Reaction of Allenyl Esters with Sodium Azide: An Efficient Synthesis of *E*-Vinyl Azides and Polysubstituted Pyrroles

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Supporting Information

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1. Experiment procedures

General. All ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. Reagents in liquid state were purified by distillation and Reagents in solid state used as received without further purification. Petroleum ether refers to the fraction with boiling point in the range 60–90 °C. 1, 2-allenyl esters **1** and **1'** were prepared according to the known method by treatment of the acid chlorides with the corresponding ethyl 2-(triphenylphoranylidene) propionate.[1]

NOTE: there exist potential dangers of using azides on large scale, and the workup involving quenching with ammonium chloride described in this paper can result in ammonium azide or hydrazoic acid which may cause explosion. No hazard evaluation was conducted on the reaction. Therefore special caution should be taken before carrying on the reaction on large scale.

The reaction of 1,2-allenyl esters with NaN_3 at room temperature. Preparation of 2 or 3. Typical procedure. To a solution of NaN_3 (1mmol) in *t*-BuOH/H_2O (v/v=4:1, 2ml), ethyl 4-phenylbuta-2,3-dienoate (0.5mmol) was added at room temperature with stirring. After the reaction was complete (30 min), the reaction was quenched with saturated NH_4Cl and extracted with EtOAc (3×10mL). The organic phase was

washed with saturated brine and dried over $MgSO_4$. After filtration and removal of the solvent in vacuo, the residues were purified with flash chromatography (silica/ Petroleum ether - ethyl acetate 20:1 v/v) to afford 110 mg (95%) of **2a**. *NOTE:* ***E*-2** and ***Z*-2** were inseparable and obtained as mixture; ***E*-3** and ***Z*-3** were obtained respectively.

The reaction of 1-allylic 1,2-allenyl esters with NaN_3 at 65 ^oC. Preparation of 5. Typical procedure.

A solution of 3 mmol of NaN_3, 1 mmol ethyl 2-vinylidenepent-4-enoate in 3 mL of *t*-BuOH was heated to 65 ^oC with stirring. After the reaction was complete (monitored by TLC), the reaction was quenched with saturated NH_4Cl and extracted with EtOAc (3 × 15mL). The organic phase was washed with saturated brine and dried over $MgSO_4$. After filtration and removal of the solvent in vacuo, the residues were purified with flash chromatography (silica/ Petroleum ether - ethyl acetate 6:1 v/v) to afford 152 mg (91%) of **5a**.

Procedure for thermal reaction of *E*-3c to afford 5a.

A solution of 0.5 mmol ***E*-3c** in 1mL *t*-BuOH was heated to 80 ^oC with stiring. After the reaction was complete (3 hours, monitored by TLC), the mixture was directly purified with flash chromatography (silica/ Petroleum ether - ethyl acetate 6:1 v/v) to afford 79mg (95%) of **5a**.

2. Characterization data of key compounds

(*E*)-ethyl 3-azido-4-phenylbut-3-enoate (*E*-2a)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.36-7.23 (m, 5H), 6.41 (s, 1H), 4.24 (q, *J* = 7.6 Hz, 2H), 3.30 (s, 2H), 1.30 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.5, 135.0, 133.0, 128.5, 128.3, 127.2, 118.6, 61.4, 35.9, 14.1. IR (neat): 2982, 2100, 1737, 1666, 1609 cm^{-1}. MS: m/z (%) 231 (M^+, 4), 203 (8), 105 (100). Anal. Calcd for $C_{12}H_{13}N_3O_2$ (231.25): C 62.33, H 5.67, N 18.17. Found: C 62.41, H 5.56, N 18.06.

(*E*)-ethyl 3-azidopent-3-enoate (*E*-2b)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 5.34 (q, *J* = 7.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.09 (s, 2H), 1.69 (d, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.3, 131.0, 112.8, 61.1, 34.4, 14.0, 12.7. IR neat): 2926, 2118, 1740, 1655 cm^{-1}. MS: m/z (%) 169 (M^+, 3), 141 (16), 43 (100). Anal. Calcd for $C_7H_{11}N_3O_2$ (169.18): C 49.70, H 6.55, N 24.84. Found: C 49.59, H 6.46, N 25.01.

(*E*)-ethyl 3-azidohex-3-enoate (*E*-2c)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 5.30 (t, *J* = 7.6 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.10 (s, 2H), 2.15-2.08 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.4, 130.1, 120.1, 61.2, 34.8, 21.0, 14.2, 14.1. IR (neat): 2970, 2100, 1740, 1658 cm^{-1}. MS: m/z (%) 183 (M^+, 2), 155 (18), 41(100). Anal.

Calcd for $C_8H_{13}N_3O_2$ (183.21): C 52.45, H 7.15, N 22.94. Found: C 52.51, H 7.28, N 22.76.

(*E*)-ethyl 3-azido-4-(naphthalen-8-yl)but-3-enoate (*E*-2d)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.97-7.80 (m, 3H), 7.53-7.40 (m, 4H), 6.85 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.23 (s, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.5, 134.5, 133.5, 132.1, 131.9, 128.4, 128.1, 126.7, 126.3, 126.1, 125.4, 124.6, 116.5, 61.3, 35.9, 14.0. IR (neat): 2981, 2103, 1736, 1646 cm^{-1}. MS: m/z (%) 281 (M^+, 1), 253 (36), 180 (100). Anal. Calcd for $C_{16}H_{15}N_3O_2$ (281.31): C 68.31, H 5.37, N 14.94. Found: C 68.18, H 5.31, N 15.06.

(*E*)-ethyl 3-azidooct-3-enoate (*E*-2e)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 5.25 (t, J = 7.6 Hz, 1H), 4.12 (q, J = 7.2 Hz, 2H), 3.06 (s, 2H), 2.07-2.01 (m, 2H), 1.34-1.27 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.3, 130.3, 118.5, 61.0, 34.6, 31.6, 27.1, 22.0, 13.9, 13.7. IR (neat): 2959, 2099, 1741, 1656 cm^{-1}. MS: m/z (%) 212 (M^++1, 1), 180 (76), 41 (100). Anal. Calcd for $C_{10}H_{17}N_3O_2$ (211.26): C 56.85, H 8.11, N 19.89. Found: C 57.03, H 7.98, N 19.78.

(*E*)-ethyl 3-azidoundec-3-enoate (*E*-2f)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 5.27 (t, J = 7.2 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H),

3.08 (s, 2H), 2.08-2.02 (m, 2H), 1.37-1.32 (m, 2H), 1.26-1.23 (m, 11H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.3, 130.3, 118.7, 61.1, 34.7, 31.7, 29.5, 29.0, 28.9, 27.5, 22.5, 13.99, 13.96. IR (neat): 2928, 2102, 1742, 1657 cm^{-1}. MS: m/z (%) 254 (M^++1, 2), 226 (100). Anal. Calcd for $C_{13}H_{23}N_3O_2$ (253.34): C 61.63, H 9.15, N 16.59. Found: C 61.71, H 9.31, N 16.46.

(*E*)-ethyl 3-azidobut-2-enoate (*E*-3a)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 5.50 (s, 1H), 4.14 (q, J = 6.8 Hz, 2H), 2.32 (s, 3H), 1.26 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 154.6, 105.1, 59.9, 16.2, 14.2. IR (neat): 2983, 2098, 1713, 1628 cm^{-1}. MS: m/z (%) 155 (M^+, 6), 127 (9), 43 (100). Anal. Calcd for $C_6H_9N_3O_2$ (155.15): C 46.45, H 5.85, N 27.08. Found: C 46.61, H 5.78, N 26.96.

(*E*)-ethyl 3-azido-2-methylbut-2-enoate (*E*-3b)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 4.17 (q, J = 7.2 Hz, 2H), 2.4 (d, J = 1.4 Hz, 3H), 1.8 (d, J = 1.4 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.0, 143.9, 114.5, 60.3, 16.0, 14.2, 13.9. IR (neat): 2118, 1724, 1665 cm^{-1}. MS: m/z (%) 169 (M^+, 16), 141 (18), 43 (100). Anal. Calcd for $C_7H_{11}N_3O_2$ (169.18): C 49.70, H 6.55, N 24.84. Found: C 49.63, H 6.69, N 25.01.

(*E*)-ethyl 2-(1-azidoethylidene)pent-4-enoate (*E*-3c)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 5.81-5.71 (m, 1H), 4.96-5.03 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.09 (d, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 167.4, 144.7, 135.6, 117.0, 115.1, 60.3, 32.2, 16.1, 14.1. IR (neat): 2982, 2119, 1704, 1619, 1280 cm^{-1}. MS: m/z (%) 195 (M^+, 1), 167 (15), 43 (100). Anal. Calcd for $C_9H_{13}N_3O_2$ (195.22): C 55.37, H 6.71, N 21.52. Found: C 55.45, H 6.85, N 21.66.

(*E*)-ethyl 3-azido-2-benzylbut-2-enoate (*E*-3d)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.25-7.15 (m, 5H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 2H), 2.48 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 167.4, 145.1, 140.2, 128.4, 128.1, 125.9, 118.3, 60.4, 33.6, 16.2, 14.1. IR (neat): 2982, 2118, 1705, 1618, 1280 cm^{-1}. MS: m/z (%) 246 (M^++1, 4), 245 (M^+, 1), 218 (100). Anal. Calcd for $C_{13}H_{15}N_3O_2$ (245.28): C 63.66, H 6.16, N 17.13. Found: C 63.53, H 6.25, N 17.29.

(*Z*)-ethyl 3-azido-2-benzylbut-2-enoate (*Z*-3d)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.27-7.15 (m, 5H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 2H), 2.13 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.9, 139.7, 138.9, 128.5, 128.0, 126.3, 117.8, 60.6, 35.2, 15.9, 14.1. IR (neat): 2968, 2101, 1715, 1619, 1278 cm^{-1}. MS: m/z (%) 246 (M^++1, 4), 245 (M^+, 1), 218 (100).

(*E*)-ethyl 2-(1-azidoethylidene)-4-methylpent-4-enoate (*E*-3e)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 4.68 (s, 1H), 4.56 (s, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.05 (s, 2H), 2.43 (s, 3H), 1.70 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 167.6, 144.4, 143.5, 117.5, 110.0, 60.3, 35.7, 22.7, 16.0, 14.1. IR (neat): 2980, 2118, 1705, 1621, 1288 cm^{-1}. MS: m/z (%) 209 (M^+, 2), 181 (19), 43 (100). Anal. Calcd for $C_{10}H_{15}N_3O_2$ (209.24): C 57.40, H 7.23, N 20.08. Found: C 57.53, H 7.35, N 19.93.

(E)-ethyl 2-(1-(4-phenyl-1H-1,2,3-triazol-1-yl)ethylidene)pent-4-enoate (4a)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (s, 1H), 7.86-7.84 (m, 2H), 7.47-7.43 (m, 2H), 7.38-7.36 (m, 1H), 5.88-5.78 (m, 1H), 5.12-5.04 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.99-2.97 (m, 2H), 2.54 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 147.3, 139.8, 134.3, 129.9, 128.9, 128.6, 128.4, 125.7, 119.9, 116.9, 61.4, 33.8, 21.2, 14.1. IR (neat): 3137, 2924, 1722, 1647 cm^{-1}. MS: m/z (%) 298 (M^++1, 18), 240 (77), 117 (100). Anal. Calcd for $C_{17}H_{19}N_3O_2$ (297.35): C 68.67, H 6.44, N 14.13. Found: C 68.61, H 5.36, N 14.25.

(E)-ethyl 3-(4-phenyl-1H-1,2,3-triazol-1-yl)undec-3-enoate (4b)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (s, 1H), 7.85-7.83 (m, 2H), 7.42-7.38 (m, 2H), 7.33-7.30 (m, 1H), 6.09 (t, *J* = 7.6 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 2H),

2.26-2.21 (m, 2H), 1.52-1.45 (m, 2H), 1.34-1.25 (m, 8H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.2, 147.3, 130.3, 129.8, 128.7, 128.1, 125.8, 125.6, 117.8, 61.2, 34.5, 31.6, 29.1, 29.0, 28.9, 27.4, 22.5, 14.0, 13.9. IR (neat): 3141, 2928, 1741, 1460 cm^{-1}. MS: m/z (%) 356 (M^++1, 7), 327 (39), 81 (100). Anal. Calcd for $C_{21}H_{29}N_3O_2$ (355.47): C 70.95, H 8.22, N 11.82. Found: C 70.81, H 8.30, N 11.85.

ethyl 1-[(E)-1-(ethoxycarbonyl)-3-(naphthalen-1-yl)prop-2-en-2-yl]-1H-1,2,3-triazole-4-carboxylate (4c)

oil. ^{1}H NMR (400 MHz, $CDCl_3$): 8.58 (s, 1H), 7.92-7.87 (m, 3H), 7.65 (s, 1H), 7.54-7.48 (m, 4H), 4.44 (q, *J* = 7.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 2H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 169.0, 160.5, 140.1, 133.4, 132.2, 131.6, 130.2, 129.3, 128.6, 126.8, 126.5, 126.4, 125.9, 125.3, 124.3, 124.0, 61.5, 61.4, 35.7, 14.2, 13.9. IR (neat): 3141, 2982, 1736, 1591 cm^{-1}. MS: m/z (%) 379 (M^+, 9), 351 (12), 165 (100). Anal. Calcd for $C_{21}H_{21}N_3O_4$ (379.41): C 66.48, H 5.58, N 11.08. Found: C 66.41, H 5.53, N 11.15.

ethyl 2,5-dimethyl-1H-pyrrole-3-carboxylate (5a)[2, 3]

m.p. 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (br, 1H), 6.20 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.48 (s, 3H), 2.19 (s, 3H), 1.33 (t, *J* =7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.9, 134.2, 125.6, 111.5, 107.4, 59.2, 14.5, 13.1, 12.6.

ethyl 2-ethyl-5-methyl-1H-pyrrole-3-carboxylate (5b)[4]

m.p. 54-56°C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (br, 1H), 6.20 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.94 (q, *J* =7.6 Hz, 2H), 2.21 (s, 3H), 1.32 (t, *J* =7.2 Hz, 3H), 1.23 (t, *J* =7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.6, 140.1, 125.5, 110.8, 107.5, 59.2, 20.5, 14.5, 13.6, 12.6. IR (neat): 3320, 1671, 1463, 1223, 1096 cm^{-1}.

ethyl 5-ethyl-2-methyl-1H-pyrrole-3-carboxylate (5c)

Low melting point solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (br, 1H), 6.23 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.54 (q, *J* =7.6 Hz, 2H), 2.49 (s, 3H), 1.33 (t, *J* =7.2 Hz, 3H), 1.22 (t, *J* =7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 134.1, 132.1, 111.4, 105.8, 59.2, 20.4, 14.5, 13.3, 13.1. IR (neat): 3294, 1664, 1459, 1245, 1096 cm^{-1}. MS: m/z (%) 181 (M^+, 83), 152 (100). Anal. Calcd for $C_{10}H_{15}NO_2$ (181.23): C 66.27, H 8.34, N 7.73. Found: C 66.16, H 8.42, 7.83.

ethyl 5-methyl-2-propyl-1H-pyrrole-3-carboxylate (5d)[3, 4]

m.p. 72-74 °C . ^{1}H NMR (400 MHz, $CDCl_3$): 8.12 (br, 1H), 6.20 (m, 1H), 4.24 (q, *J* =7.2 Hz, 2H), 2.86 (t, *J* =7.6 Hz, 2H), 2.20 (s, 3H), 1.68-1.59 (m, 2H), 1.32 (t, *J* =7.2 Hz, 3H), 0.94 (t, *J* =7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.7, 138.9, 125.5, 111.1, 107.5, 59.1, 29.2, 22.9, 14.4, 13.9, 12.6.

ethyl 5-methyl-2-octyl-1H-pyrrole-3-carboxylate (5e)

Low melting point solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 (br, 1H), 6.20 (m, 1H), 4.24 (q, *J* =7.2 Hz, 2H), 2.88 (t, *J* =8.0 Hz, 2H), 2.20 (s, 3H), 1.62-1.58 (m, 2H), 1.34-1.26 (m, 10H), 1.32 (t, *J* =7.2 Hz, 3H), 0.87 (t, *J* =6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.6, 139.1, 125.5, 111.1, 107.5, 59.1, 31.8, 29.6, 29.5, 29.4, 29.2, 27.3, 22.6, 14.5, 14.1, 12.6. IR (neat): 3315, 1671, 1462, 1223, 1084 cm^{-1}. MS: m/z (%) 265 (M^+, 29), 166 (86), 69 (100). Anal. Calcd for $C_{16}H_{27}NO_2$ (265.39): C 72.41, H 10.25, N 5.28. Found: C 72.29, H 10.33, N 5.37.

ethyl 5-isopropyl-2-methyl-1H-pyrrole-3-carboxylate (5f)

Low melting point solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (br, 1H), 6.22 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.86-2.79 (m, 1H), 2.49 (s, 3H), 1.33 (t, *J* =7.2 Hz, 3H), 1.23 (d, *J* =7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 136.8, 134.0, 111.2, 104.5, 59.2, 26.7, 22.4, 14.5, 13.2. IR (neat): 3320, 1671, 1446, 1238, 1097 cm^{-1}. MS: m/z (%) 195 (M^+, 54), 180 (100). Anal. Calcd for $C_{11}H_{17}NO_2$ (195.26): C 67.66, H 8.78, N 7.17. Found: C 67.57, H 8.91, N 7.25.

ethyl 4,5,6,7-tetrahydro-2-methyl-1H-indole-3-carboxylate (5g)[5]

m.p. 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.25 (br, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.71-2.68 (m, 2H), 2.48 (m, 5H), 1.76-1.74 (m, 4H), 1.33 (t, *J* =7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 134.2, 125.4, 118.4, 109.3, 58.9, 23.4, 23.2, 22.9, 22.3, 14.5, 13.5.

