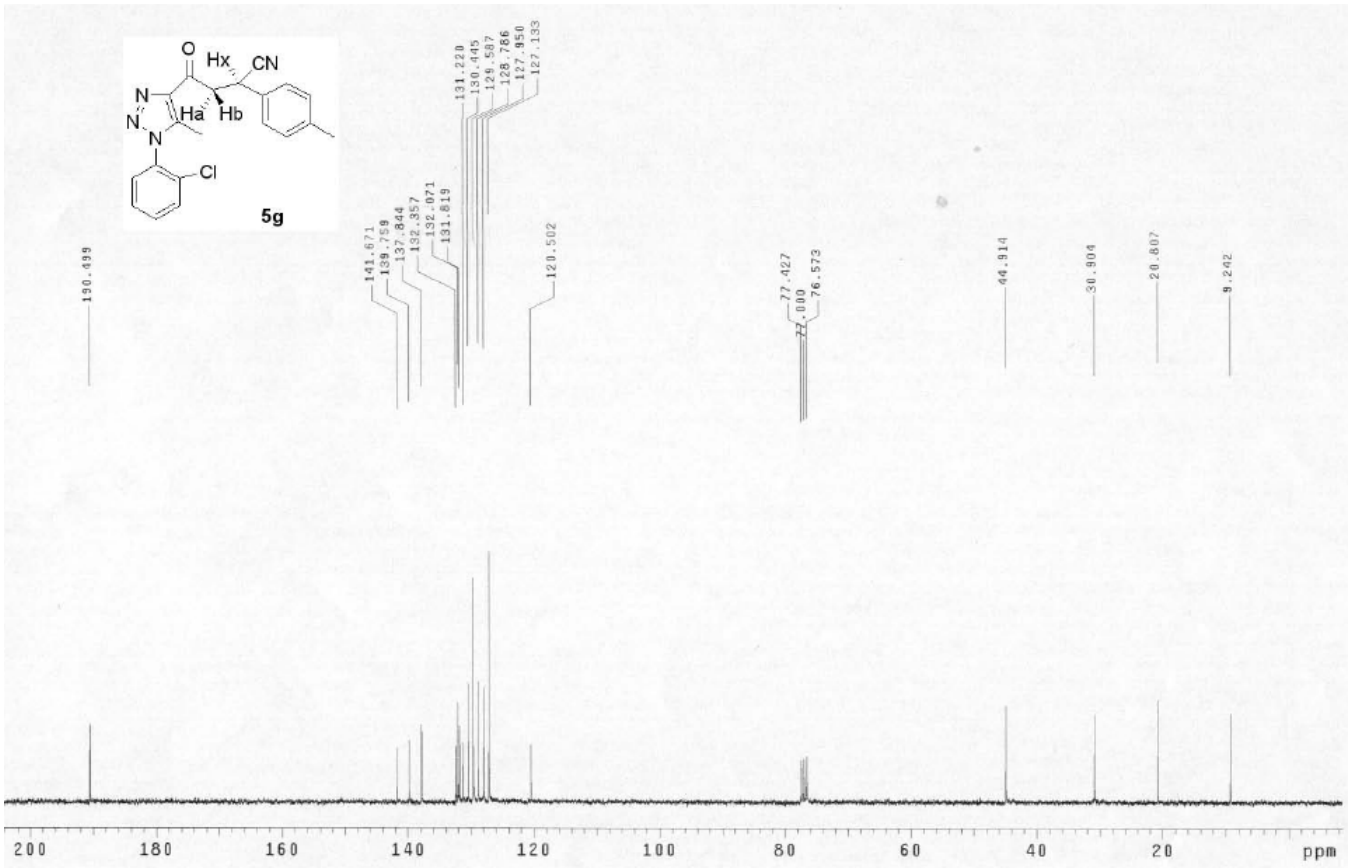
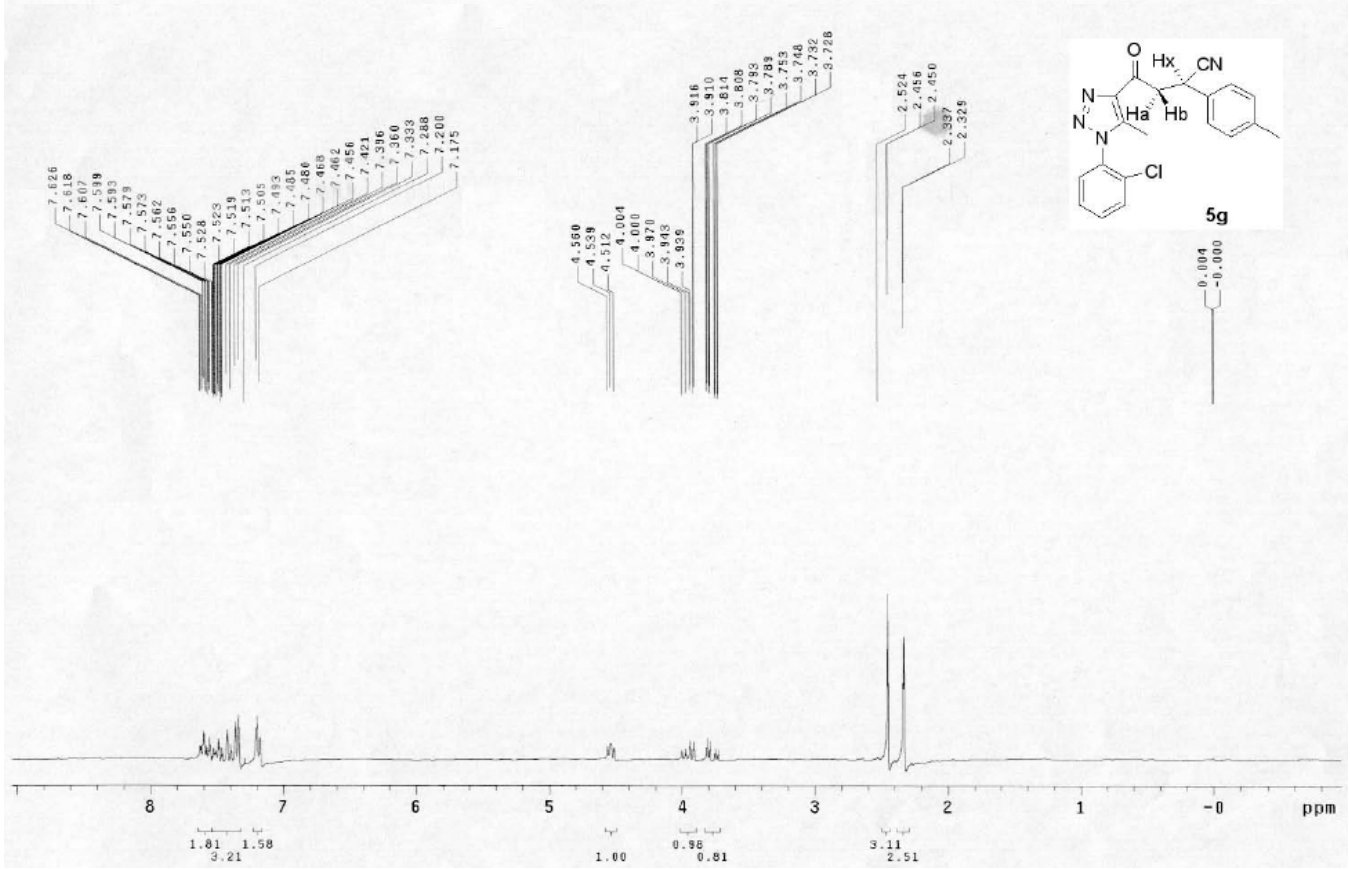
1.00
0.96
0.72
2.91
2.51


O
Hx
CN
N
N
Ha
Hb
5f
Cl
190.587
142.400
138.107
136.226
134.883
133.353
129.881
129.060
128.175
127.362
126.305
120.357
77.424
77.000
76.576
44.995
31.426
9.948
200
180
160
140
120
100
80
60
40
20
ppm
7.564
7.546
7.538
7.517
7.460
7.437
7.411
7.407
7.390
7.382
7.360
7.341
7.337
7.319
7.296
7.276
4.570
4.551
4.543
4.523
4.435
4.209
3.980
3.959
3.953
3.931
3.920
3.898
3.892
3.871
3.837
3.787
3.767
3.746
3.728
3.707
3.687
2.634
2.610
2.583
2.571
2.567
-0.004
-0.000
-0.021
9
8
7
6
5
4
3
2
1
0
ppm
2.05
7.47
1.00
1.01
1.01
3.02


O
Hx
CN
N
N
Ha
Hb
Cl
5g
190.499
141.671
139.759
137.844
132.357
132.071
131.819
131.220
130.445
129.587
128.766
127.950
127.133
120.502
77.427
77.000
76.573
44.914
30.904
20.807
9.242
200
180
160
140
120
100
80
60
40
20
ppm


