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Supporting Information

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Controllable [2+2]-Cycloadditions of 1,5-Bisallenes

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Index

I General Procedure I and analytical data for compounds **7a-k** S2

II General Procedure II and analytical data for compounds **8a-c, 81-m** S9

III General Procedure III and analytical data for compounds **9n** S13

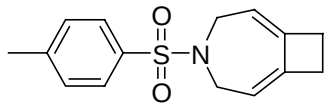
IV ^{1}H NMR and ^{13}C NMR spectra for compounds **7**, **8**, and **9** S14

General Procedure I:

A solution of bisallene **6** (0.25 mmol) in 6 mL of dry xylene was refluxed under Ar. After the reaction was complete as monitored by TLC (petroleum ether: ethyl acetate = 5: 1), rotary evaporation and flash chromatography on silica gel (eluent: petroleum ether: ethyl ether = 20: 1) afforded the product **7**.

The following compounds were prepared according to **General Procedure I:**

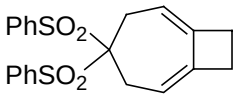
(1) 4-(*p*-Toluenesulfonyl)-4-azabicyclo[5.2.0]nona-1,6-diene (7a)



7a

A solution of bisallene **6a** (145 mg, 0.53 mmol) in 12 mL of dry xylene was refluxed under Ar for 24 hours to afford 62 mg (43 %) of the product **7a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 5.22 (s, 2 H), 4.12 (d, *J* = 2.7 Hz, 4 H), 2.39 (s, 3 H), 2.28 (s, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.2, 142.7, 137.9, 128.8, 127.7, 119.6, 50.7, 26.0, 21.4; MS (ESI) *m/z* (%) 274 (M^+-H, 100), 275 (M^+, 45), 277 (MNa^+-H, 40); IR (neat) 2926, 1710, 1674, 1598, 1495, 1448, 1338, 1161 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}NO_2S$ (M^+-H) 274.0896. Found 274.0890.

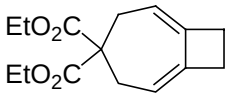
(2) 4,4-Bis(benzenesulfonyl)bicyclo[5.2.0]nona-1,6-diene (7b)



7b

A solution of bisallene **6b** (49 mg, 0.123 mmol) in 3 mL of dry xylene was refluxed under Ar for 3 hours to afford 30 mg (61 %) of the product **7b**: solid, m.p. 146-147 ^{o}C (petroleum ether, ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 4 H), 7.66 (t, *J* = 6.9 Hz, 2 H), 7.52 (t, *J* = 8.1 Hz, 4 H), 5.10-5.00 (m, 2 H), 3.24 (d, *J* = 4.2 Hz, 4 H), 2.21 (s, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.4, 138.0, 134.3, 131.6, 128.1, 114.9, 89.4, 32.1, 26.1; MS (ESI) *m/z* (%) 401 (MH^+, 17.5), 418 (MNH_4^+, 24.0), 423 (MNa^+, 6.0); IR (neat) 2929, 1710, 1583, 1478, 1448, 1330, 1311, 1147 cm^{-1}; Anal Calcd for $C_{21}H_{20}O_4S_2$: C, 62.98; H, 5.03. Found: C, 63.20; H, 5.41.

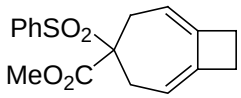
(3) 4,4-Bis(ethoxycarbonyl)bicyclo[5.2.0]nona-1,6-diene (7c)



7c

A solution of bisallene **6c** (119 mg, 0.44 mmol) in 10 mL of dry xylene was refluxed under Ar for 46 hours to afford 45 mg (38 %) of the product **7c**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.35-5.25 (t, *J* = 4.2 Hz, 2 H), 4.16 (q, *J* = 6.9 Hz, 4 H), 2.79 (d, *J* = 4.2 Hz , 4 H), 2.53 (s, 4 H), 1.22 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 171.4, 141.7, 118.5, 61.2, 56.1, 36.1, 26.2, 14.0; MS (EI) *m/z* (%) 264 (M^+, 7.20), 117 (100); IR (neat) 2929, 1732, 1244, 1187 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}O_4$ 264.1362. Found 264.1357.

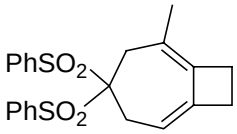
(4) 4-(Benzenesulfonyl)-4-(methoxycarbonyl)bicyclo[5.2.0]nona-1,6-diene (7d)



7d

A solution of bisallene **6d** (80 mg, 0.25 mmol) in 6 mL of dry xylene was refluxed under Ar for 8 hours to afford 49 mg (61 %) of the product **7d**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2 H), 7.68 (t, *J* = 7.8 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 2 H), 5.27 (d, *J* = 6.0 Hz, 2 H), 3.63 (s, 3 H), 3.20 (dd, *J* = 15.6, 6.9 Hz, 2 H), 2.77 (d, *J* = 16.2 Hz, 2 H), 2.51 (s, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 167.2, 141.9, 135.3, 134.3, 130.4, 128.8, 116.6, 74.7, 52.9, 32.8, 26.2; MS (ESI) *m/z* (%) 319 (MH^+, 70), 336 (MNH_4^+, 100), 341 (MNa^+, 72); IR (neat) 2942, 1738, 1446, 1307, 1212, 1147 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{18}O_4SNa$ (MNa^+) 341.0818. Found 341.0821.

(5) 4,4-Bis(benzenesulfonyl)-2-methylbicyclo[5.2.0]nona-1,6-diene (7e)



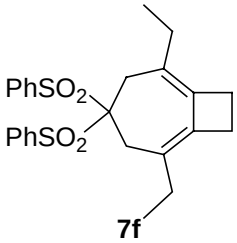
7e

A solution of bisallene **6e** (104 mg, 0.25 mmol) in 6 mL of dry xylene was refluxed under Ar for 1.5 hours to afford 72 mg (69 %) of the product **7e**: solid, m.p. 140-141 ^{o}C (petroleum ether / ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.90 (m, 4 H), 7.70-7.55 (m, 2 H), 7.55-7.40 (m, 4 H), 4.97-4.87 (m, 1 H), 3.25-3.15 (m, 4 H), 2.03 (s, 4 H), 1.54 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.4, 138.3, 137.6, 134.2, 131.3, 128.0, 123.4, 112.5, 89.5, 37.0, 31.7, 25.5, 25.0, 19.4; MS (ESI) *m/z* (%)

415 (MH^+, 100), 432 (MNH_4^+, 72), 437 (MNa^+, 10.0); IR (neat) 2921, 1689, 1583, 1478, 1447, 1320, 1309, 1152, 1143, 1075 cm^{-1}; Anal Calcd for $C_{22}H_{22}O_4S_2$: C, 63.74; H, 5.35. Found: C, 63.71; H, 5.35.

The structure of bicyclic compound **7e** was further confirmed by single crystal X-ray diffraction study.

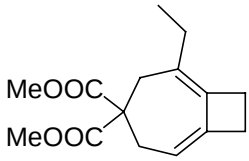
(6) 4,4-Bis(benzenesulfonyl)-2,6-diethylbicyclo[5.2.0]nona-1,6-diene (7f)



7f

A solution of bisallene **6f** (114 mg, 0.25 mmol) in 6 mL of dry xylene was refluxed under Ar for 1 hour to afford 84 mg (74 %) of the product **7f**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 4 H), 7.61 (t, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.2 Hz, 4 H), 3.16 (s, 4 H), 1.94 (s, 4 H), 1.83 (q, *J* = 7.5 Hz, 4 H), 0.96 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.6, 136.3, 134.1, 131.0, 127.9, 126.0, 90.0, 34.7, 27.1, 24.5, 11.9; MS (ESI) *m/z* (%) 457 (MH^+, 48), 474 (MNH_4^+, 100), 479 (MNa^+, 20); IR (neat) 2963, 1583, 1447, 1326, 1310, 1148, 1076 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}O_4S_2Na$ 479.1321. Found 479.1319.

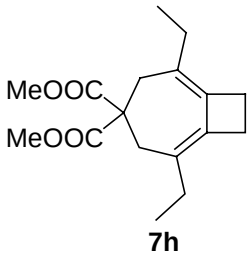
(7) 4,4-Bis(methoxycarbonyl)-2-ethylbicyclo[5.2.0]nona-1,6-diene (7g)



7g

A solution of bisallene **6g** (134 mg, 0.5 mmol) in 12 mL of dry xylene was refluxed under Ar for 10 hours to afford 75 mg (56 %) of the product **7g**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.25-5.18 (m, 1 H), 3.68 (s, 6 H), 2.76 (s, 4 H), 2.48 (s, 4 H), 1.97 (q, *J* = 7.2 Hz, 2 H), 0.99 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.1, 141.2, 134.9, 132.5, 116.2, 55.7, 52.5, 39.2, 35.9, 26.9, 26.0, 25.0, 12.0; MS (EI) *m/z* (%) 264 (M^+, 69.73), 189 (100); IR (neat) 2960, 2929, 1736, 1245, 1200 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}O_4$ 264.1362. Found 264.1373.

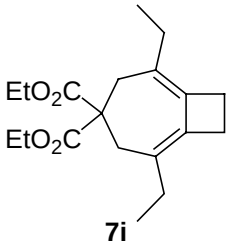
(8) 4,4-Bis(methoxycarbonyl)-2,6-diethylbicyclo[5.2.0]nona-1,6-diene (7h)



7h

A solution of bisallene **6h** (142 mg, 0.49 mmol) in 12 mL of dry xylene was refluxed under Ar for 24 hours to afford 99 mg (70 %) of the product **7h**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (s, 6 H), 2.69 (s, 4 H), 2.42 (s, 4 H), 1.93 (q, *J* = 7.5 Hz, 4 H), 0.97 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.1, 134.2, 130.0, 55.4, 52.4, 38.7, 26.8, 24.6, 12.0; MS (EI) *m/z* (%) 292 (M^+, 31.76), 217 (100); IR (neat) 2962, 1736, 1435, 1244 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{24}O_4$ 292.1675. Found 292.1661.

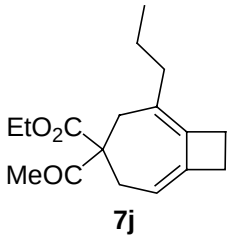
(9) 4,4-Bis(ethoxycarbonyl)-2,6-diethylbicyclo[5.2.0]nona-1,6-diene (7i)



7i

A solution of bisallene **6i** (122 mg, 0.38 mmol) in 9 mL of dry xylene was refluxed under Ar for 6 hours to afford 84 mg (69 %) of the product **7i**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (q, *J* =7.2 Hz, 4 H), 2.69 (s, 4 H), 2.43 (s, 4 H), 1.95 (q, *J* =7.5 Hz, 4 H), 1.20 (t, *J* =7.2 Hz, 6 H) , 0.98 (t, *J* =7.2 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 171.7, 134.1, 130.2, 61.1, 55.4, 38.7, 26.9, 24.6, 13.9, 12.1; MS (EI) *m/z* (%) 320 (M^+, 34.12), 217 (100); IR (neat) 2975, 1735, 1459, 1236 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{28}O_4$ 320.1988. Found 320.1969.

(10) 4-(Ethoxycarbonyl)-4-acetyl-2-propylbicyclo[5.2.0]nona-1,6-diene (7j)

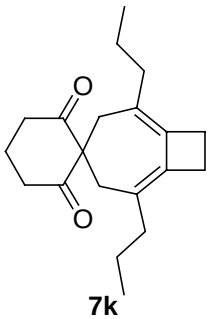


7j

A solution of bisallene **6j** (130 mg, 0.5 mmol) in 12 mL of dry xylene was refluxed under Ar for 5 hours to afford 91 mg (70 %) of the product **7j**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.24 (t, *J* = 4.8 Hz, 1 H), 4.14 (q, *J* = 7.2 Hz, 2 H), 2.72-2.62 (m, 4 H), 2.46 (s, 4 H), 2.17 (s, 3 H), 1.93 (t, *J* = 7.2 Hz, 2 H), 1.52-1.38 (m, 2 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$)

δ 204.7, 172.2, 141.5, 135.8, 131.3, 116.2, 61.20, 61.18, 38.9, 36.1, 35.1, 25.8, 25.7, 25.2, 20.6, 13.99, 13.96; MS (EI) *m/z* (%) 276 (M^+, 16.25), 43 (100); IR (neat) 2959, 2930, 1747, 1716, 1464, 1224, 1202 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{24}O_3$ 276.1725. Found 276.1714.

(11) 4,4-(pentamethylene-1',5'-dioxo)-2,6-dipropylbicyclo[5.2.0]nona-1,6-diene (7k)



7k

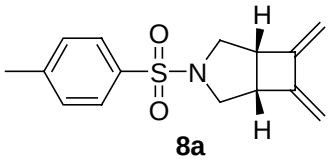
A solution of bisallene **6k** (121 mg, 0.4 mmol) in 10 mL of dry xylene was refluxed under Ar for 0.5 hours to afford 94 mg (78 %) of the product **7k**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 2.57 (t, *J* = 6.9 Hz, 4 H), 2.43 (s, 4 H), 2.34 (s, 4 H), 1.88 (t, *J* = 7.2 Hz, 4 H), 1.81 (t, *J* = 6.9 Hz, 2 H), 1.45-1.30 (m, 4 H), 0.81 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 206.4, 136.3, 127.6, 67.3, 37.8, 36.4, 36.2, 24.8, 20.9, 18.6, 13.9; MS (EI) *m/z* (%) 300 (M^+, 59.99), 257 (100); IR (neat) 2956, 1728, 1698, 1458, 1429, 1317 cm^{-1}; HRMS (MALDI) calcd for $C_{20}H_{29}O_2$ (M^++H) 301.2162. Found 301.2151.

General Procedure II:

To a stirred solution of bisallene **6** (0.25 mmol) and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 5 mol%) in 5 mL of dry toluene were added K_2CO_3 (138 mg, 1 mmol, 4 equiv) and *n*-Bu_4NI (185 mg, 0.5 mmol, 2 equiv). The reaction mixture was refluxed under Ar for 4 hours. After the reaction was complete as monitored by TLC (petroleum ether: ethyl acetate = 5: 1), rotary evaporation and flash chromatography on silica gel (petroleum ether: ethyl ether = 20: 1) afforded the product **8**.

The following compounds were prepared according to **General Procedure II:**

(1) 6,7-Dimethylene-3-(*p*-toluenesulfonyl)-3-azabicyclo[3.2.0]heptane (8a)[7h]

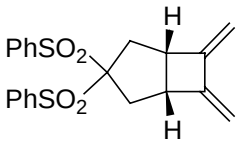


8a

Bisallene **6a** (140 mg, 0.51 mmol), $Pd(PPh_3)_4$ (27 mg, 0.023 mmol, 5 mol%), K_2CO_3 (281 mg, 2.04 mmol, 4 equiv), *n*-Bu_4NI (369 mg, 1 mmol, 2 equiv) and 10 mL of dry toluene were added to a flame-dried argon-flushed Schlenk tube. After heating at 80-85^oC for 4 hours and usual workup, the reaction afforded 82 mg (59 %) of the product **8a**: solid, m.p. 77-79 ^oC (petroleum ether, ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 5.21 (s, 2 H), 4.79 (s, 2 H), 3.62 (d, *J* = 9.9 Hz, 2 H), 3.30 (d, *J* = 4.5 Hz, 2 H), 2.72 (dd, *J* = 9.9, 4.5 Hz, 2 H), 2.42 (s, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 149.0, 143.5, 132.1, 129.4, 128.0, 105.5, 53.3, 44.6, 21.5; MS (EI) *m/z* (%) 275 (M^+, 4.41); 91 (100); IR (neat) 2923, 2851, 1459, 1344, 1167 cm^{-1}.

The structure of bicyclic compound **8a** was further confirmed by the single crystal X-ray diffraction study.