(Z)-ethyl 4,7,8,9-tetrahydro-2-methyl-1H-cycloocta[b]pyrrole-3-carboxylate (5h)

m.p. 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (br, 1H), 5.99-5.92 (m, 1H), 5.47-5.54 (m, 1H), 4.26 (q, *J* =7.2 Hz, 2H), 3.57 (d, *J* =6.4 Hz, 2H), 2.67 (t, *J* =6.4 Hz, 2H), 2.44 (s, 3H), 2.21-2.16 (m, 2H), 1.57-1.51 (m, 2H), 1.34 (t, *J* =7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 132.5, 130.2, 128.8, 125.3, 120.6, 110.8, 59.0, 25.6, 25.5, 25.1, 25.0, 14.5, 14.0. IR (KBr): 3278, 1657, 1478, 1443, 1165 cm^{-1}. MS: m/z (%) 233 (M^+, 57), 166 (100). Anal. Calcd for $C_{14}H_{19}NO_2$ (233.31): C 72.07, H 8.21, N 6.00. Found: C 71.95, H 8.29, 6.05.

ethyl 5-butyl-2-methyl-1H-pyrrole-3-carboxylate (5k)

Low melting point solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (br, 1H), 6.22 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.51 (t, *J* =7.2 Hz, 2H), 2.49 (s, 3H), 1.61-1.53 (m, 2H), 1.39-1.32 (m, 2H), 1.33 (t, *J* =7.2 Hz, 3H), 0.92 (t, *J* =7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 134.0, 130.7, 111.5, 106.5, 59.2, 31.4, 27.0, 22.3, 14.5, 13.8, 13.2. IR (neat): 3324, 1669, 1446, 1232, 1095 cm^{-1}. MS: m/z (%) 209 (M^+, 41), 166 (100). Anal. Calcd for $C_{12}H_{19}NO_2$ (209.28): C 68.87, H 9.15, N 6.69. Found: C 69.01, H 9.30, N 6.75.

ethyl 5-hexyl-2-methyl-1H-pyrrole-3-carboxylate (5l)[6]

m.p. 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.00 (br, 1H), 6.21 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.50 (t, *J* =7.6 Hz, 2H), 2.48 (s, 3H), 1.62-1.54 (m, 2H), 1.34-1.28 (m, 6H), 1.33 (t, *J* =7.2 Hz, 3H), 0.88 (t, *J* =7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 134.0, 130.8, 111.5, 106.5, 59.2, 31.6, 29.3, 28.9, 27.3, 22.5, 14.5, 14.0, 13.2.

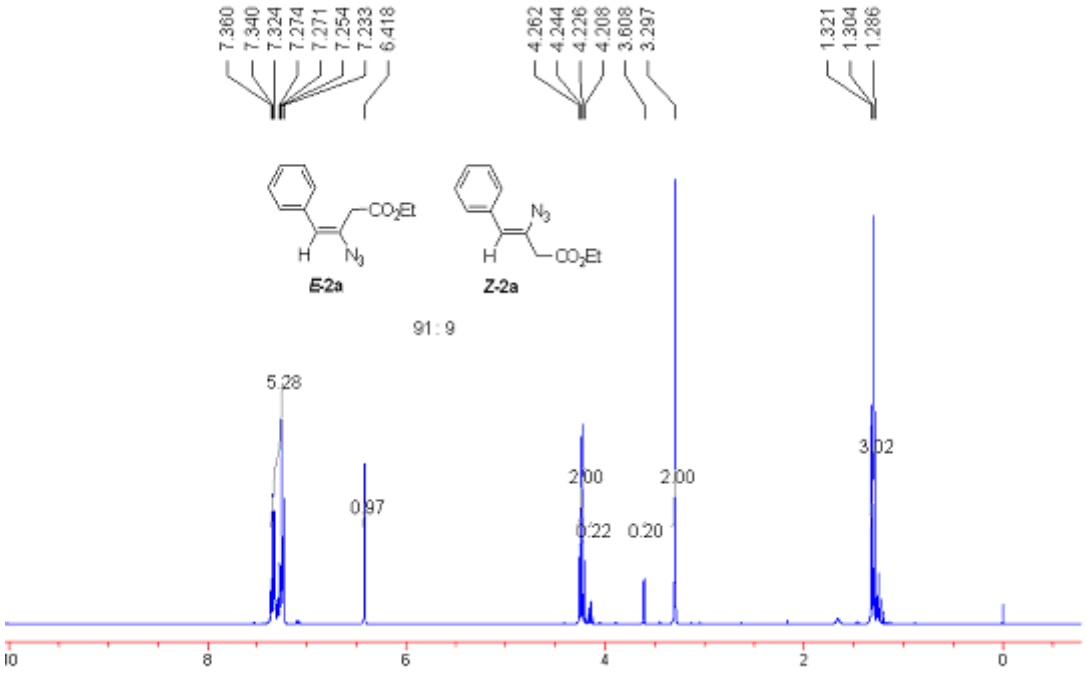
ethyl 2-methyl-5-(6-methylhept-5-en-2-yl)-1H-pyrrole-3-carboxylate (5m)

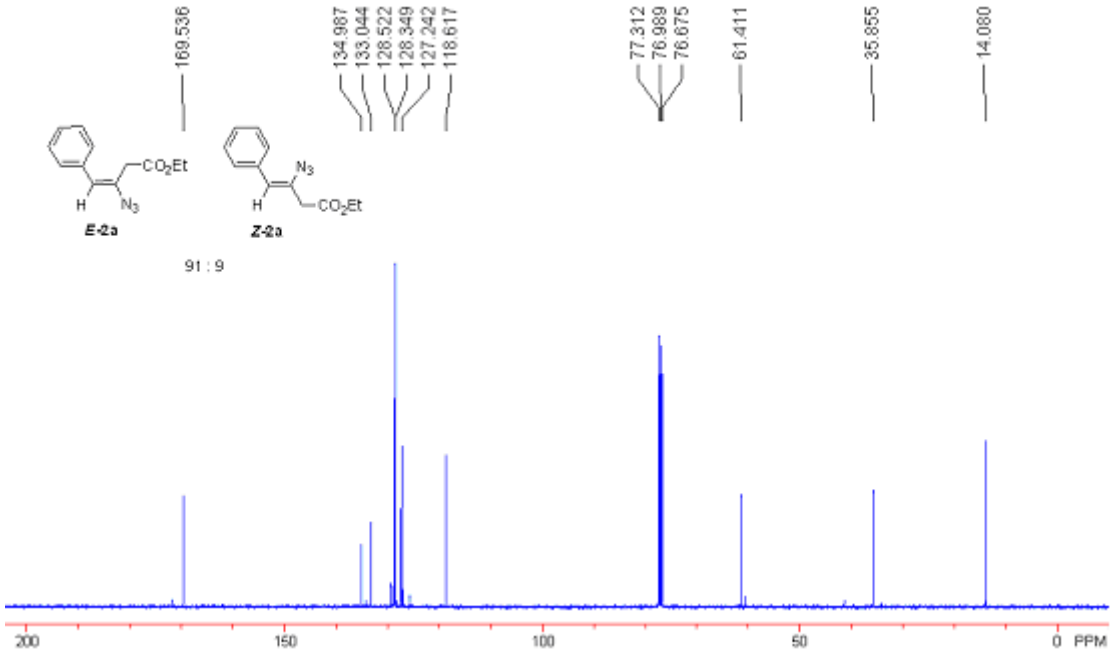
Low melting point solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (br, 1H), 6.22 (m, 1H), 5.09-5.06 (m, 1H), 4.25 (q, *J* =7.2 Hz, 2H), 2.69-2.63 (m, 1H), 2.48 (s, 3H), 1.98-1.92 (m, 2H), 1.68 (s, 3H), 1.56 (s, 3H), 1.62-1.48 (m, 2H), 1.33 (t, *J* =7.2 Hz, 3H), 1.21 (d, *J* =6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 135.6, 133.8, 131.8, 124.1, 111.3, 105.3, 59.2, 37.2, 31.7, 25.68, 25.65, 20.4, 17.7, 14.5, 13.2. IR (neat): 3316, 1670, 1449, 1233, 1091 cm^{-1}. MS: m/z (%) 263 (M^{+}, 37), 180 (97), 108 (100). Anal. Calcd for $C_{16}H_{25}NO_2$ (263.38): C 72.96, H 9.57, N 5.32. Found: C 72.91, H 9.68, N 5.41.

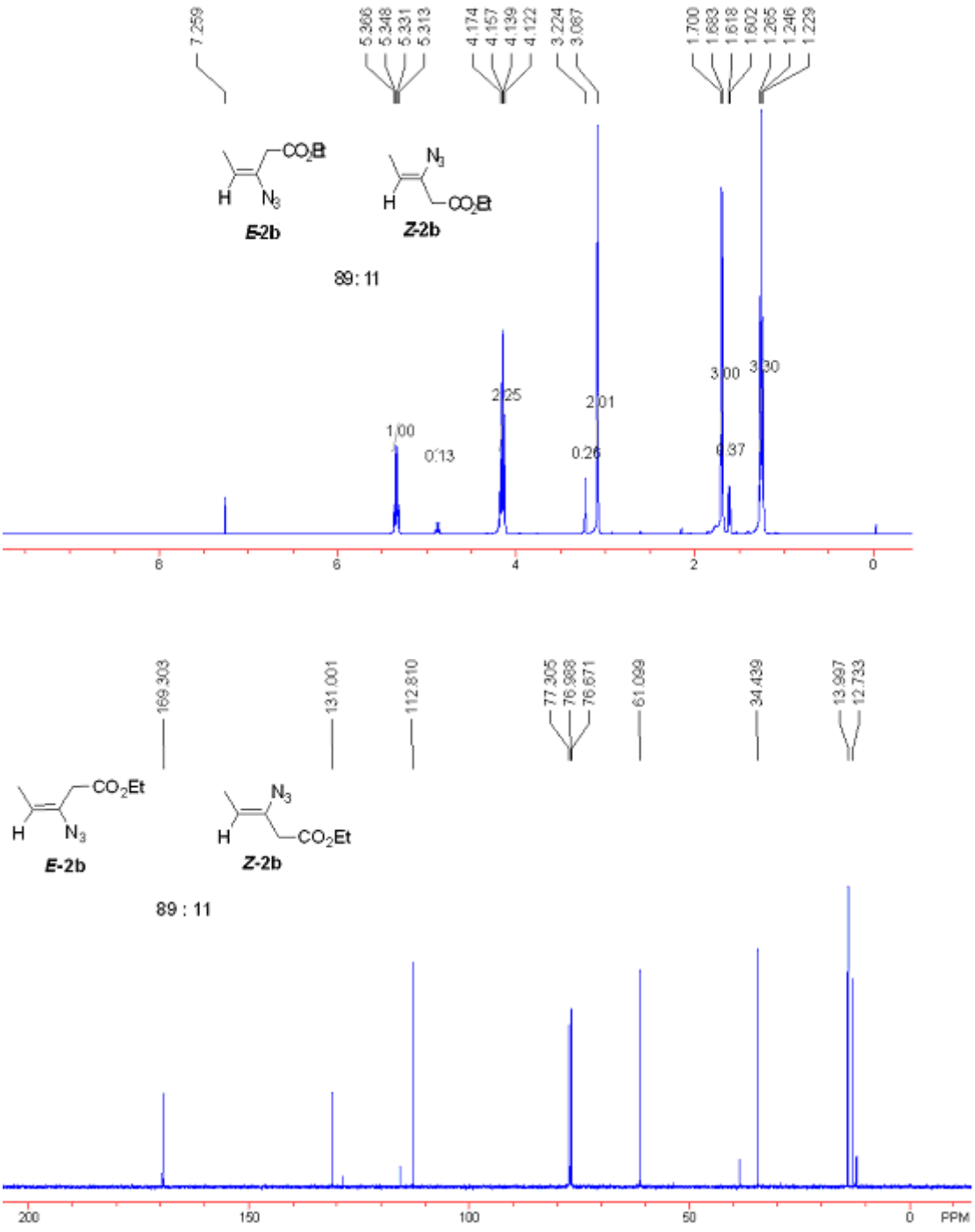
Reference:

1. Lang, R. W.; Hansen, H.-J. *Org. Synth.* **1984**, *62*, 202.
2. Alberola A.; Ortega A. G., Sádaba M. L.; Sañudo C. *Tetrahedron* **1999**, 55, 6555.
3. Yu, M.; Pagenkopf, B. L. *Org. Lett.* **2003**, **5**, 5099.
4. Roomi, M. W.; Macdonald, S. F. *Can. J. of Chem.* **1970**, 48, 1689.
5. Chiu P.-K.; Sannes M. P. *Tetrahedron* **1990**, 46, 3439.
6. Araki S.; Tanaka T.; Toumatsu S.; Hirashita T. *Org. Biomol. Chem.* **2003**, 1, 4025.

