Supplementary Material (ESI) for Chemical Communications

Thiazepine Moiety-Controlled Regioselective Rearrangements of 7-Oxanorbornadiene Derivatives

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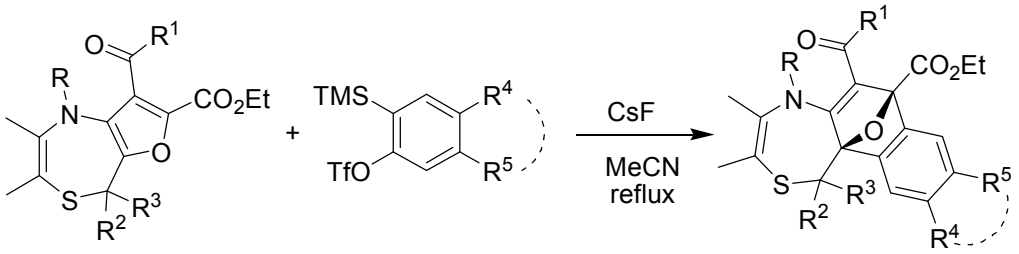
Contents

General

Benzyne precursors were prepared according to literatures.[1-6] Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents in anhydrous conditions. Dichloromethane was distilled from calcium hydride immediately prior to use. All chemicals were distilled or recrystallized before use, when necessary.

All reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates using UV-light (254 and 365 nm). Flash chromatography was performed on neutral Al_2O_3 (200-300 mesh). NMR spectra were recorded in $CDCl_3$, d_4-Methanol, d_6-Acetone or d_6-DMSO. High resolution mass spectral (HRMS) analyses were measured using ESI (electrospray ionosation) techniques. Melting points are uncorrected.

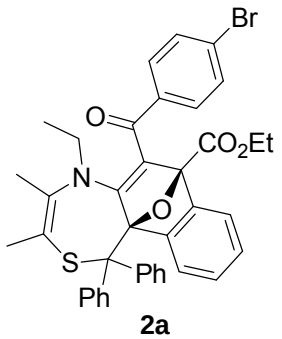
Preparation and characterization data for the thiazepine-fused 7-oxanorbornadienes 2a–m, 7a–i and 12a–c [7]



2, 7 and 12

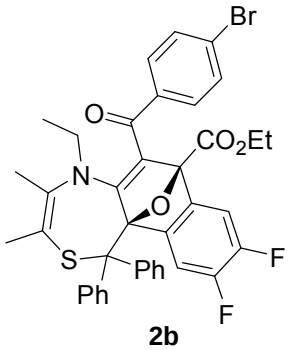
To a solution of furan-fused 1,4-thiazpines (0.15 mmol) and benzyne precursors (0.3 mmol) in anhydrous MeCN was added CsF (0.6 mmol). The mixture was heated to reflux for 1.5 h. On completion of the reaction, the solvent was removed under vacuum, ethyl ether was added to precipitate the salt. The solid was filtered off through a short pad of neutral Al_2O_3 column and the filtrate was concentrated. The residue was then recrystallized from CH_2Cl_2/Hexane to afford the desired products **2a–k, 7a–i** and **12a–c**.

Compound **2a:** 95 % yield, yellow solid; m.p.213–215 ^oC; **IR** (KBr) ν_{max} 3058, 2979, 2932, 1749, 1613, 1444, 1318, 1180, 1067, 850, 749, 698 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane) δ = 7.73–7.62 (m, 8H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.25–7.10 (m, 6H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 4.19–4.13 (m, 2H), 2.85 (q, *J* = 6.4 Hz, 2H), 2.42 (q, *J* = 6.8 Hz, 2H), 1.61 (s, 3H), 1.24 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.52 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane) δ = 189.7, 168.4, 166.6, 148.1, 147.6, 143.1, 142.0, 141.8, 138.7, 131.8, 130.5, 130.4, 130.0, 129.5, 127.2, 127.0, 126.9, 126.8, 126.4, 125.5, 124.9, 124.2, 120.6, 119.4, 96.4, 88.2, 61.7, 58.5, 51.4, 22.9, 16.6, 13.8, 13.1 ppm; **HRMS (ESI)**: calcd for $C_{39}H_{34}BrNO_4SNa$: $[M+Na]^+$ 714.1284, found 714.1269.