7.626
7.618
7.607
7.599
7.593
7.579
7.573
7.562
7.556
7.550
7.528
7.523
7.519
7.513
7.505
7.493
7.485
7.486
7.468
7.462
7.456
7.421
7.396
7.360
7.333
7.288
7.200
7.175
4.560
4.539
4.512
4.004
4.000
3.970
3.943
3.939
3.916
3.910
3.814
3.808
3.793
3.789
3.753
3.748
3.732
3.728
2.524
2.456
2.450
2.397
2.329
O
Hx
CN
N
N
Ha
Hb
Cl
5g
0.004
0.000
8
7
6
5
4
3
2
1
-0
ppm
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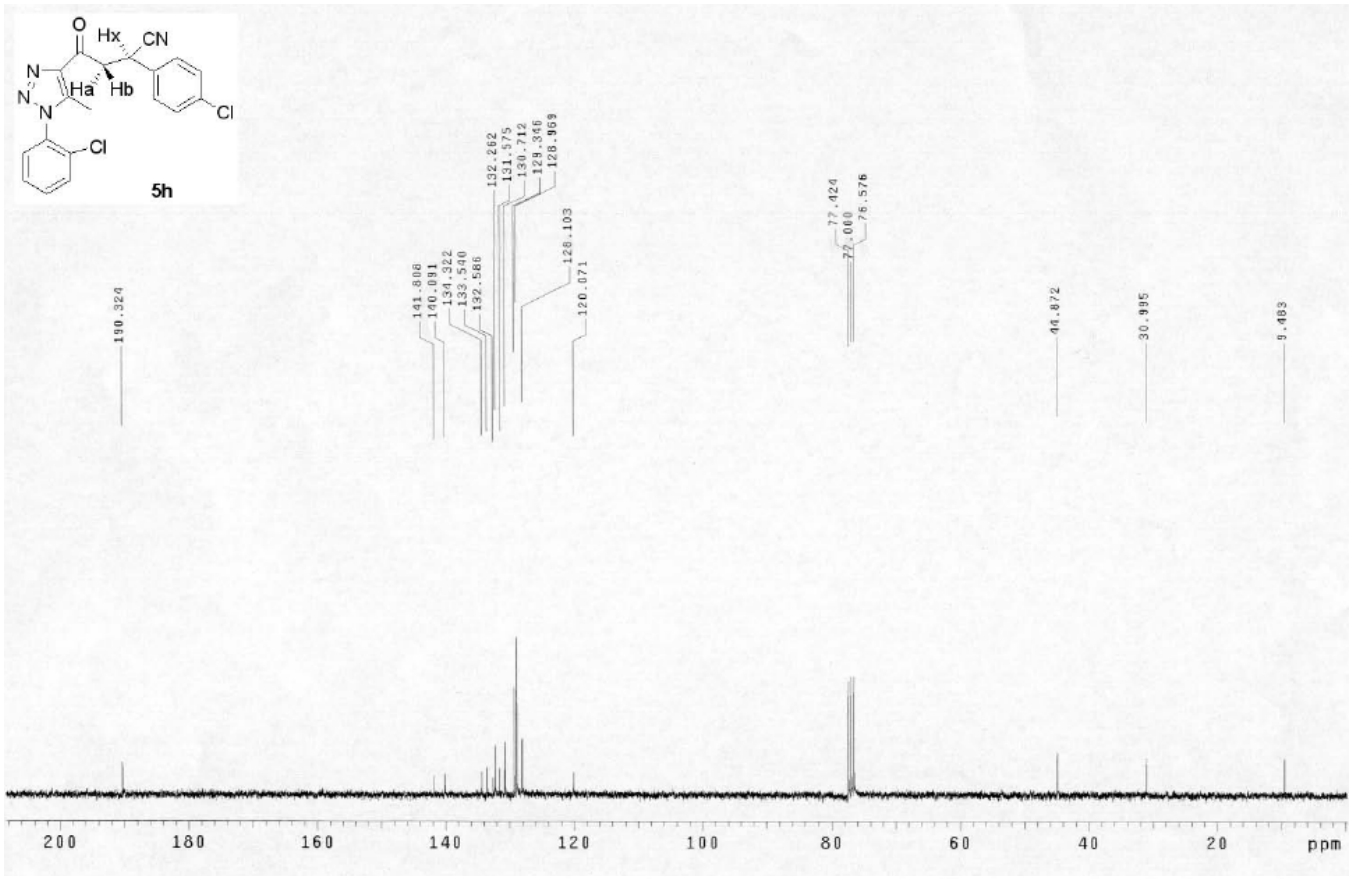
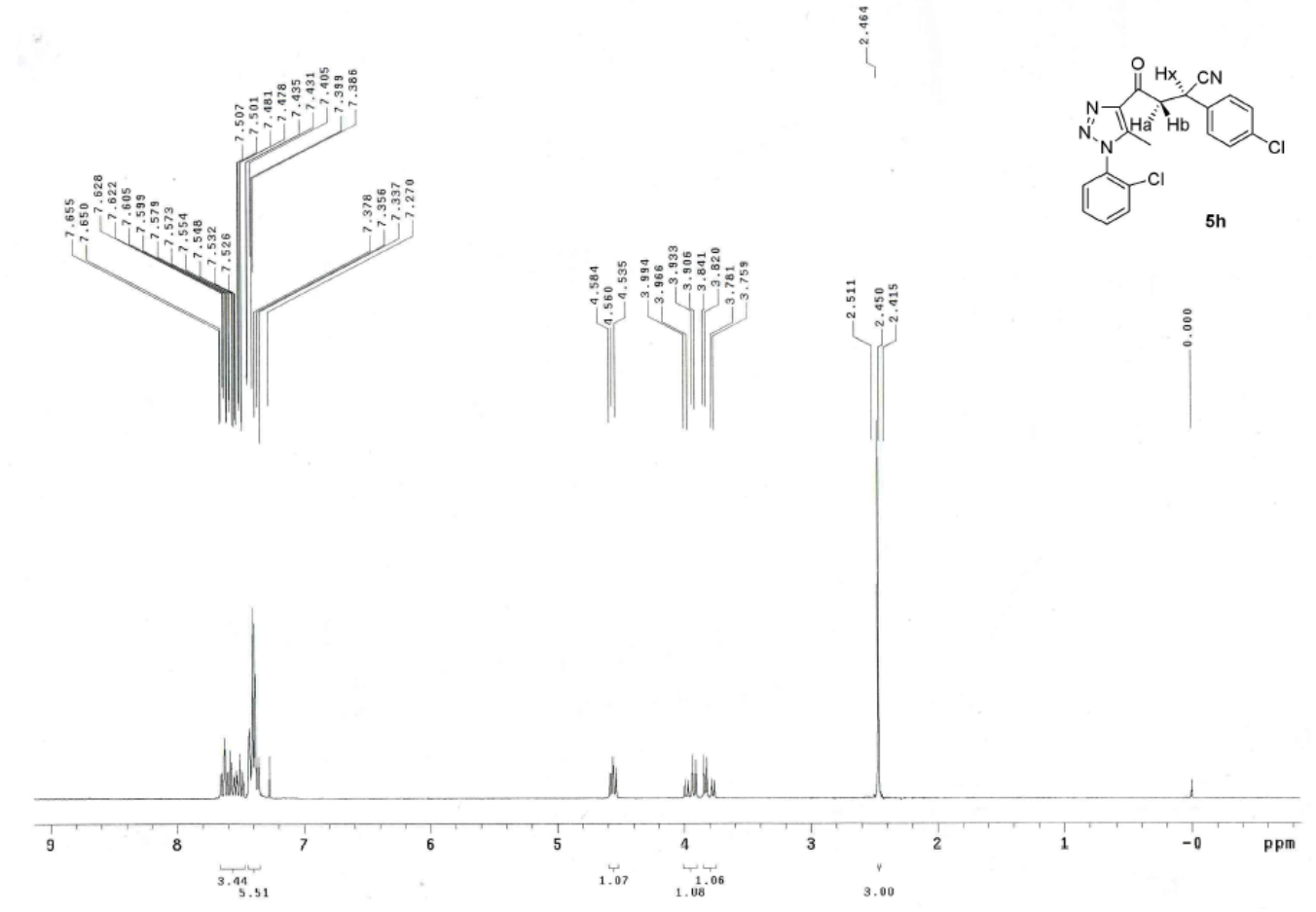
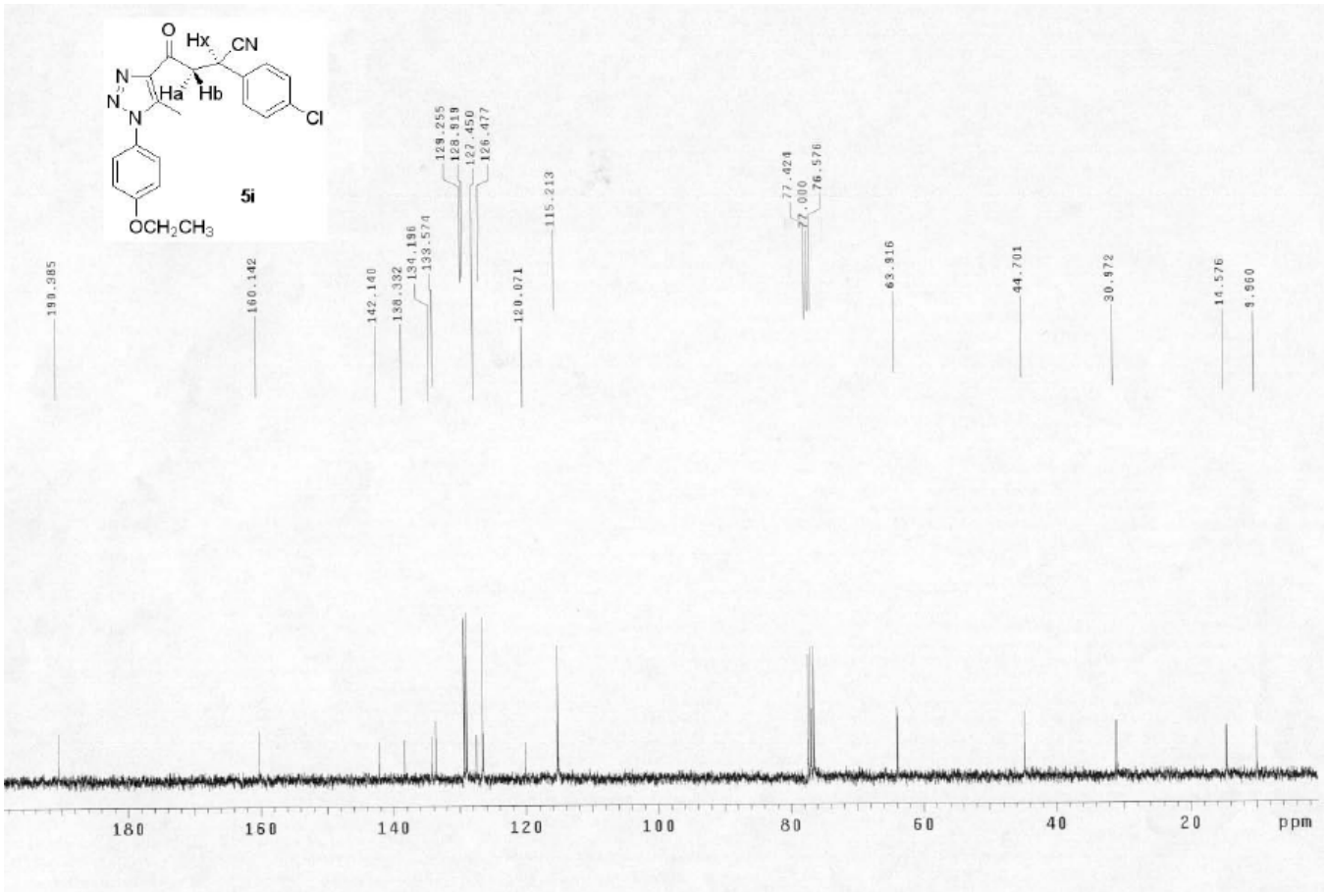
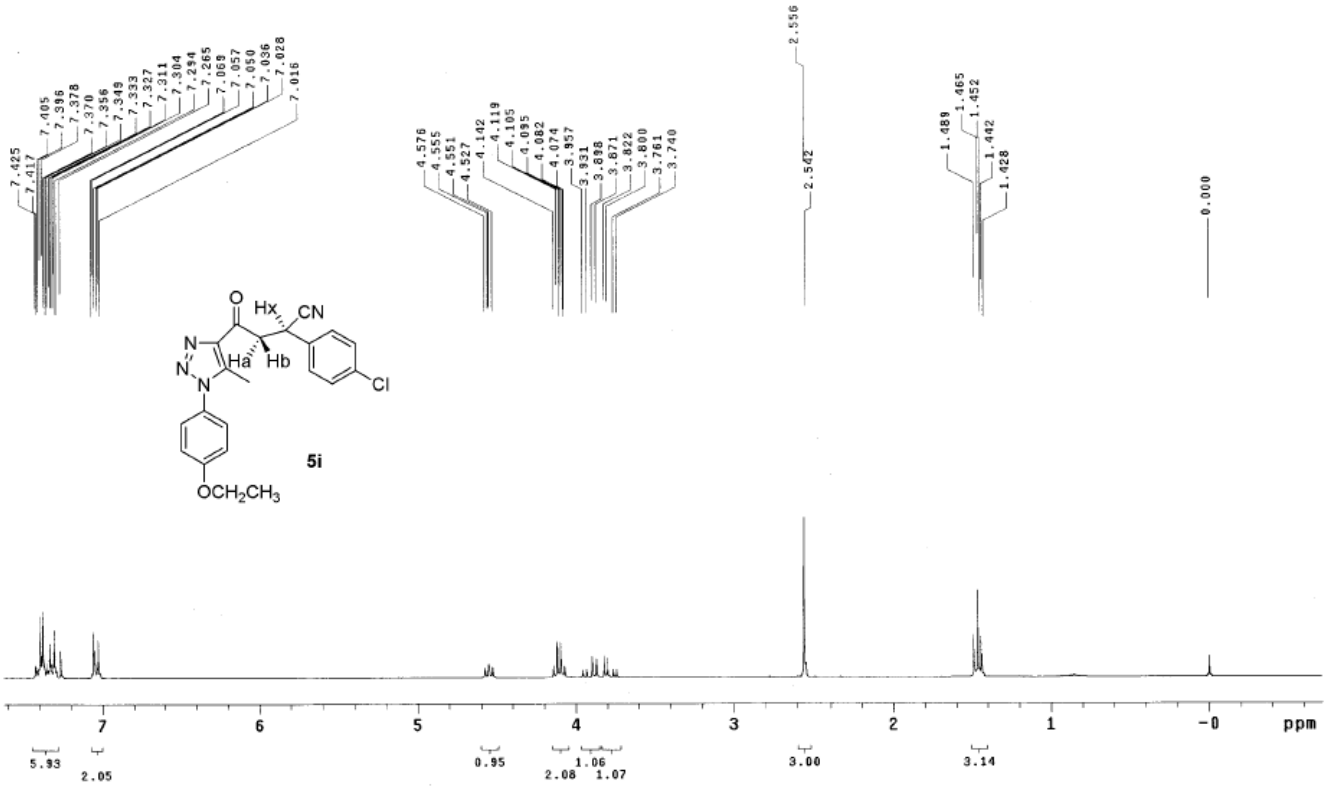
1.58
3.21
1.00
0.98
0.81
3.11
2.51


5h
190.324
141.806
140.091
134.322
133.540
132.586
132.262
131.575
130.712
129.346
128.959
128.103
120.071
77.424
77.000
76.576
44.872
30.995
9.483
200
180
160
140
120
100
80
60
40
20
ppm


5h
2.464
7.655
7.650
7.628
7.622
7.605
7.599
7.579
7.573
7.554
7.548
7.532
7.526
7.507
7.501
7.481
7.478
7.435
7.431
7.405
7.399
7.386
7.378
7.356
7.337
7.270
4.584
4.560
4.535
3.994
3.966
3.933
3.906
3.841
3.820
3.781
3.759
2.511
2.450
2.415
0.000
9
8
7
6
5
4
3
2
1
-0
ppm
3.44
5.51
1.07
1.08
1.06
3.00


O
Hx
CN
N
N
N
Ha
Hb
Cl
5i
OCH2CH3
190.985
160.142
142.140
138.332
134.196
133.574
129.255
128.819
127.450
126.477
120.071
115.213
77.424
77.000
76.576
63.916
44.701
30.972
14.576
9.960
180
160
140
120
100
80
60
40
20
ppm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7.417
7.405
7.396
7.378
7.370
7.356
7.349
7.333
7.327
7.311
7.304
7.294
7.265
7.069
7.057
7.050
7.036
7.028
7.016
4.576
4.555
4.551
4.527
4.142
4.119
4.105
4.095
4.082
4.074
3.957
3.931
3.888
3.871
3.822
3.800
3.761
3.740
2.556
2.542
1.489
1.465
1.452
1.442
1.428
0.000
O
Hx
CN
N
N
N
Ha
Hb
Cl
5i
OCH2CH3
7
6
5
4
3
2
1
-0
ppm
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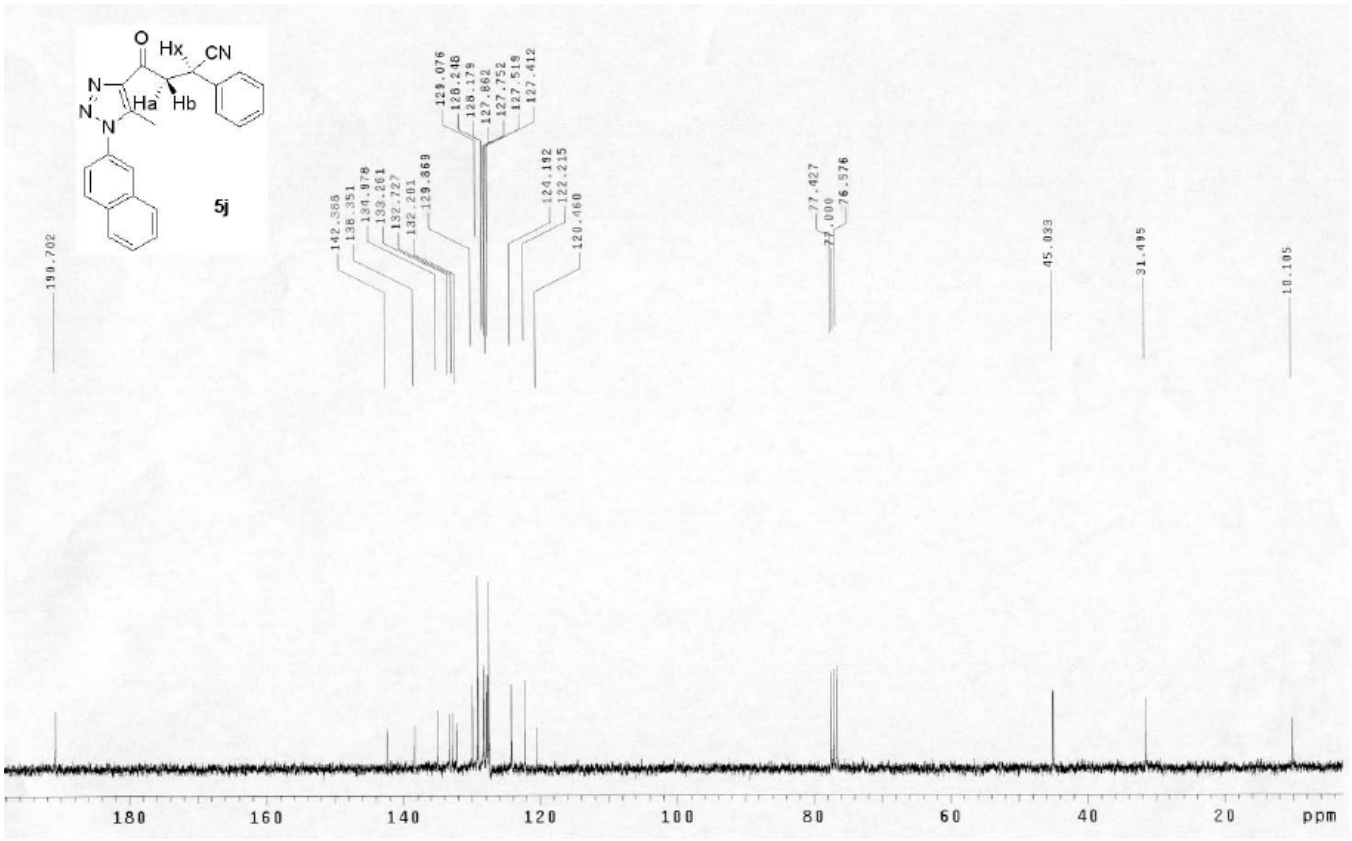
2.05
0.95
2.08
1.06
1.07
3.00
3.14