3. ^{1}H NMR and ^{13}C NMR spectra of key compounds



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1.265
1.246
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H
N3
E-2b
N3
H
CO2Et
Z-2b
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0.13
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0.26
3.00
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0.37
8
6
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2
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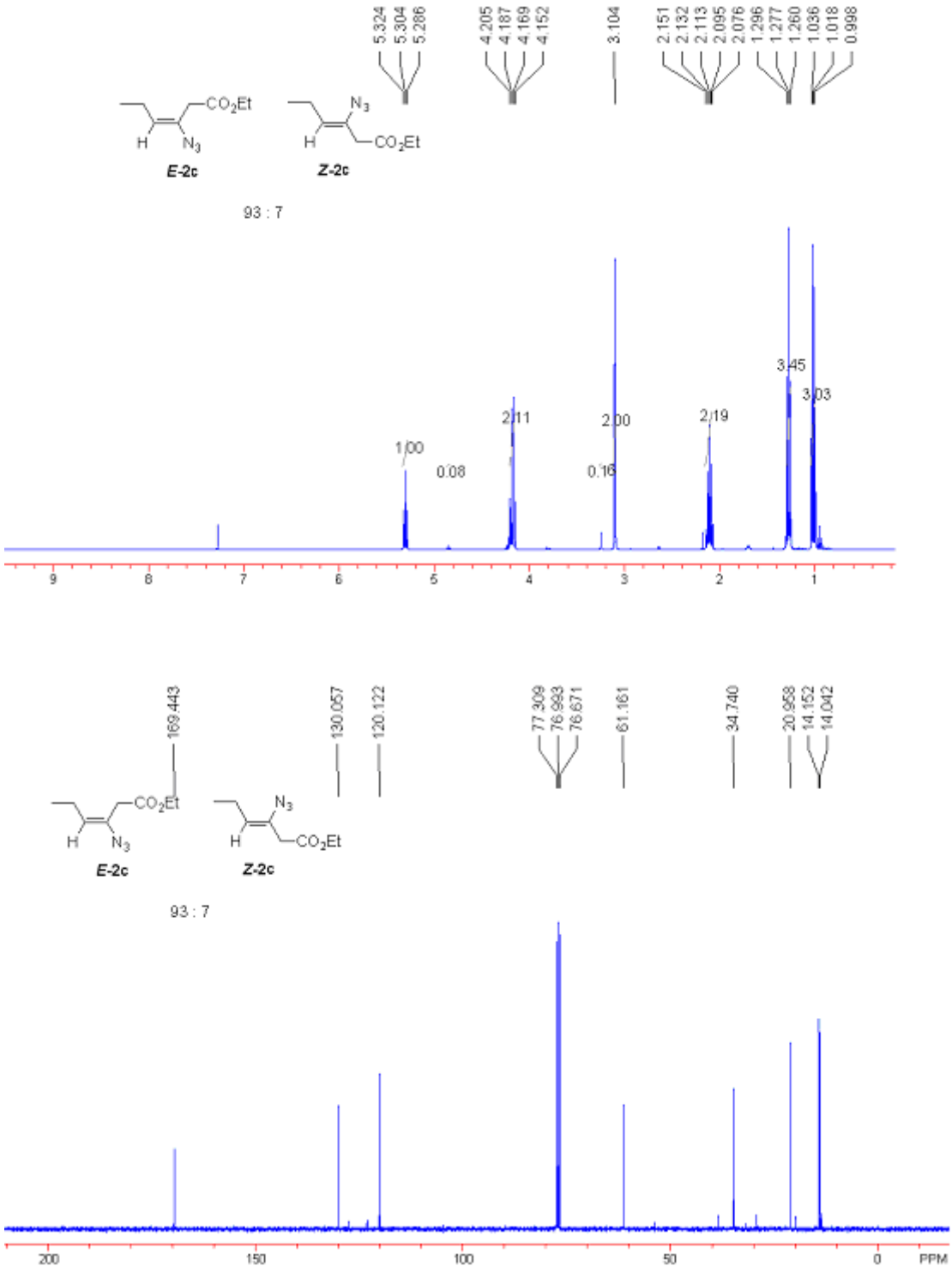
S15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9
8
7
6
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4
3
2
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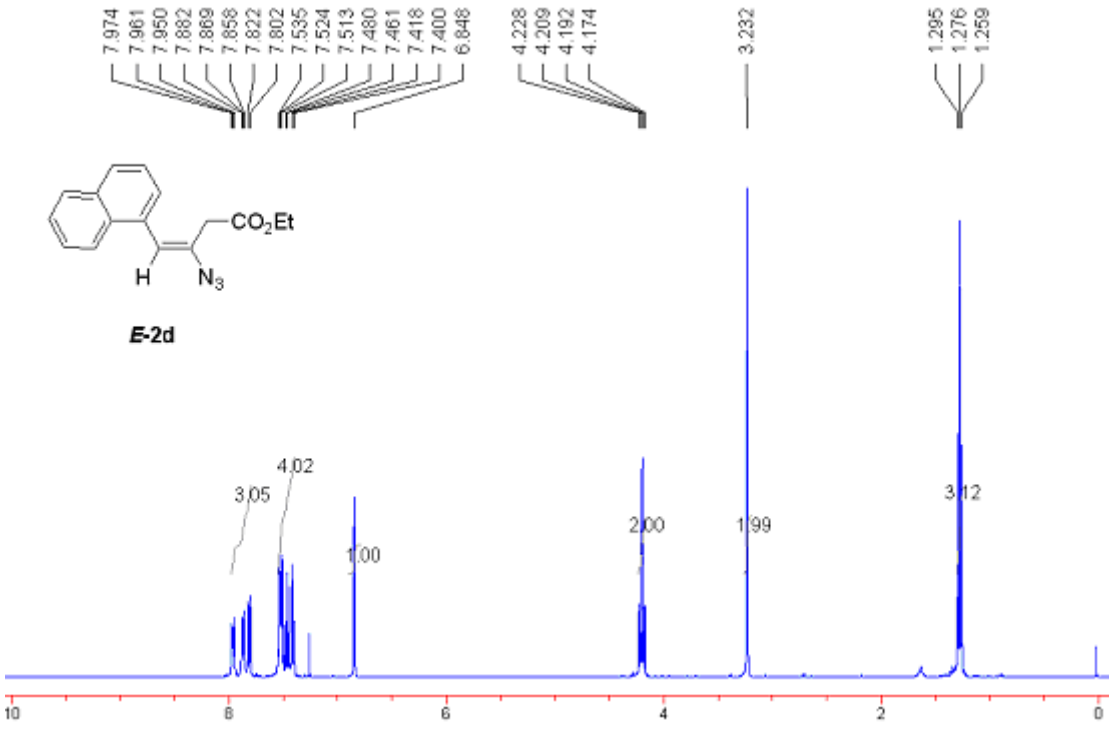
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1.276
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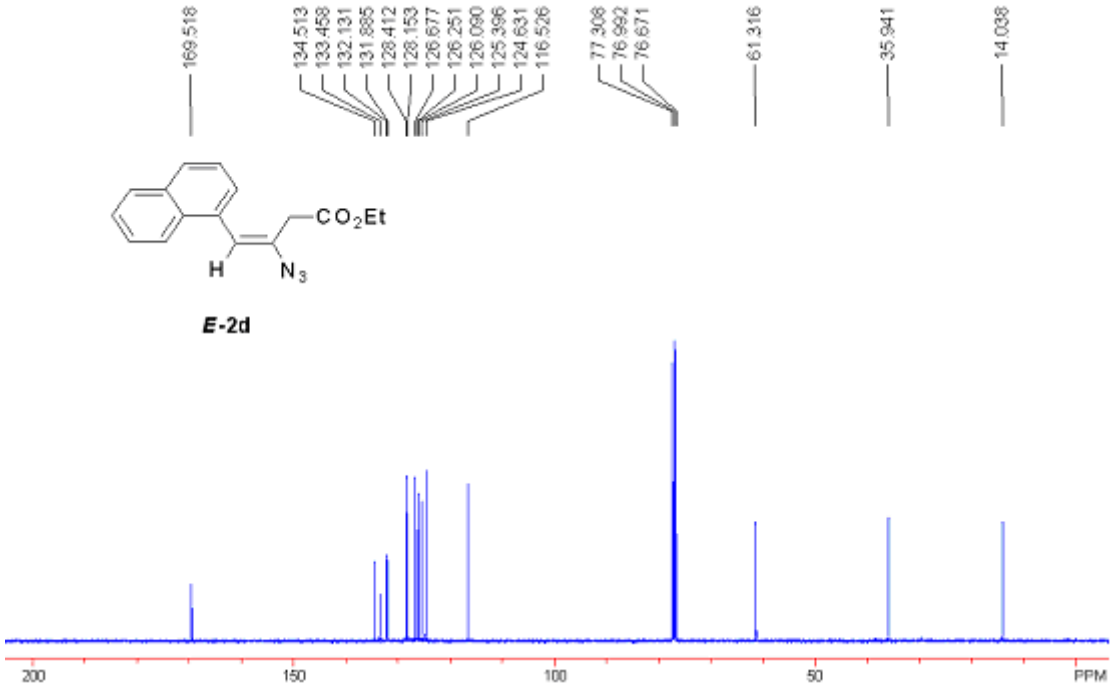
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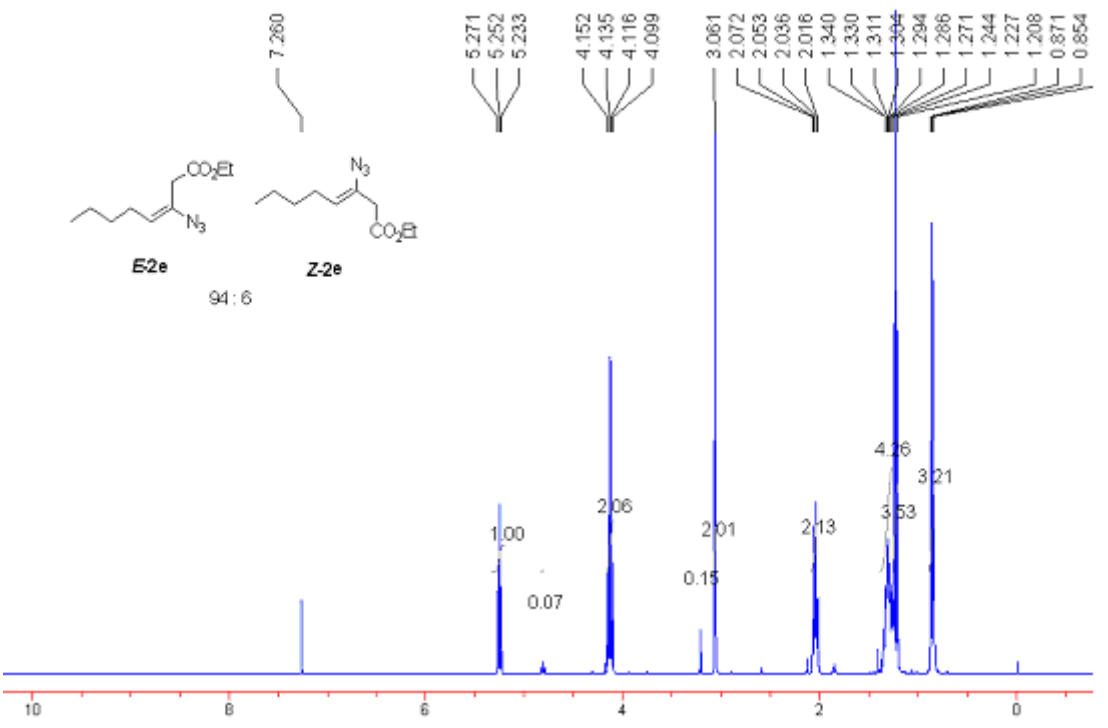
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1.330
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E-2e
Z-2e
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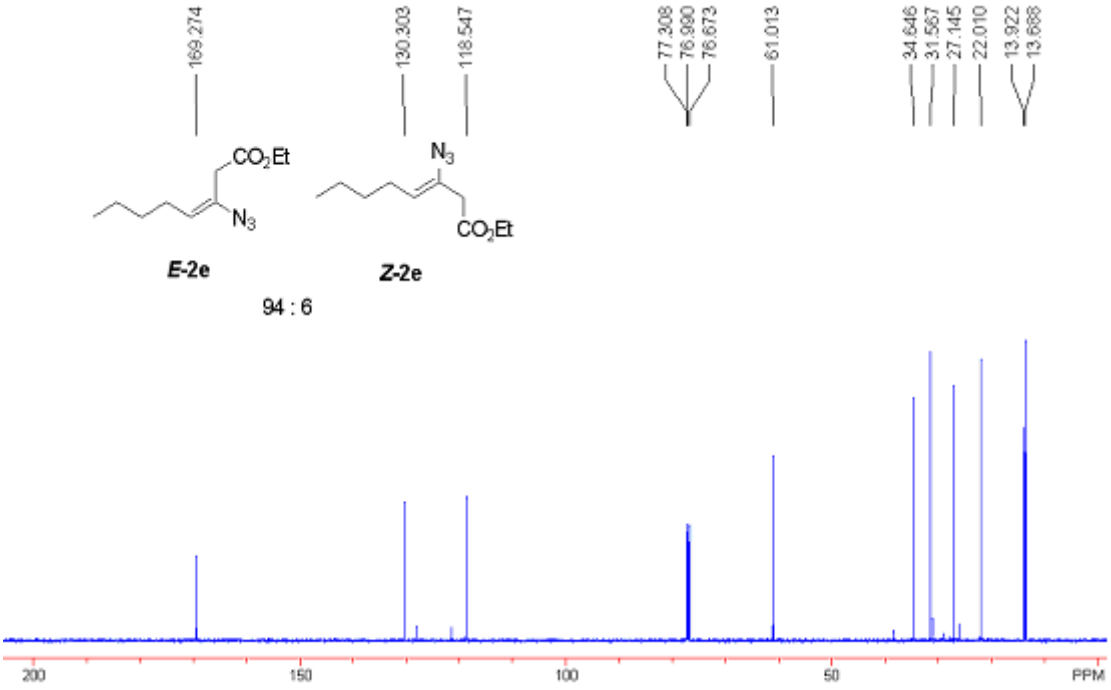
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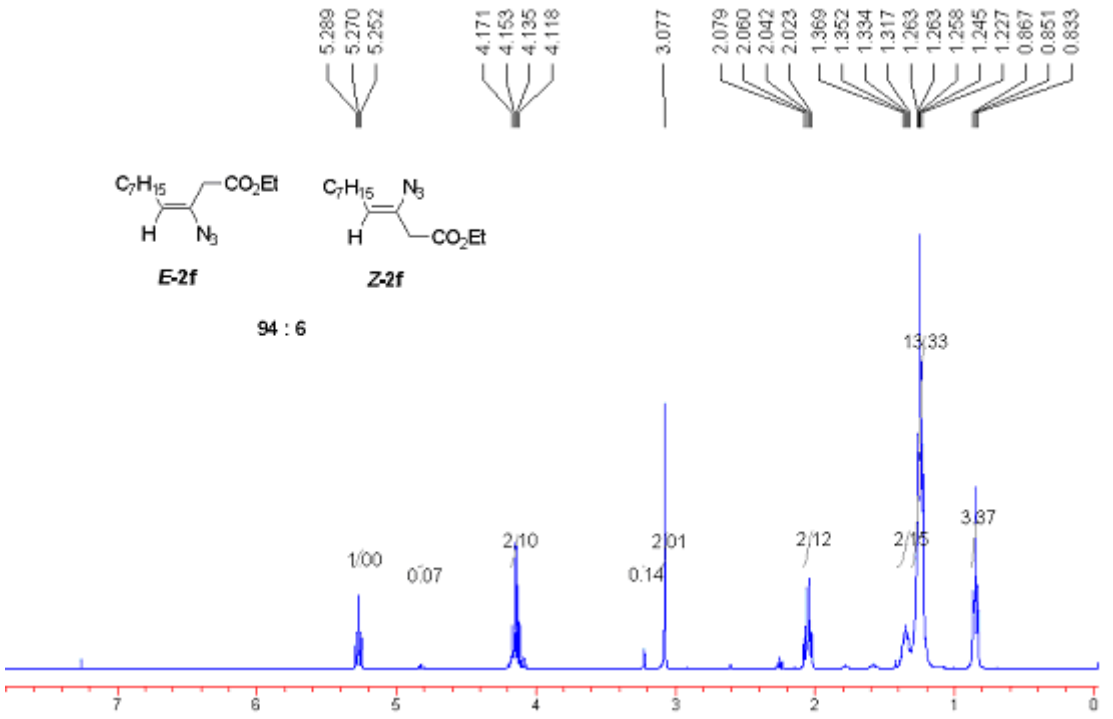
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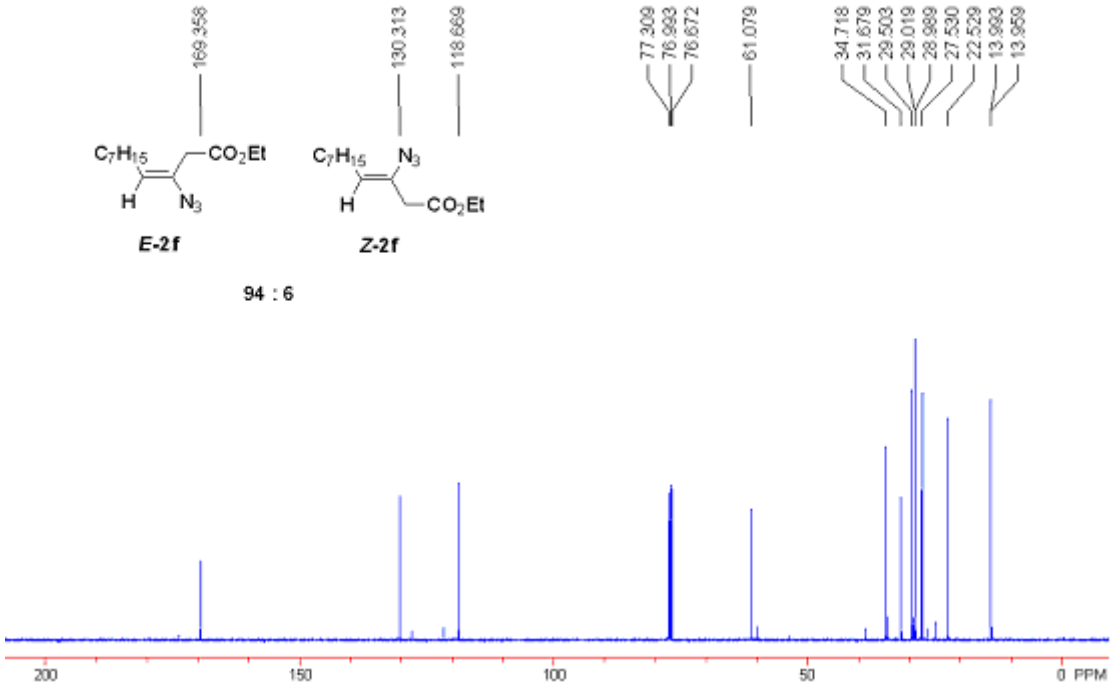