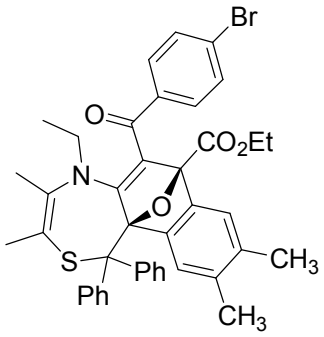
2a

Compound **2b:** 93 % yield, pale yellow solid; m.p.198–200 °C; **IR** (KBr) ν_{max} 3059, 2980, 2935, 1754, 1614, 1466, 1322, 1126, 1070, 772, 699 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane) δ = 7.60 (s, 6H), 7.60 (dd, J_1 = 6.4 Hz, J_2 = 6.8 Hz ,1H), 7.51–7.43 (m, 3H), 7.27–7.16 (m, 6H), 4.23–4.18 (m, 2H), 2.80 (q, J = 6.8 Hz, 1H), 2.40 (q, J = 6.8 Hz, 1H), 1.58 (s, 3H), 1.25 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 0.57 ppm (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane) δ = 190.0, 167.5, 166.0, 147.6 (dd, J = 247, 13.8 Hz), 146.5 (dd, J = 244, 12.8 Hz), 144.5 (q, J^3 = 3.0 Hz), 144.2 (d, J^3 = 2.0 Hz), 144.1 (d, J^3 = 1.4 Hz), 142.8, 141.9, 141.5, 138.5, 132.1, 130.4, 130.1, 129.2, 127.7, 127.4, 127.3, 127.0, 126.8, 119.7, 115.2 (d, J^2 = 21.8 Hz), 111.3 (d, J^2 = 21.4 Hz), 96.5 (d, J^3 = 2.0 Hz), 88.0 (d, J^3 = 1.8 Hz), 62.1, 58.5, 52.1, 23.1, 16.7, 13.9, 13.6 ppm; **HRMS (ESI)**: calcd for $C_{39}H_{32}BrF_2NO_4SNa$: $[M+Na]^+$ 750.1096, found 714.1085.



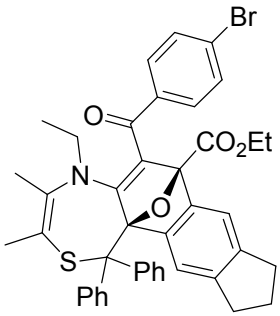
2b

Compound **2c:** 96 % yield, yellow solid; m.p.224–226 °C; **IR** (KBr) ν_{max} 3059, 2978, 2929, 1748, 1586, 1444, 1314, 1129, 1079, 753, 696 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane) δ = 7.70–7.61 (m, 6H), 7.46 (t, J = 7.6 Hz, 3H), 7.41(s, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 6.8 Hz, 3H), 7.11 (d, J = 6.8 Hz, 1H), 4.15 (q, J = 3.6 Hz, 2H), 2.85 (q, J = 6.4 Hz, 1H), 2.42 (q, J = 6.4 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 1.60 (s, 3H), 1.24 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H), 0.55 ppm (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane) δ = 189.4, 168.8, 166.5, 145.2, 145.0, 142.9, 141.6, 141.6, 138.5, 132.8, 131.4, 130.2, 130.1, 129.7, 129.3, 126.7, 126.6, 126.4, 126.1, 126.0, 121.8, 119.2, 96.0, 87.9, 61.3, 58.3, 51.3, 22.7, 19.6, 19.5, 16.3, 13.5, 13.0 ppm; **HRMS (ESI)**: calcd for $C_{41}H_{38}BrNO_4SNa$: $[M+Na]^+$ 742.1597, found 742.1586.