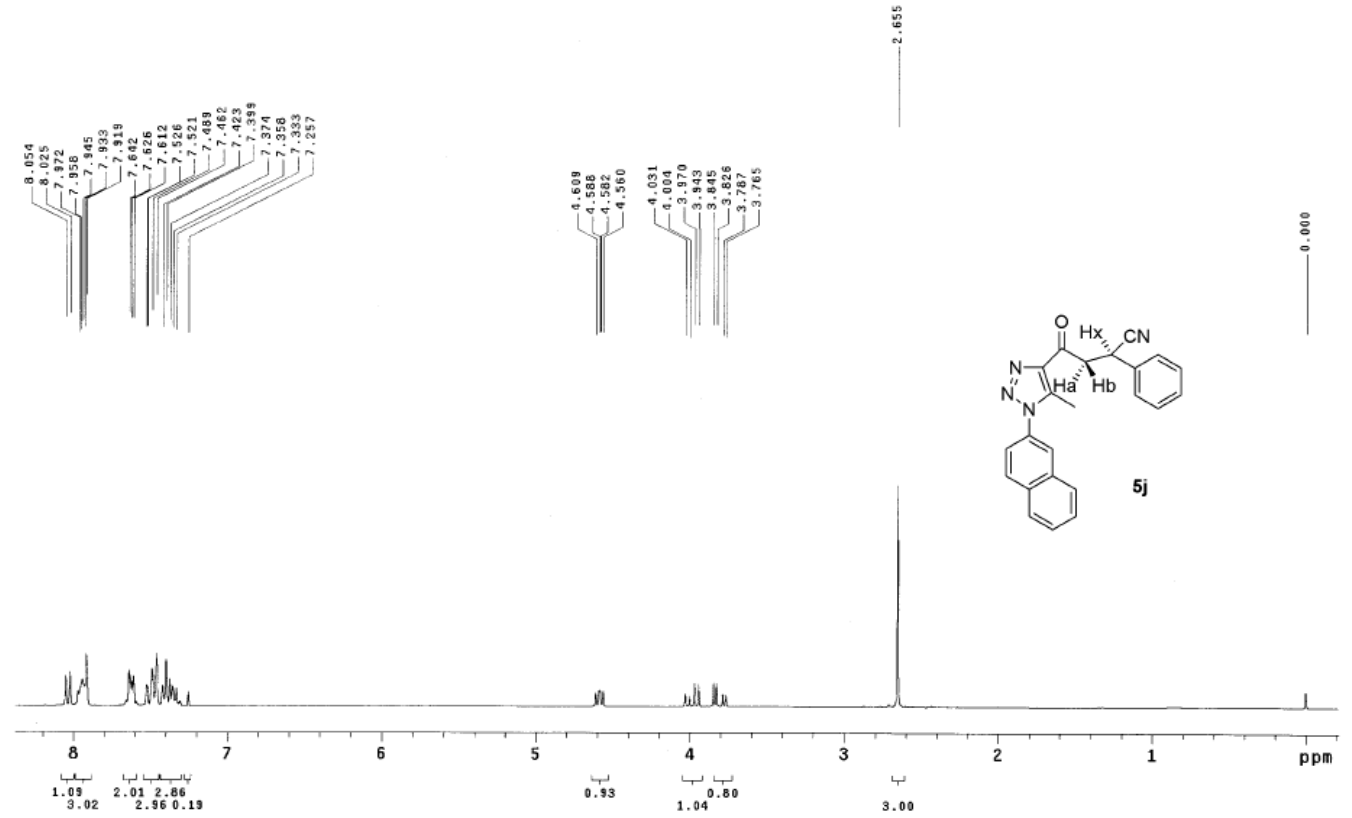
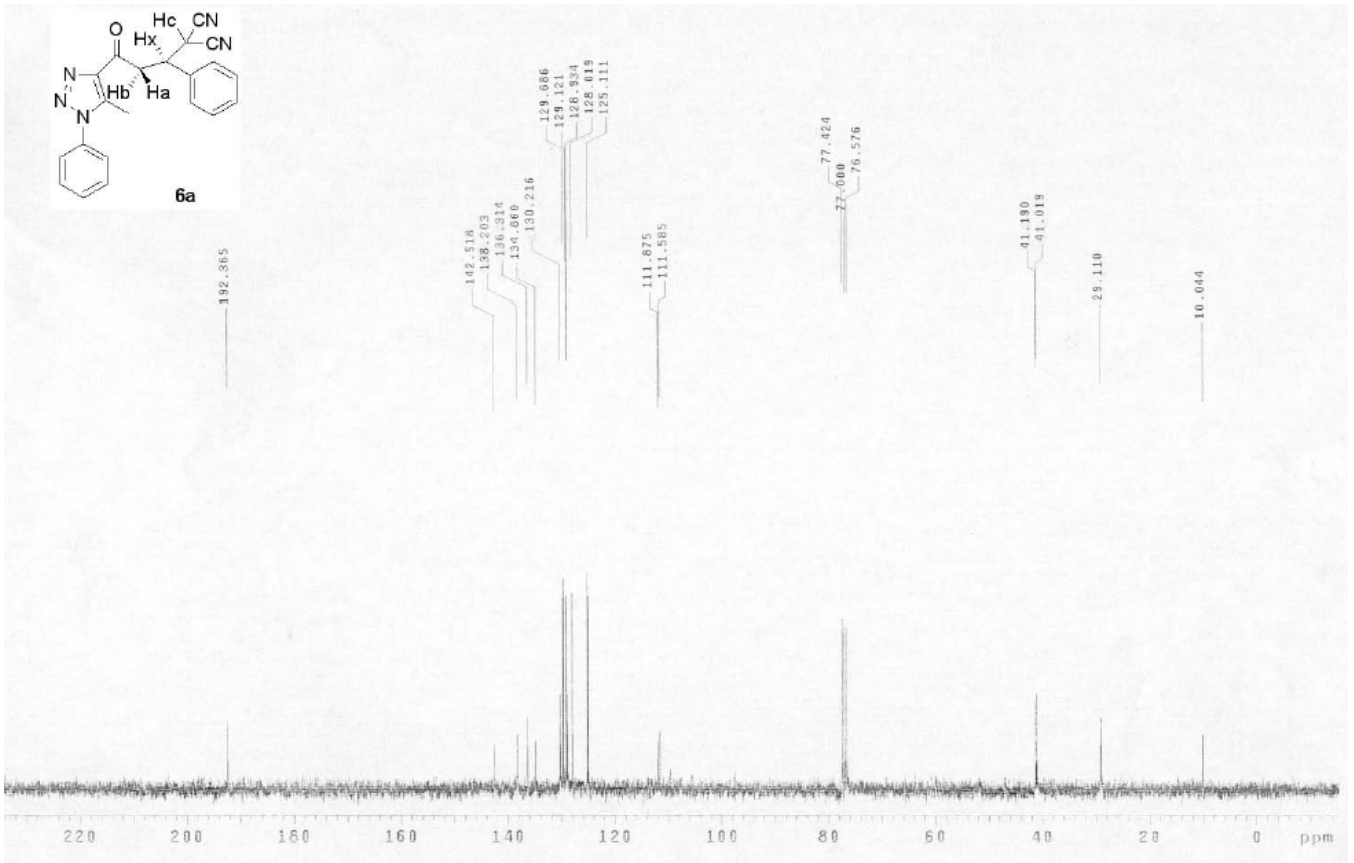
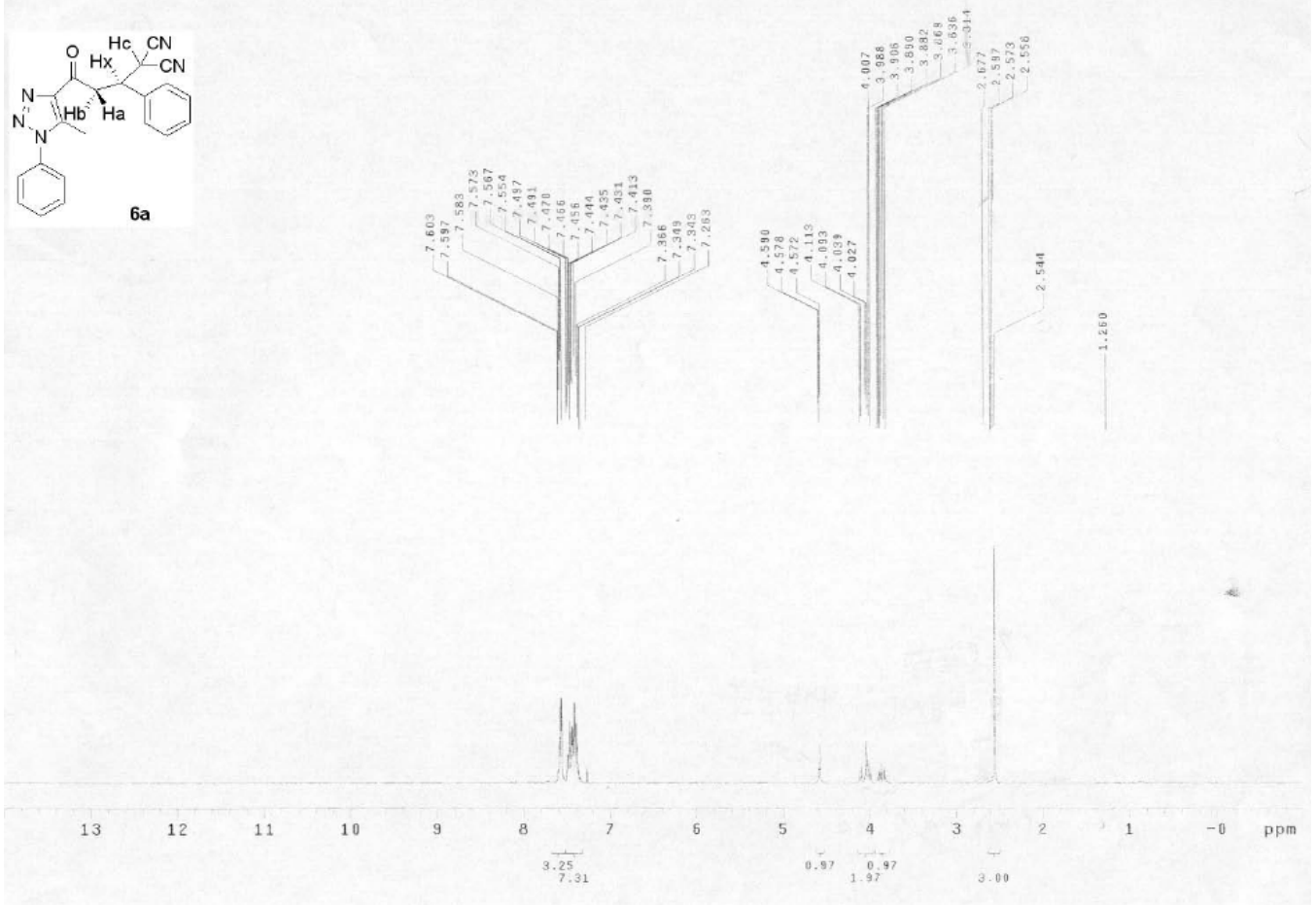
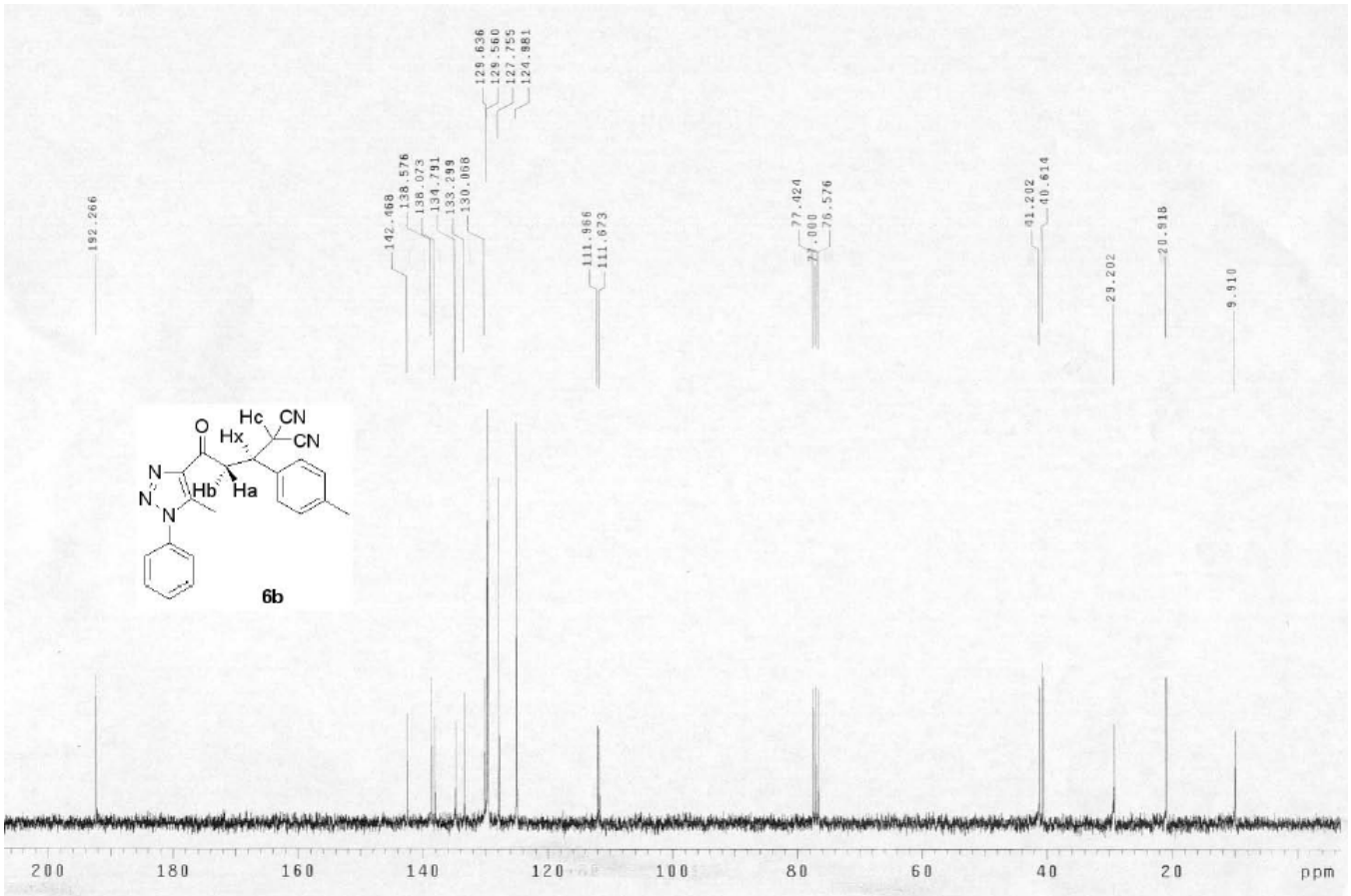
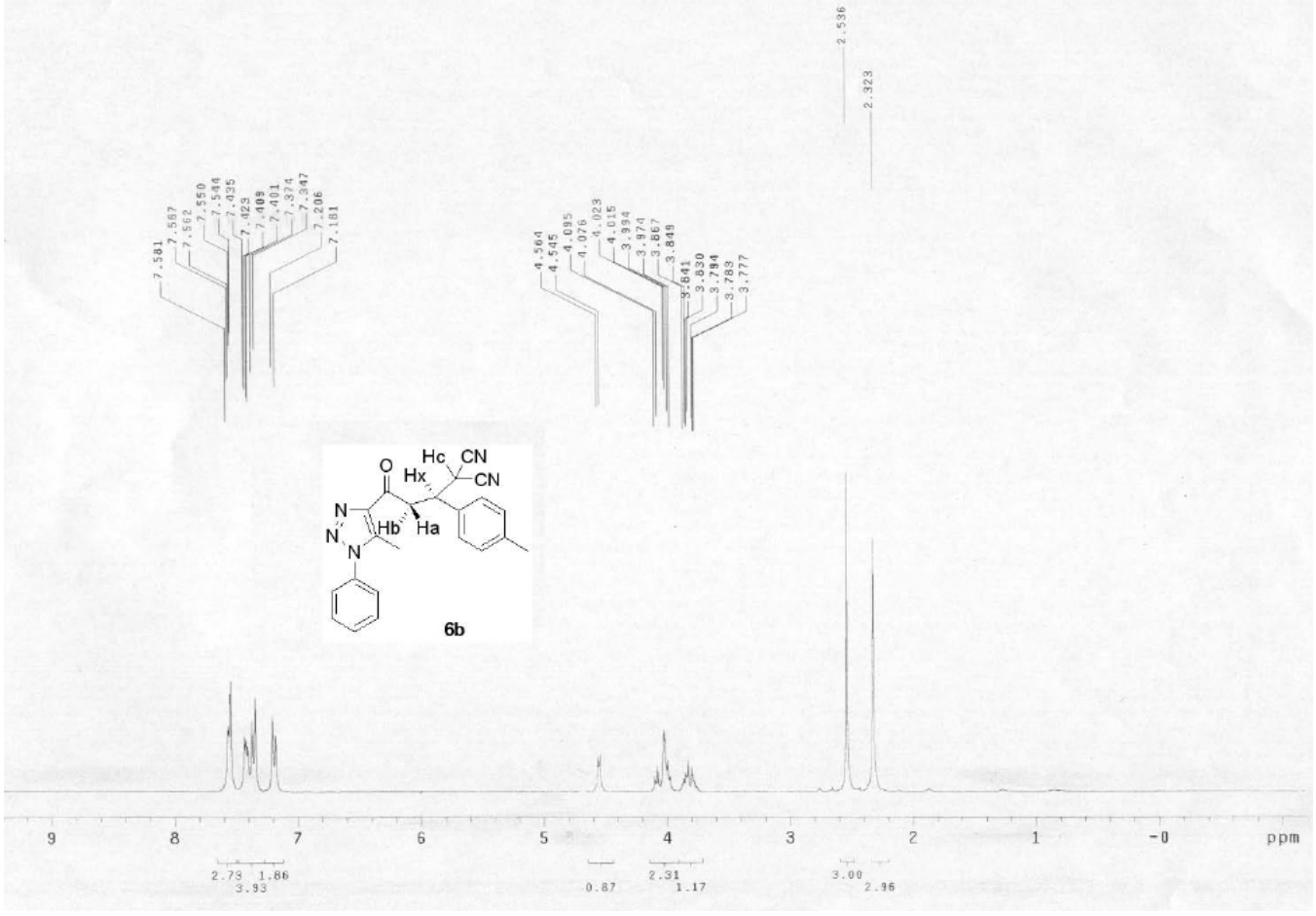