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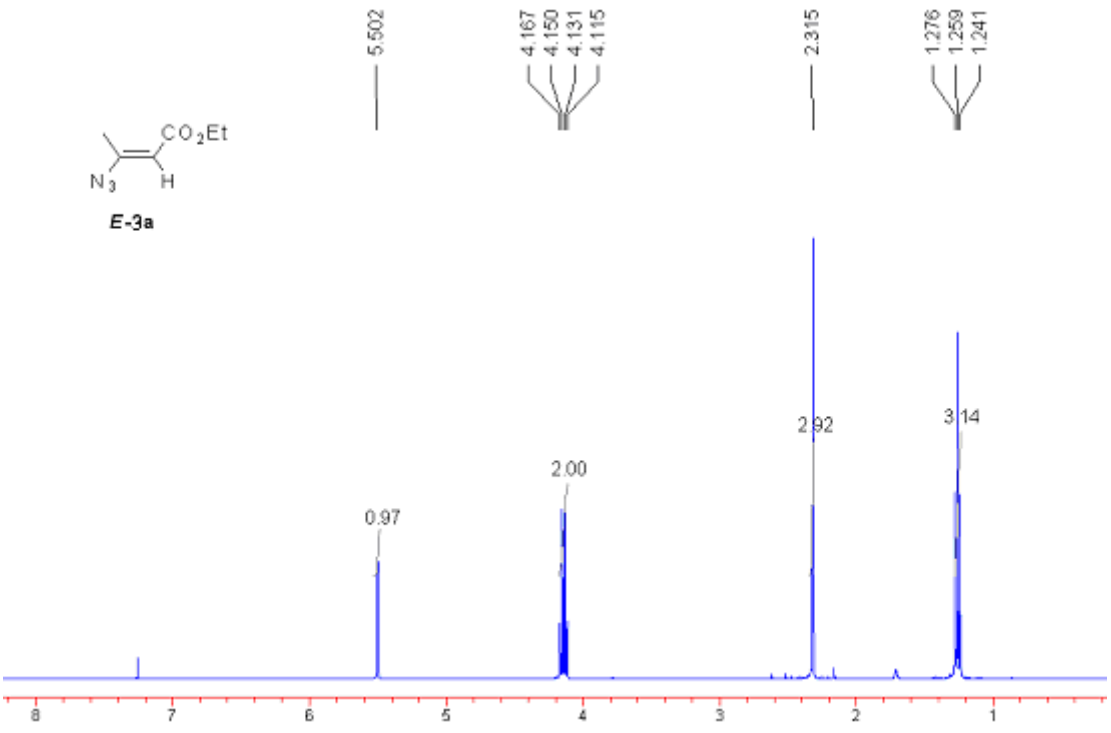
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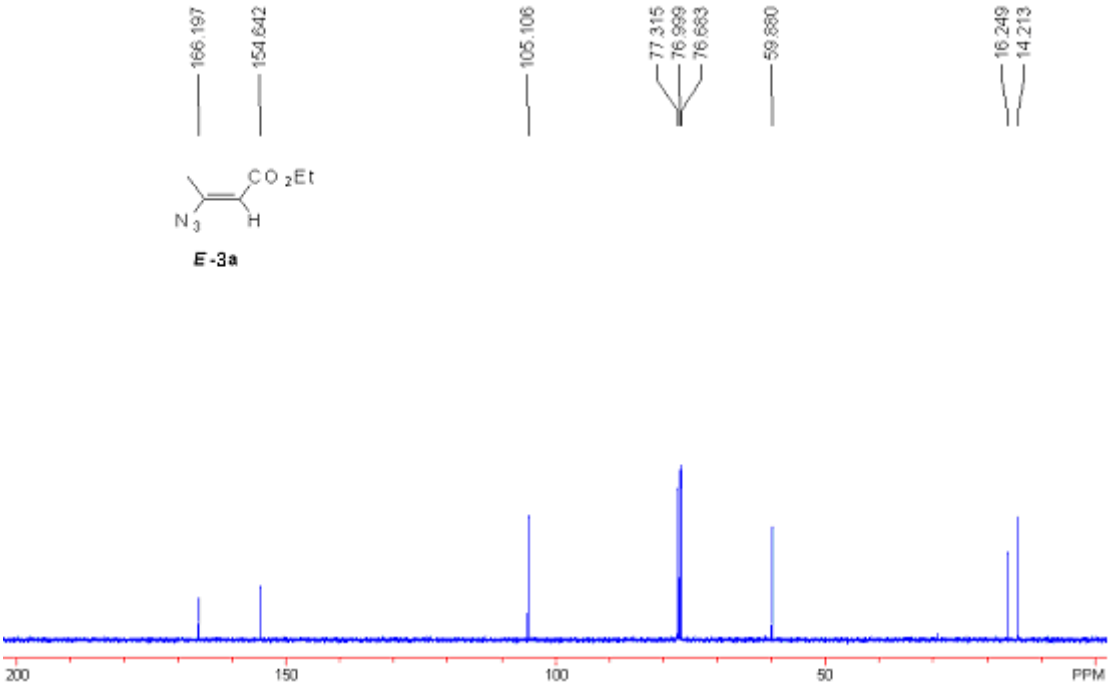
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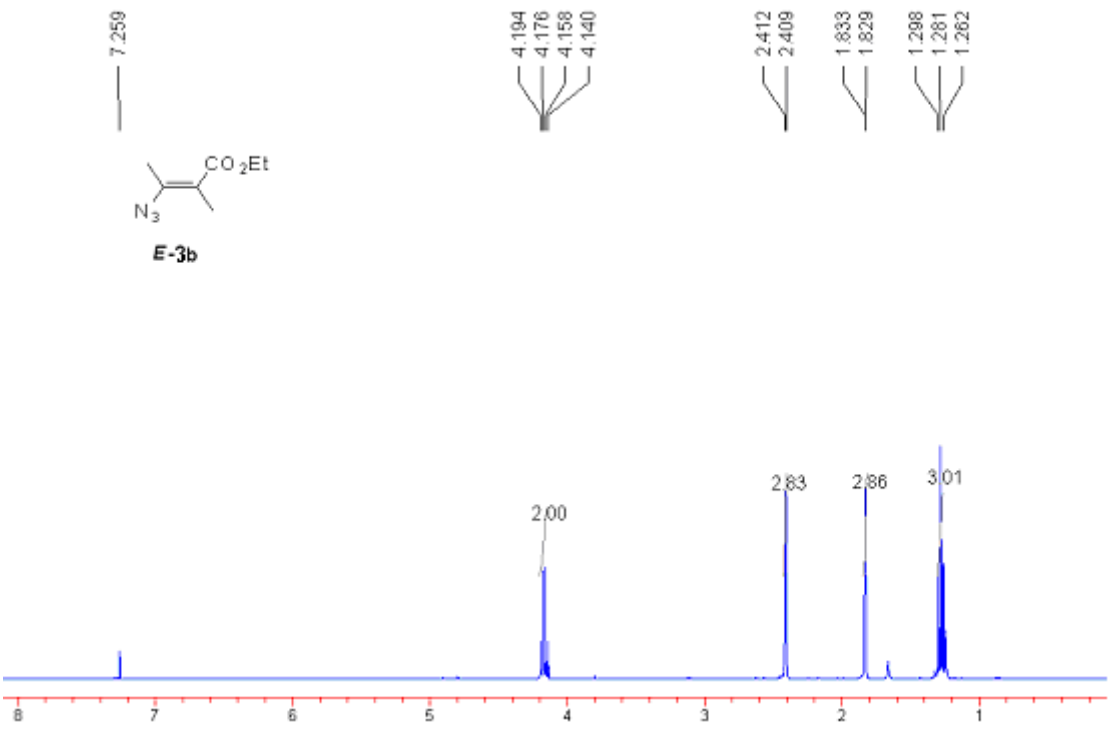
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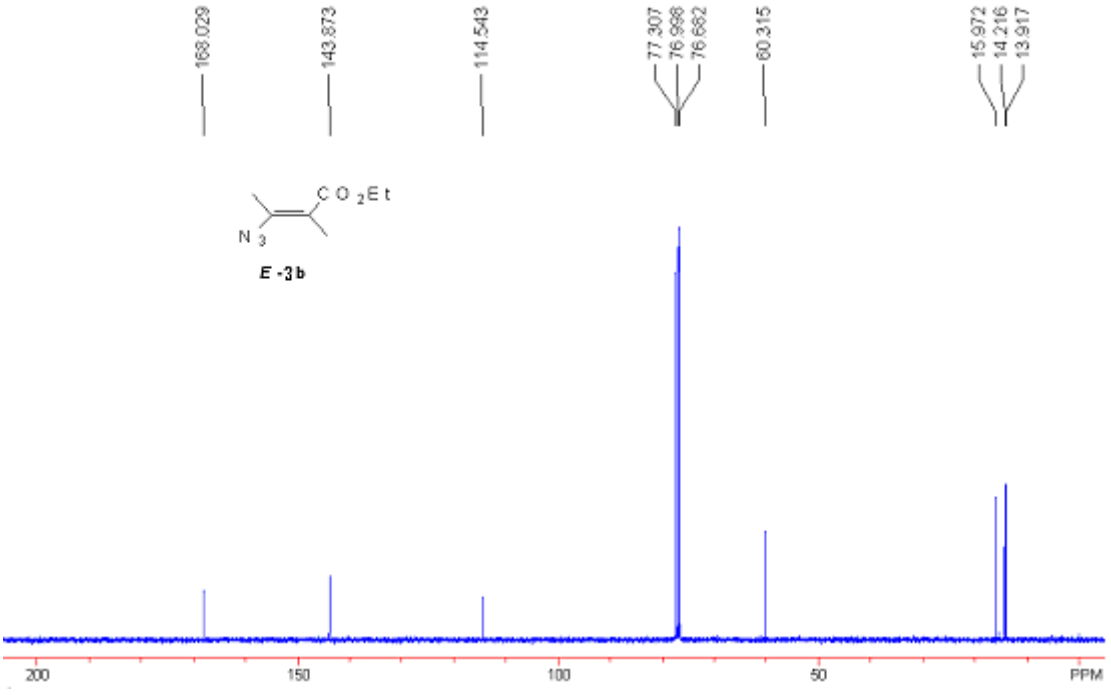
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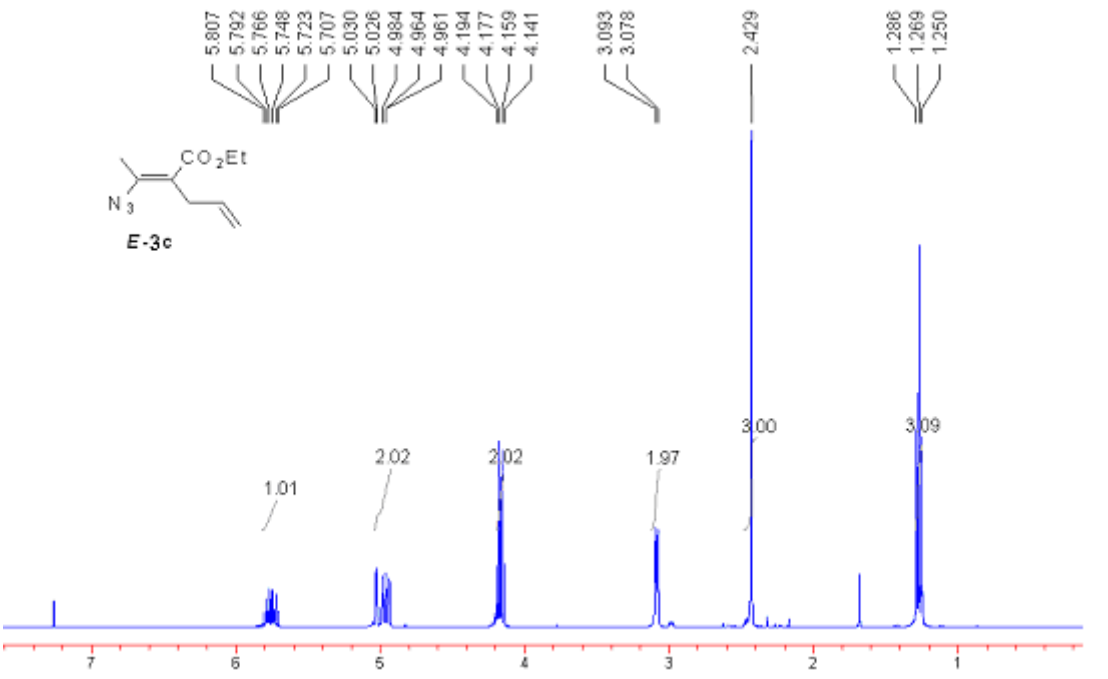
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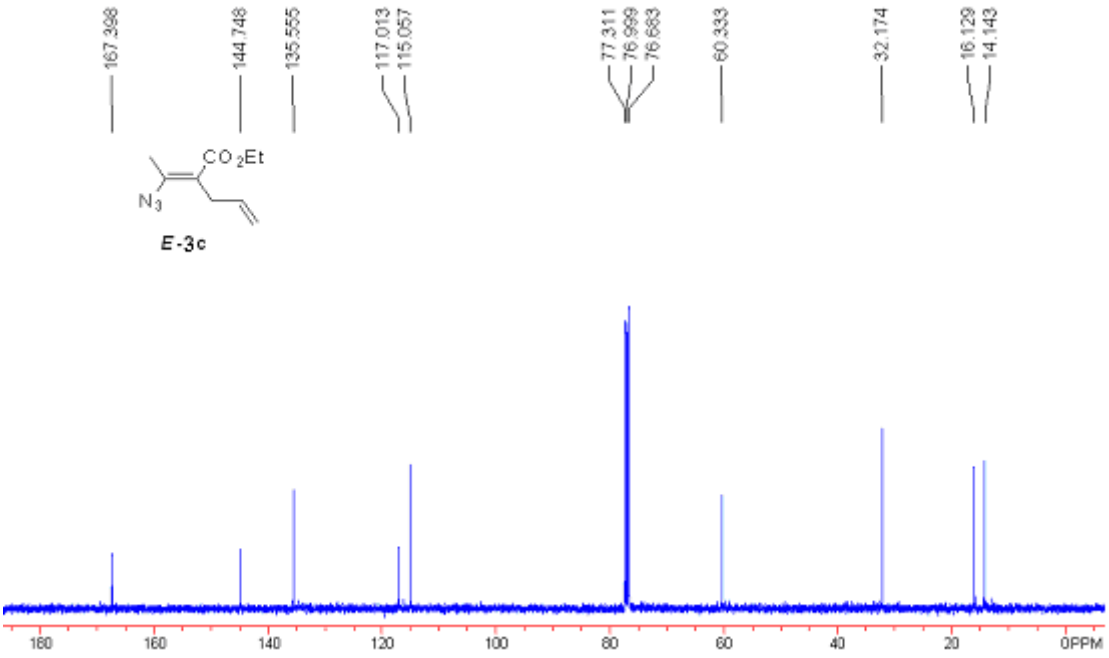
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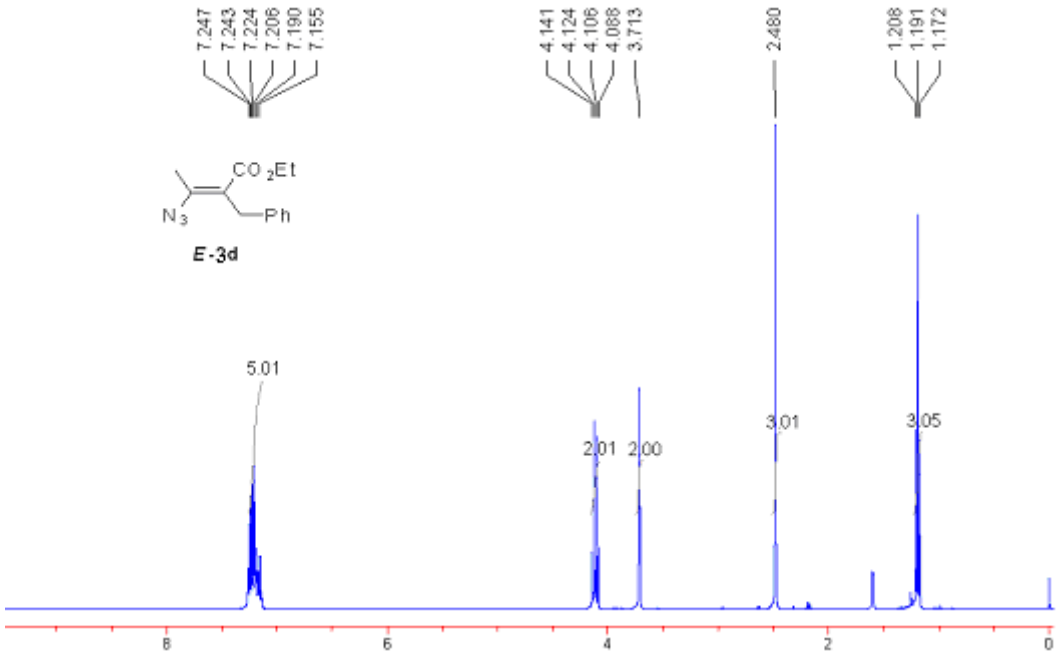
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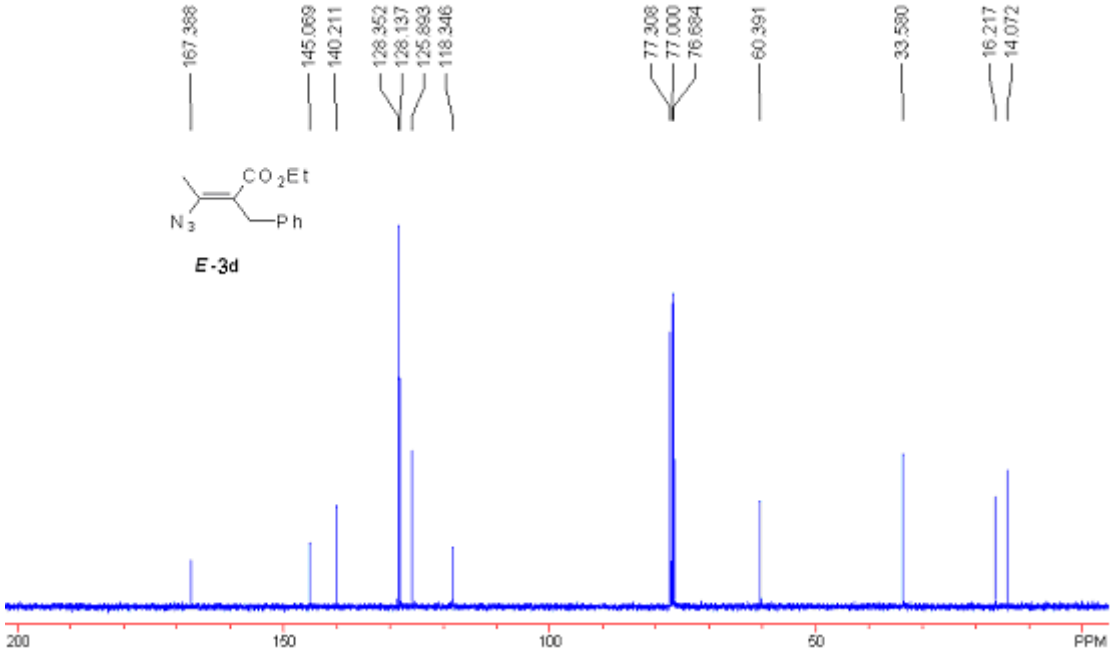
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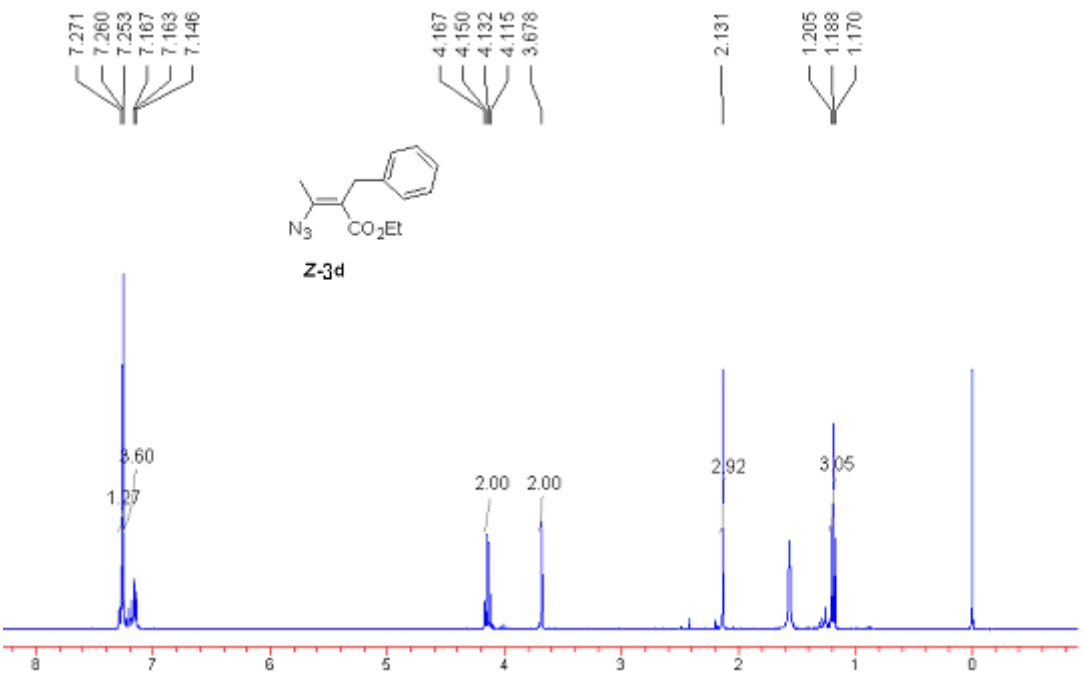
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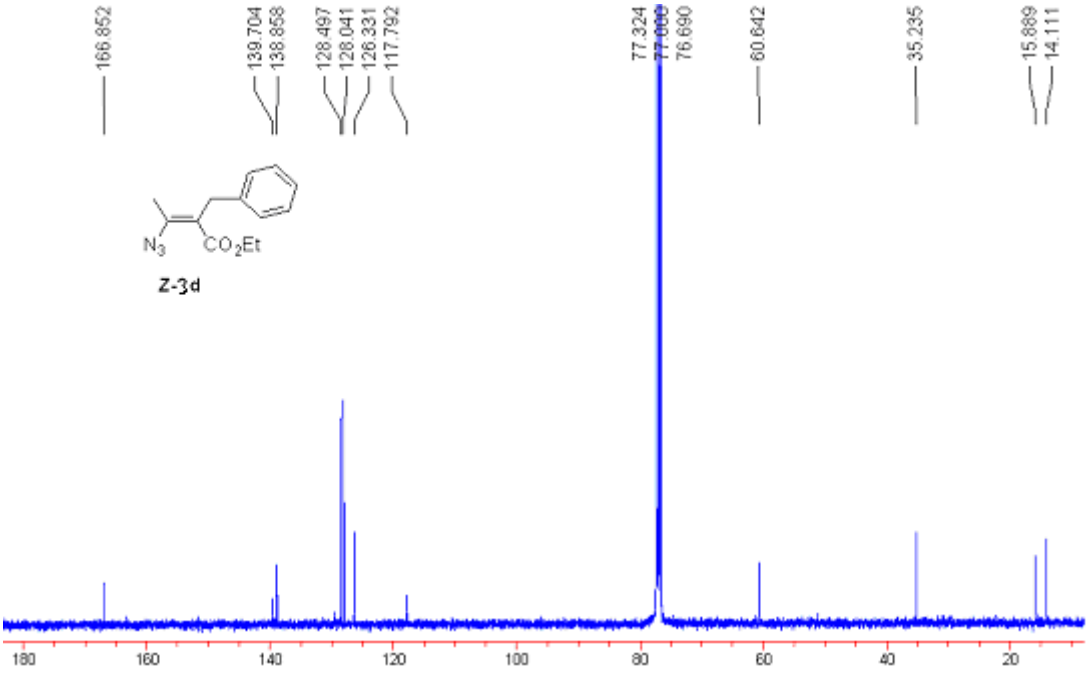
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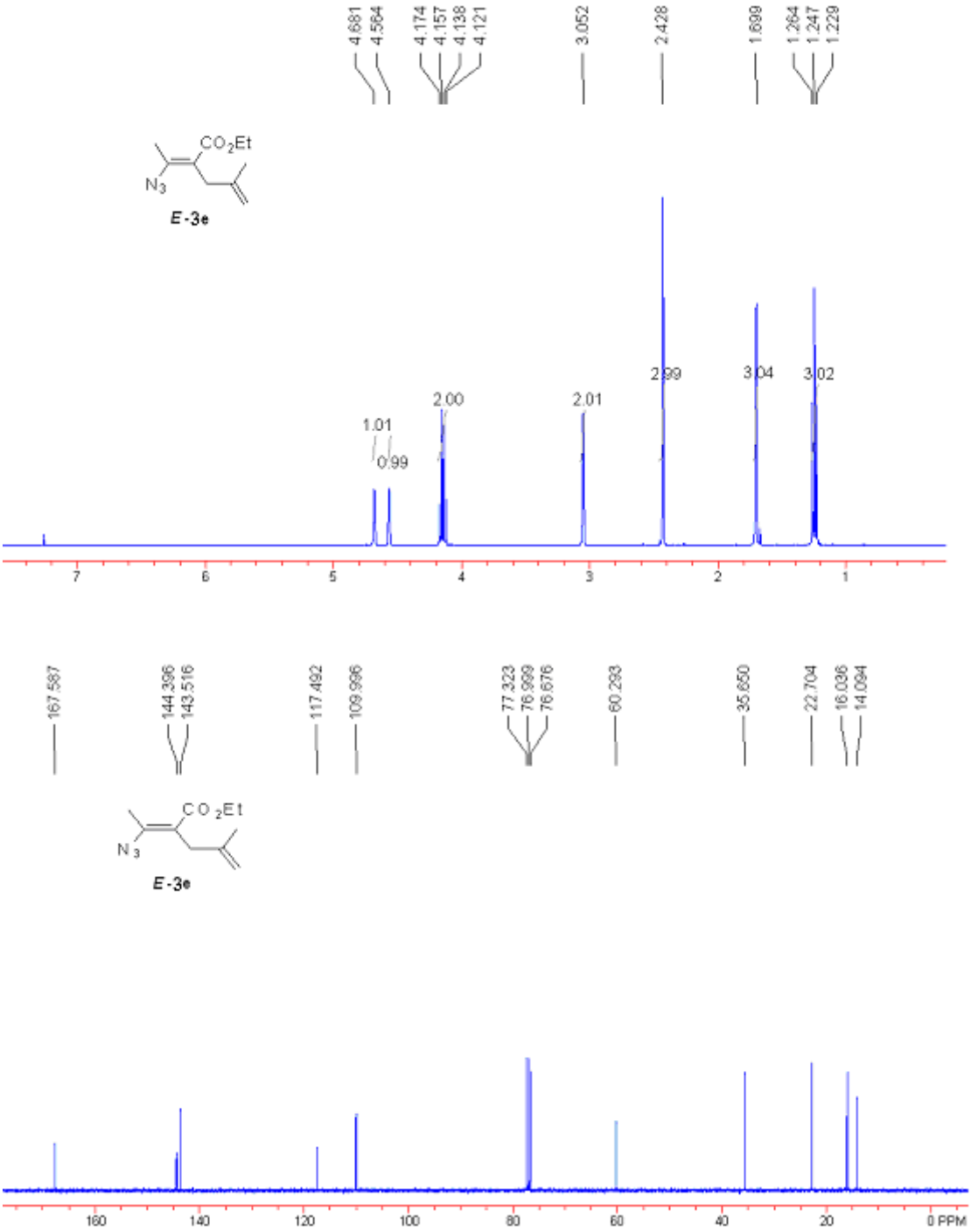
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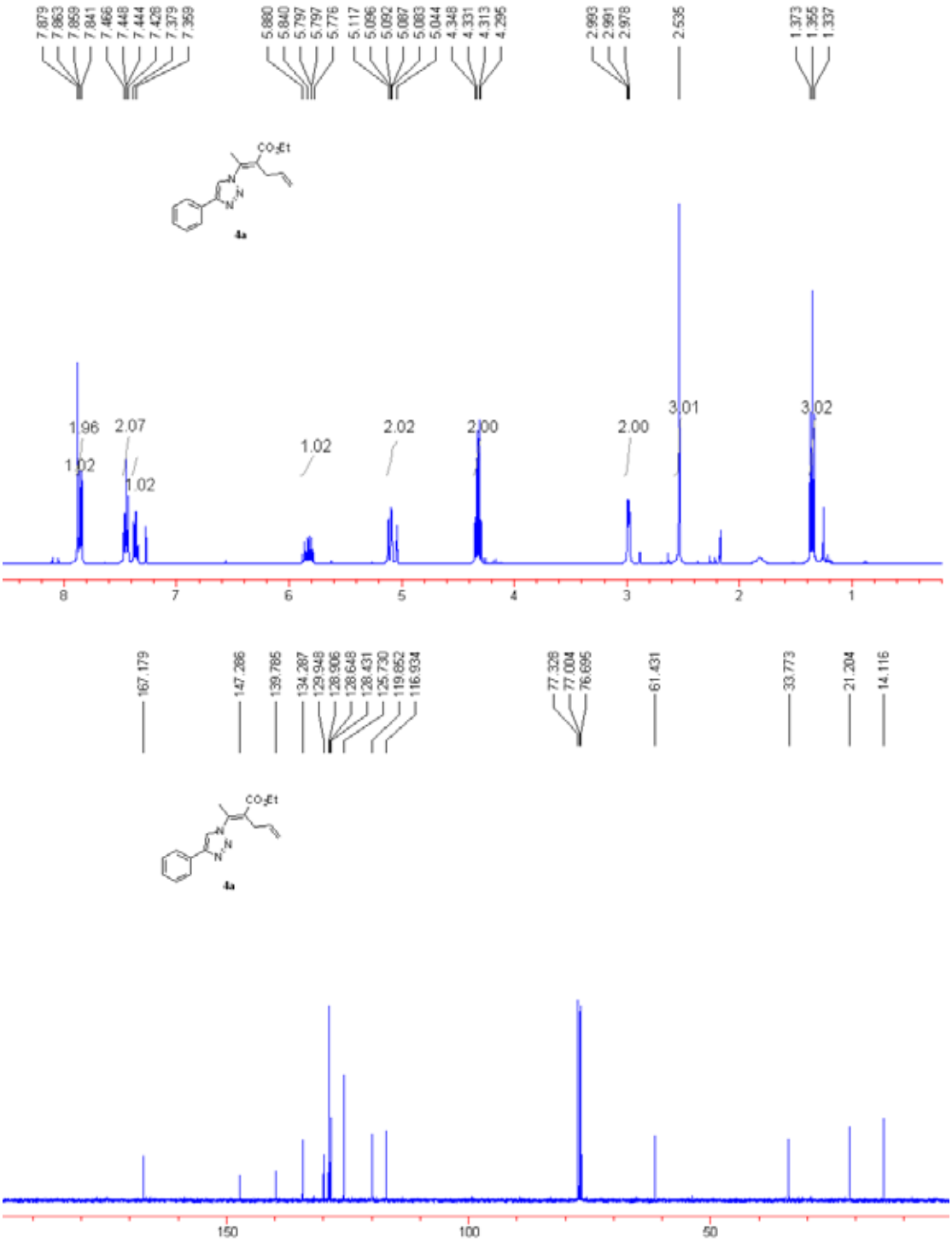
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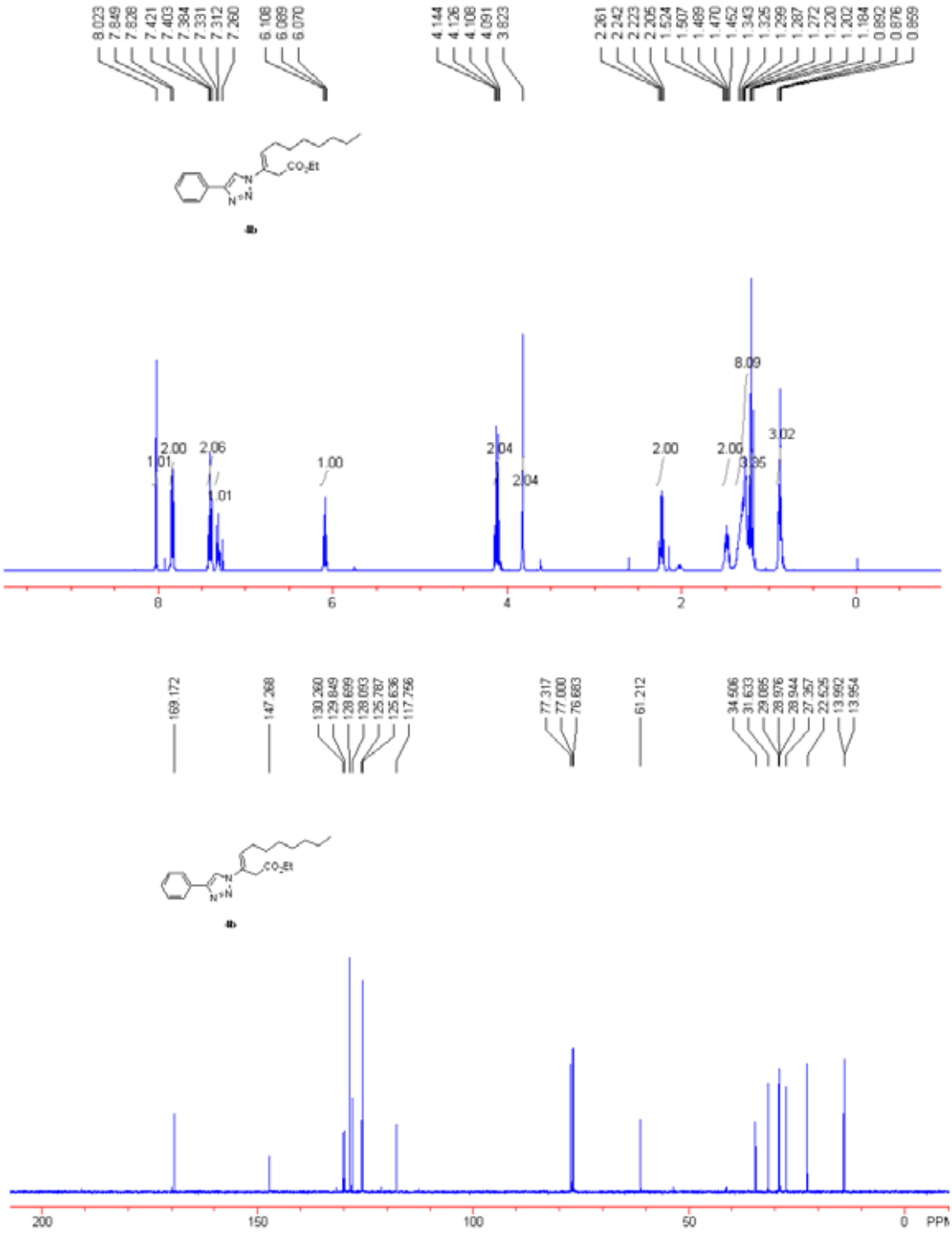
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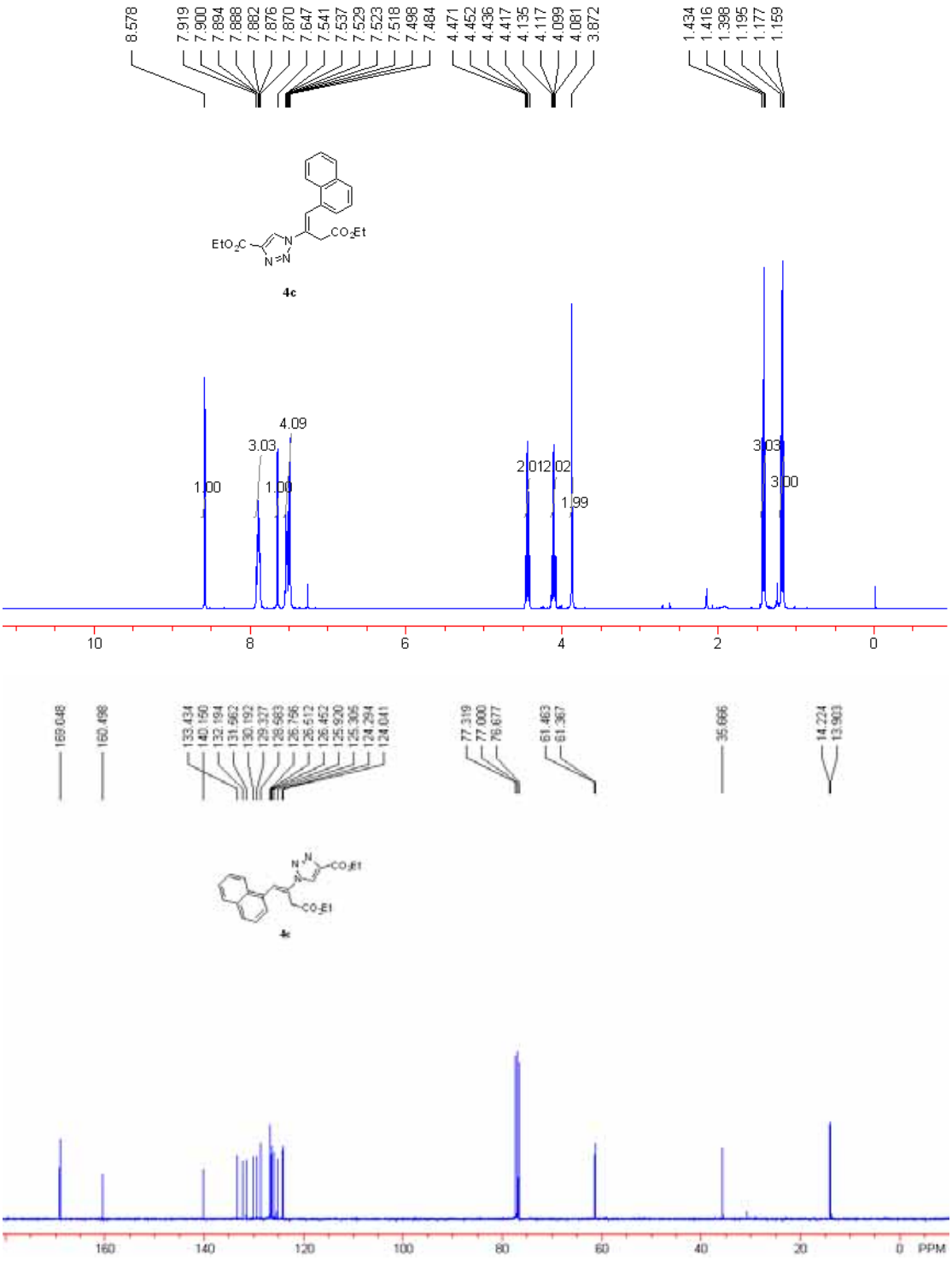