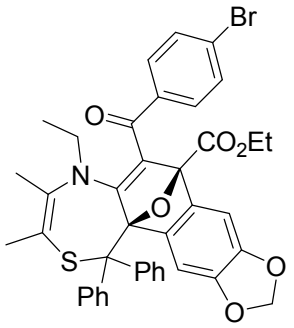
2c

Compound **2d:** 93 % yield, yellow solid; m.p.228–230 ^{o}C; **IR** (KBr) ν_{max} 3057, 2978, 2932, 1751, 1586, 1400, 1323, 1071, 750, 697 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.71–7.62 (m, 6H), 7.54 (s, 1H), 7.47 (d, *J* = 10.0 Hz, 3H), 7.26–7.10 (m, 6H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.88–2.62 (m, 5H), 2.43 (q, *J* = 6.8 Hz, 1H), 1.97 (t, *J* = 7.6 Hz, 2H), 1.59 (s, 3H), 1.23 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.56 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 189.8, 169.2, 166.8, 146.5, 146.2, 143.3, 142.0, 141.8, 141.1, 139.8, 138.9, 131.7, 130.6, 130.5, 130.0, 129.7, 127.1, 126.9, 126.8, 126.8, 126.3, 121.4, 119.5, 117.0, 96.2, 88.1, 61.6, 58.6, 32.4, 32.4, 25.3, 23.0, 16.6, 13.8, 13.4 ppm; **HRMS (ESI)**: calcd for $C_{42}H_{38}BrNO_4SNa$: $[M+Na]^+$ 754.1597, found 754.1584.



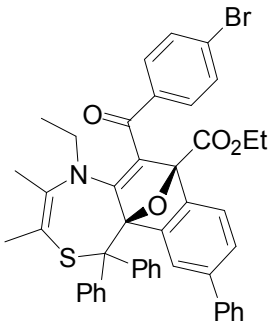
2d

Compound **2e:** 90 % yield, pale yellow solid; m.p.209–211 ^{o}C; **IR** (KBr) ν_{max} 3059, 2980, 2897, 1749, 1586, 1460, 1275, 1070, 1037, 858, 750, 699 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.70–7.65 (m, 6H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.33 (s, 1H), 7.26–7.14 (m, 7H), 5.85 (d, *J* = 8.8 Hz, 2H), 4.17 (q, *J* = 6.8 Hz, 2H), 2.85 (q, *J* = 6.8 Hz, 1H), 2.46 (q, *J* = 6.8 Hz, 1H), 1.59 (s, 3H), 1.23 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.60 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 189.7, 169.5, 166.6, 144.6, 143.6, 143.0, 142.7, 142.4, 141.9, 141.8, 138.8, 131.8, 130.5, 130.4, 130.0, 129.8, 127.2, 127.1, 127.0, 126.8, 126.5, 119.5, 107.7, 103.9, 101.2, 96.4, 88.2, 61.8, 58.5, 51.8, 23.0, 16.6, 13.8, 13.5 ppm; **HRMS (ESI)**: calcd for $C_{40}H_{34}BrNO_6SNa$: $[M+Na]^+$ 758.1182, found 758.1160.



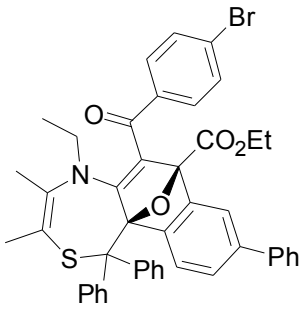
2e

Compound **2f:** 46 % yield, white solid; m.p.223–225 ^{o}C; **IR** (KBr) ν_{max} 3056, 2978, 2895, 1744, 1582, 1456, 1270, 1068, 1035, 855, 745, 698 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.96 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.71–7.64 (m, 5H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.42–7.41 (m, 4H), 7.35–7.32 (m, 1H), 7.25–7.12 (m, 7H), 4.21–4.16 (m, 2H), 2.86 (q, *J* = 6.8 Hz, 1H), 2.45 (q, *J* = 6.8 Hz, 1H), 1.62 (s, 3H), 1.24(s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.53 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 189.9, 168.2, 166.6, 149.0, 146.7, 143.1, 142.0, 141.9, 141.4, 138.7, 137.4, 131.9, 130.6, 130.5, 130.1, 129.4, 128.6, 127.3, 127.15, 127.11, 127.08, 127.0, 126.9, 126.5, 124.7, 124.3, 120.6, 119.5, 96.4, 88.3, 61.8, 58.6, 51.6, 23.0, 16.6, 13.8, 13.4 ppm; **HRMS (ESI)**: calcd for $C_{45}H_{38}BrNO_4SNa$: $[M+Na]^+$ 790.1597, found 790.1592.