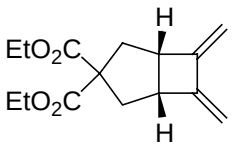
(2) 6,7-Dimethylene-3,3-bis(benzenesulfonyl)bicyclo[3.2.0]heptane (8b)



8b

Bisallene **6b** (99 mg, 0.25 mmol), $Pd(PPh_3)_4$ (18 mg, 0.016 mmol, 5 mol%) K_2CO_3 (141 mg, 1.02 mmol, 4 equiv), *n*-Bu_4NI (181 mg, 0.49 mmol, 2 equiv) and 5 mL of dry toluene were added to a flame-dried argon-flushed Schlenk tube. After heating at 80-85^{o}C for 4 hours and usual workup, the reaction afforded 61 mg (62 %) of the product **8b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (t, *J* = 7.5 Hz, 4 H), 7.71 (q, *J* = 7.5 Hz, 2 H), 7.59 (q, *J* = 7.5 Hz, 4 H), 5.18 (s, 2 H), 4.80 (s, 2 H), 3.47 (m, 2 H), 2.90-2.68 (m, 4 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 150.3, 137.2, 135.8, 134.6, 134.4, 131.1, 130.9, 128.7, 128.6, 105.9, 98.9, 46.5, 37.2; MS (ESI) *m/z* (%) 401 (MH^+, 100), 418 (MNH_4^+, 60), 423 (MNa^+, 35); IR (neat) 3071, 1711, 1448, 1329, 1311, 1146 cm^{-1}. HRMS (MALDI) calcd for $C_{21}H_{20}O_4S_2Na$ (MNa^+) 423.0695. Found 423.0708.

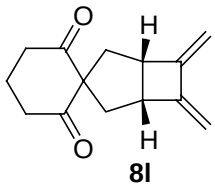
(3) 6,7-Dimethylene-3,3-bis(ethoxycarbonyl)bicyclo[3.2.0]heptane (8c)



8c

To a stirred solution of bisallene **6c** (131 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.025 mmol, 5 mol%) in 10 mL of dry toluene were added K_2CO_3 (284 mg, 2.06 mmol, 4 equiv) and *n*-Bu_4NI (370 mg, 1 mmol, 2 equiv) under Ar, After heating at 80-85^oC for 19 hours and usual workup, the reaction afforded 59 mg (45 %) of the product **8c**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.11 (d, *J* = 1.5 Hz, 2 H), 4.73 (s, 2 H), 4.20-4.00 (m, 4 H), 3.35 (m, 2 H), 2.62 (d, *J* = 13.8 Hz, 2 H), 2.27 (dd, *J* = 13.8, 8.1 Hz, 2 H), 1.30-1.16 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.1, 171.3, 150.9, 104.7, 62.8, 61.5, 61.2, 45.9, 39.3, 13.9, 13.7; MS (EI) *m/z* (%) 265 (MH^+, 4.84), 117 (100); IR (neat) 2981, 1735, 1258, 1188 cm^{-1}. HRMS (MALDI) calcd for $C_{15}H_{20}O_4Na$ (MNa^+) 287.1254. Found 287.1262.

(4) 6,7-Dimethylene-3,3-(pentamethylene-1',5'-dioxo)bicyclo[3.2.0]heptane (8l)

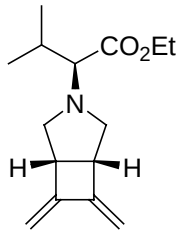


8l

To a stirred solution of bisallene **6l** (105 mg, 0.49 mmol) and $Pd(PPh_3)_4$ (32 mg, 0.028 mmol, 5 mol%) in 10 mL of dry toluene were added K_2CO_3 (278 mg, 2 mmol, 4 equiv) and *n*-Bu_4NI (366 mg, 0.99 mmol, 2 equiv) under Ar. After heating at 80-85^oC for 8 hours and usual workup, the reaction afforded 57 mg (54 %) of the product **8l**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.11 (s, 2 H), 4.75 (s, 2 H), 3.31 (m, 2 H), 2.70 (t, *J* = 6.6 Hz, 2 H), 2.62 (d, *J* = 6.6 Hz, 2 H), 2.40-2.20 (m, 4 H), 1.90-1.82 (m, 2 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 207.4, 206.5, 151.4, 104.8, 77.9, 45.9, 38.0, 37.7, 37.6, 18.3; MS (ESI) *m/z* (%) 217 (MH^+, 100); IR (neat) 2930, 1725, 1693, 1437,

1314, 1215 cm^{-1}. HRMS (MALDI) calcd for $C_{14}H_{17}O_2$ (MH^+) 217.1223. Found 217.1225.

(5) 6,7-Dimethylene-3-[1'-(S)-1'-ethoxycarbonyl-1'-isopropyl]-3-azabicyclo[3.2.0] heptane (8m)

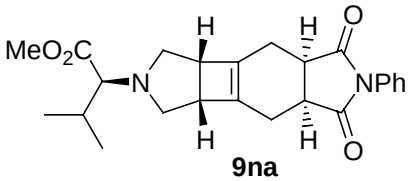


8m

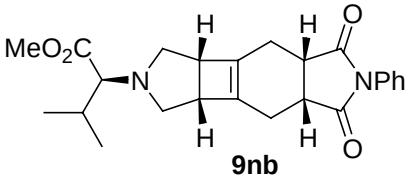
To a stirred solution of bisallene **6m** (58 mg, 0.25 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.025 mmol, 10 mol%) in 5 mL of dry toluene were added K_2CO_3 (136 mg, 1 mmol, 4 equiv) and *n*-Bu_4NI (183 mg, 0.5 mmol, 2 equiv) under Ar. After refluxing for 5 hours and usual workup, the reaction afforded 38 mg (66 %) of the product **8m** with >99% ee as determined by HPLC analysis (AD-H, *n*-Hexane : *i*-PrOH = 99.5 : 0.5, 230 nm), t_r 7.2 (major), 7.7 (minor); $[\alpha]^{20}_D$ = -45.1 (c = 0.50, Et_2O): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.12 (d, *J* = 1.2 Hz, 2 H), 4.69 (d, *J* = 0.9 Hz, 2 H), 4.14 (q, *J* = 5.1 Hz, 2 H), 3.26-3.10 (m, 2 H), 3.00-2.92 (m, 3 H), 2.60-2.45 (m, 2 H), 2.10-1.90 (m, 1 H), 1.26 (t, *J* = 7.2 Hz, 3 H), 0.93 (d, *J* = 6.6 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 171.9, 152.05, 151.95, 102.6, 102.5, 70.0, 59.5, 57.6, 51.8, 44.4, 43.9, 28.6, 19.7, 19.1, 14.6; MS (EI) *m/z* (%) 249 (MH^+, 1.18), 250 (MH^+, 2.35), 176 (100); IR (neat) 2960, 2928, 2872, 2854, 2800, 1729, 1467, 1369, 1262, 1235, 1177, 1028 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{23}NO_2$ 249.1729. Found 249.1727.

Diels-Alder reaction of [3.2.0]-bicyclic compounds with *N*-phenyl maleimide

Tetracyclic compound 9n



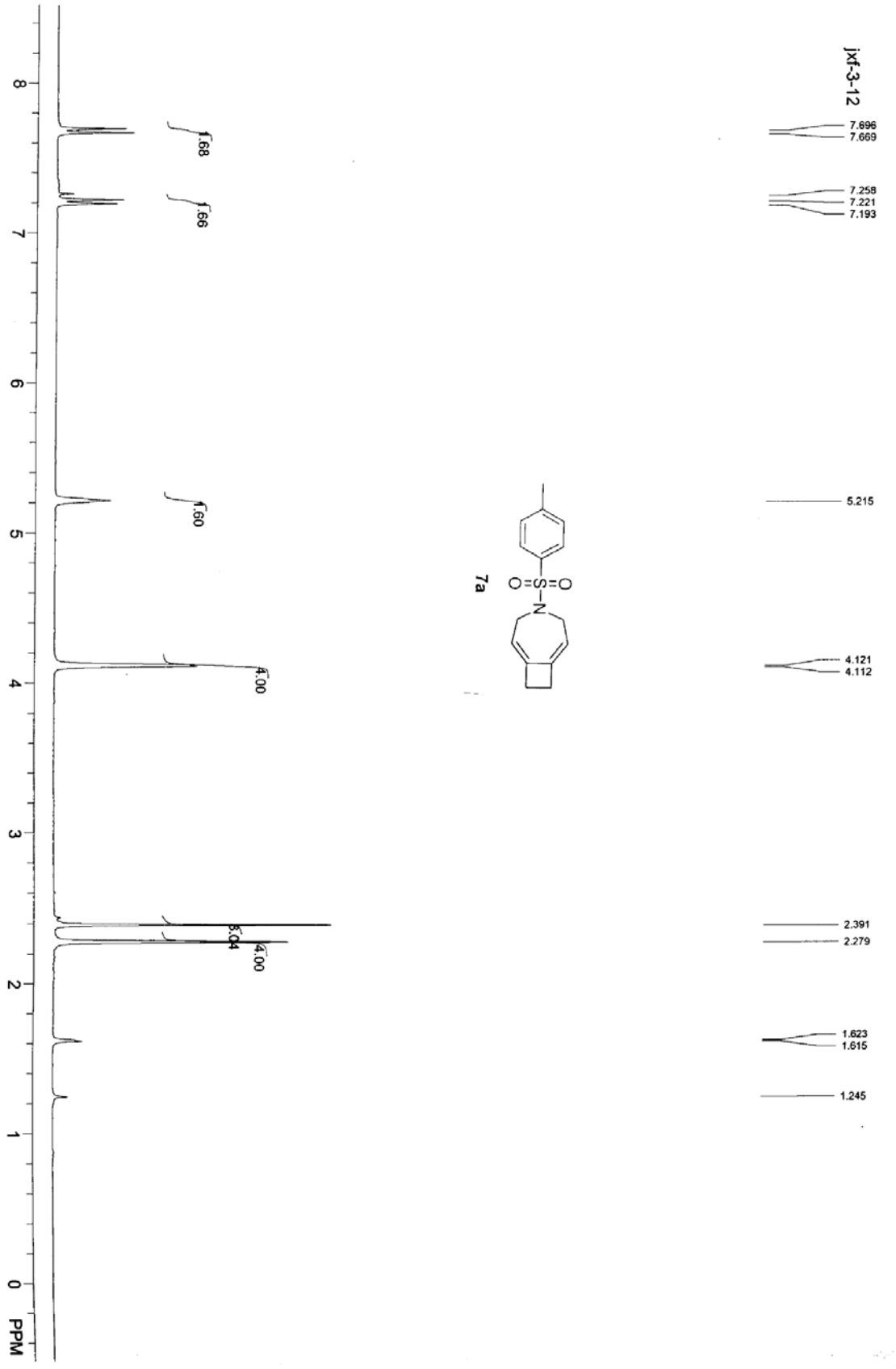
9na



9nb

A solution of **8n** (13 mg, 0.055 mmol) and *N*-phenyl maleimide (19 mg, 0.11 mmol, 2 equiv) in 2 mL of dry toluene were refluxed under Ar for 8 hours to afford 24 mg (100 %) of the product **9n** (**9na : 9nb** = 100 : 3 determined by ^{1}H NMR analysis)**,** $[\alpha]^{20}_{D}$ = -20.6 (c = 1.00, $CHCl_3$): solid, m.p. 123-124 ^{o}C (petroleum ether / ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.41 (m, 2 H), 7.41-7.32 (m, 1 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 3.67 (s, 3 H), 3.30-3.22 (m, 2 H), 3.22-3.10 (m, 2 H), 2.95 (d, *J* = 10.5 Hz, 1 H), 2.80-2.68 (m, 2 H), 2.58-2.30 (br, 4 H), 2.18-2.04 (m, 2 H), 2.10-1.85 (m, 1 H), 0.91 (d, *J* = 6.9 Hz, 3 H), 0.87 (d, *J* = 6.9 Hz, 3 H); The following data are disernible for the minor isomer: 3.65 (s), 0.79 (d, *J* = 6.6 Hz), 0.76 (d, *J* = 6.6 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 178.88, 178.85, 172.5, 138.4, 132.0, 129.1, 128.4, 126.3, 70.0, 50.5, 50.3, 46.6, 46.0, 44.3, 37.8, 37.7, 28.0, 20.7, 20.5, 19.6, 19.2; MS (ESI) *m/z* (%) 409 (MH^+, 100) , 441 (MNa^+, 30); IR (neat) 2924, 2854, 1714, 1500, 1457, 1379, 1171, 1150 cm^{-1}; HRMS (MALDI/DHB) calcd for $C_{24}H_{29}N_2O_4$ (MH^+) 409.2122. Found 409.2129.

The structure of tetracyclic compound **9na** was further confirmed by the single crystal X-ray diffraction study.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7.221
7.193
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1.615
1.245
7a
1.68
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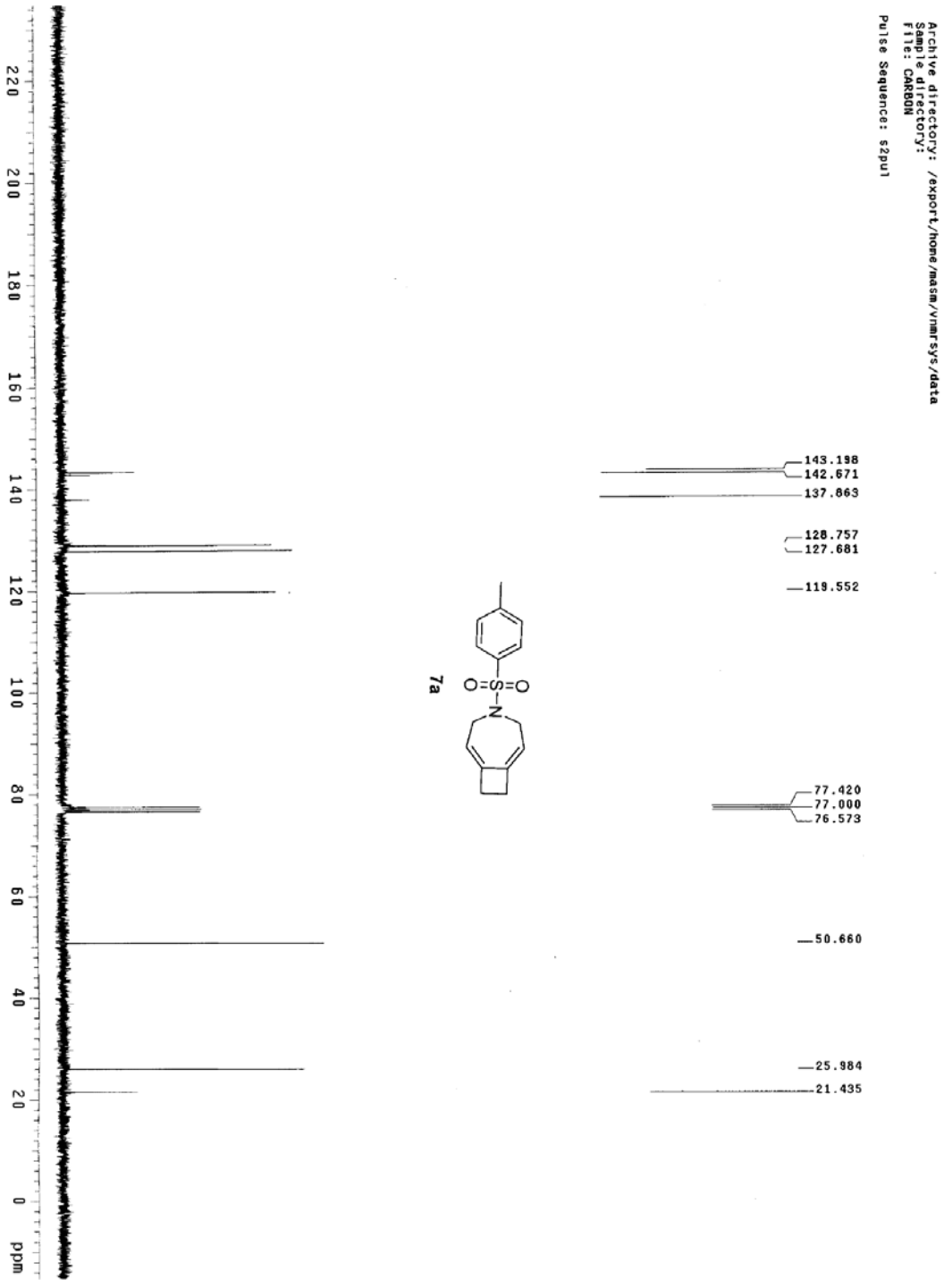
1.60
4.00
3.04
4.00
PPM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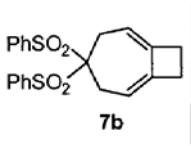
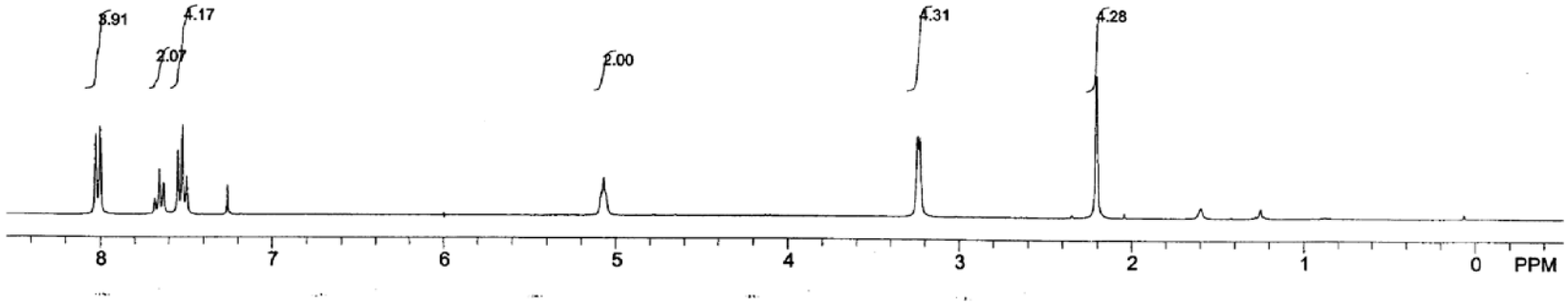
128.757
127.681
119.552
77.420
77.000
76.573
50.660
25.984
21.435
7a
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.028
8.002
7.679
7.656
7.632
7.547
7.520
7.496
7.259
jxf-2-105-2-h
5.071
3.242
3.228
2.205