Figure of compounds 6a-j


Hc
CN
Hx
CN
O
N
N
N
Hb
Ha
6a
192.365
142.518
138.203
136.314
134.860
130.216
129.686
129.121
128.934
128.019
125.111
111.875
111.585
77.424
77.000
76.576
41.130
41.019
29.110
10.044
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Hc
CN
Hx
CN
O
N
N
N
Hb
Ha
6a
7.603
7.597
7.583
7.573
7.567
7.554
7.497
7.491
7.470
7.466
7.456
7.444
7.435
7.431
7.413
7.390
7.366
7.349
7.343
7.263
4.590
4.578
4.572
4.113
4.093
4.039
4.027
4.007
3.988
3.906
3.890
3.882
3.668
3.636
3.614
2.672
2.597
2.573
2.556
2.544
1.260
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
3.25
7.31
0.97
0.97
1.97
3.00


192.266
142.468
138.576
138.073
134.791
133.299
130.068
129.636
129.560
127.755
124.881
111.986
111.673
77.424
77.000
76.576
41.202
40.614
29.202
20.918
9.910
Hc
CN
CN
Hx
O
N
N
N
Hb
Ha
6b
200
180
160
140
120
100
80
60
40
20
ppm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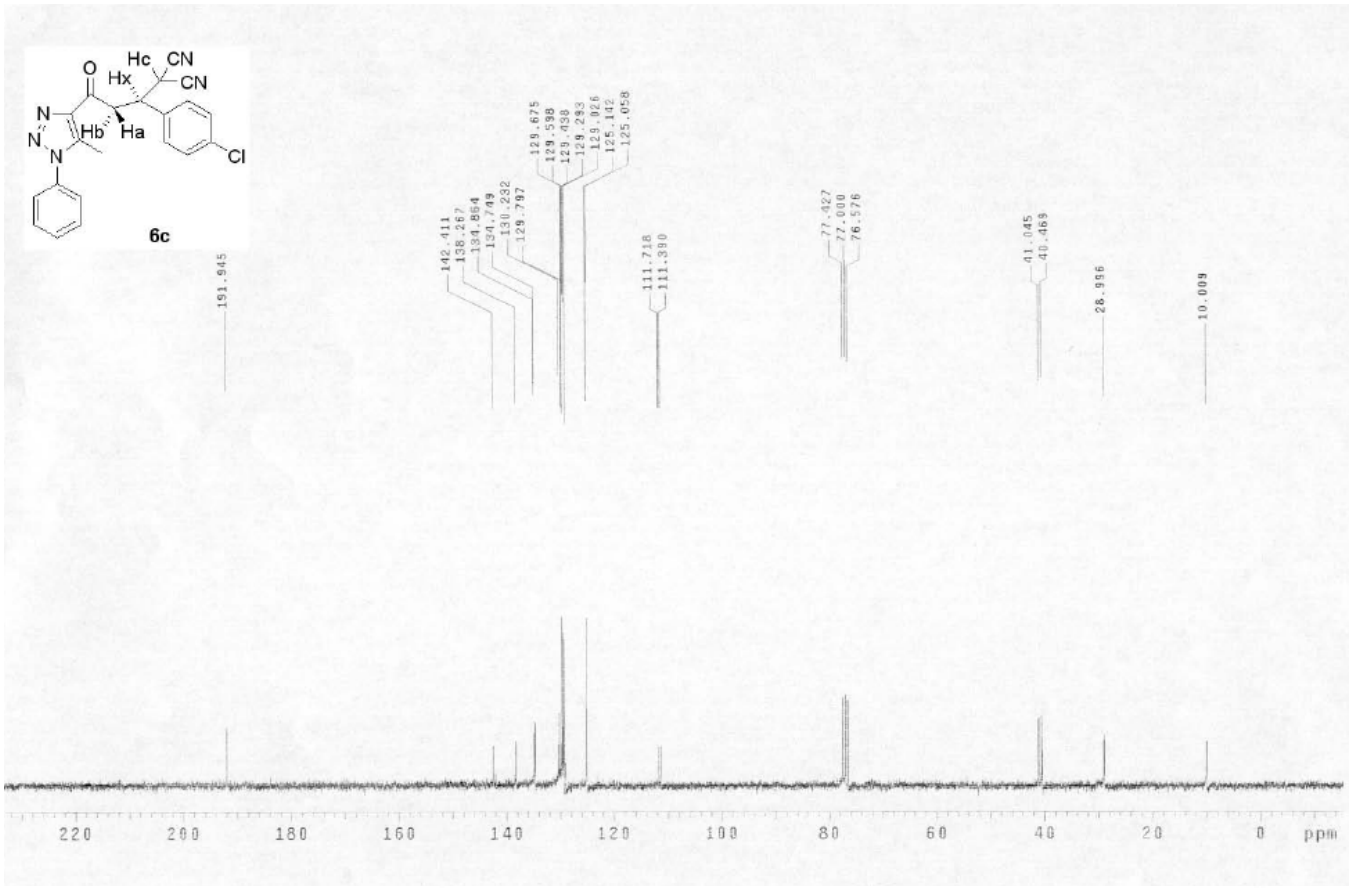
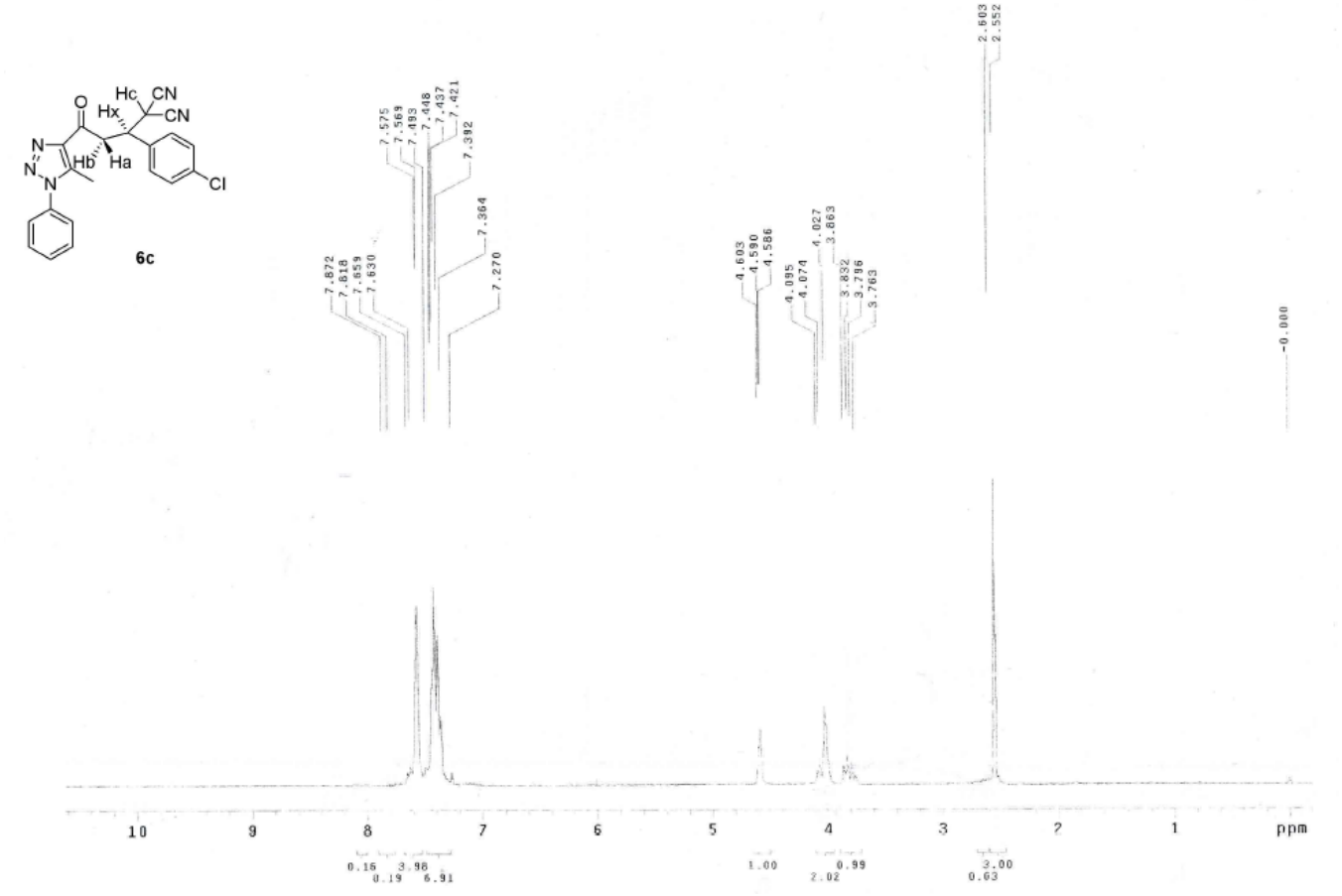
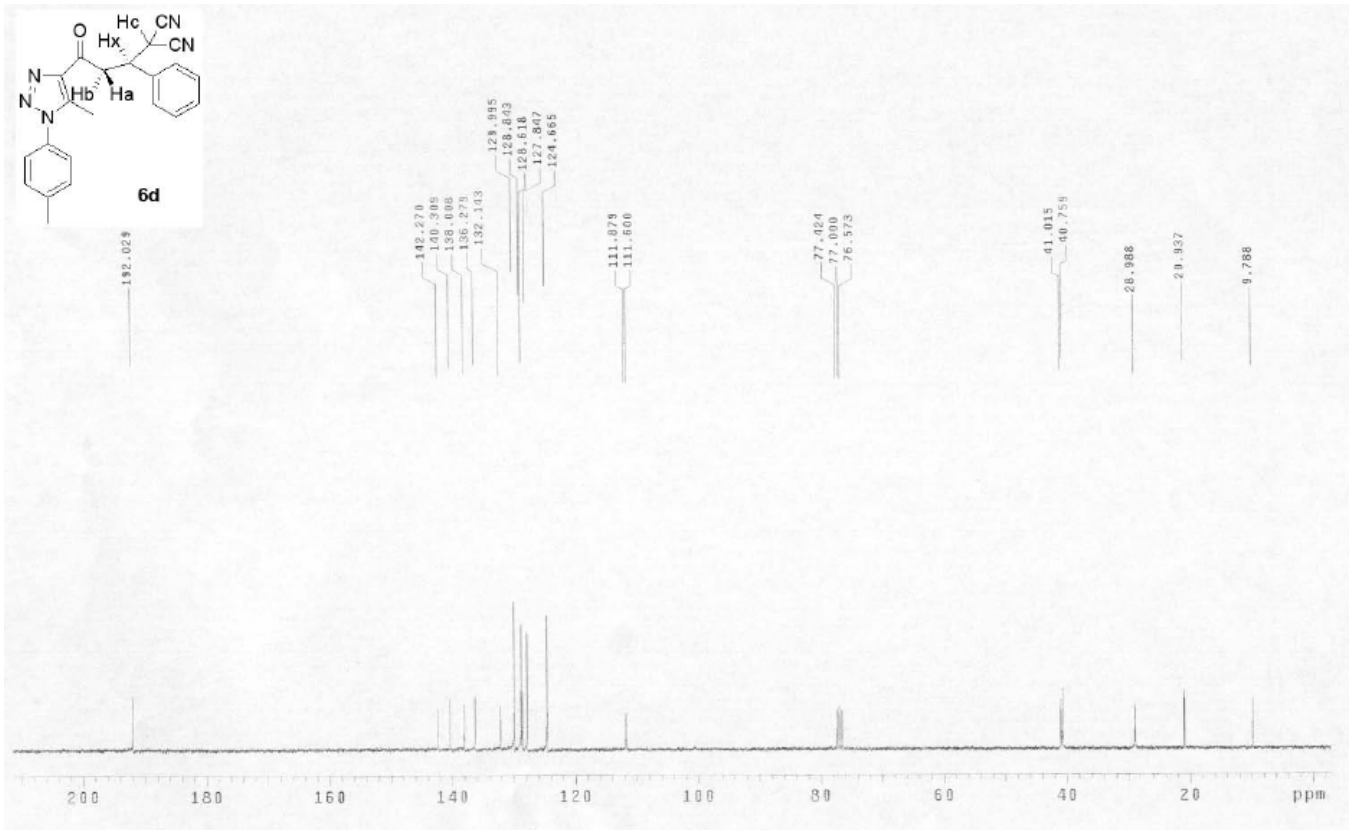
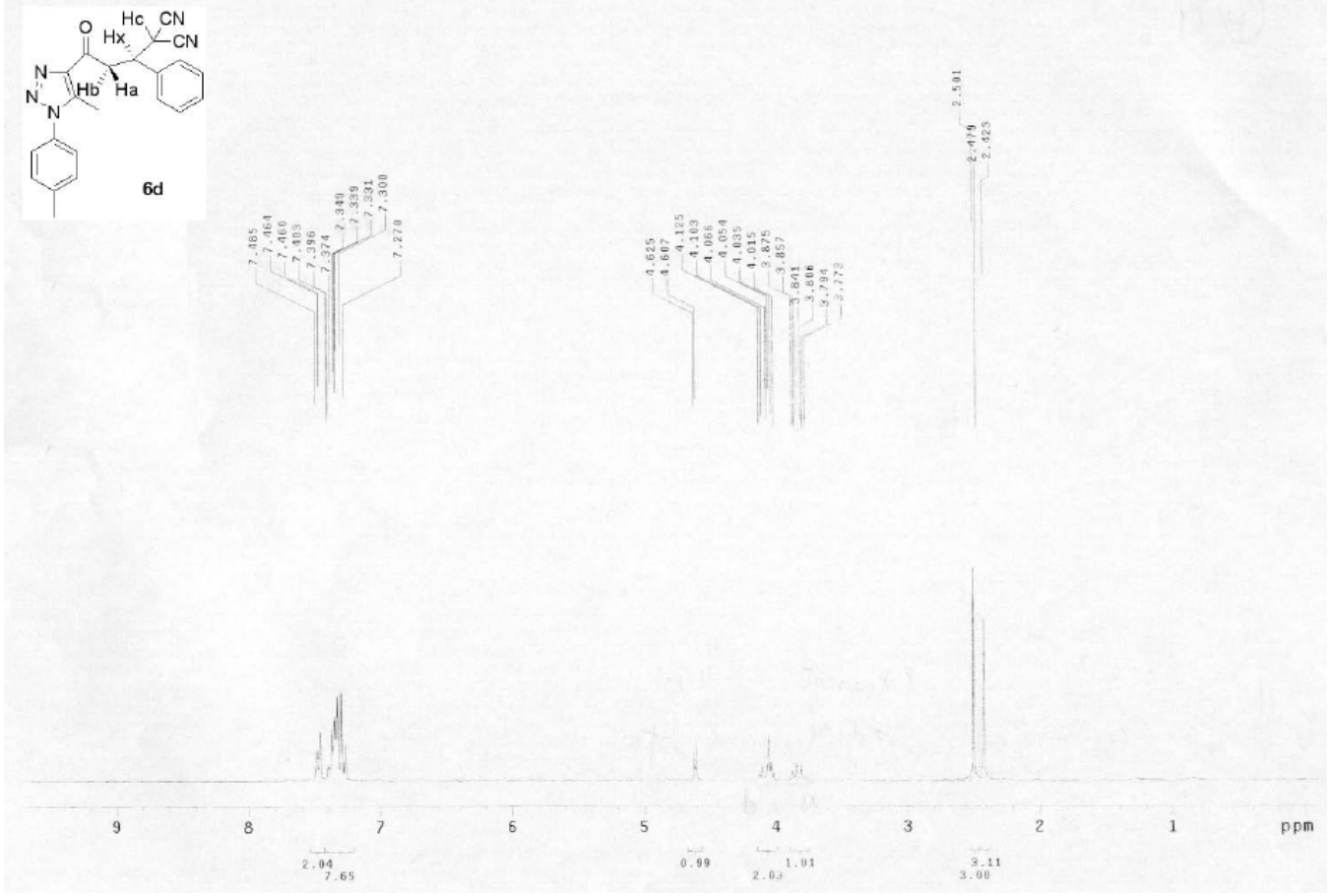
2.323
7.587
7.562
7.550
7.544
7.435
7.429
7.408
7.401
7.374
7.347
7.206
7.181
4.564
4.545
4.095
4.076
4.023
4.015
3.994
3.974
3.867
3.849
3.641
3.830
3.794