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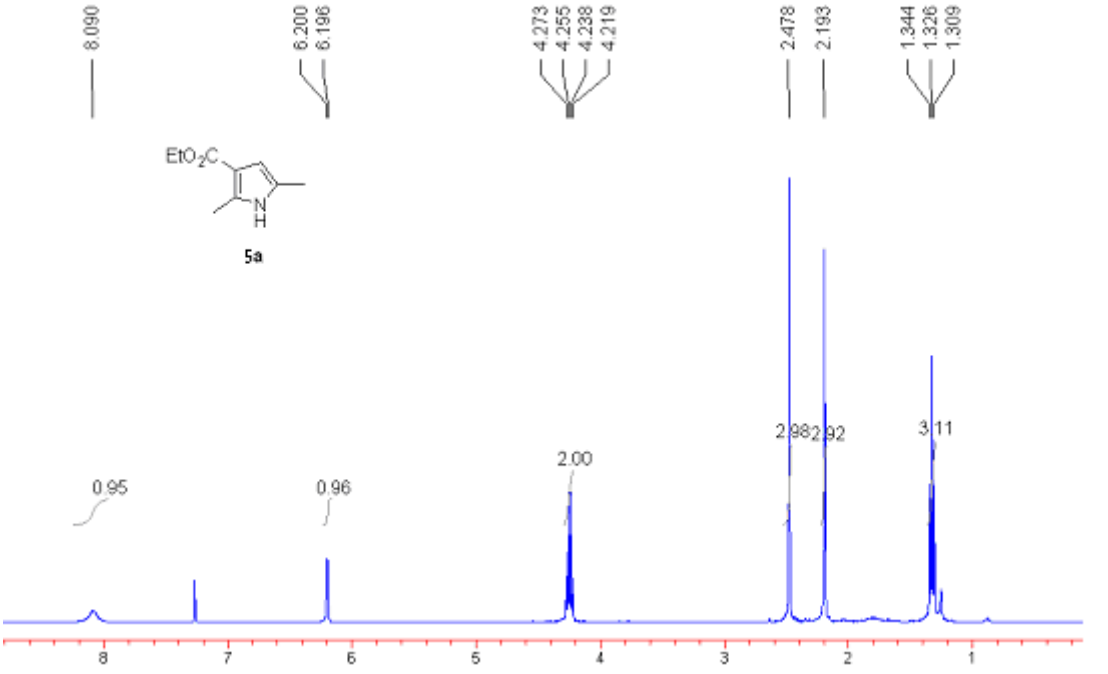
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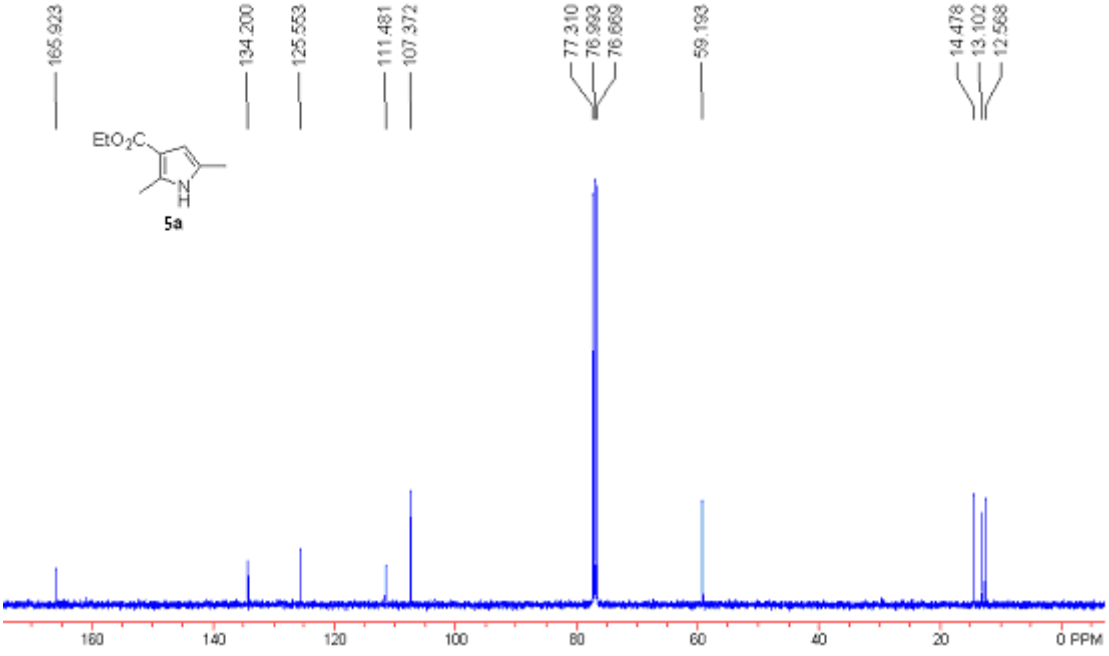
6.200
6.196
4.273
4.255
4.238
4.219
2.478
2.193
1.344
1.326
1.309
EtO2C
5a
0.95
0.96
2.00
2.98
2.92
3.11
8
7
6
5
4
3
2
1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134.200
125.553
111.481
107.372
77.310
76.993
76.669
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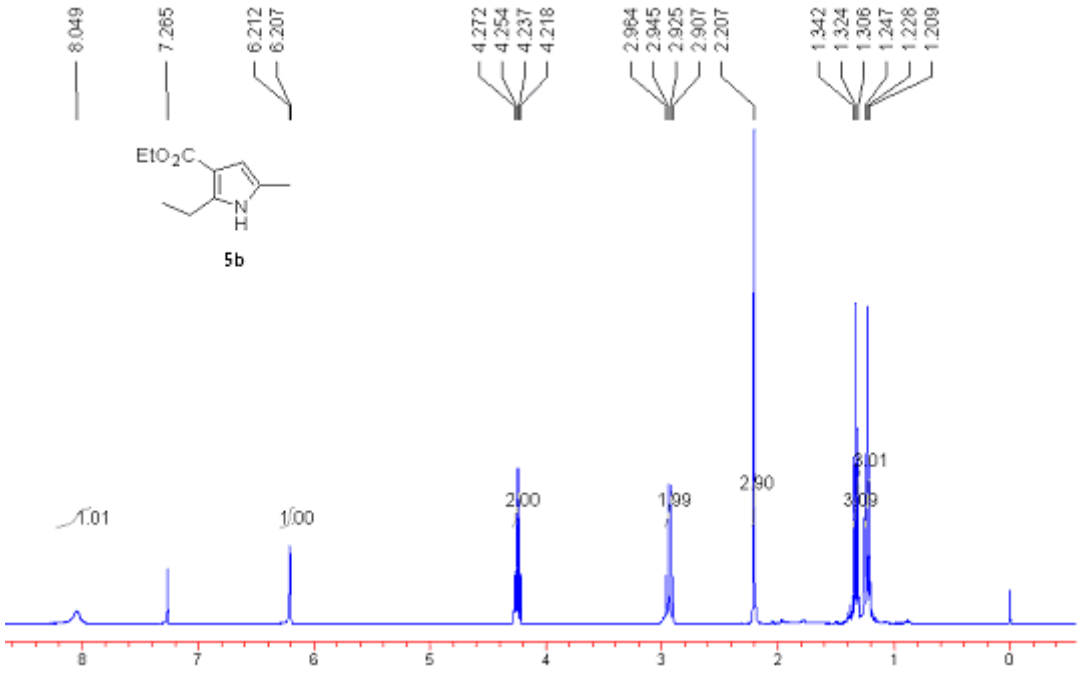
13.102
12.568
EtO2C
5a
160
140
120
100
80
60
40
20
0 PPM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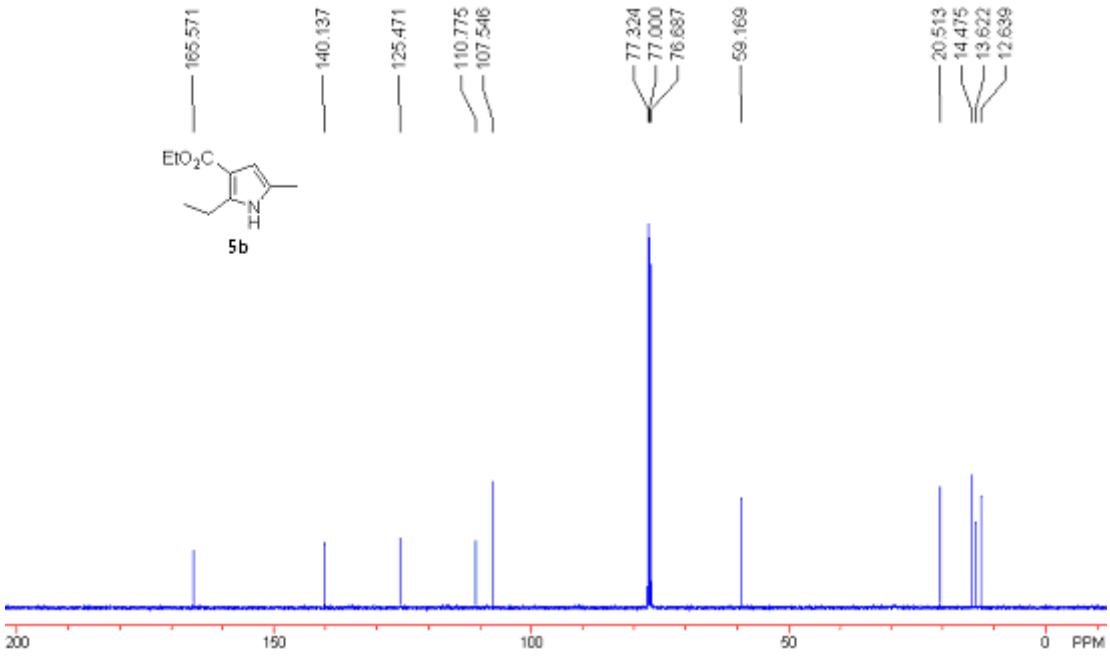
7.265
6.212
6.207
4.272
4.254
4.237
4.218
2.964
2.945
2.925
2.907
2.207
1.342
1.324
1.306
1.247
1.228
1.209
EtO2C
5b
1.01
1.00
2.00
1.99
2.90
3.01
3.09
8
7
6
5
4
3
2
1
0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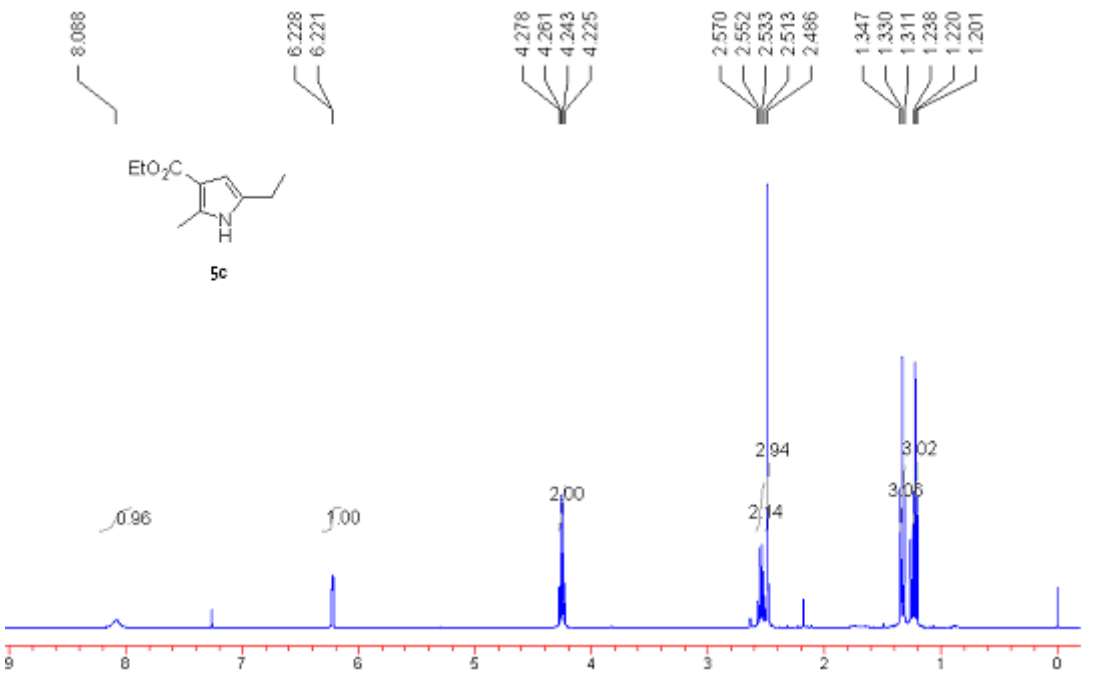
140.137
125.471
110.775
107.546
77.324
77.000
76.687
59.169
20.513
14.475
13.622
12.639
EtO2C
5b
200
150
100
50
0
PPM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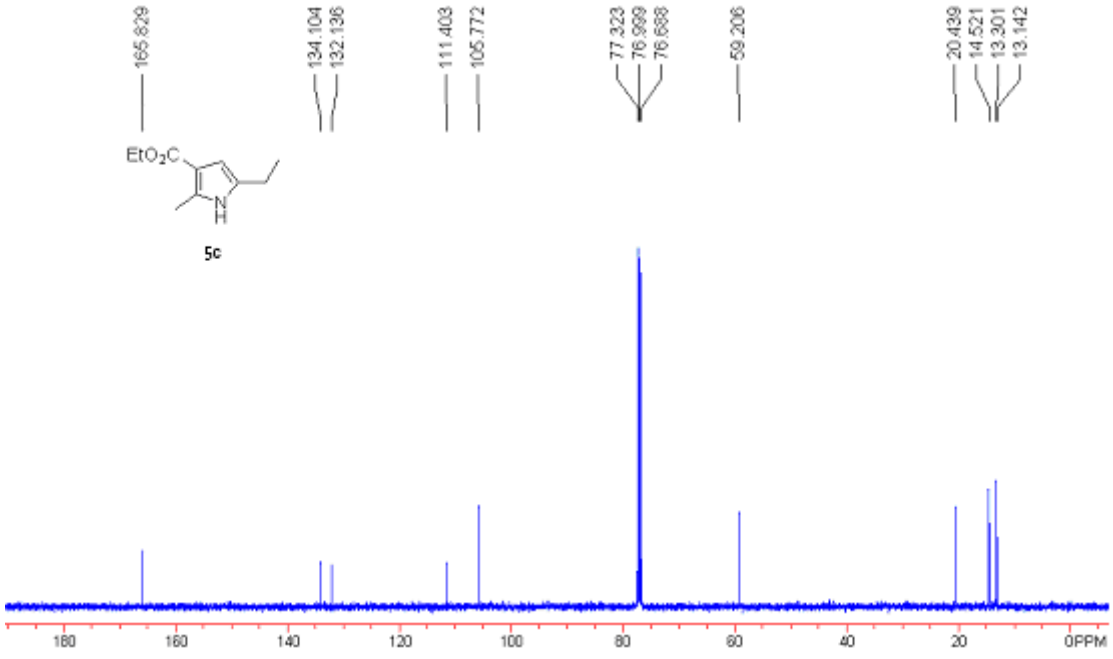
6.228
6.221
4.278
4.261
4.243
4.225
2.570
2.552
2.533
2.513
2.486
1.347
1.330
1.311
1.238
1.220
1.201
EtO2C
5c
0.96
1.00
2.00
2.94
2.14
3.02
3.06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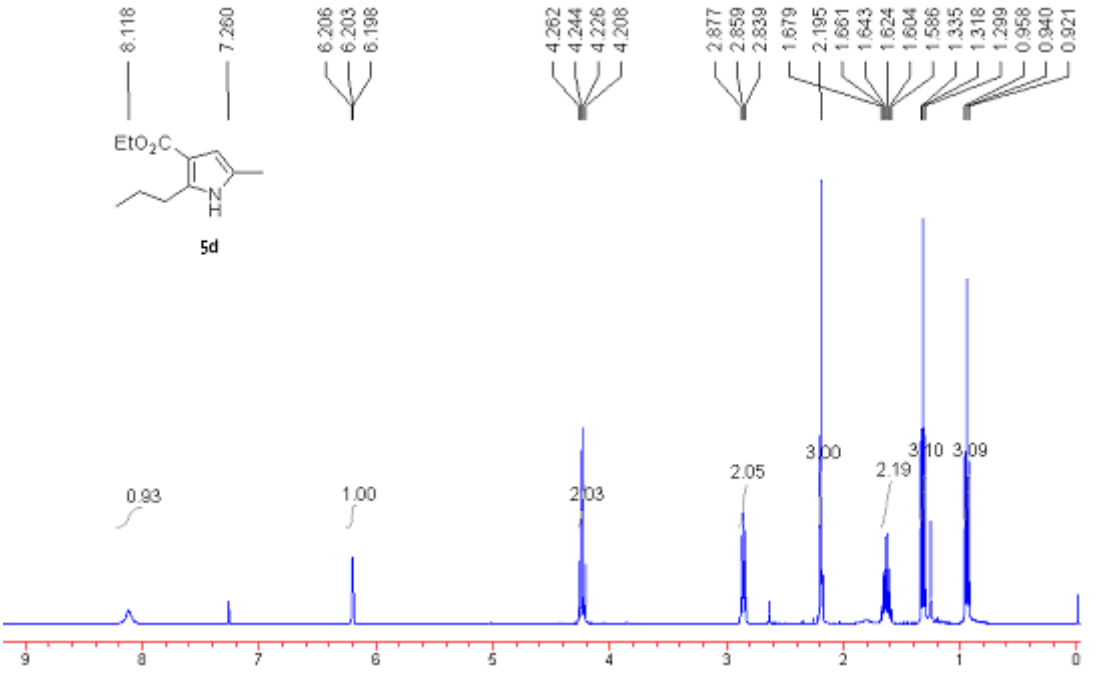
134.104
132.136