PhSO2
PhSO2

7b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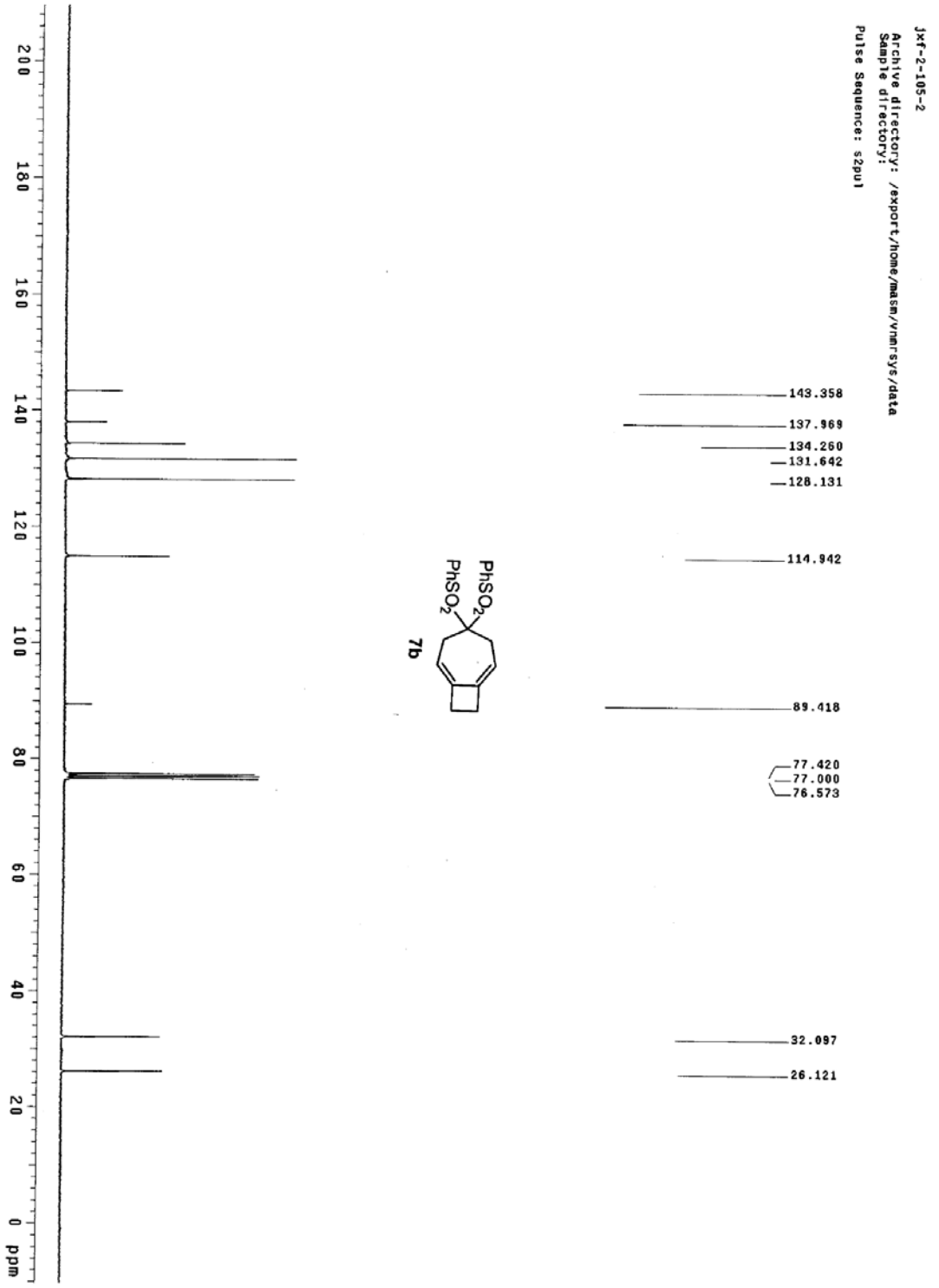
8
7
6
5
4
3
2
1
0
PPM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128.131
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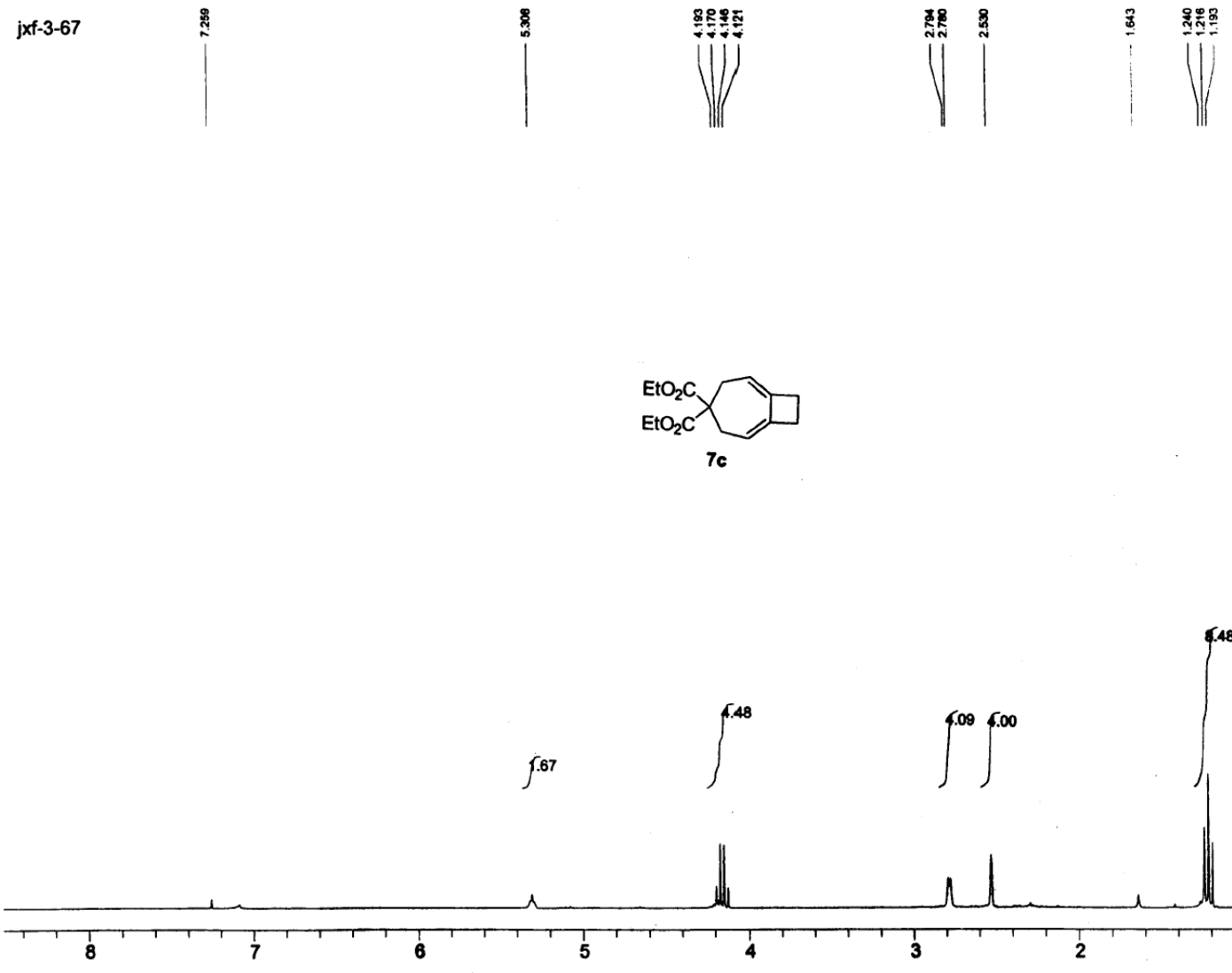
77.000
76.573
32.097
26.121
PhSO2
PhSO2
7b
200
180
160
140
120
100
80
60
40
20
0 ppm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4.193
4.170
4.146
4.121
2.794
2.780
2.530
1.643
1.240
1.216
1.193
EtO2C
EtO2C
7c
1.67
4.48
4.09
4.00
8.48
8
7
6
5
4
3
2
1
0
PPM

jxf-3-67-c2

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File: CARBON

Pulse Sequence: s2pul

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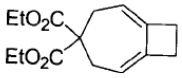
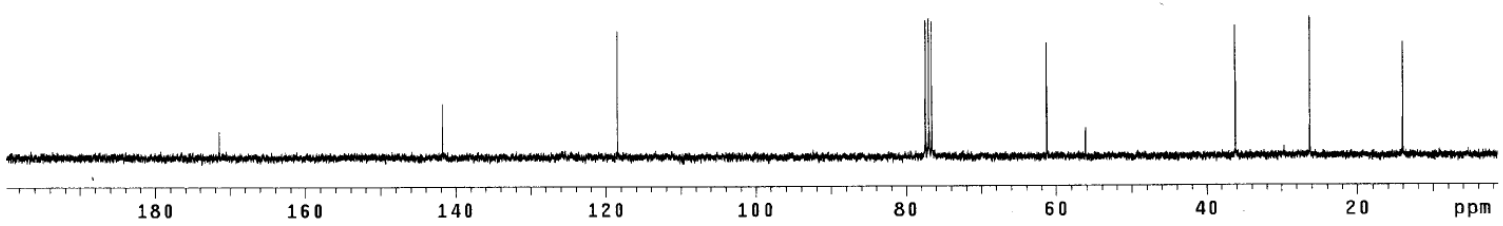
77.000
76.573
61.231
56.110
36.143
26.235
14.000



7c




jxf-3-200
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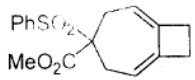
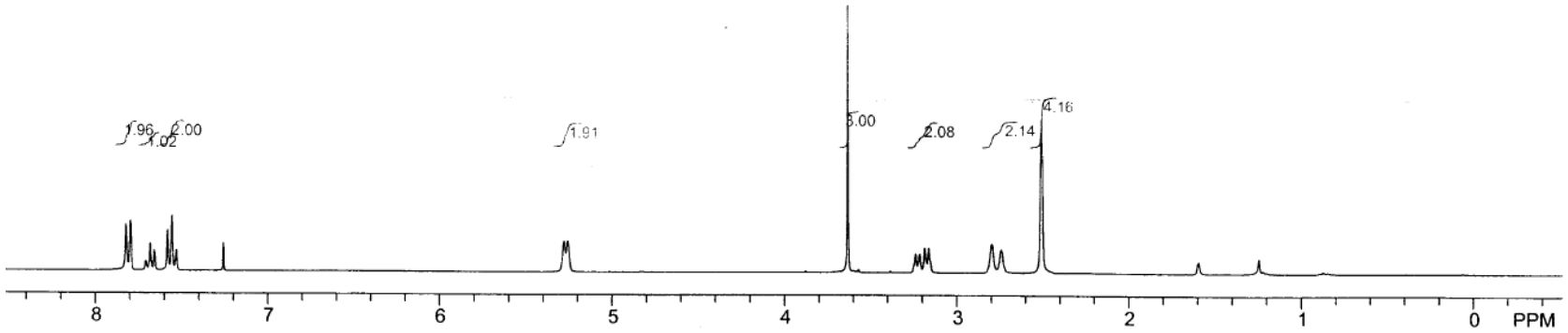
7.795
7.708
7.682
7.658
7.581
7.556
7.529
7.258
5.278
5.258
3.634
3.238
3.215
3.186
3.163
2.796
2.742
2.509
1.595
1.244


PhSO2
MeO2C

7d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1.91
5.00
2.08
2.14
4.16
8
7
6
5
4
3
2
1
0
PPM

jxf-3-200-c-2

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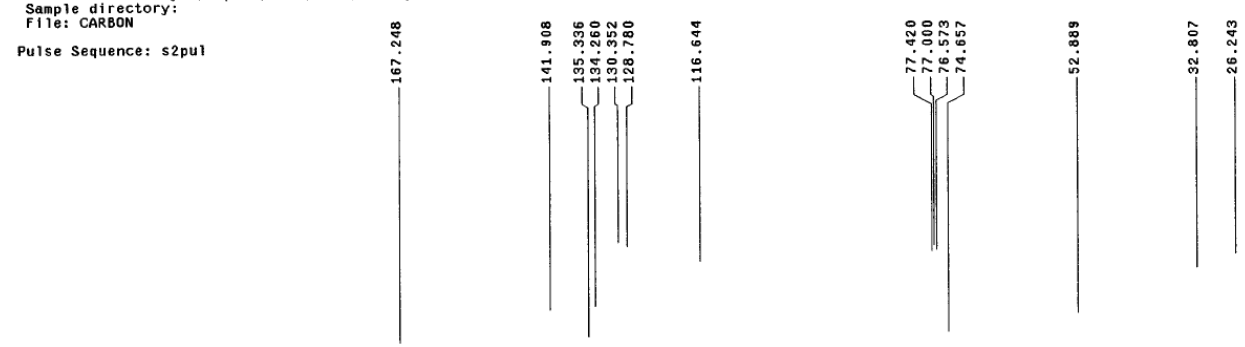
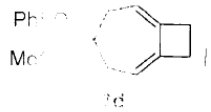
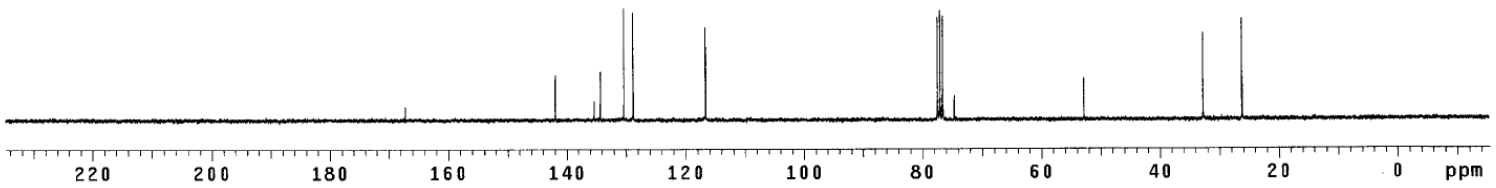
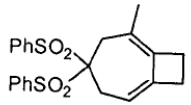
Pulse Sequence: s2pul