3.783
3.777
Hc
CN
CN
Hx
O
N
N
N
Hb
Ha
6b
9
8
7
6
5
4
3
2
1
-0
ppm
2.73
1.86
3.93
0.87
2.31
1.17
3.00
2.96


6c
191.945
142.411
138.267
134.864
134.749
130.232
129.797
129.675
129.598
129.438
129.293
129.026
125.142
125.058
111.718
111.390
77.427
77.000
76.576
41.045
40.463
28.956
10.009
220
200
180
160
140
120
100
80
60
40
20
0
ppm


6c
7.672
7.618
7.659
7.630
7.575
7.569
7.493
7.448
7.437
7.421
7.392
7.364
7.270
4.603
4.590
4.586
4.095
4.074
4.027
3.863
3.832
3.796
3.763
2.603
2.552
0.000
10
9
8
7
6
5
4
3
2
1
ppm
0.15
3.98
0.19
6.91
1.00
0.99
2.02
3.00
0.63


Hc
CN
Hx
CN
O
N
N
N
Hb
Ha
6d
192.029
142.270
140.305
138.088
136.279
132.143
129.985
128.843
128.618
127.847
124.665
111.879
111.600
77.424
77.000
76.573
41.015
40.759
28.988
28.937
9.788
200
180
160
140
120
100
80
60
40
20
ppm


Hc
CN
Hx
CN
O
N
N
N
Hb
Ha
6d
7.485
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7.460
7.403
7.396
7.374
7.349
7.339
7.331
7.300
7.270
4.625
4.607
4.125
4.103
4.066
4.054
4.035
4.015
3.875
3.857
3.841
3.806
3.794
3.773
2.501
2.479
2.423
9
8
7
6
5
4
3
2
1
ppm
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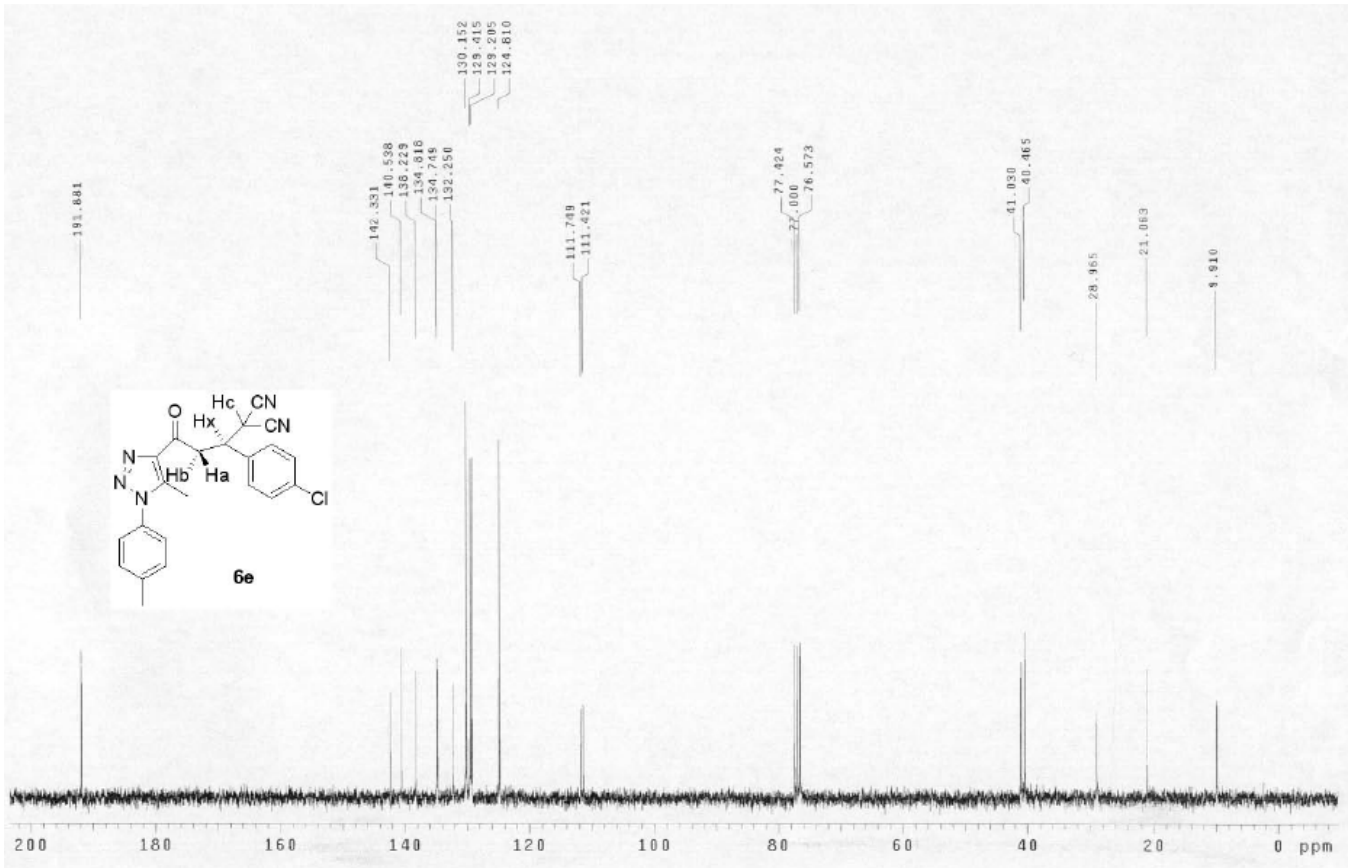
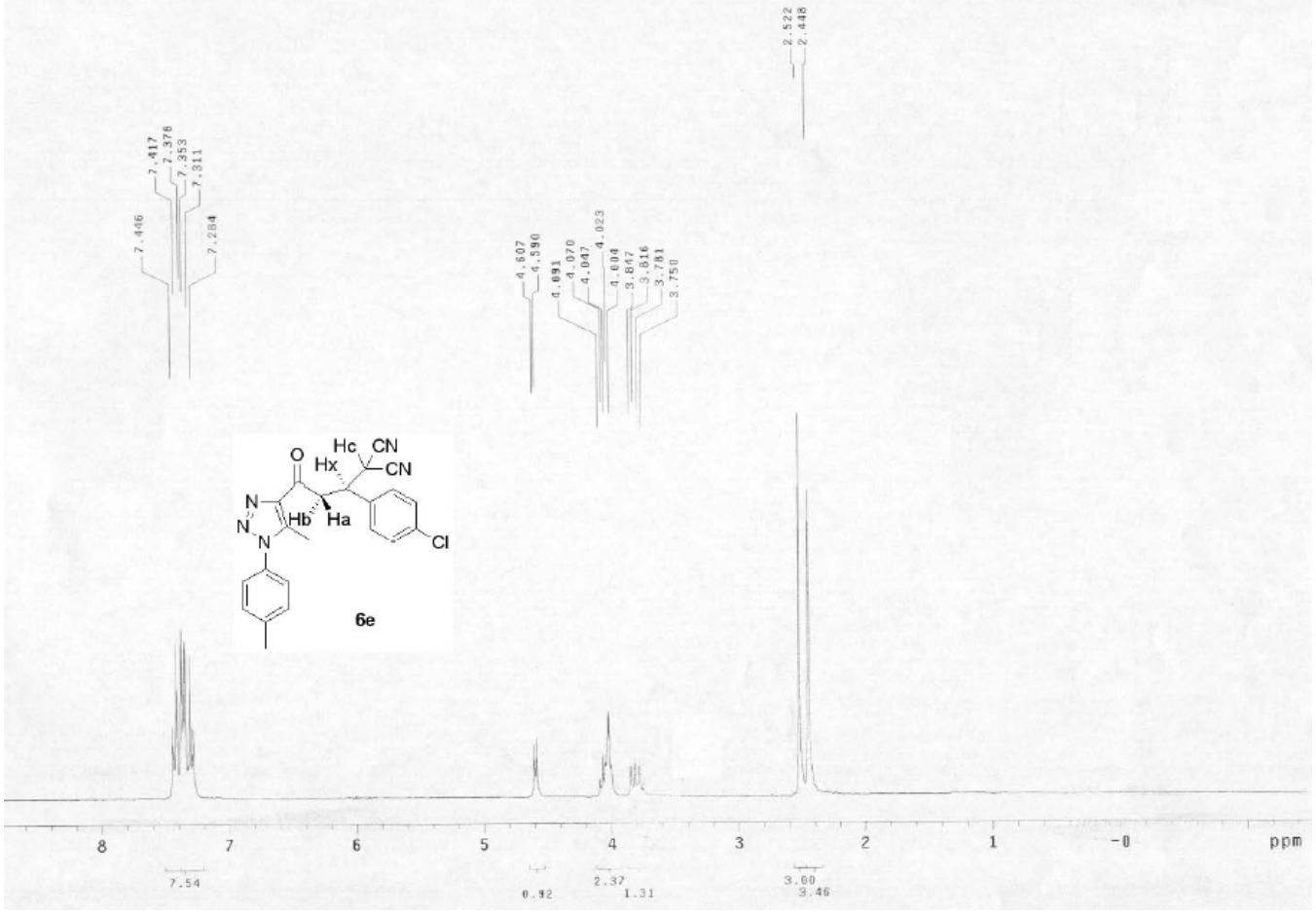
0.99
2.03
1.01
3.11
3.00