111.403
105.772
77.323
76.999
76.688
59.206
20.439
14.521
13.301
13.142
EtO2C
5c
0PPM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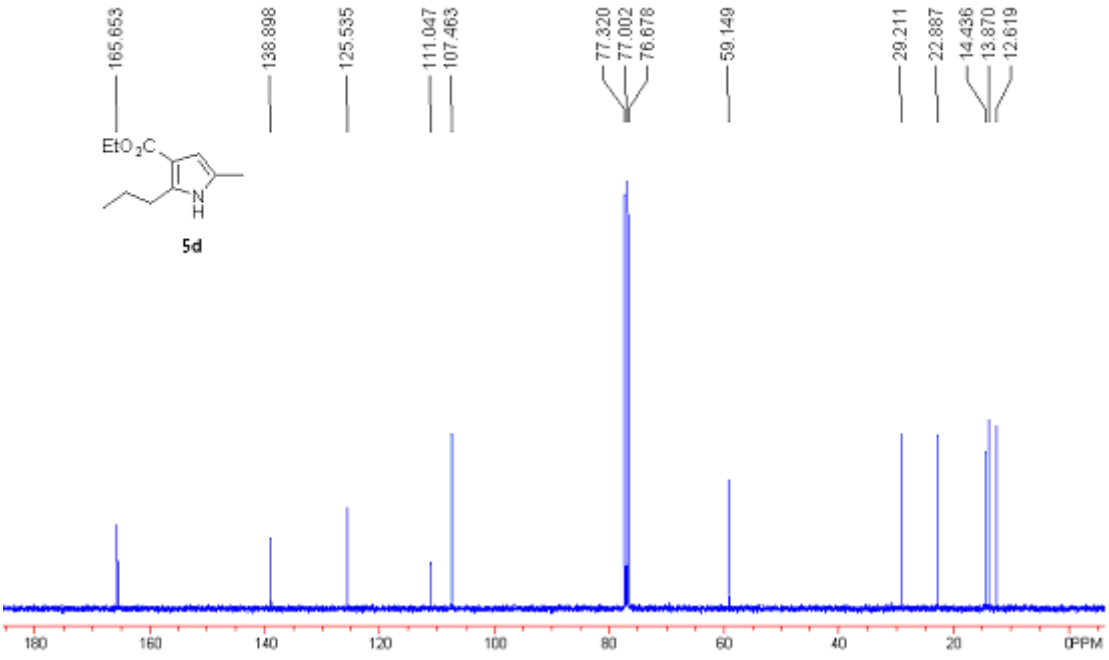
7.260
6.206
6.203
6.198
4.262
4.244
4.226
4.208
2.877
2.859
2.839
1.679
2.195
1.661
1.643
1.624
1.604
1.586
1.335
1.318
1.299
0.958
0.940
0.921
EtO2C
5d
0.93
1.00
2.03
2.05
3.00
2.19
3.10
3.09
9
8
7
6
5
4
3
2
1
0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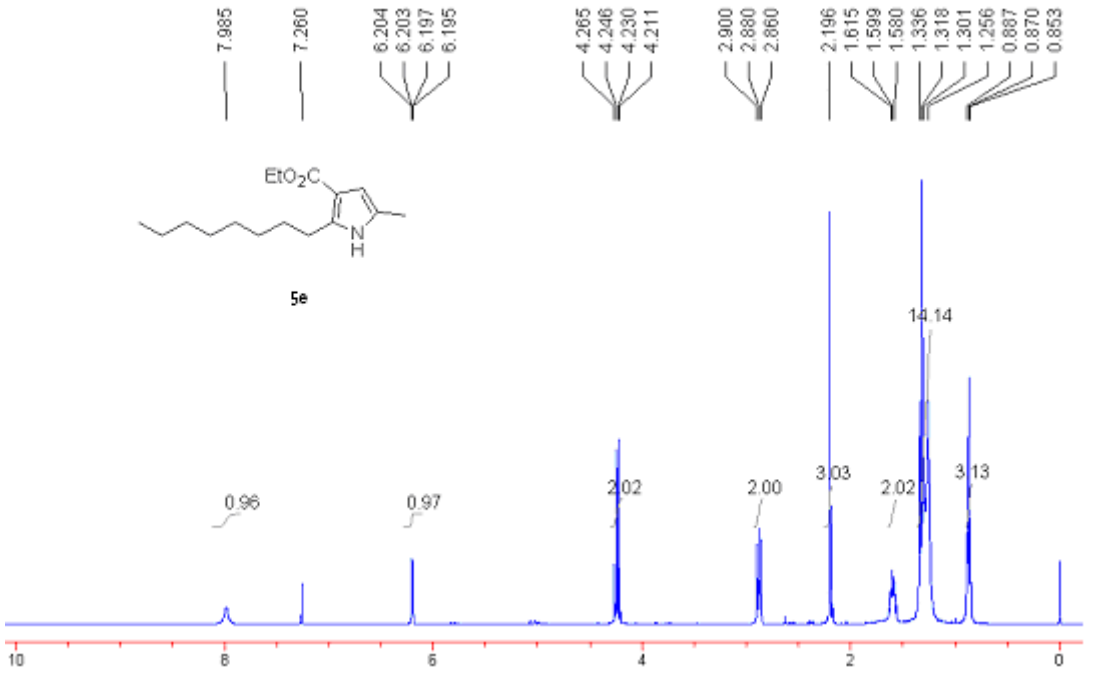
138.898
125.535
111.047
107.463
77.320
77.002
76.678
59.149
29.211
22.887
14.436
13.870
12.619
EtO2C
5d
180
160
140
120
100
80
60
40
20
0PPM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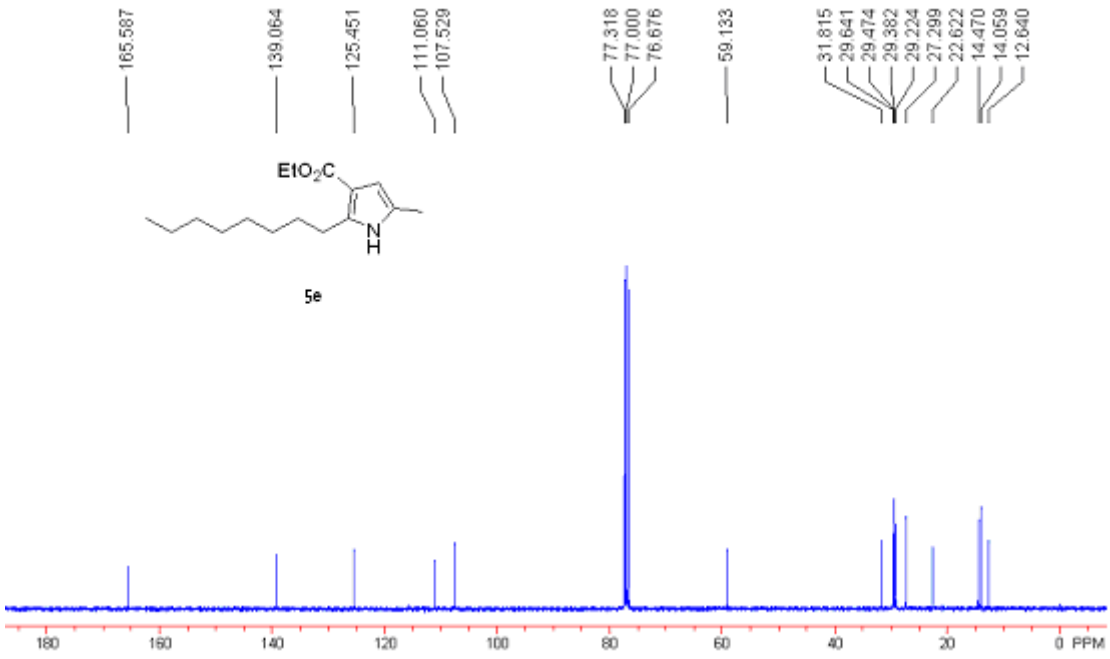
7.260
6.204
6.203
6.197
6.195
4.265
4.246
4.230
4.211
2.900
2.880
2.860
2.196
1.615
1.599
1.580
1.336
1.318
1.301
1.256
0.887
0.870
0.853
EtO2C
N
H
5e
14.14
0.96
0.97
2.02
2.00
3.03
2.02
3.13
10
8
6
4
2
0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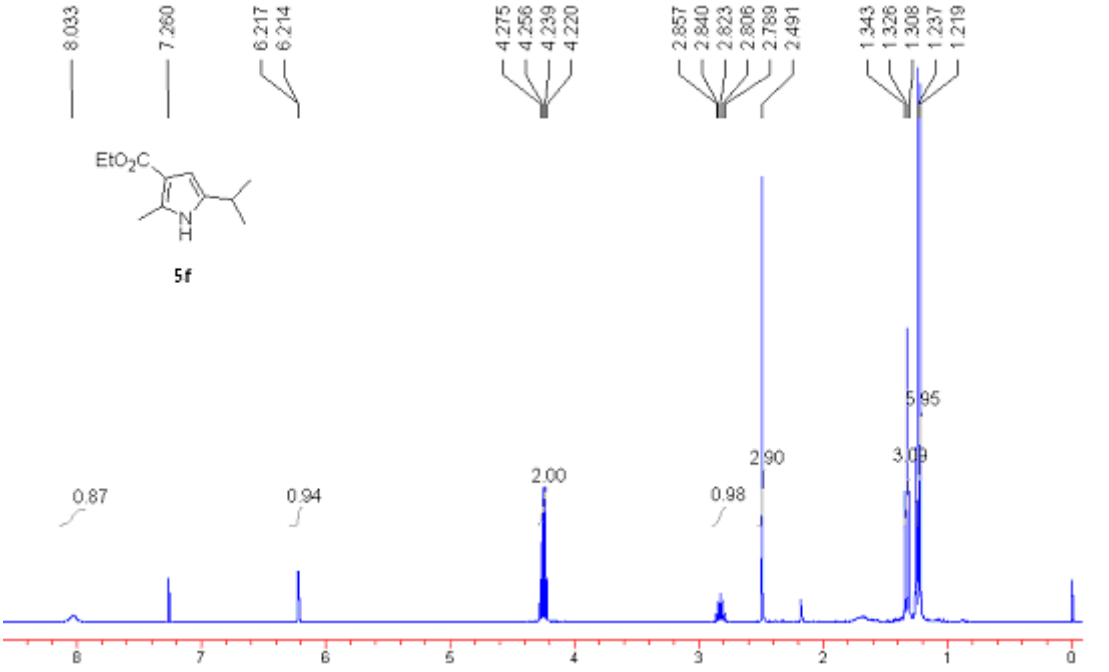
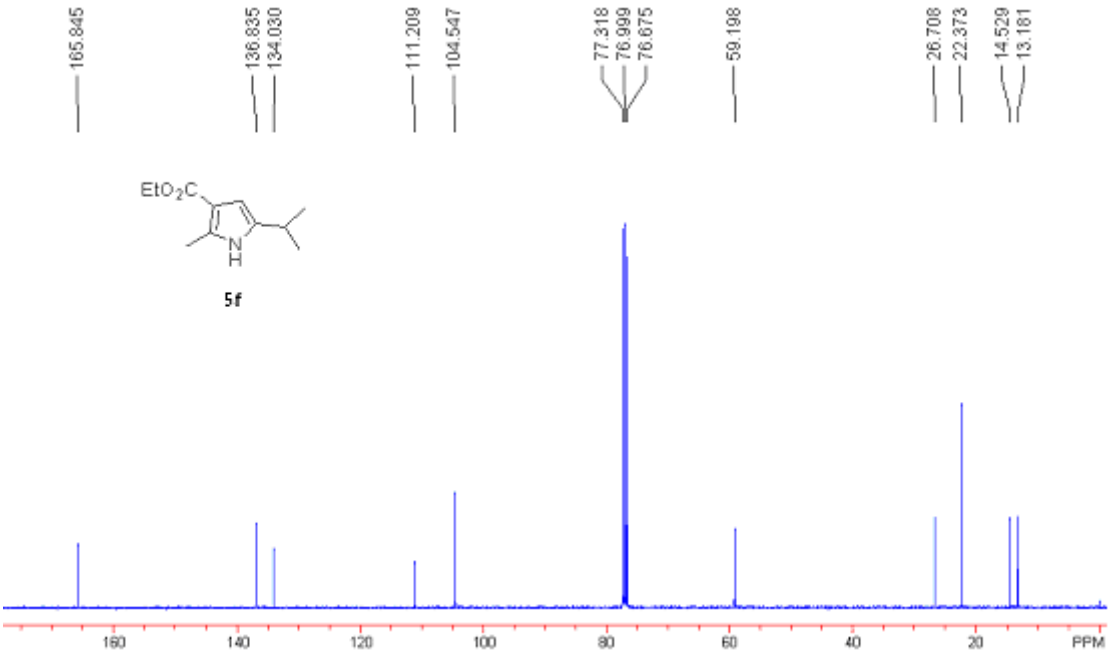
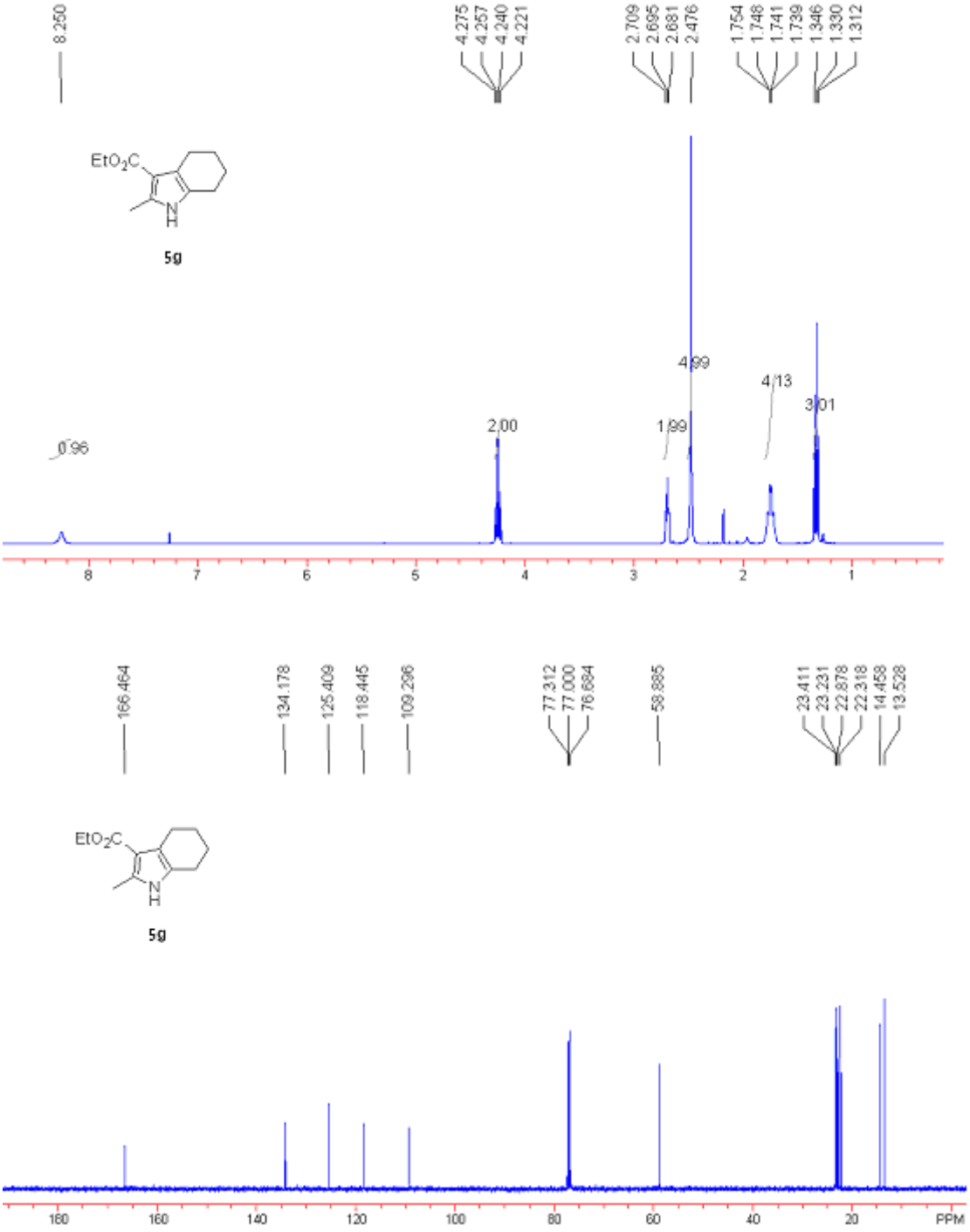
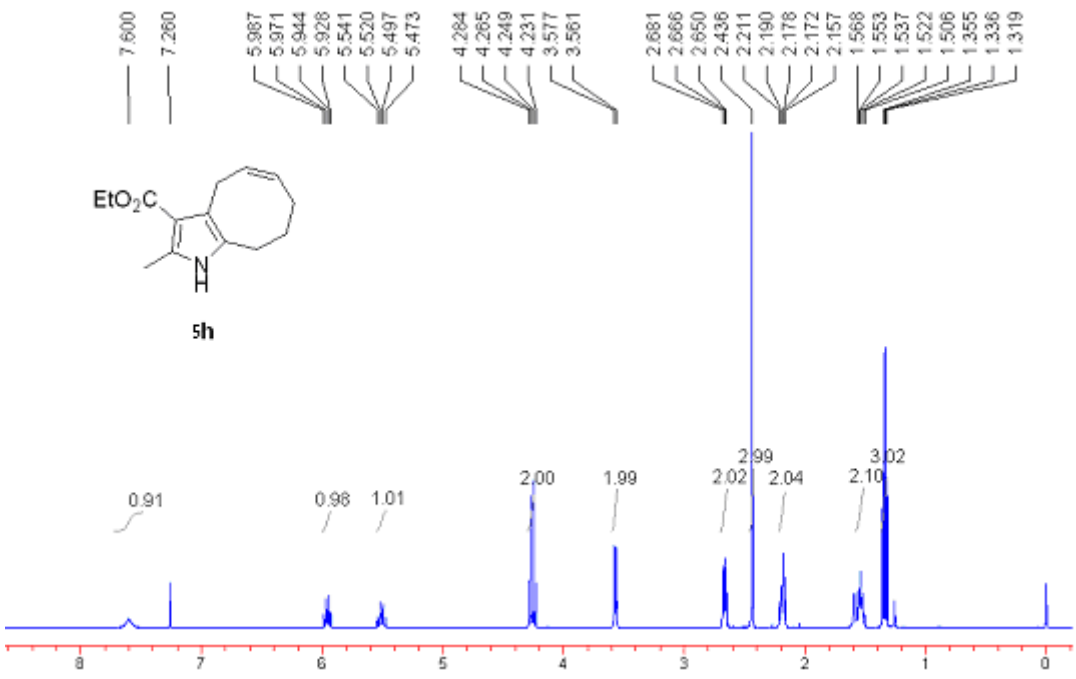
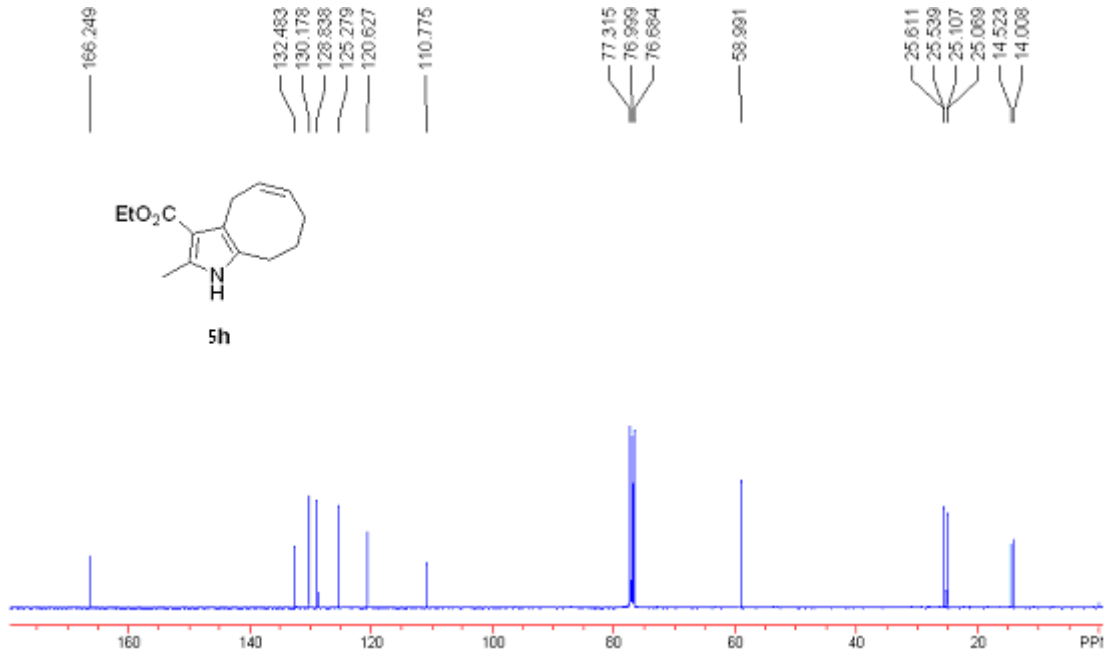
139.064
125.451
111.060
107.529
77.318
77.000
76.676
59.133
31.815
29.641
29.474
29.382
29.224
27.299
22.622
14.470
14.059
12.640
EtO2C
N
H
5e
180
160
140
120
100
80
60
40
20
0 PPM