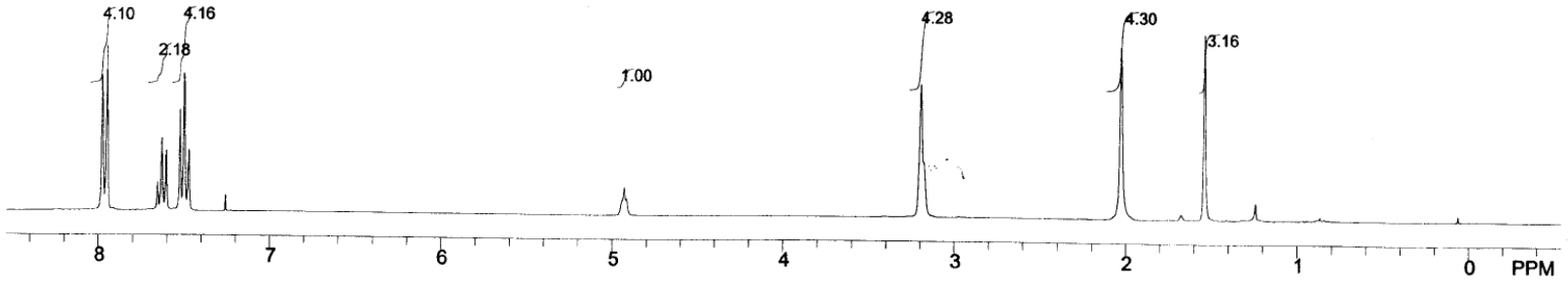





7.979
7.976
7.952
7.946
7.659
7.654
7.631
7.624
7.609
7.606
7.602
7.525
7.518
7.501
7.499
7.473
jxf-40-3-c
4.930
3.194
3.178
2.027
1.538


PhSO2
PhSO2

7e


4.10
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1.00
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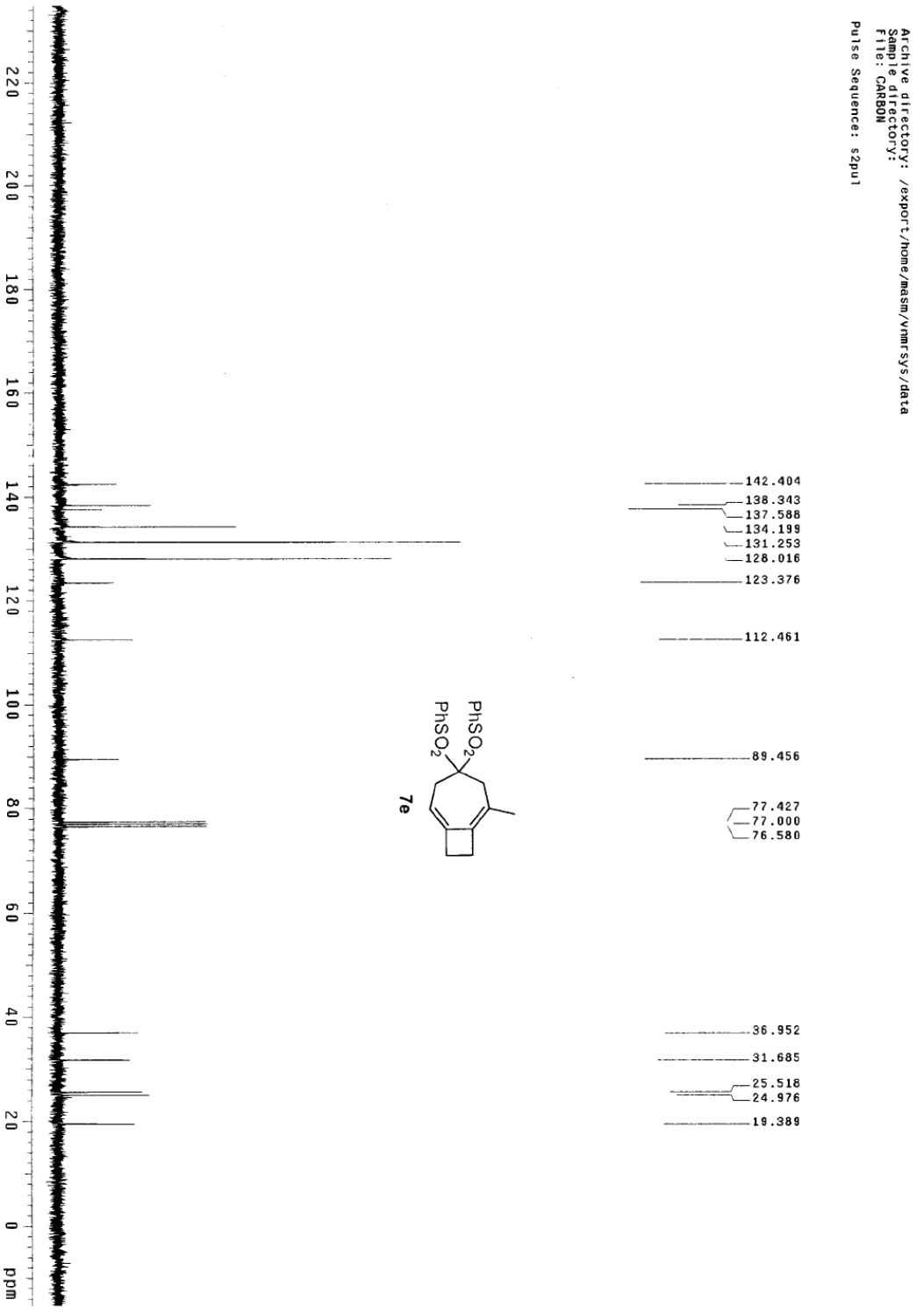
3.16
8
7
6
5
4
3
2
1
0
PPM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134.199
131.253
128.016
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112.461
89.456
77.427
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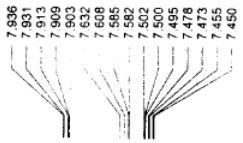
36.952
31.685
25.518
24.976
19.389
PhSO2
PhSO2
7e
220
200
180
160
140
120
100
80
60
40
20
0
ppm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7.903
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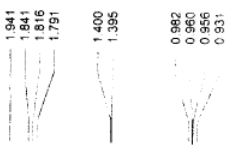
7.473
7.455
7.450

jxf-2-131-h

3.160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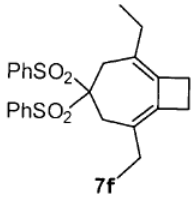
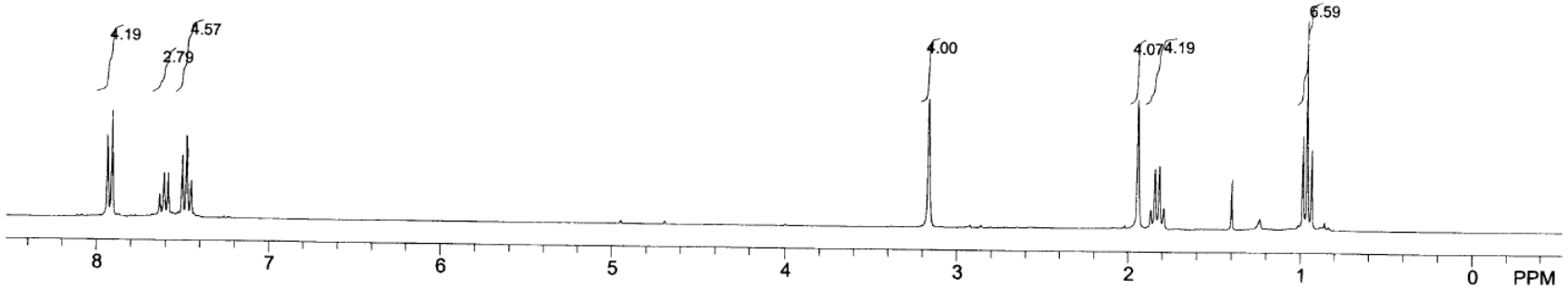
0.960
0.956
0.931


PhSO2
PhSO2

7f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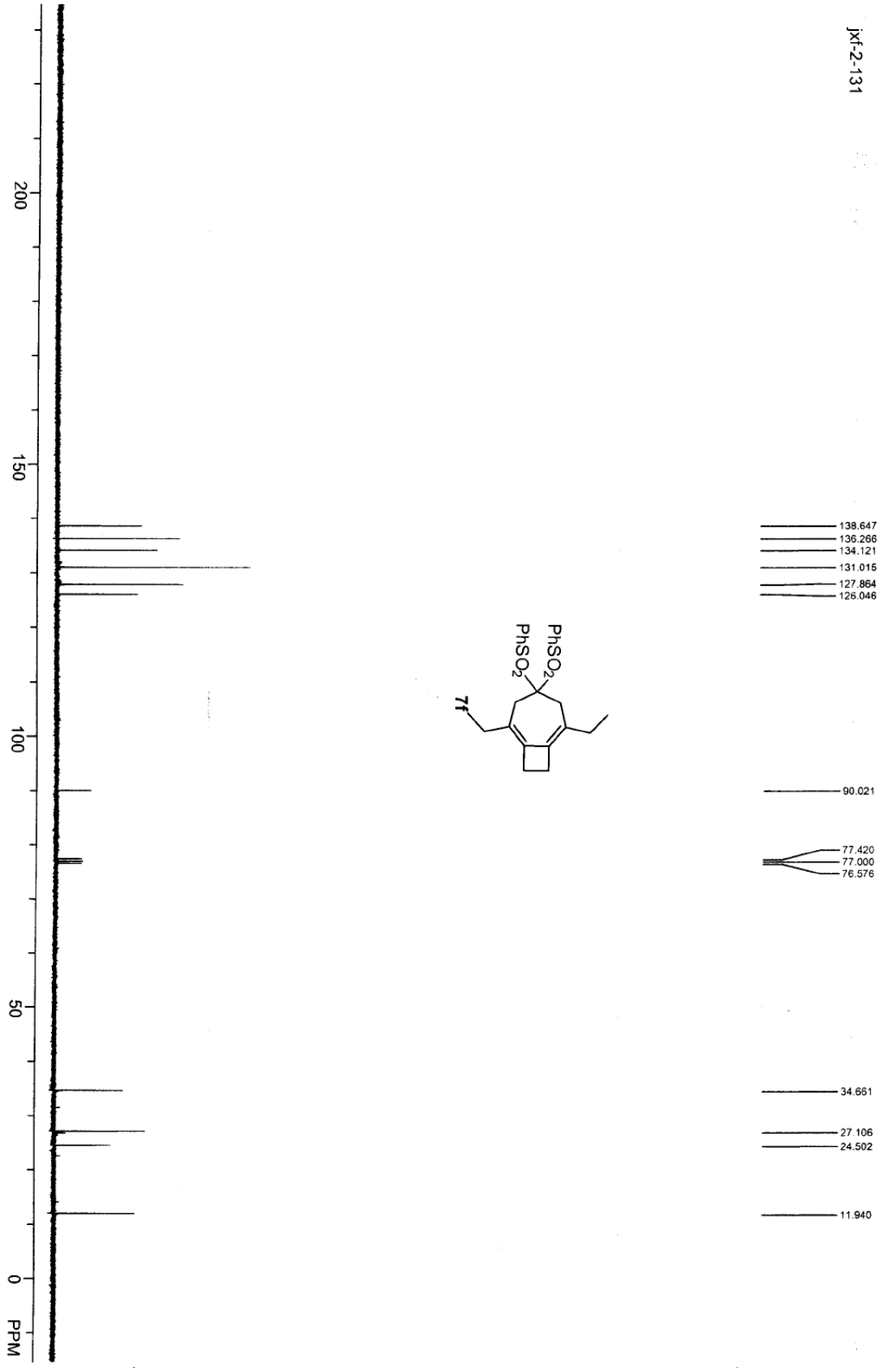
4.19
6.59
8
7
6
5
4
3
2
1
0
PPM