191.881
142.331
140.538
138.229
134.816
134.749
132.250
130.152
129.415
129.205
124.610
111.749
111.421
77.424
77.000
76.573
41.030
40.465
28.955
21.063
9.910
Hc
CN
Hx
CN
O
N
N
Hb
Ha
Cl
6e
200
180
160
140
120
100
80
60
40
20
0 ppm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2.448
7.417
7.376
7.353
7.311
7.446
7.284
4.607
4.590
4.691
4.070
4.047
4.023
4.004
3.847
3.816
3.781
3.750
Hc
CN
Hx
CN
O
N
N
Hb
Ha
Cl
6e
8
7
6
5
4
3
2
1
-0
ppm
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0.92
2.37
1.31
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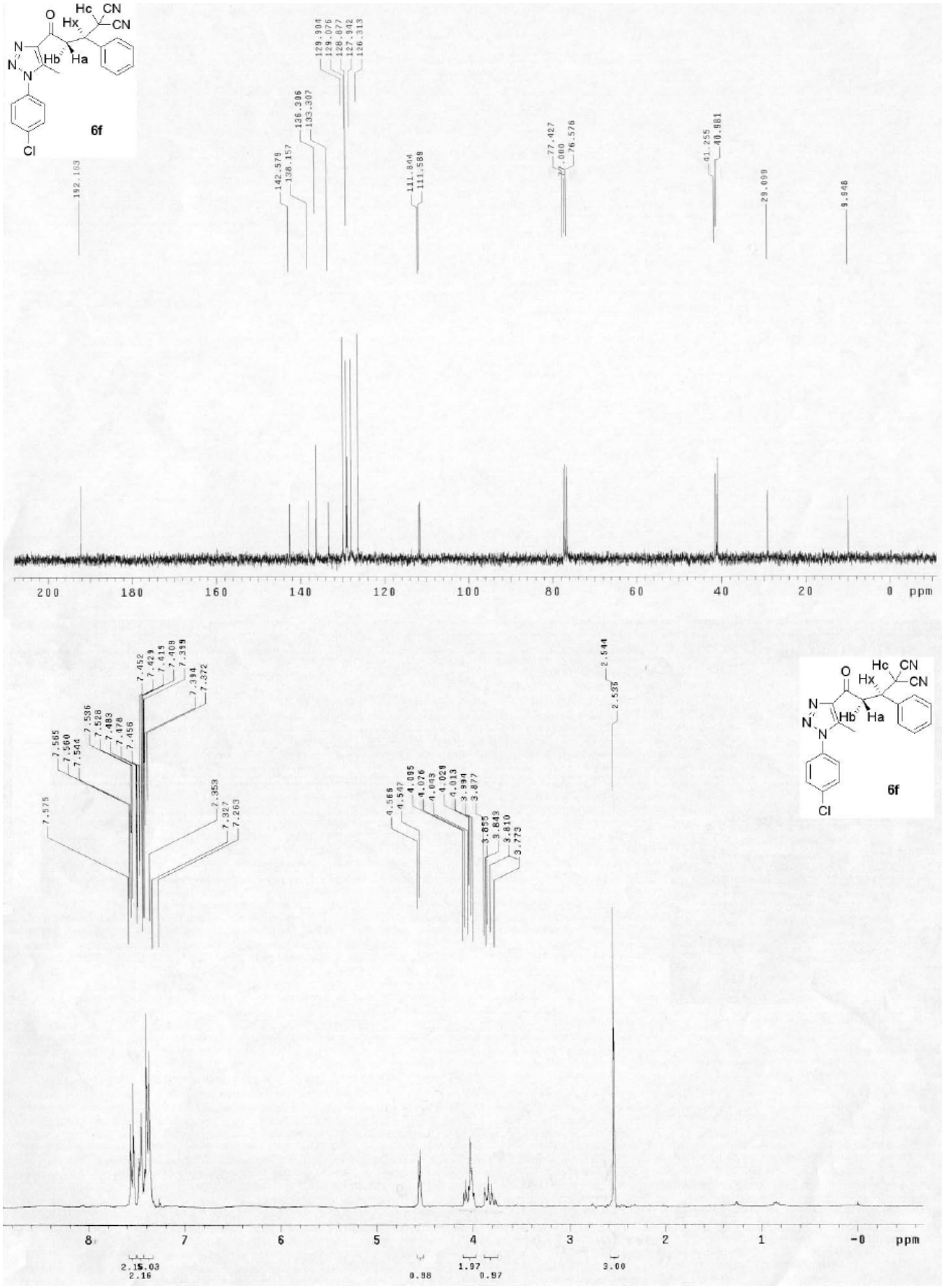
3.46