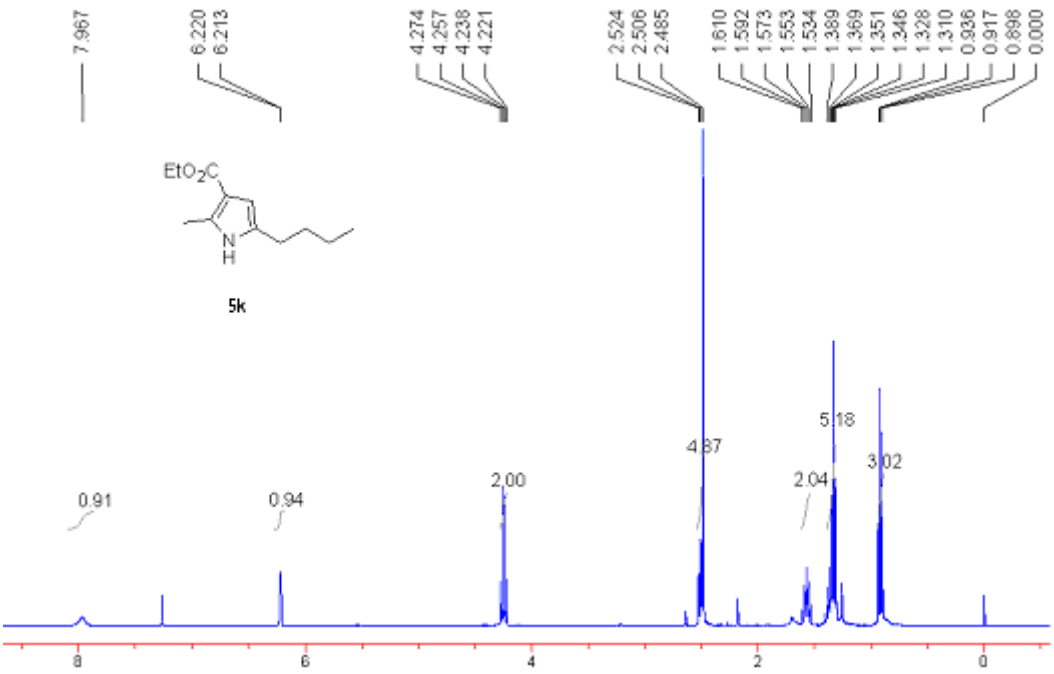

8.033
7.260
6.217
6.214
4.275
4.256
4.239
4.220
2.857
2.840
2.823
2.806
2.789
2.491
1.343
1.326
1.308
1.237
1.219
EtO2C
5f
0.87
0.94
2.00
0.98
2.90
3.09
5.95
8
7
6
5
4
3
2
1
0