jxf-2-131
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100
50
0
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134.121
131.015
127.864
126.046
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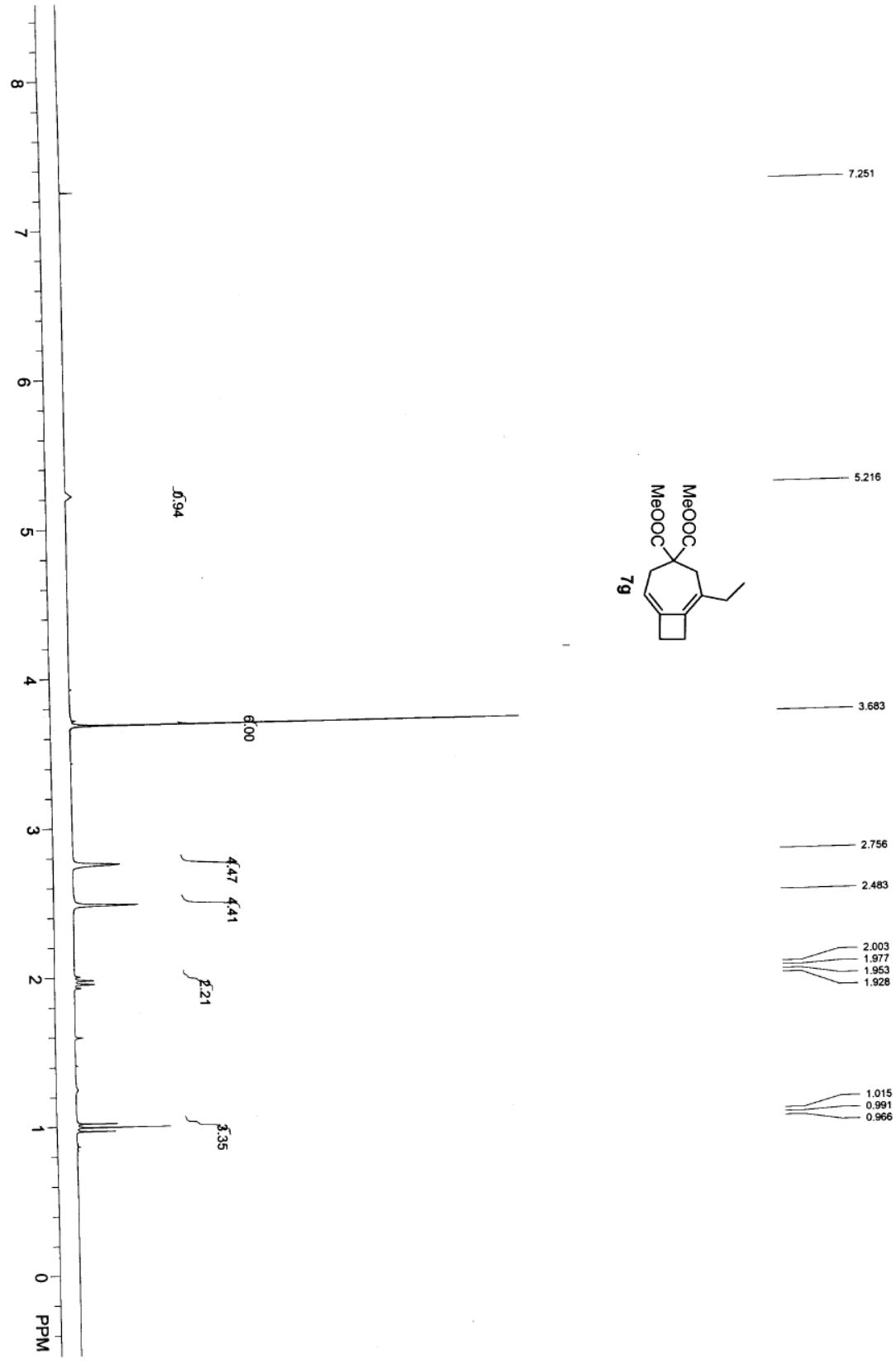
77.420
77.000
76.576
34.661
27.106
24.502
11.940
PhSO2
PhSO2
7f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2.483
2.003
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1.953
1.928
1.015
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MeOOC
MeOOC
7g
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6.00
4.47
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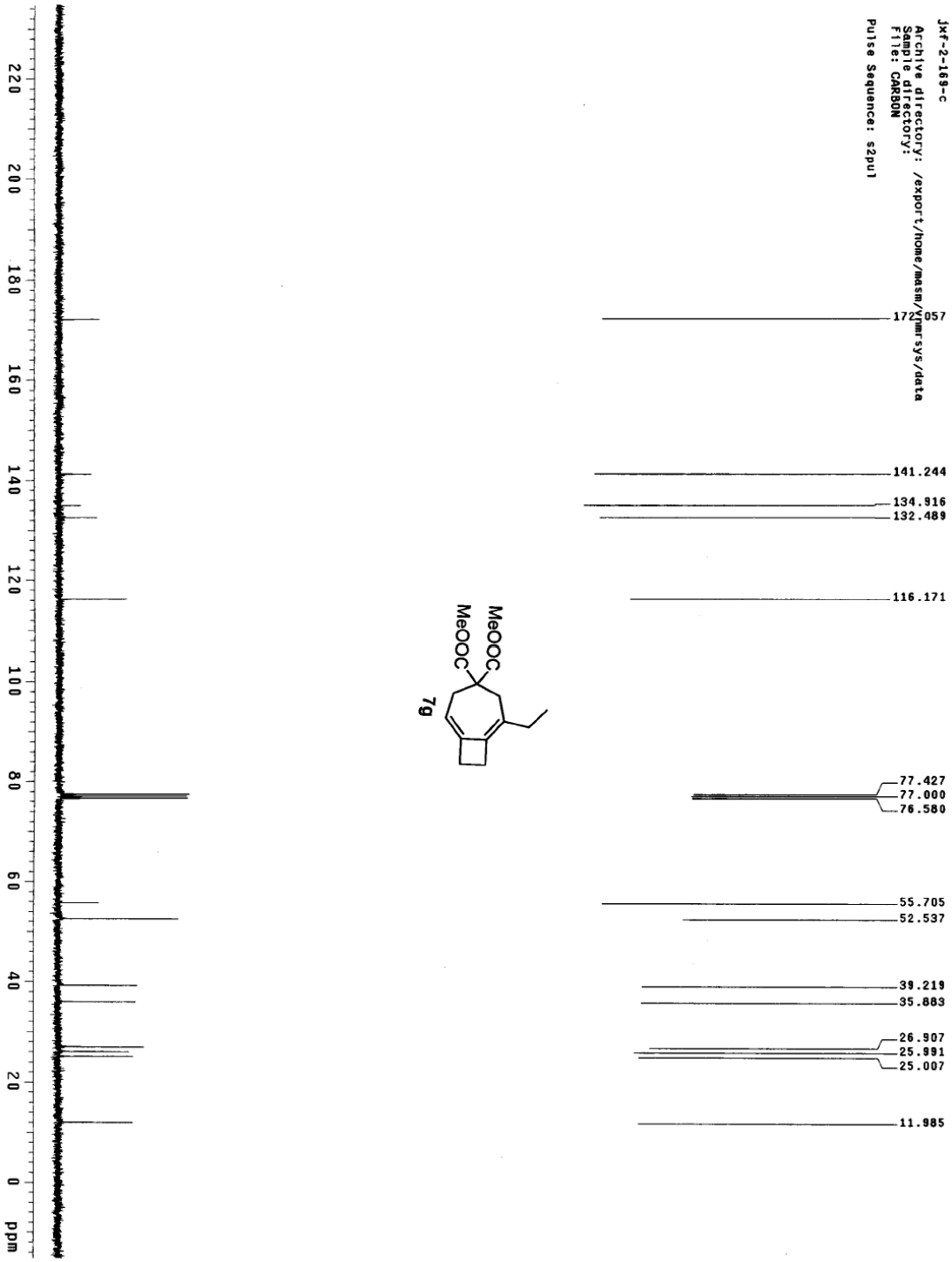
PPM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132.489
116.171
77.427
77.000
76.580
55.705
52.537
39.219
35.883
26.907
25.991
25.007
11.985
MeOOC
MeOOC
7g
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200
180
160
140
120
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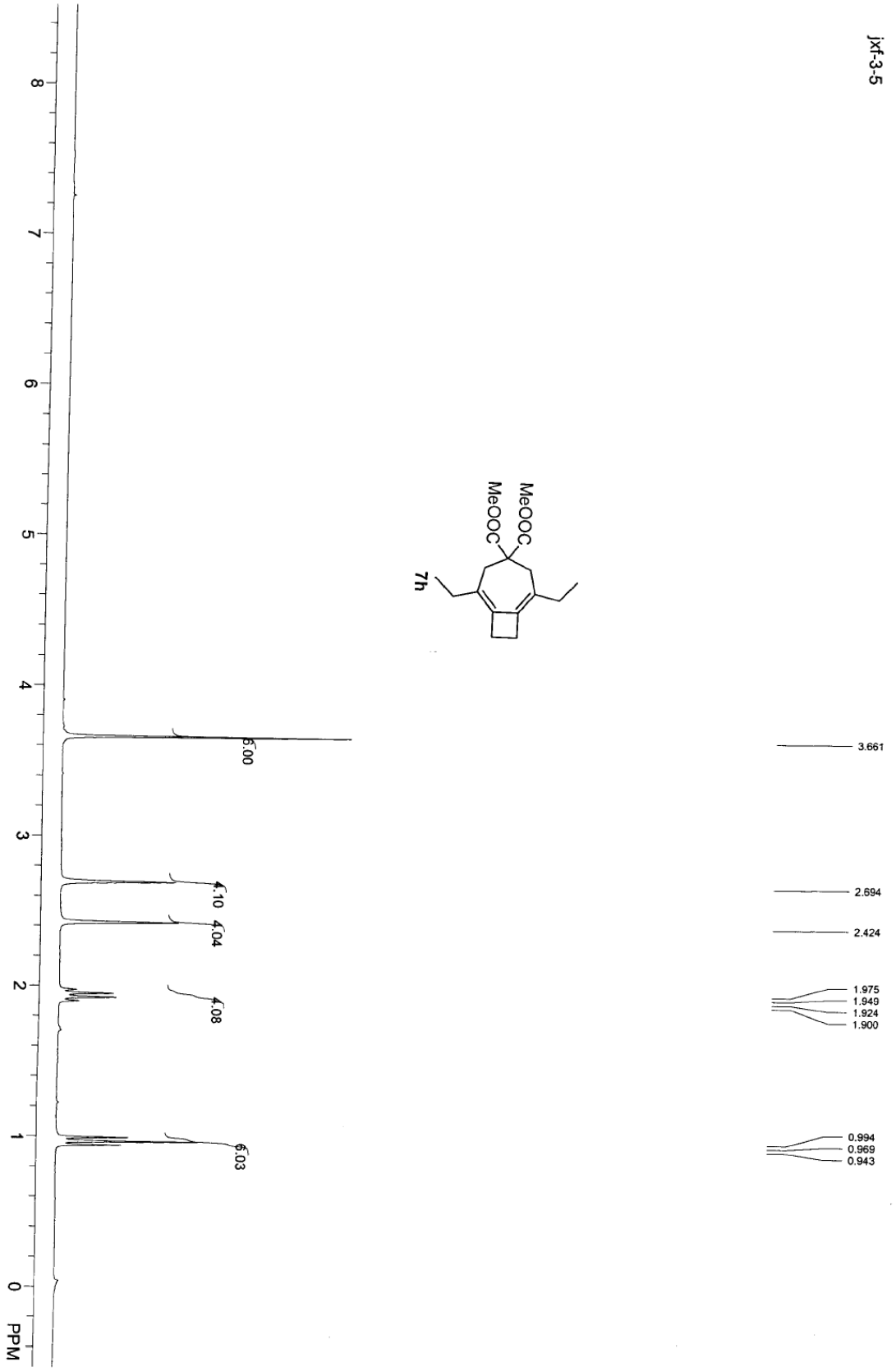
80
60
40
20
0
ppm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MeOOC
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2.424
1.975
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1.924
1.900
0.994
0.969
0.943
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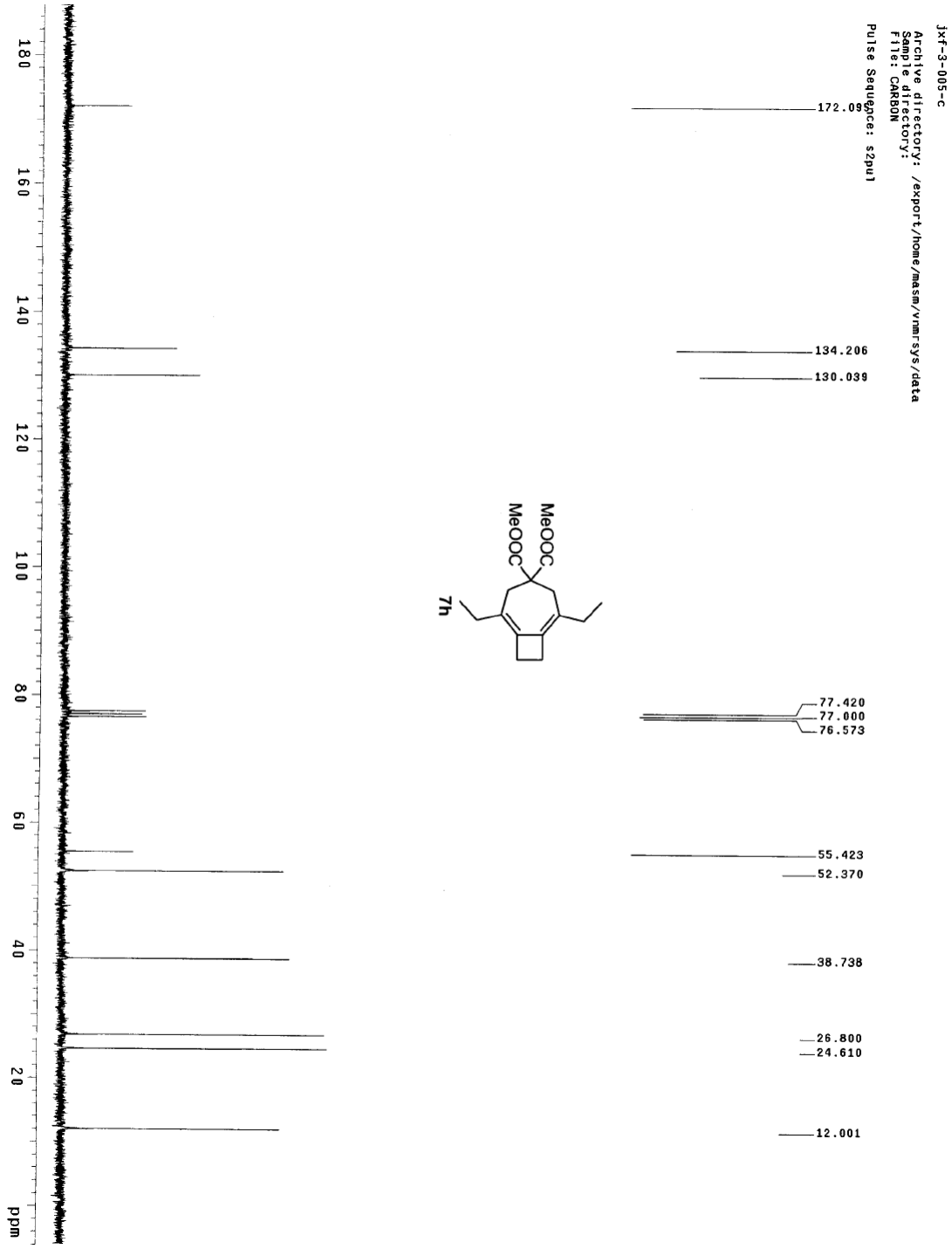
4.10
4.04
4.08
6.03
PPM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52.370
38.738
26.800
24.610
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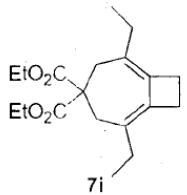
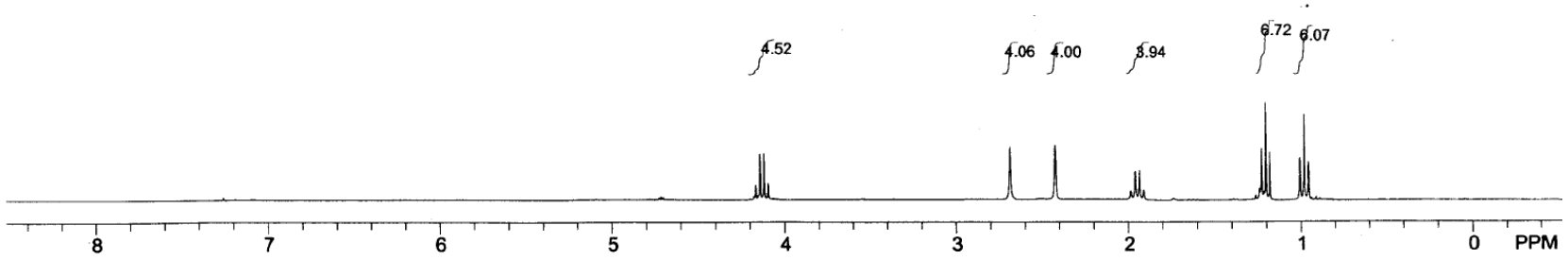
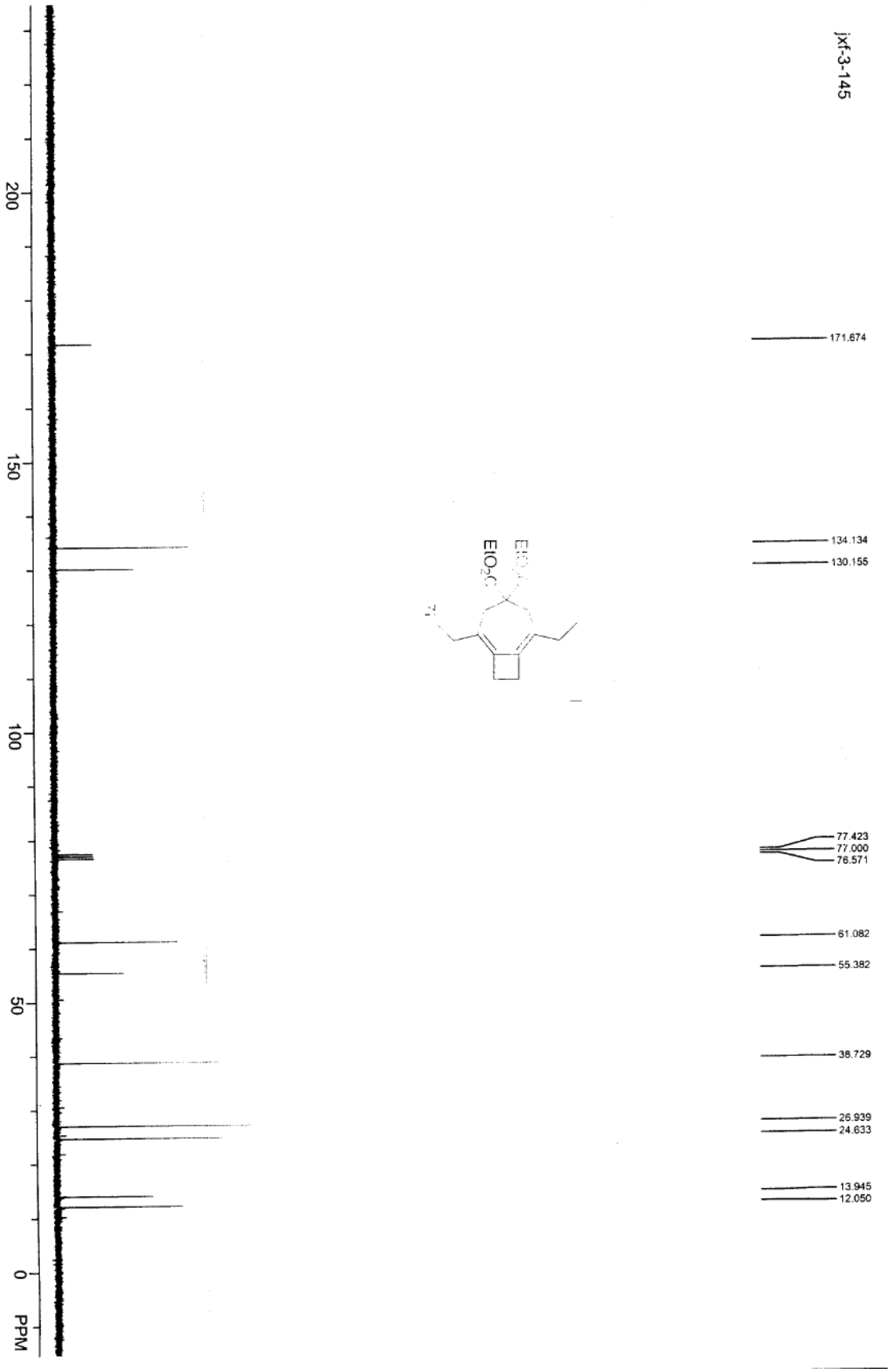
MeOOC
MeOOC
7h
180
160
140
120
100
80
60
40
20
ppm

jxf-3-145-1-h



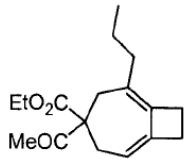
7i



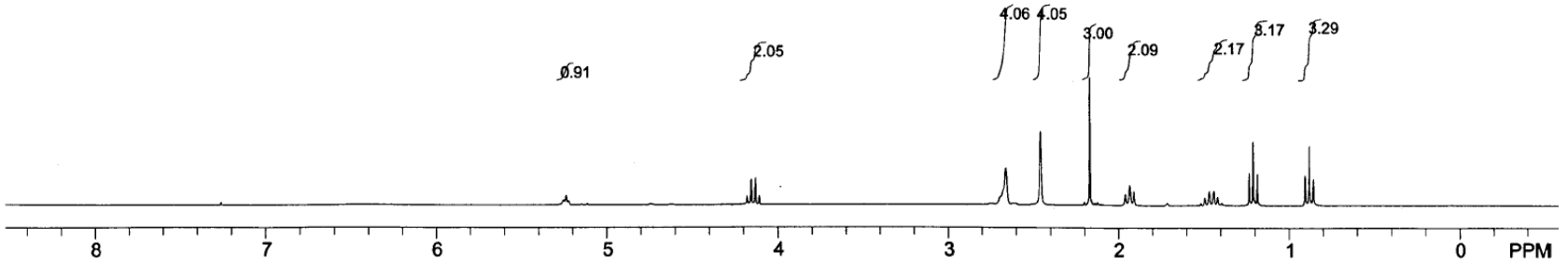

jxf-3-145
171.674
134.134
130.155
77.423
77.000
76.571
61.082
55.382
38.729
26.939
24.633
13.945
12.050
200
150
100
50
0
PPM