Hc
CN
CN
O
Hx
N
N
N
Hb
Ha
Cl
6f
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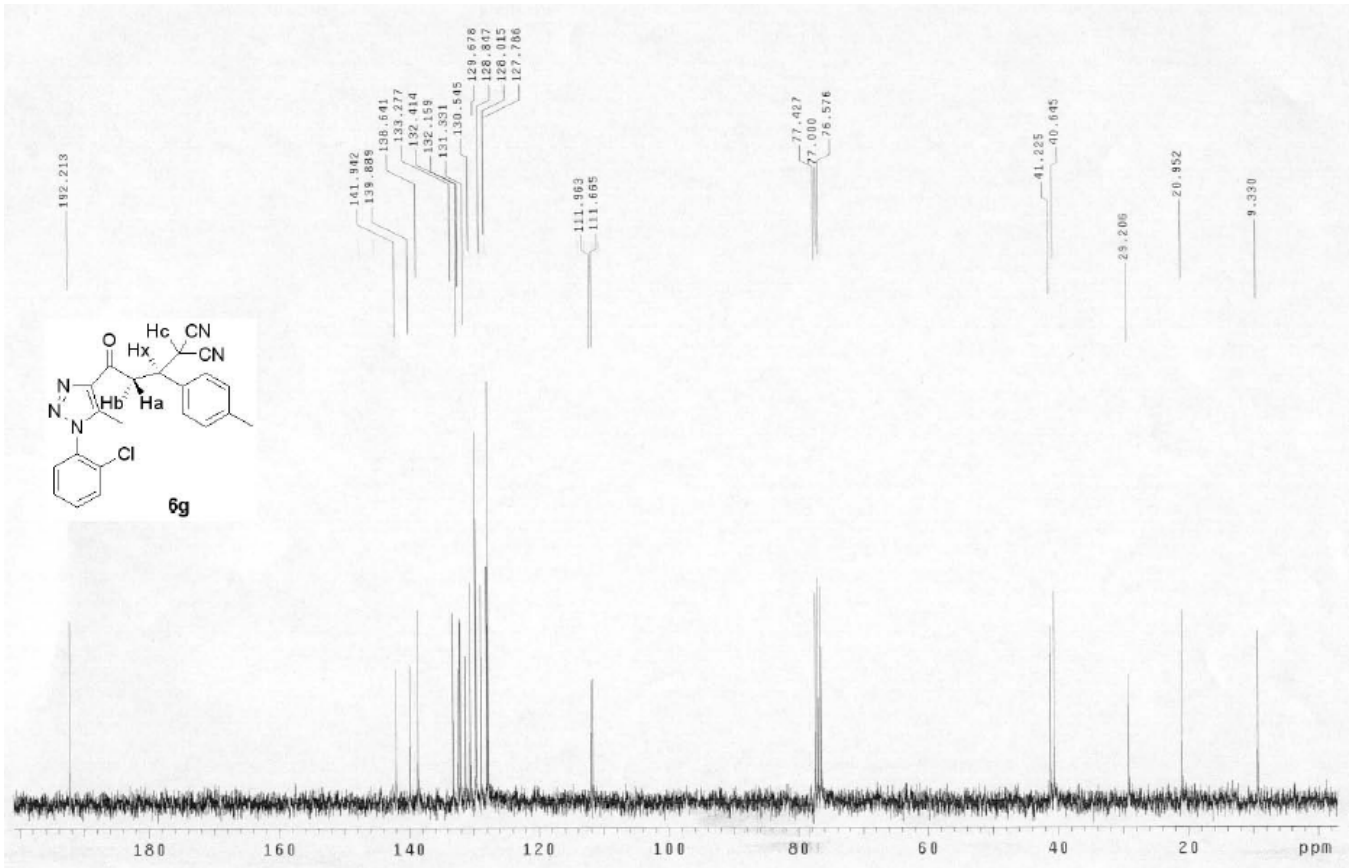
133.307
129.904
129.076
128.877
127.942
126.313
111.844
111.589
77.427
77.000
76.576
41.255
40.881
29.699
9.848
200
180
160
140
120
100
80
60
40
20
0 ppm
7.575
7.565
7.560
7.544
7.536
7.528
7.483
7.478
7.456
7.452
7.429
7.415
7.408
7.399
7.394
7.372
7.353
7.327
7.263
4.566
4.547
4.095
4.076
4.063
4.029
4.013
3.994
3.877
3.855
3.843
3.810
3.773
2.544
2.535
8
7
6
5
4
3
2
1
-0 ppm
2.15
5.03
2.16
0.98
1.97
0.97
3.00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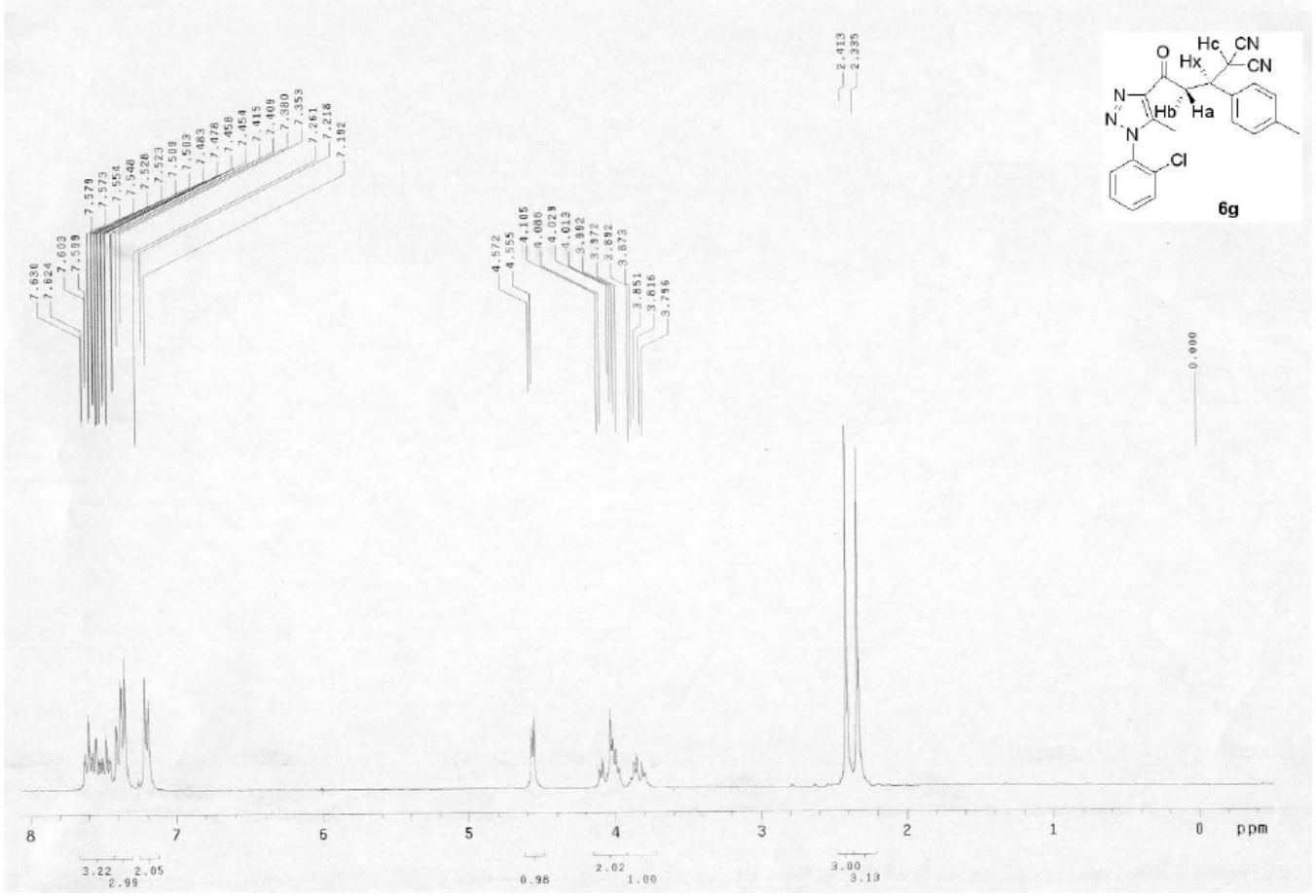
138.641
133.277
132.414
132.159
131.331
130.545
129.678
128.847
126.015
127.706
111.963
111.665
77.427
77.000
76.576
41.225
40.645
29.206
20.952
9.330
Hc
CN
CN
Hx
O
N
N
N
Hb
Ha
Cl
6g
180
160
140
120
100
80
60
40
20
ppm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2.335
7.630
7.624
7.603
7.599
7.579
7.573
7.554
7.540
7.528
7.523
7.509
7.503
7.483
7.478
7.458
7.454
7.415
7.409
7.380
7.353
7.261
7.218
7.192
4.572
4.555
4.105
4.086
4.029
4.013
3.992
3.972
3.892
3.873
3.851
3.816
3.796
0.000
Hc
CN
CN
Hx
O
N
N
N
Hb
Ha
Cl
6g
8
7
6
5
4
3
2
1
0
ppm
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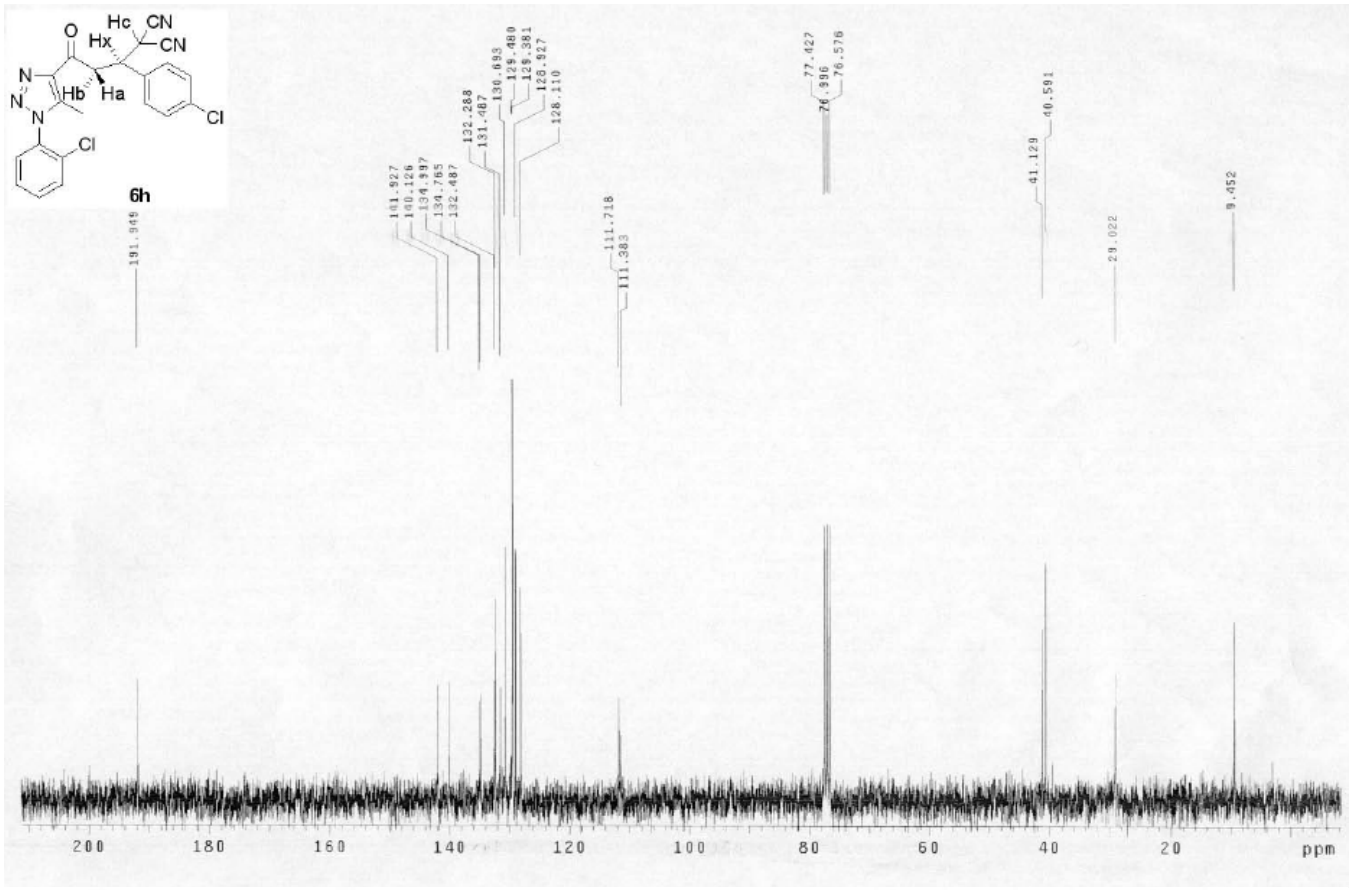
0.98
2.02
1.00
3.00
3.13


Hc
CN
Hx
CN
O
N
N
N
Hb
Ha
Cl
Cl
6h
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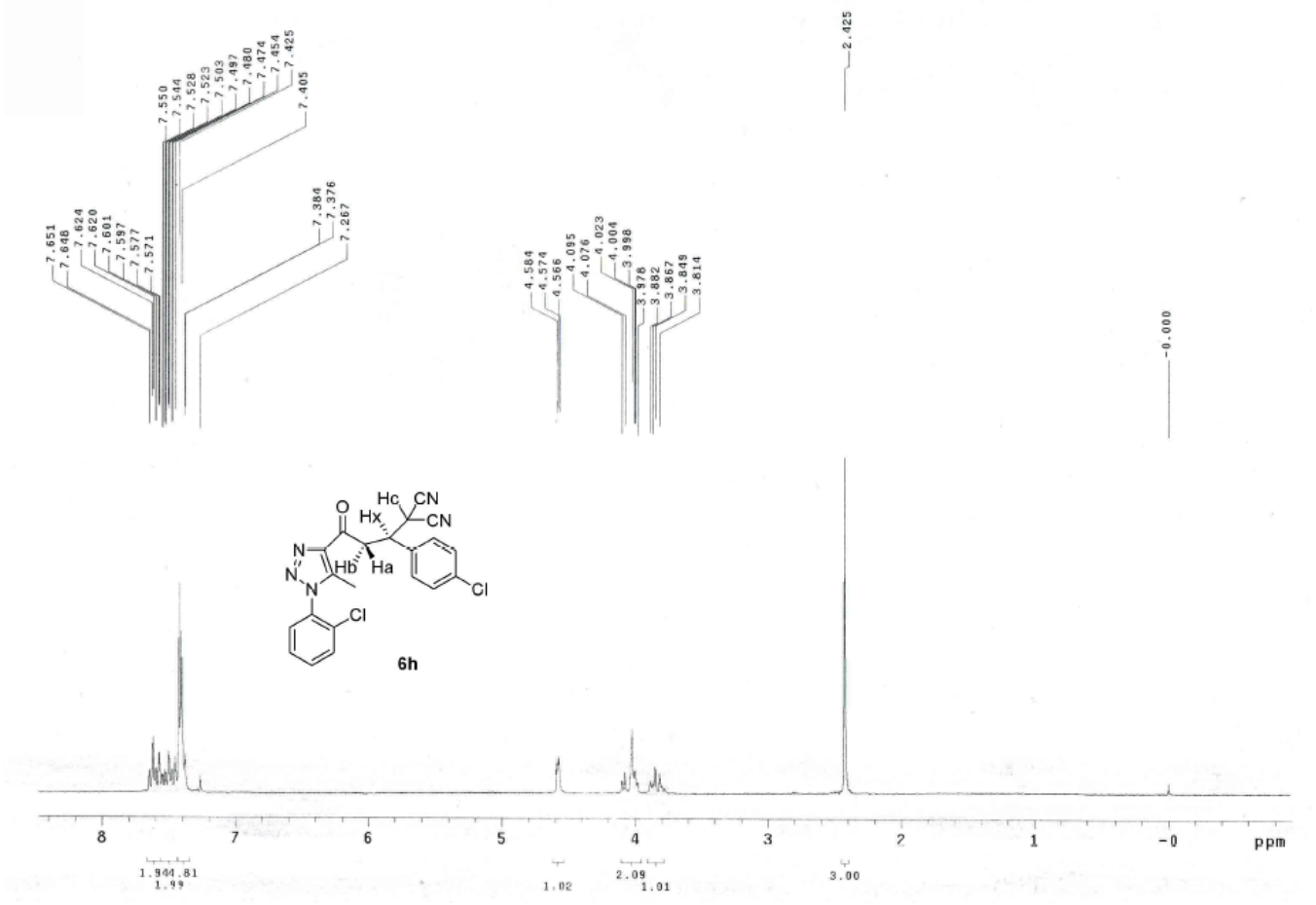
161.927
160.126
134.997
134.765
132.487
132.288
131.487
130.693
129.480
129.381
128.927
128.110
111.718
111.383
77.427
76.996
76.576
41.129
40.591
29.022
9.452
200
180
160
140
120
100
80
60
40
20
ppm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7.648
7.624
7.620
7.601
7.597
7.577
7.571
7.550
7.544
7.528
7.523
7.503
7.497
7.480
7.474
7.454
7.425
7.405
7.384
7.376
7.267
4.584
4.574
4.566
4.095
4.076
4.023
4.004
3.998
3.978
3.882
3.867
3.849
3.814
2.425
-0.000
Hc
CN
Hx
CN
O
N
N
N
Hb
Ha
Cl
Cl
6h
8
7
6
5
4
3
2
1
-0
ppm
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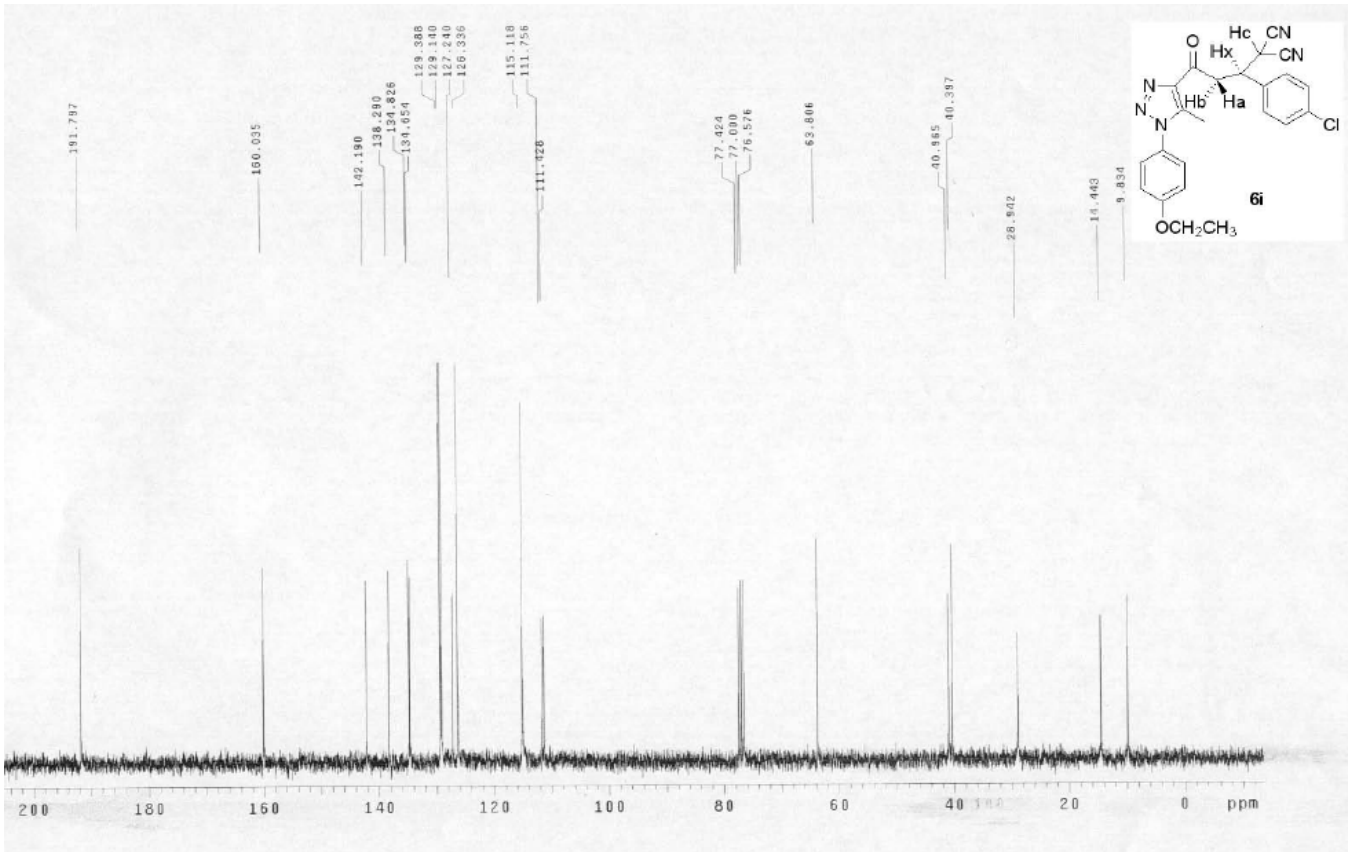
1.01
3.00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160.035
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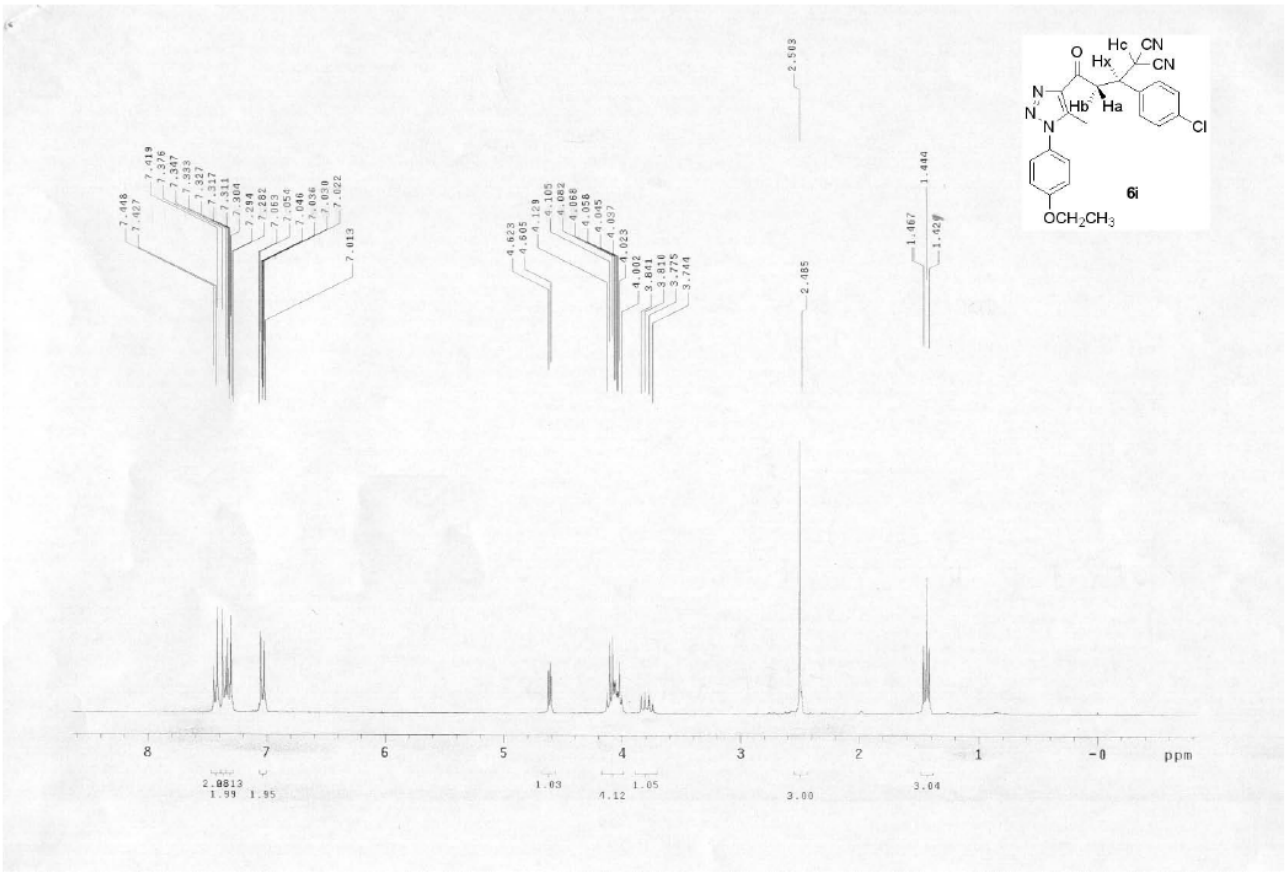
131.654
129.388
129.140
127.240
126.336
115.118
111.756
111.426
77.424
77.000
76.576
63.806
40.965
40.397
28.942
14.443
9.834
Hc
CN
CN
O
Hx
N
N
N
Hb
Ha
Cl
6i
OCH2CH3
200
180
160
140
120
100
80
60
40
20
0
ppm