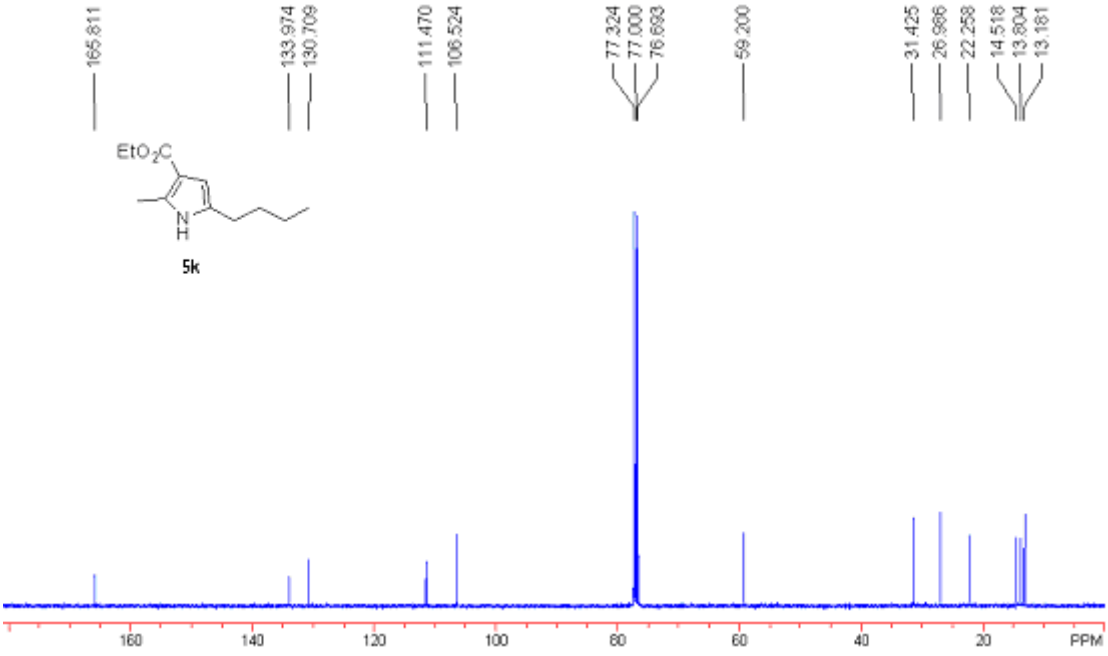

165.845
136.835
134.030
111.209
104.547
77.318
76.999
76.675
59.198
26.708
22.373
14.529
13.181
EtO2C
5f
160
140
120
100
80
60
40
20
PPM


8.250
4.275
4.257
4.240
4.221
2.709
2.695
2.681
2.476
1.754
1.748
1.741
1.739
1.346
1.330
1.312
EtO2C
5g
0.96
2.00
1.99
4.99
4.13
3.01
166.464
134.178
125.409
118.445
109.296
77.312
77.000
76.684
58.885
23.411
23.231
22.878
22.318
14.458
13.528
EtO2C
5g
PPM


7.600
7.260
5.987
5.971
5.944
5.928
5.541
5.520
5.497
5.473
4.284
4.265
4.249
4.231
3.577
3.561
2.681
2.666
2.650
2.436
2.211
2.190
2.178
2.172
2.157
1.568
1.553
1.537
1.522
1.506
1.355
1.336
1.319
EtO2C
N
H
5h
0.91
0.98
1.01
2.00
1.99
2.02
2.99
2.04
2.10
3.02
8
7
6
5
4
3
2
1
0


166.249
132.483
130.178
128.838
125.279
120.627
110.775
77.315
76.999
76.684
58.991
25.611
25.539
25.107
25.069
14.523
14.008
EtO2C
N
H
5h
160
140
120
100
80
60
40
20
PPI


7.967
6.220
6.213
4.274
4.257
4.238
4.221
2.524
2.506
2.485
1.610
1.592
1.573
1.553
1.534
1.389
1.369
1.351
1.346
1.328
1.310
0.936
0.917
0.898
0.000
EtO2C
5k
0.91
0.94
2.00
4.87
2.04
5.18
3.02
8
6
4
2
0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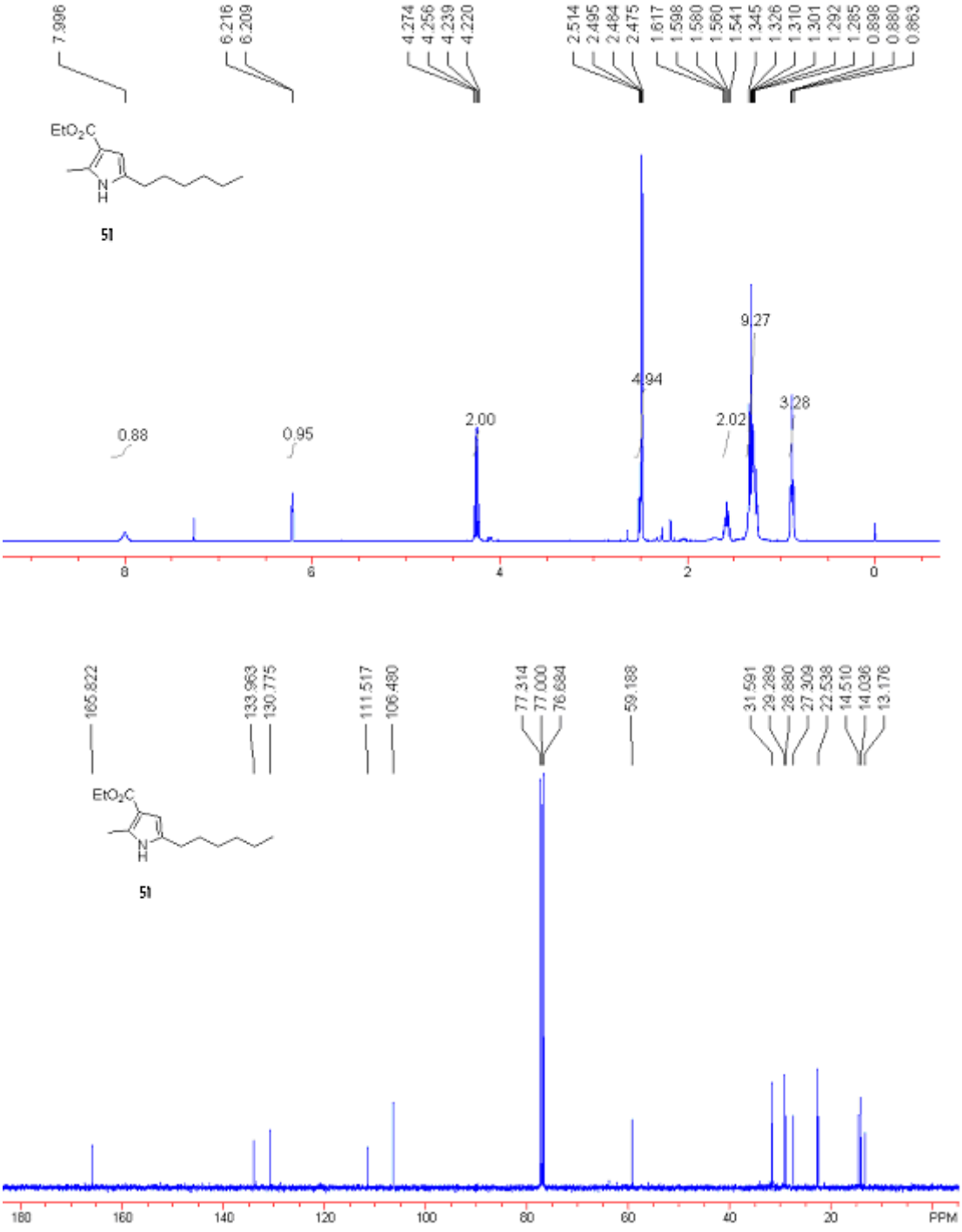
130.709
111.470
106.524
77.324
77.000
76.693
59.200
31.425
26.986
22.258
14.518
13.804
13.181
EtO2C
5k
160
140
120
100
80
60
40
20
PPM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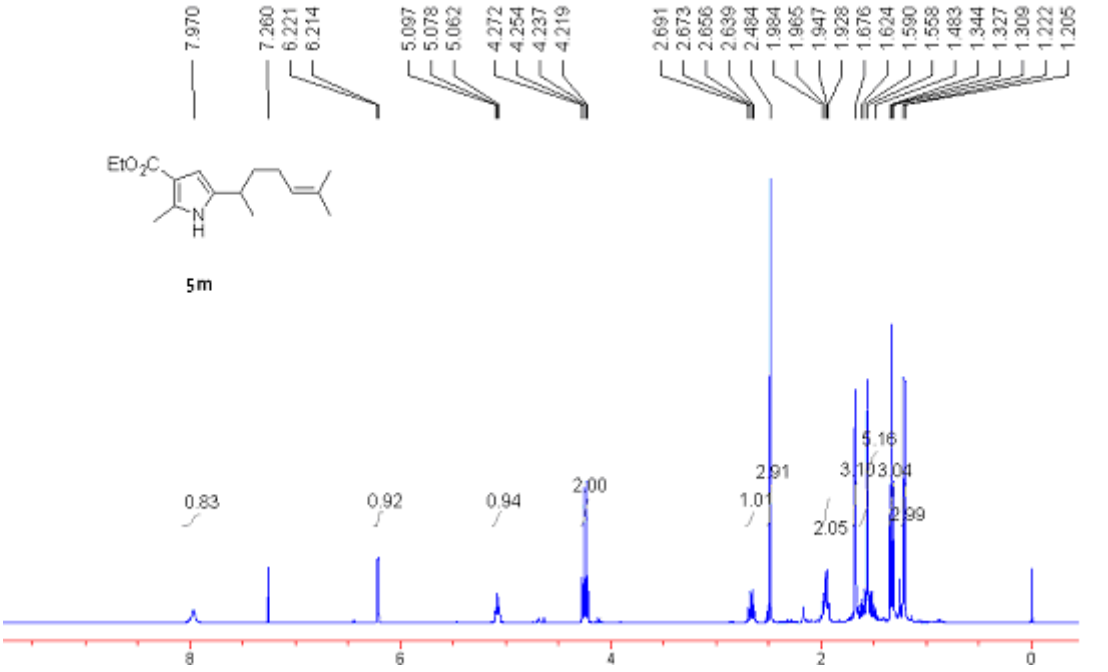
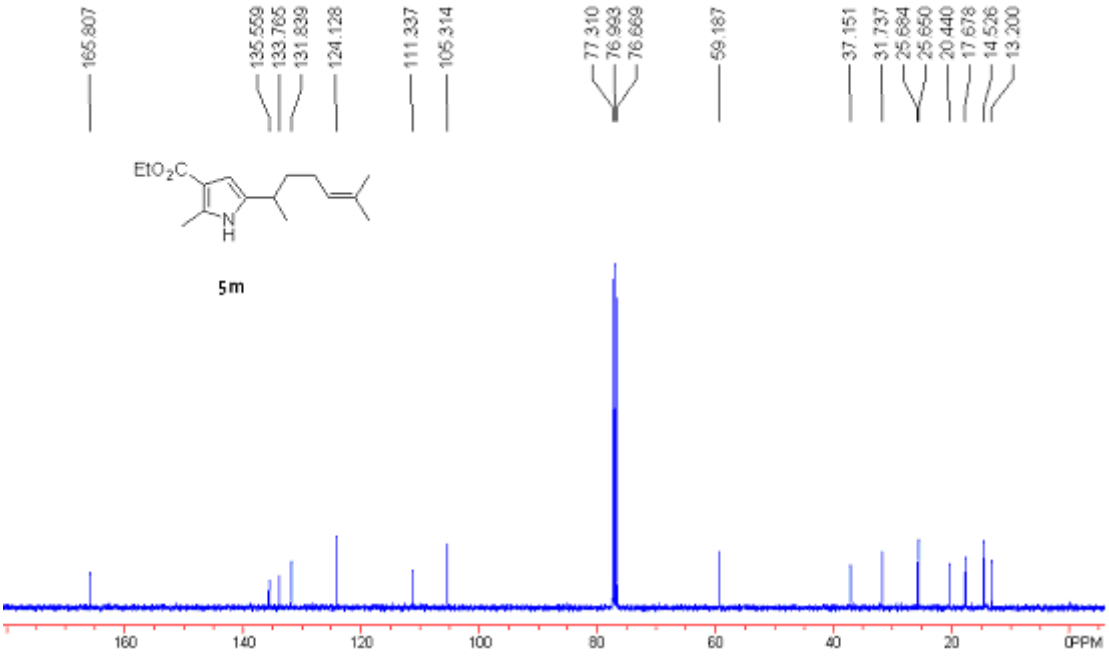
6.209
4.274
4.256
4.239
4.220
2.514
2.495
2.484
2.475
1.617
1.598
1.580
1.560
1.541
1.345
1.326
1.310
1.301
1.292
1.285
0.898
0.880
0.863
EtO2C
N
H
51
0.88
0.95
2.00
4.94
2.02
9.27
3.28
8
6
4
2
0
165.822
133.963
130.775
111.517
106.480
77.314
77.000
76.684
59.188
31.591
29.289
28.880
27.309
22.538
14.510
14.036
13.176
EtO2C
N
H
51
180
160
140
120
100
80
60
40
20
PPM


7.970
7.260
6.221
6.214
5.097
5.078
5.062
4.272
4.254
4.237
4.219
2.691
2.673
2.656
2.639
2.484
1.984
1.965
1.947
1.928
1.676
1.624
1.590
1.558
1.483
1.344
1.327
1.309
1.222
1.205
EtO2C
5m
0.83
0.92
0.94
2.00
1.01
2.91
2.05
3.10
5.16
3.04
2.99
8
6
4
2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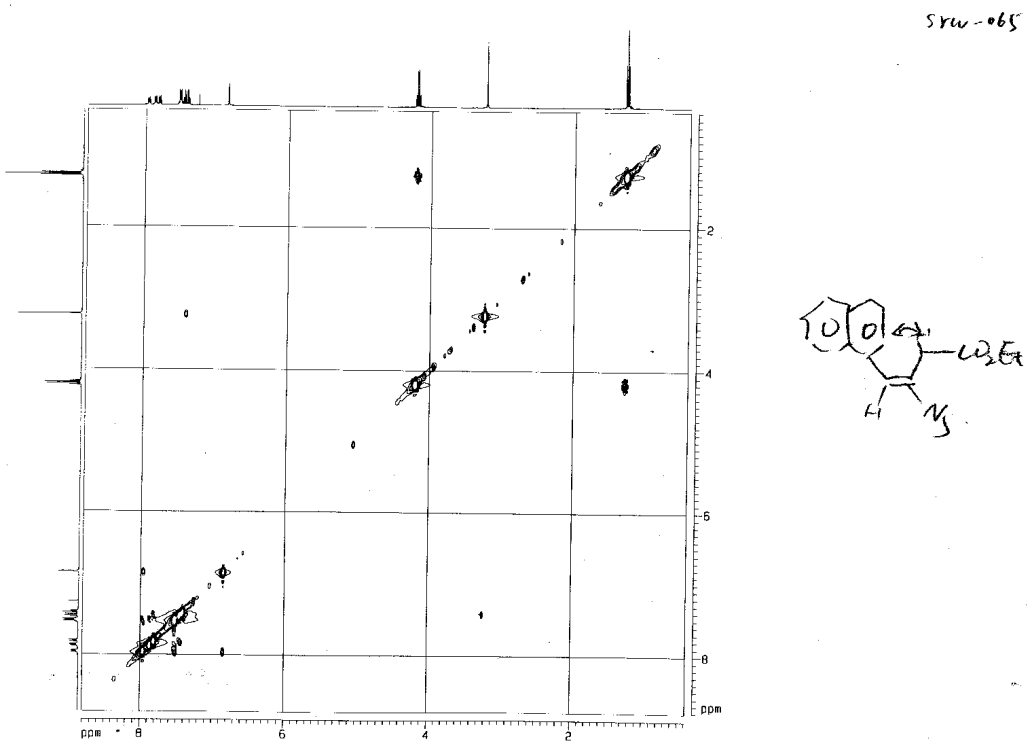
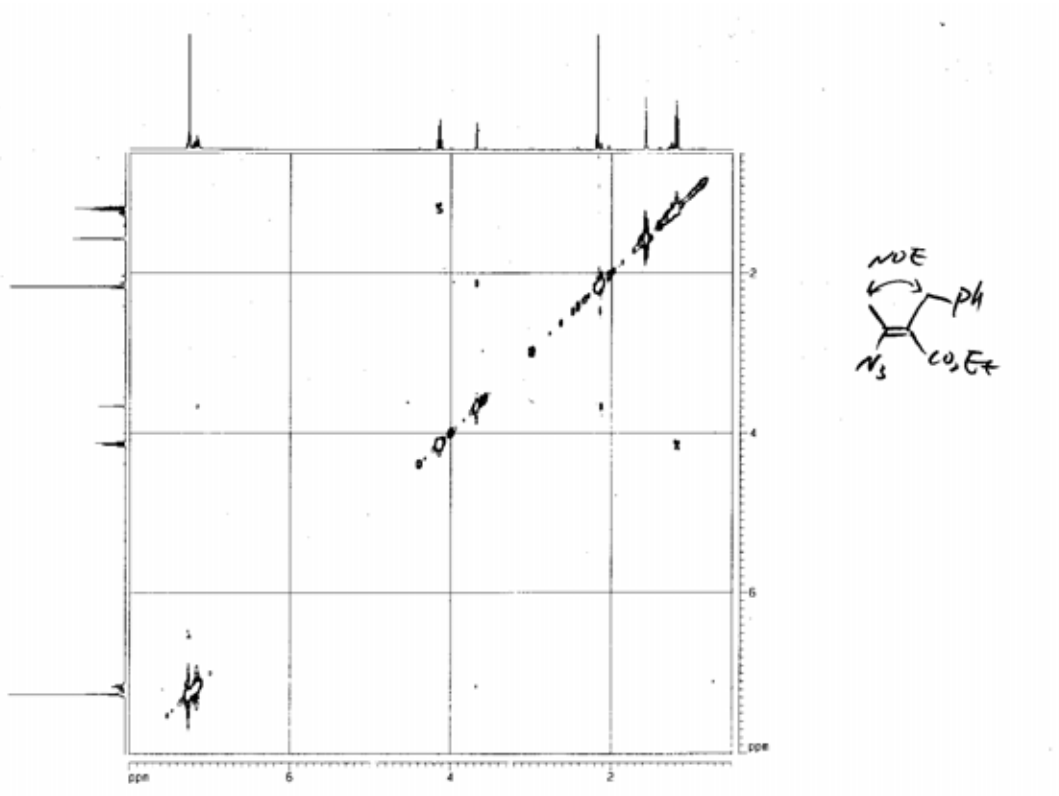
135.559
133.765
131.839
124.128
111.337
105.314
77.310
76.983
76.669
59.187
37.151
31.737
25.684
25.650
20.440
17.678
14.526
13.200
EtO2C
5m
160
140
120
100
80
60
40
20
0PPM

4. NOESY spectra for compounds *E*-2d and *Z*-3d

E-2d



Z-3d



E-3d