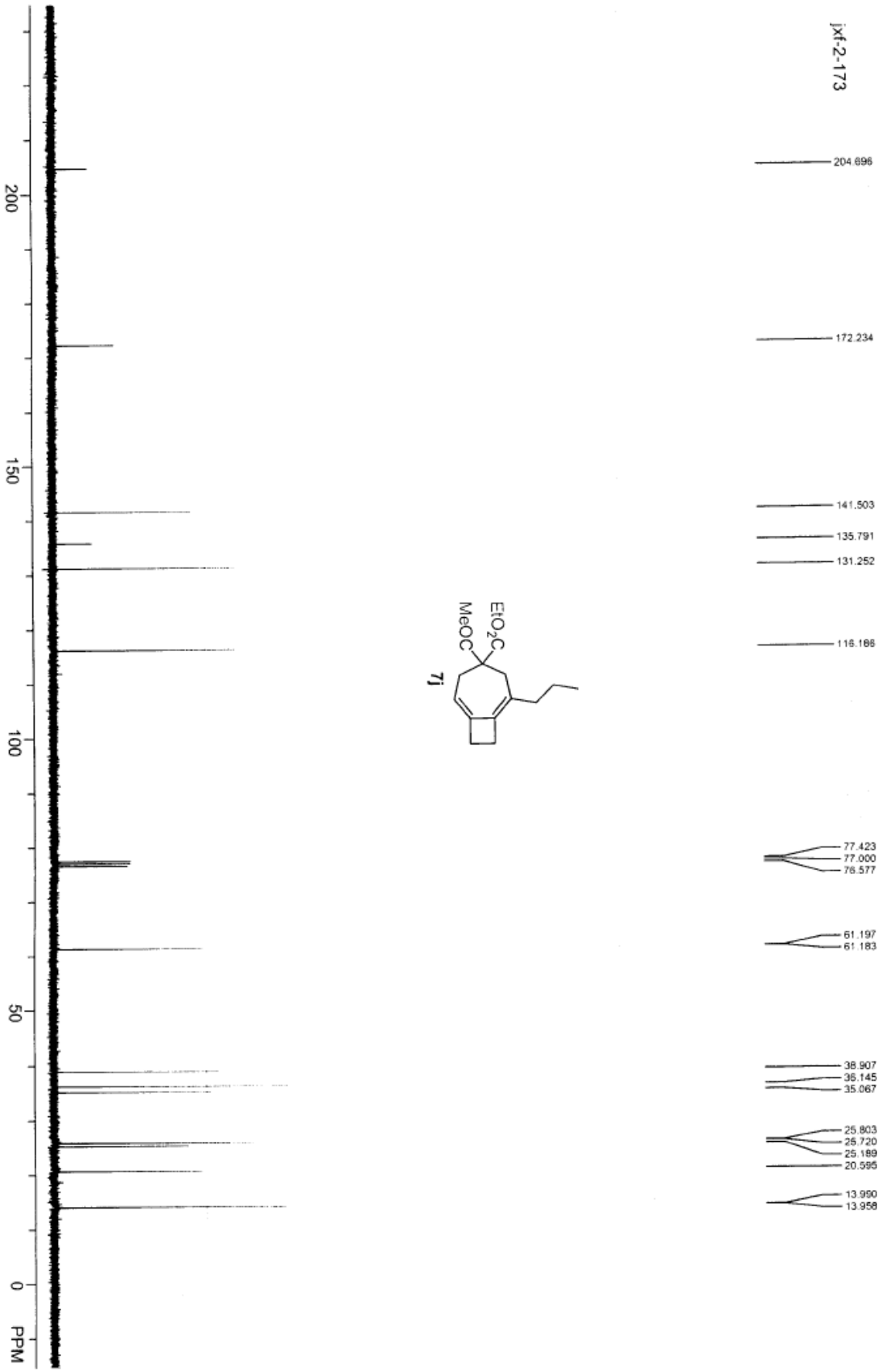
jxf-2-173-h


5.254
5.238
5.225
4.177
4.153
4.130
4.106
2.696
2.661
2.458
2.201
2.174
2.167
2.159
2.156
1.958
1.934
1.908
1.491
1.466
1.440
1.416
1.233
1.227
1.225
1.217
1.210
1.205
1.203
1.195
1.186
0.906
0.882
0.858


EtO2C
MeOC

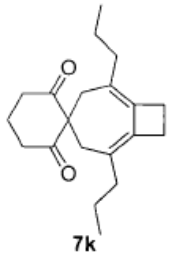
7j


0.91
2.05
4.06
4.05
3.00
2.09
2.17
3.17
3.29
8
7
6
5
4
3
2
1
0
PPM

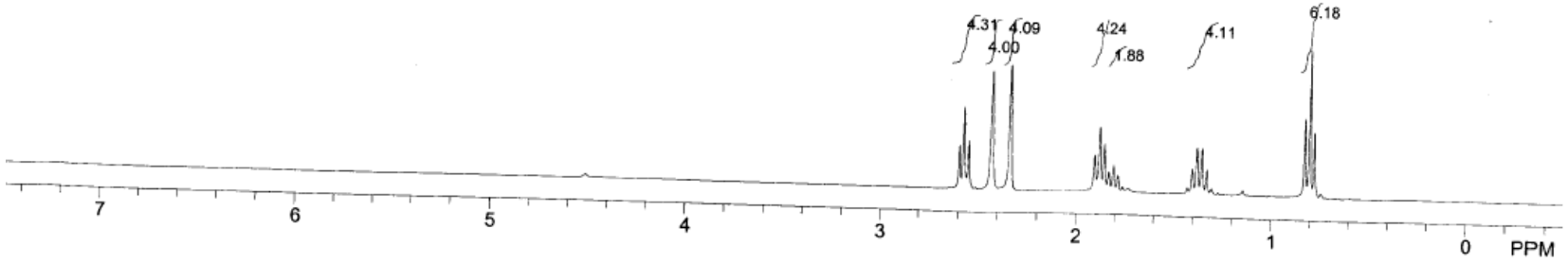

jxf-2-173
204.696
172.234
141.503
135.791
131.252
116.188
77.423
77.000
76.577
61.197
61.183
38.907
36.145
35.067
25.803
25.720
25.189
20.595
13.990
13.958
200
150
100
50
0
PPM
MeOC
EtO2C
7j

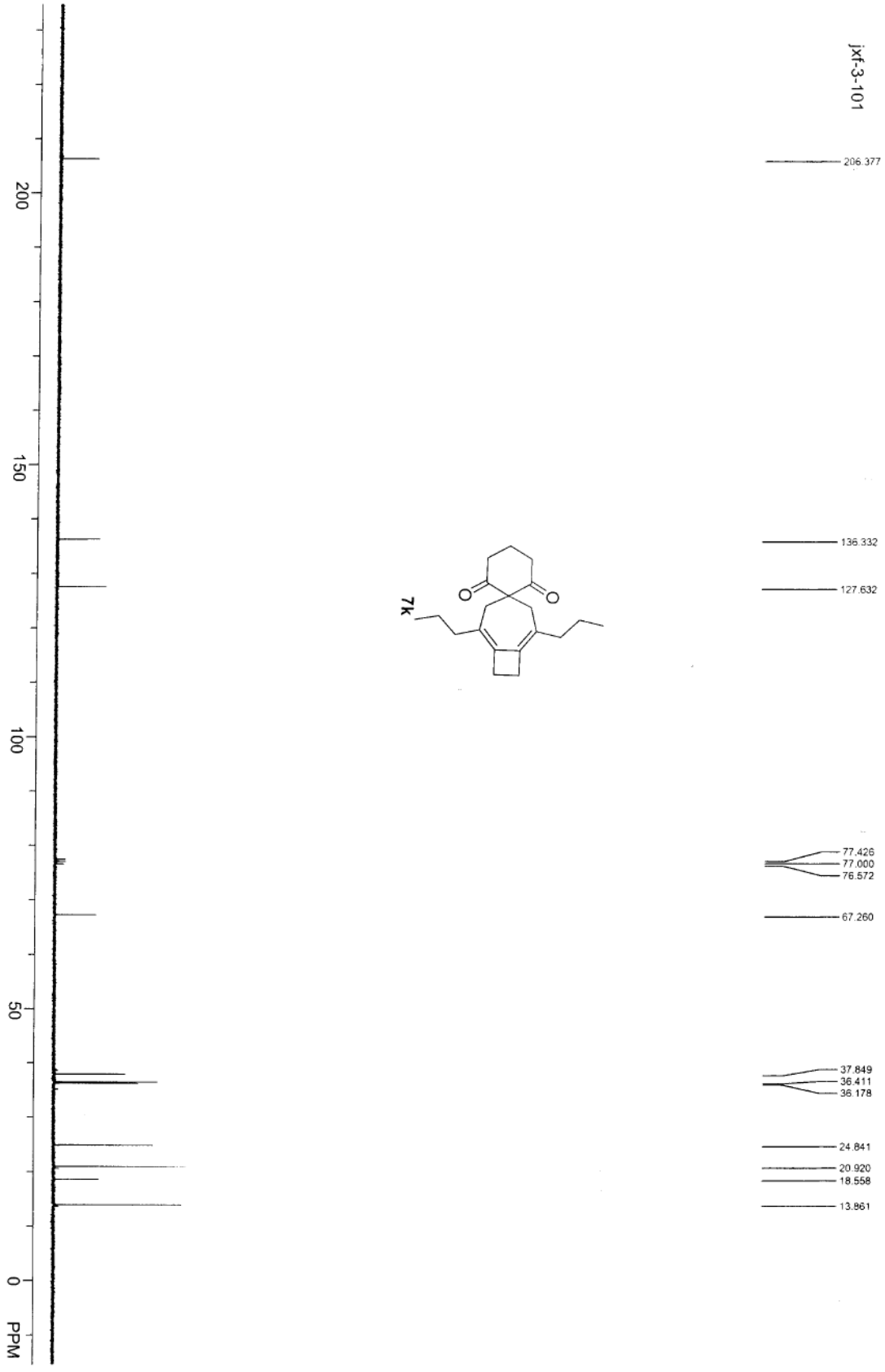
jxf-3-101-h

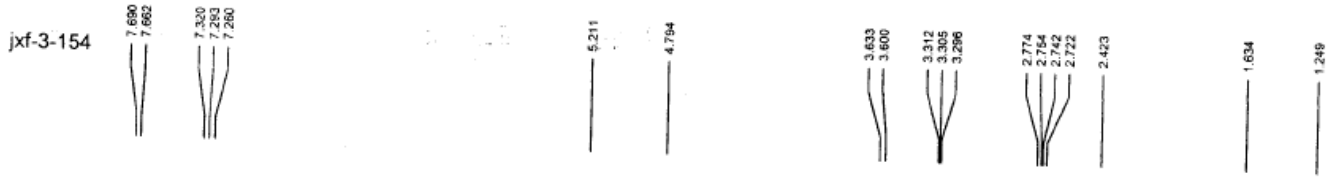

2.595
2.572
2.548
2.431
2.337
1.904
1.880
1.854
1.830
1.808
1.785
1.403
1.378
1.354
1.329
0.829
0.805
0.780

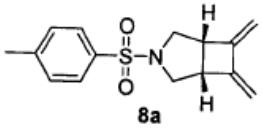

O
O

7k

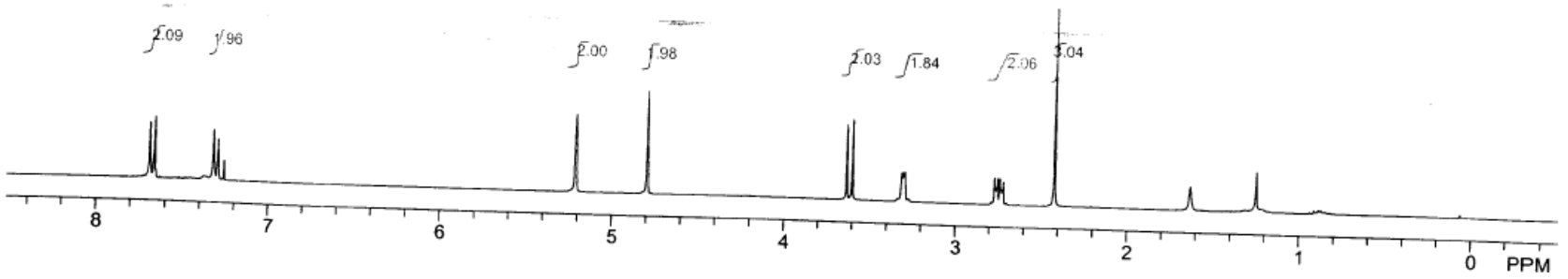

4.31
4.09
4.00
4.24
1.88
4.11
6.18
7
6
5
4
3
2
1
0
PPM

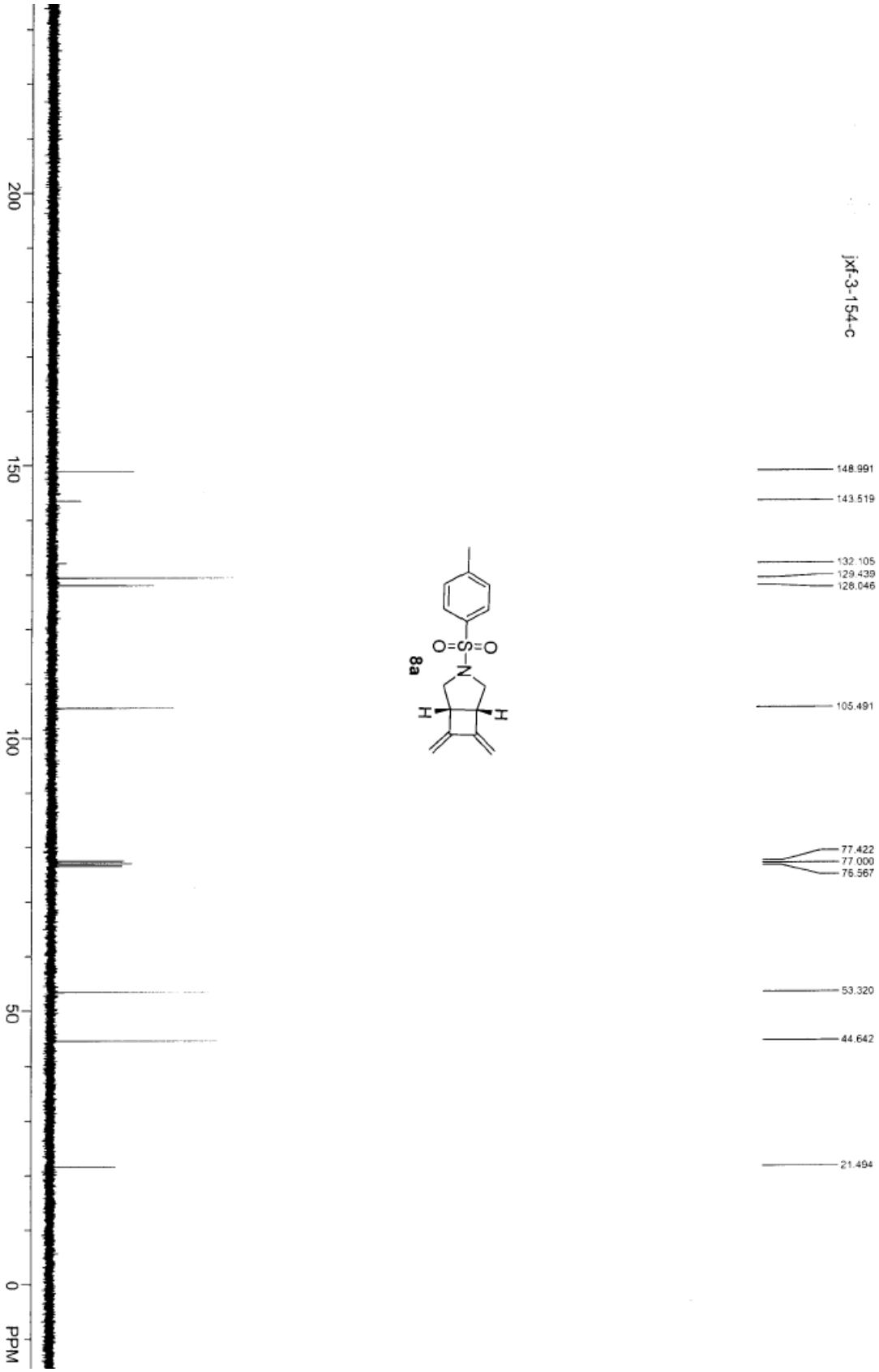

jxf-3-101
206.377
136.332
127.632
77.426
77.000
76.572
67.260
37.849
36.411
36.178
24.841
20.920
18.558
13.861
7k
200
150
100
50
0
PPM