7.448
7.427
7.419
7.376
7.347
7.333
7.327
7.317
7.311
7.304
7.294
7.282
7.063
7.054
7.046
7.036
7.030
7.022
7.013
4.623
4.605
4.129
4.105
4.082
4.068
4.058
4.045
4.037
4.023
4.002
3.841
3.810
3.775
3.744
2.563
2.485
1.467
1.444
1.429
Hc
CN
CN
O
Hx
N
N
N
Hb
Ha
Cl
6i
OCH2CH3
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7
6
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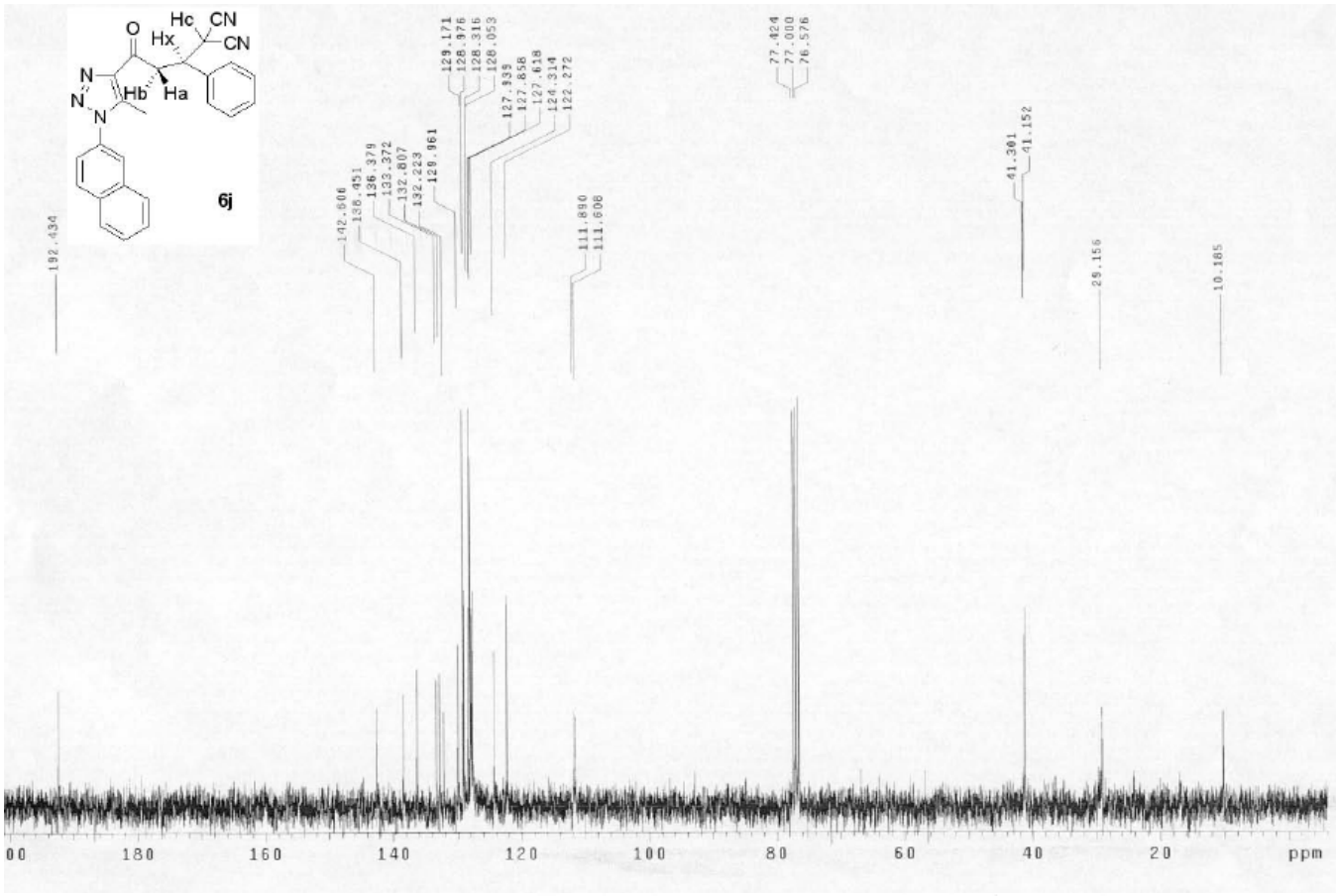
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CN
O
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N
Hb
Ha
6j
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111.608
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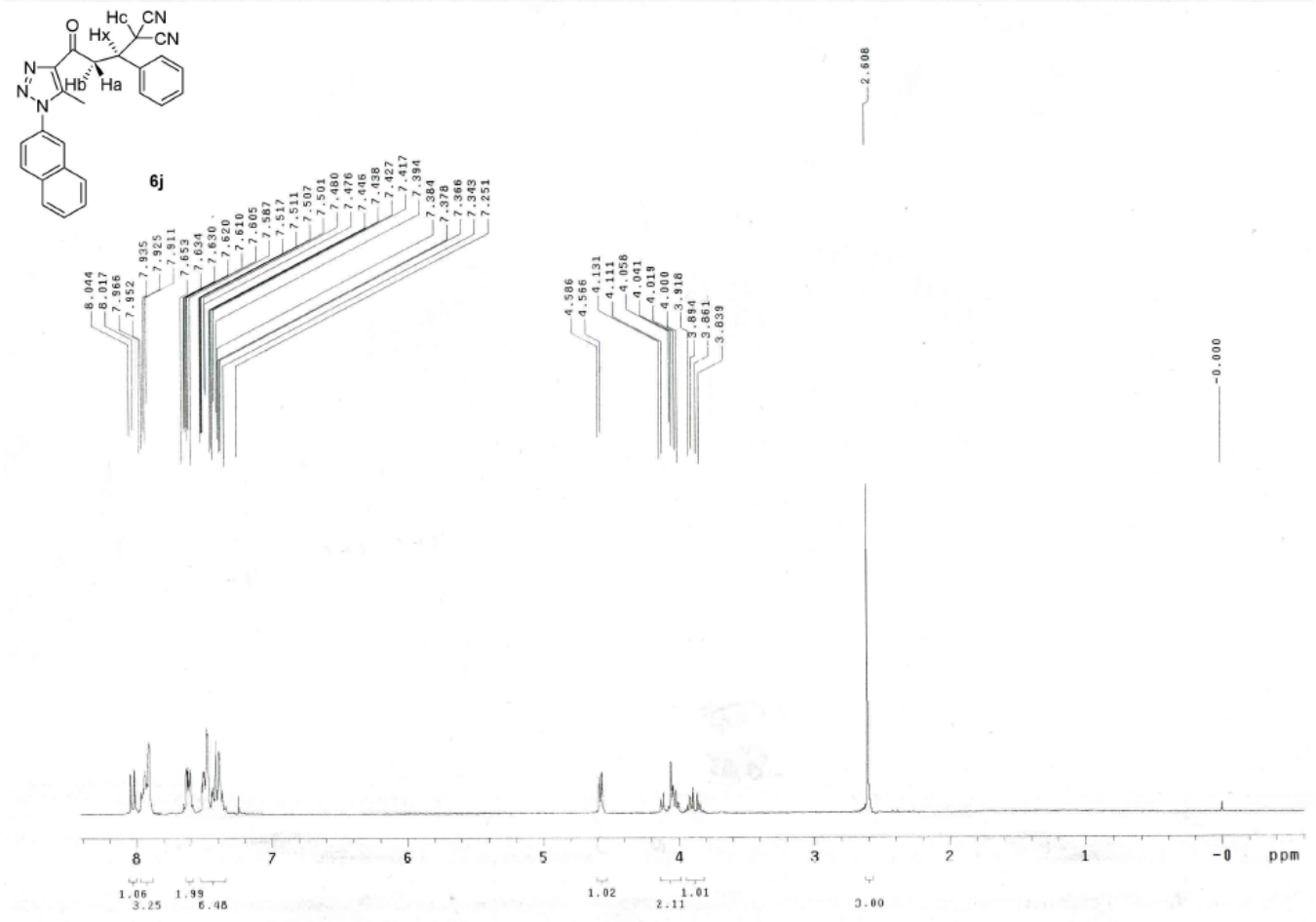
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CN
Hx
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N
Hb
Ha
6j
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7.925
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7.630
7.620
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7.517
7.511
7.507
7.501
7.480
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7.343
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3.894
3.861
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-0.000
8
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6
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4
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-0
ppm
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1.99
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2.11
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