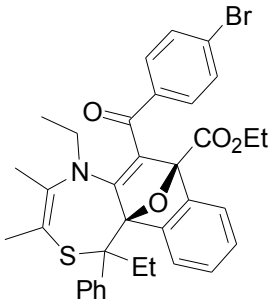
2f

Compound **2g:** 46 % yield, white solid; m.p.230–232 ^{o}C; **IR** (KBr) ν_{max} 3056, 2976, 2898, 1746, 1586, 1457, 1272, 1067, 1036, 854, 745, 699 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.93 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.68 (dd, $J_1 = J_2$ = 8.4 Hz, 4H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.31–7.24 (m, 3H), 7.20–7.17 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 6.8 Hz, 1H), 4.21–4.18 (m, 2H), 2.86 (q, *J* = 6.8 Hz, 1H), 2.45 (q, *J* = 7.2 Hz, 1H), 1.61 (s, 3H), 1.26 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.56 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 189.6, 168.4, 166.6, 148.6, 147.1, 143.1, 141.92, 141.86, 140.6, 138.8, 138.3, 131.8, 130.54, 130.50, 130.0, 129.3, 128.5, 127.2, 127.11, 127.05, 126.94, 126.87, 126.5, 125.0, 123.1, 119.60, 119.56, 96.5, 88.2, 61.8, 58.6, 51.8, 23.0, 16.7, 13.8, 13.4 ppm; **HRMS (ESI)**: calcd for $C_{45}H_{38}BrNO_4SNa$: $[M+Na]^+$ 790.1597, found 790.1595.



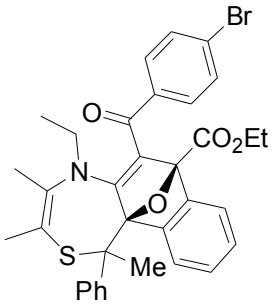
2g

Compound **2h:** 88 % yield, pale yellow oil; **IR** (film) ν_{max} 3058, 2976, 2928, 1751, 1586, 1442, 1323, 1056, 772, 699 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane) δ = 8.07 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 6.8 Hz, 3H), 7.65 (dd, $J_1 = J_2$ = 6.8 Hz, 4H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.24–7.04 (m, 3H), 4.22 (dd, $J_1 = J_2$ = 6.8 Hz, 2H), 2.69–2.33 (m, 4H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.36 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.44 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane) δ = 189.9, 170.0, 166.5, 148.5, 148.3, 140.0, 140.0, 138.8, 131.8, 130.0, 129.5, 127.7, 127.3, 127.1, 126.6, 126.0, 124.6, 124.4, 121.2, 121.1, 98.3, 88.8, 61.6, 54.8, 52.2, 31.9, 23.4, 16.5, 13.8, 13.1, 11.0 ppm; **HRMS (ESI)**: calcd for $C_{35}H_{34}BrNO_4SNa$: $[M+Na]^+$ 666.1284, found 666.1270.