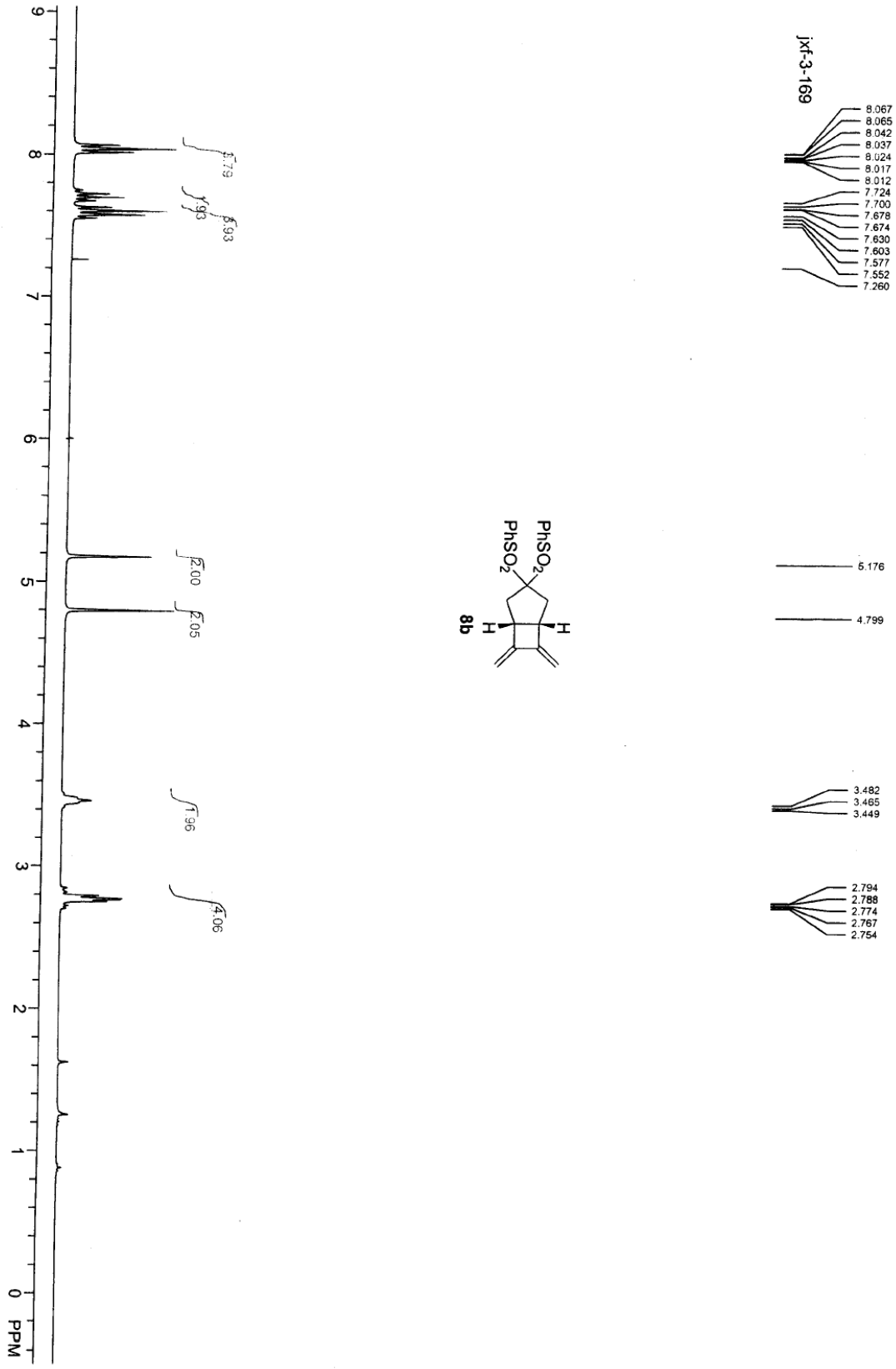

jxf-3-154
7.690
7.662
7.320
7.293
7.280
5.211
4.794
3.633
3.600
3.312
3.305
3.296
2.774
2.754
2.742
2.722
2.423
1.634
1.249

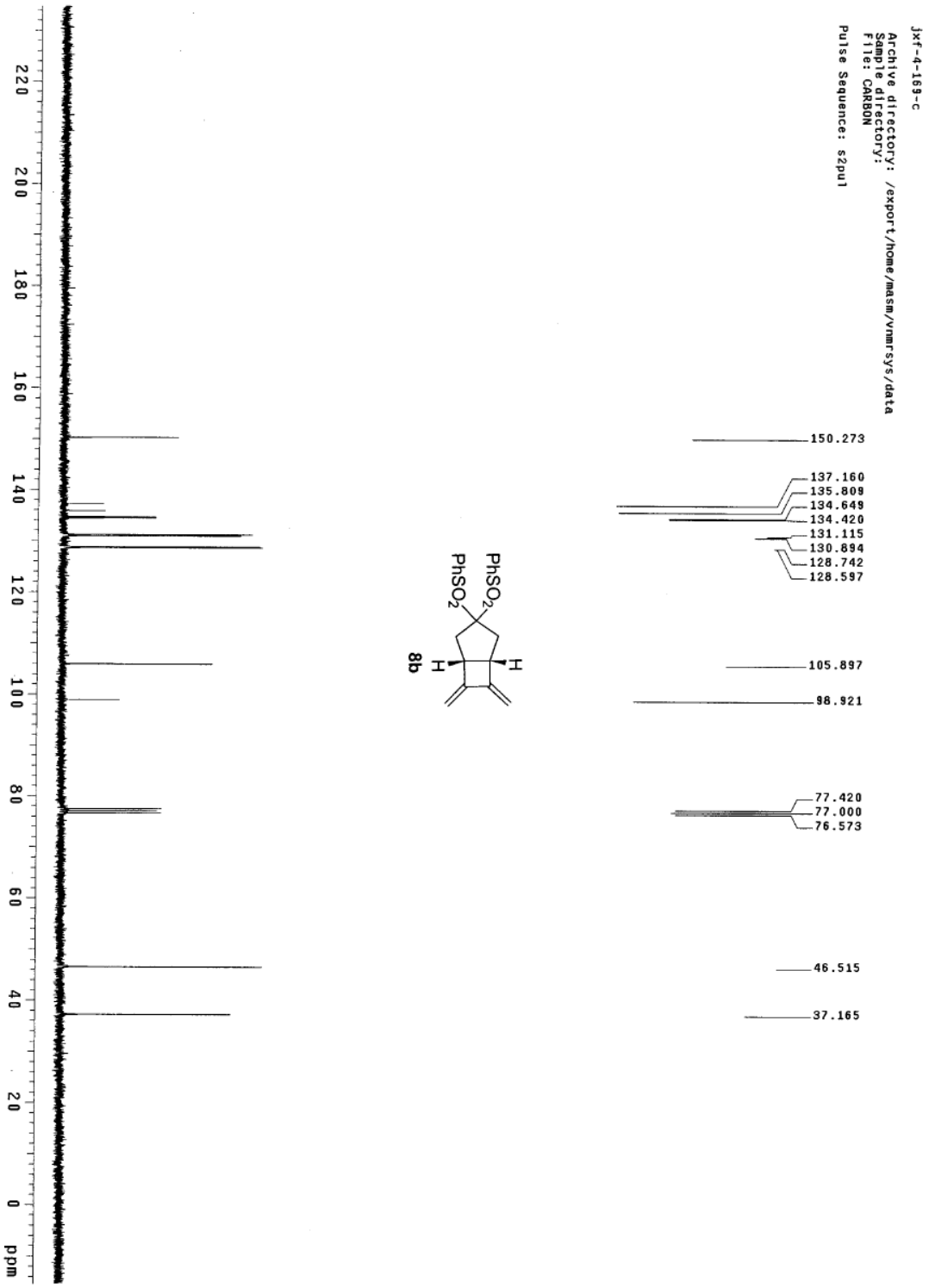

O
S
O
N
H
H

8a

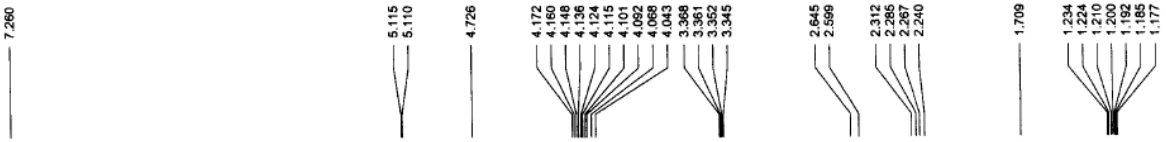

2.09
1.96
2.00
1.98
2.03
1.84
2.06
3.04
8
7
6
5
4
3
2
1
0
PPM

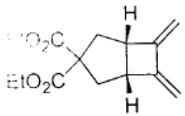

jxf-3-154-c
148.991
143.519
132.105
129.439
128.046
105.491
77.422
77.000
76.567
53.320
44.642
21.494
200
150
100
50
0
PPM
8a
O=S=O
N
H
H


jxf-3-169
8.067
8.065
8.042
8.037
8.024
8.017
8.012
7.724
7.700
7.678
7.674
7.630
7.603
7.577
7.552
7.260
PhSO2
PhSO2
H
H
8b
5.176
4.799
3.482
3.465
3.449
2.794
2.788
2.774
2.767
2.754
7.79
7.93
2.00
2.05
1.96
4.06
PPM

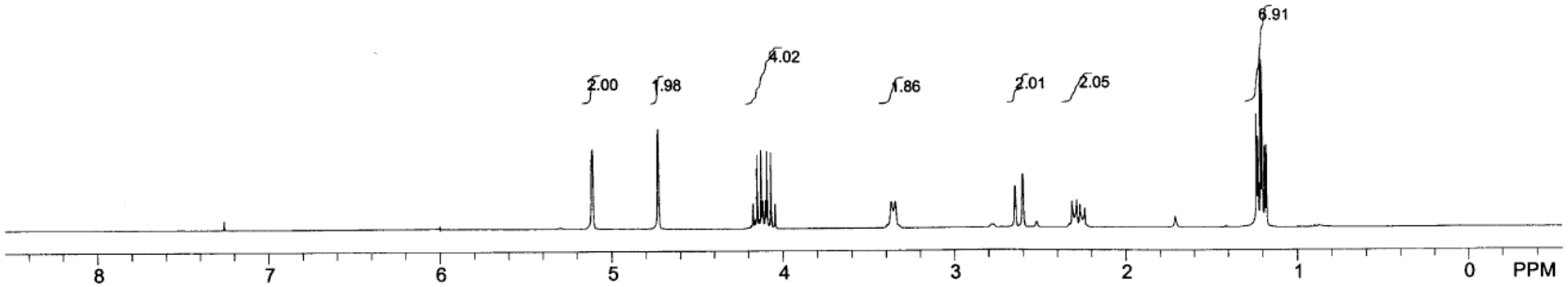

jxf-4-169-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
150.273
137.160
135.809
134.649
134.420
131.115
130.894
128.742
128.597
105.897
98.921
77.420
77.000
76.573
46.515
37.165
PhSO2
PhSO2
H
H
8b
220
200
180
160
140
120
100
80
60
40
20
0
ppm

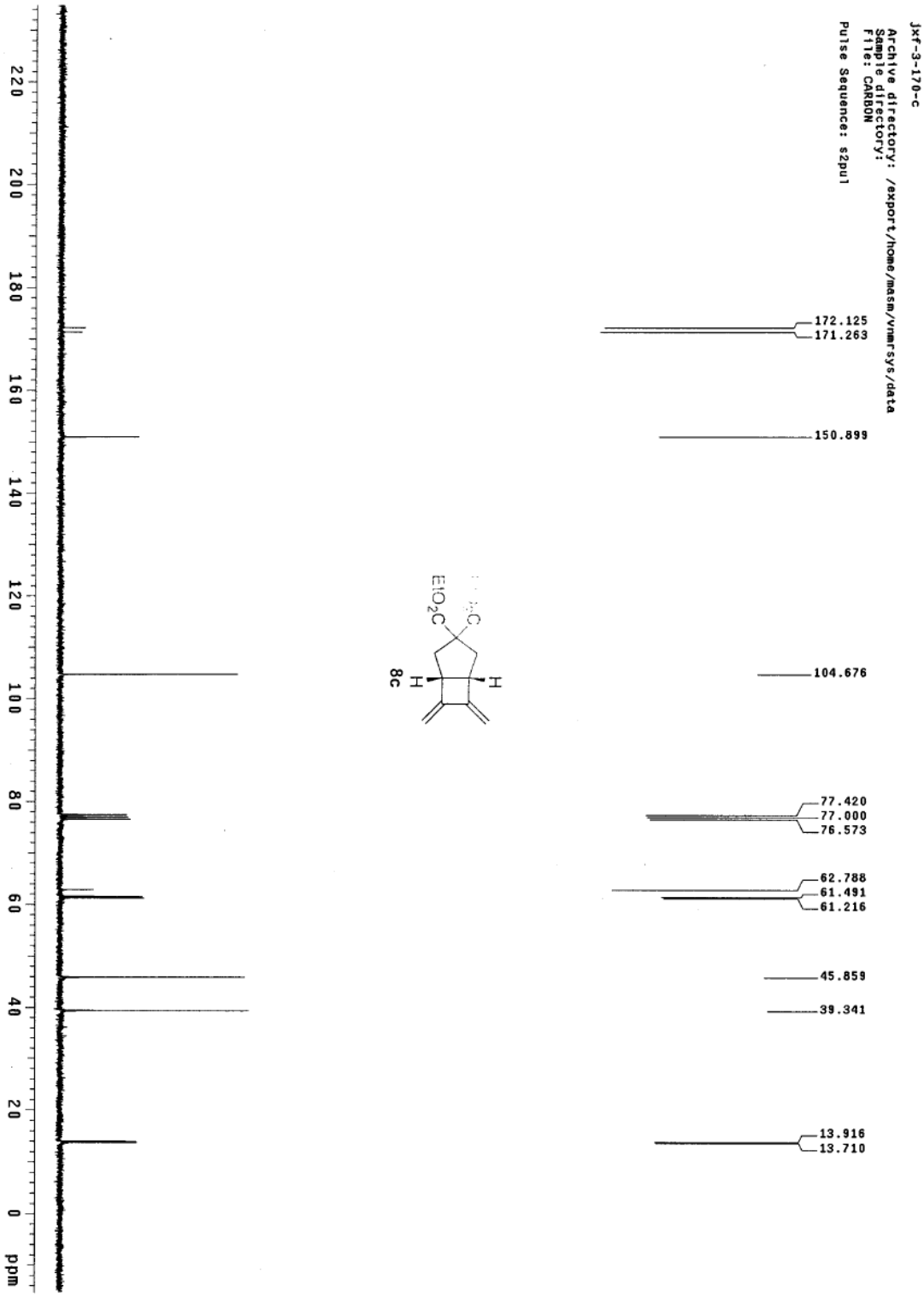
jxf-3-170-hh



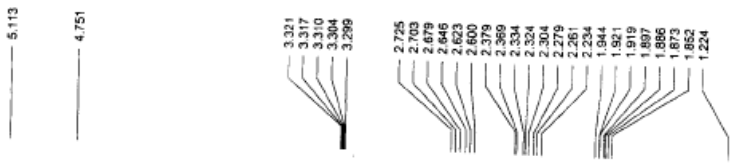


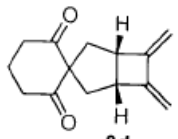
8c



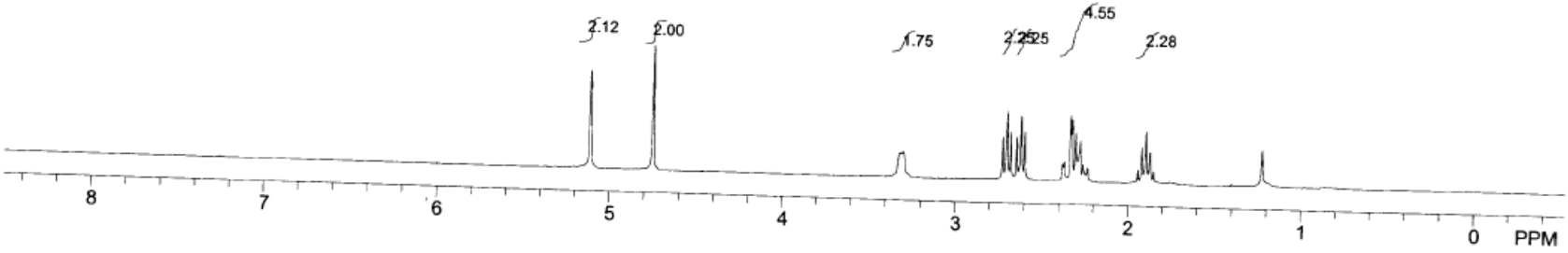

jxf-3-170-c
Archive directory: /export/home/mass/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pul
172.125
171.263
150.899
104.676
77.420
77.000
76.573
62.788
61.491
61.216
45.859
39.341
13.916
13.710
8c
H
H
ppm

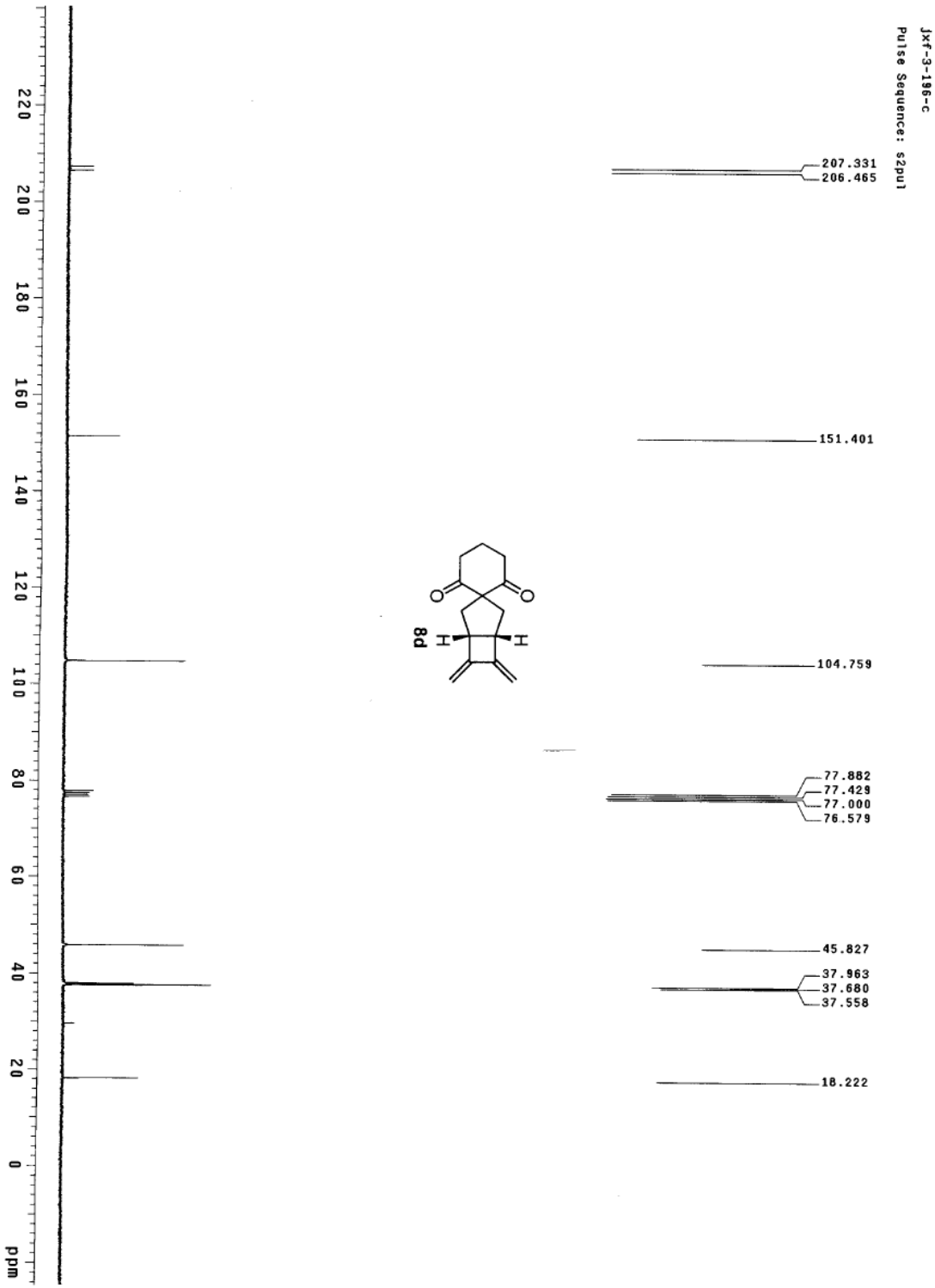
jxf-3-196-h


5.113
4.751
3.321
3.317
3.310
3.304
3.299
2.725
2.703
2.679
2.646
2.623
2.600
2.379
2.369
2.334
2.324
2.304
2.279
2.261
2.234
1.944
1.921
1.919
1.897
1.886
1.873
1.852
1.224

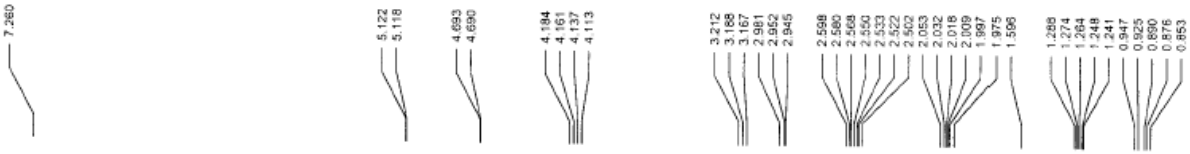


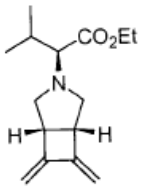
8d


2.12
2.00
1.75
2.25
2.25
4.55
2.28
8
7
6
5
4
3
2
1
0
PPM

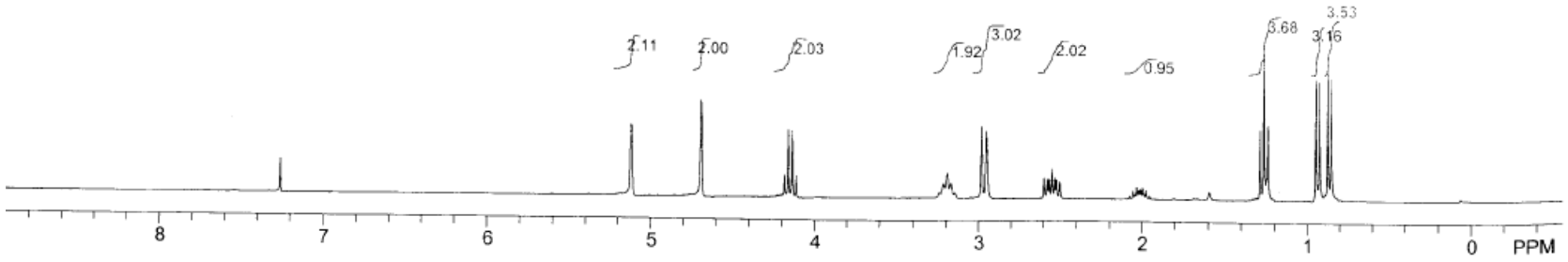

jxf-3-196-c
Pulse Sequence: s2pul
207.331
206.465
151.401
104.759
77.882
77.429
77.000
76.579
45.827
37.963
37.680
37.558
18.222
8d
ppm

jxf-7-58

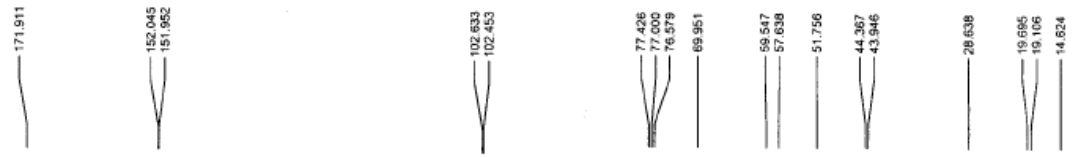

7.260
5.122
5.118
4.693
4.690
4.184
4.161
4.137
4.113
3.212
3.188
3.167
2.981
2.952
2.945
2.598
2.580
2.568
2.550
2.533
2.522
2.502
2.053
2.032
2.018
2.009
1.997
1.975
1.596
1.288
1.274
1.264
1.248
1.241
0.947
0.925
0.890
0.876
0.853

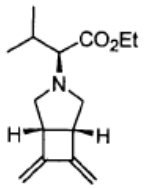

CO2Et
N
H
H

8e

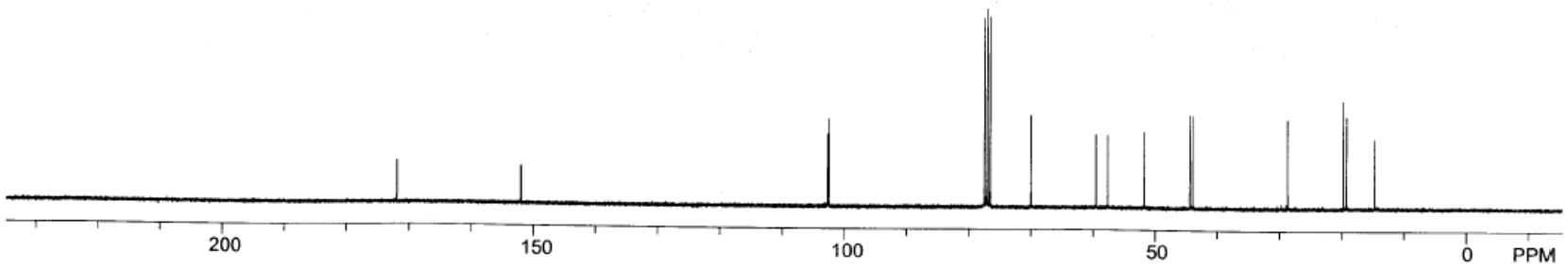

2.11
2.00
2.03
1.92
3.02
2.02
0.95
3.68
3.16
3.53
8
7
6
5
4
3
2
1
0
PPM

jxf-7-58

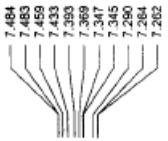

171.911
152.045
151.952
102.633
102.453
77.426
77.000
76.579
69.951
59.547
57.638
51.756
44.367
43.946
28.638
19.695
19.166
14.624

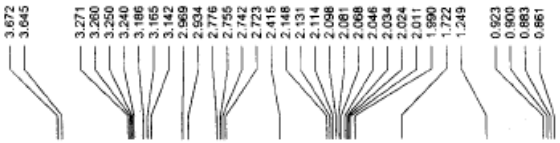

CO2Et
N
H
H

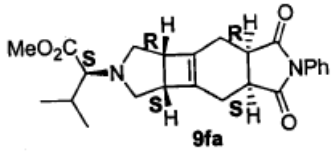
8e


200
150
100
50
0
PPM

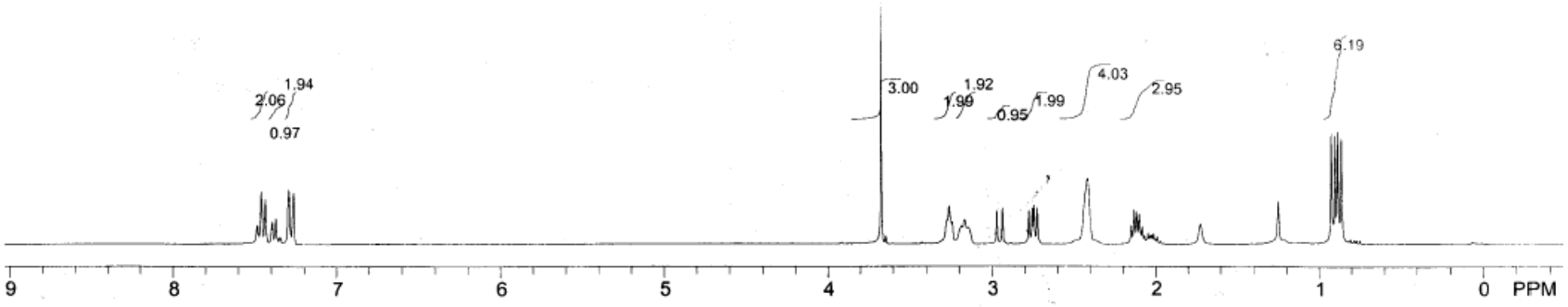
jxf-7-70


7.484
7.463
7.459
7.433
7.393
7.369
7.347
7.345
7.290
7.264
7.262


3.672
3.645
3.271
3.260
3.250
3.240
3.186
3.165
3.142
2.969
2.934
2.776
2.755
2.742
2.723
2.415
2.148
2.131
2.114
2.098
2.081
2.068
2.046
2.034
2.024
2.011
1.990
1.722
1.249
0.923
0.900
0.883
0.861


MeO2C
S
N
R
H
R
H
S
H
S
H
O
NPh
O

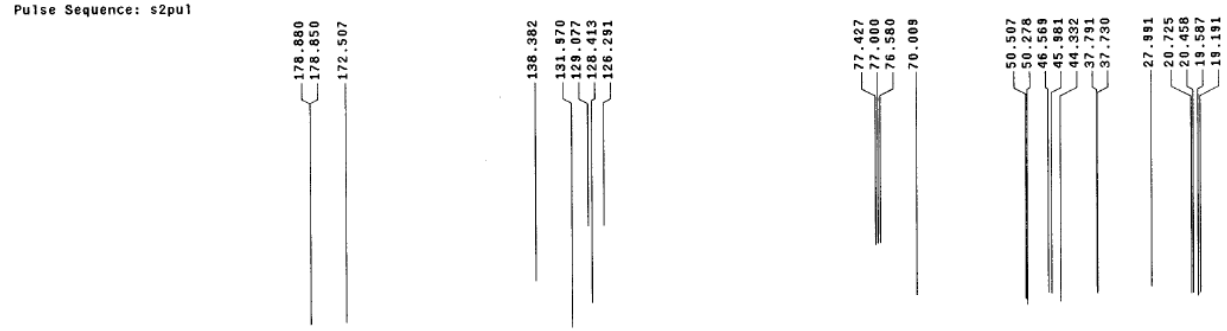
9fa

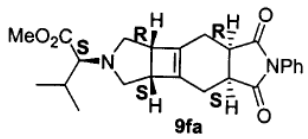

1.94
2.06
0.97
3.00
1.92
1.99
0.95
1.99
4.03
2.95
6.19
9
8
7
6
5
4
3
2
1
0
PPM

jxf-7-70-c

Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul





9fa