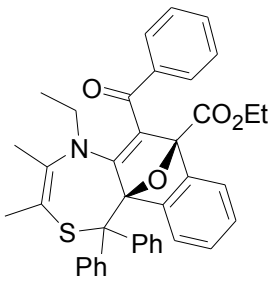
2h

Compound **2i:** 92 % yield, pale yellow oil; **IR** (film) ν_{max} 3059, 2978, 2930, 1749, 1614, 1466, 1225, 1054, 772, 699 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane) δ = 8.08 (d, *J* = 7.6 Hz, 1H), 7.85 (q, *J* = 6.8 Hz, 3H), 7.65 (dd, J_1 = 8.4 Hz, J_2 = 8.8 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07–7.03 (m, 1H), 4.24–4.18 (m, 2H), 2.70 (q, *J* = 6.8 Hz, 1H), 2.36 (q, *J* = 6.8 Hz, 1H), 1.96 (s, 3H), 1.45 (s, 3H), 1.36 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.46 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane) δ = 189.5, 168.0, 166.5, 148.8, 148.4, 142.7, 139.0, 138.8, 131.9, 130.1, 128.9, 127.7, 127.4, 127.2, 126.8, 126.1, 124.6, 124.5, 121.8, 121.2, 97.7, 88.9, 61.8, 52.2, 50.7, 25.2, 23.6, 16.8, 13.9, 13.2 ppm; **HRMS (ESI)**: calcd for $C_{34}H_{32}BrNO_4SNa$: $[M+Na]^+$ 652.1128, found 652.1116.



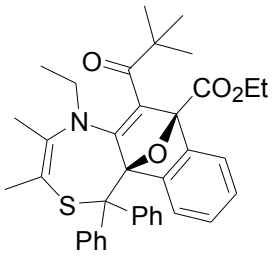
2i

Compound **2j:** 96 % yield, pale yellow solid; m.p.199–201 °C; **IR** (KBr) ν_{max} 3059, 2977, 2931, 1750, 1551, 1445, 1181, 847, 747, 699 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane) δ = 7.80–7.67 (m, 6H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.0 Hz, 4H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.18–7.09 (m, 4H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 8.0 Hz, 1H), 4.17–4.12 (m, 2H), 2.77 (q, *J* = 6.8 Hz, 1H), 2.42 (q, *J* = 6.8 Hz, 1H), 1.57 (s, 3H), 1.22 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.49 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane) δ = 191.2, 168.0, 166.8, 148.3, 147.9, 143.2, 142.4, 142.0, 140.2, 132.4, 130.7, 130.5, 130.2, 128.6, 128.5, 127.1, 126.9, 126.8, 126.4, 125.5, 124.8, 124.2, 120.7, 119.2, 96.5, 88.3, 61.7, 58.6, 51.4, 22.9, 16.5, 13.8, 13.2 ppm; **HRMS (ESI)**: calcd for $C_{39}H_{35}NO_4SNa$: $[M+Na]^+$ 636.2179, found 636.2181.



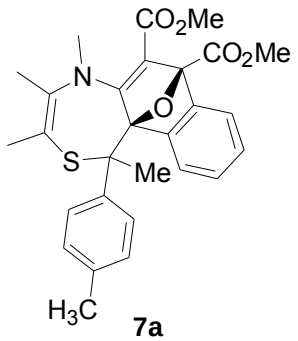
2j

Compound **2k:** 95 % yield, pale yellow solid; m.p.208–211 °C; **IR** (KBr) ν_{max} 3055, 2998, 2948, 1752, 1701, 1561, 1201, 1142, 808, 754, 697 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane) δ = 7.77 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 6.8 Hz, 1H), 7.19–7.08 (m, 6H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.16 (q, *J* = 6.9 Hz, 1H), 2.62 (q, *J* = 6.8 Hz, 1H), 1.79 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.28 (s, 9H), 1.21 (s, 3H), 0.51 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane) δ = 210.5, 167.1, 159.6, 148.8, 147.8, 143.4, 143.3, 142.4, 131.7, 130.8, 130.5, 127.0, 126.8, 126.6, 126.1, 124.8, 124.7, 124.1, 119.8, 118.3, 95.8, 89.0, 61.8, 58.0, 50.0, 45.3, 27.0, 22.8, 17.3, 14.1, 13.7 ppm; **HRMS (ESI)**: calcd for $C_{37}H_{39}NO_4SNa$: $[M+Na]^+$ 616.2492, found 616.2493.



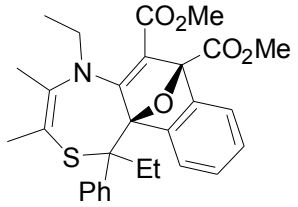
2k

Compound **7a**: 97 % yield, pale yellow solid; m.p.175–178 ^{o}C; **IR** (KBr) ν_{max} 3060, 2990, 2951, 1754, 1698, 1577, 1438, 1203, 927, 756, 691 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 8.03 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.07 (dd, J_1 = 8.4 Hz, J_2 = 8.0 Hz, 4H), 3.89 (s, 3H), 3.71(s, 3H), 2.80 (s, 3H), 2.29(s, 3H), 1.90 (s, 3H), 1.71 (s, 3H), 1.33 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 169.5, 167.6, 162.7, 148.9, 148.7, 140.9, 139.0, 136.1, 129.6, 128.0, 125.9, 124.5, 120.6, 119.3, 118.3, 96.8, 87.3, 52.5, 51.1, 50.2, 44.2, 25.0, 23.3, 20.9,17.7 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{29}NO_5SNa$: $[M+Na]^+$ 514.1659, found 514.1668.



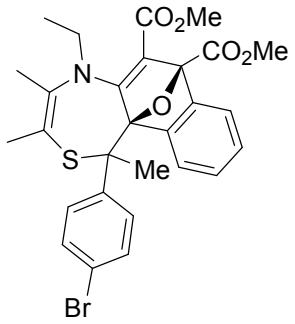
7a

Compound **7b**: 96 % yield, pale yellow solid; m.p.168–170 ^{o}C; **IR** (KBr) ν_{max} 3064, 2972, 2950, 1756, 1694, 1575, 1438, 1206, 754, 698 cm^{-1}; **^{1}H NMR** (400 MHz**,** d_6-Acetone, 25 ^{o}C, tetramethylsilane) δ = 8.03 (d, *J* = 6.4 Hz, 1H), 7.74–7.72 (m, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.32–7.28 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.68 (s, 3H), 3.43–3.35 (m, 1H), 2.90–2.82 (m, 1H), 1.71 (s, 3H), 1.25 (s, 3H), 0.72 (t, *J* = 7.6 Hz, 3H), 0.45 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, d_6-Acetone, 25 ^{o}C, tetramethylsilane) δ = 206.1, 169.4, 168.1, 163.4, 150.2, 149.6, 140.5, 130.6, 128.0, 127.3, 126.7, 125.5, 125.4, 121.9, 121.7, 98.3, 88.1, 55.3, 52.8, 51.4, 49.8, 32.0, 23.0, 17.3, 12.4, 11.2 ppm; **HRMS (ESI)**: calcd for $C_{29}H_{31}NO_5SNa$: $[M+Na]^+$ 528.1815, found 528.1810.



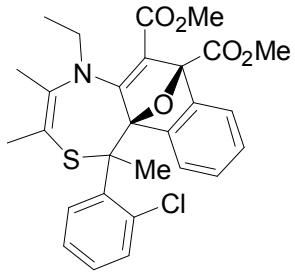
7b

Compound **7c**: 93 % yield, white solid; m.p.236–238 ^{o}C; **IR** (KBr) ν_{max} 3660, 2990, 2949, 1756, 1692, 1570, 1446, 1200, 1009, 759, 690 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.99 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.11–7.00 (m, 2H), 3.90 (s, 3H), 3.72 (s, 3H), 3.49–3.40 (m, 1H), 2.91–2.85 (m, 1H), 1.90 (s, 3H), 1.72 (s, 3H), 1.33 (s, 3H), 0.51 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 167.9, 167.4, 162.7, 148.7, 148.4, 141.5, 140.5, 130.7, 130.3, 126.0, 124.6, 124.5, 121.4, 120.8, 120.5, 120.4, 96.8, 87.2, 52.6, 51.1, 49.9, 49.6, 24.8, 23.1, 17.6, 12.1 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{28}BrNO_5SNa$: $[M+Na]^+$ 592.0764, found 592.0756.



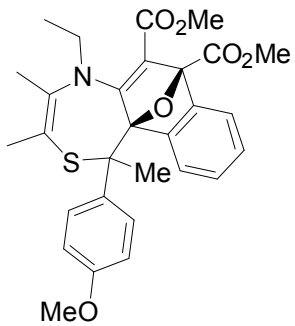
7c

Compound **7d**: 94 % yield, pale yellow solid; m.p.231–234 °C; **IR** (KBr) ν_{max} 3072, 2960, 2922, 1760, 1693, 1560, 1441, 1200, 931, 754, 671 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane) δ = 8.04 (d, *J* = 6.8 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.17–7.00 (m, 4H), 3.91 (s, 3H), 3.72 (s, 3H), 3.49–3.40 (m, 1H), 2.97–2.92 (m, 1H), 2.13 (s, 3H), 1.63 (s, 3H), 1.47 (s, 3H), 0.52 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane) δ = 167.8, 167.6, 162.7, 148.8, 148.6, 140.2, 138.4, 133.6, 132.6, 132.1, 128.1, 125.9, 125.5, 125.1, 124.5, 121.9, 120.5, 118.8, 98.6, 87.0, 52.5, 51.2, 51.1, 49.7, 22.4, 22.1, 17.4, 12.1 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{28}ClNO_5SNa$: $[M+Na]^+$ 548.1269, found 548.1247.



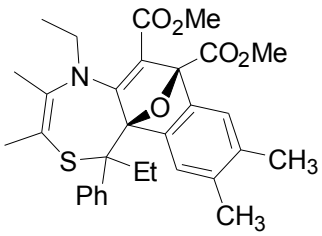
7d

Compound **7e**: 91 % yield, yellow oil; **IR** (film) ν_{max} 3059, 2950, 2839, 1755, 1693, 1569, 1444, 1199, 1031, 831, 759 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane) δ = 8.01 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 9.2 Hz, 2H), 7.10–7.00 (m, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 3.78 (s, 3H), 3.72 (s, 3H), 3.44 (q, *J* = 7.2 Hz, 1H), 2.90 (q, *J* = 6.9 Hz, 1H), 1.91 (s, 3H), 1.72 (s, 3H), 1.32 (s, 3H), 0.52 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane) δ = 168.5, 167.5, 162.7, 157.8, 148.9, 148.6, 140.1, 134.2, 130.0, 125.8, 124.6, 124.5, 122.1, 120.6, 119.9, 112.5, 97.1, 87.0, 55.1, 52.4, 51.0, 50.1, 49.5, 24.9, 23.1, 17.5, 14.0 ppm; **HRMS (ESI)**: calcd for $C_{29}H_{31}NO_6SNa$: $[M+Na]^+$ 544.1764, found 544.1752.



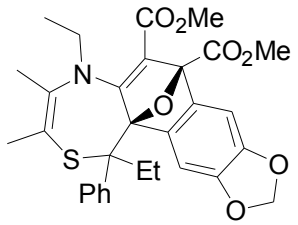
7e

Compound **7f**: 92 % yield, pale yellow solid; m.p.174–177 ^{o}C; **IR** (KBr) ν_{max} 3057, 2972, 2949, 1755, 1690, 1570, 1438, 1210, 740, 696 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.75 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.29–7.26 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.70 (s, 3H), 3.44 (q, *J* = 6.9 Hz, 1H), 2.82 (q, *J* = 7.6 Hz, 1H), 2.59–2.51 (m, 2H), 2.25 (s, 6H), 1.69 (s, 3H), 1.24 (s, 3H), 0.78 (t, *J* = 7.6 Hz, 3H), 0.53 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 170.2, 167.9, 163.0, 146.7, 145.7, 139.5, 133.6, 132.1, 129.4, 127.2, 126.4, 126.1, 122.2, 120.2, 97.3, 86.9, 54.6, 52.3, 50.9, 49.5, 31.3, 22.6, 19.9, 19.8, 17.0, 12.3, 10.8 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{35}NO_5SNa$: $[M+Na]^+$ 556.2128, found 556.2116.



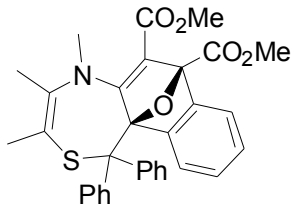
7f

Compound **7g**: 95 % yield, pale yellow solid; m.p.160–163 ^{o}C; **IR** (KBr) ν_{max} 2968, 2950, 1754, 1693, 1571, 1461, 1278, 1035, 740, 695 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.59 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.34 (s, 1H), 7.27 (t, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 7.2Hz, 1H), 5.98 (d, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.70 (s, 3H), 3.47 (q, *J* = 7.1 Hz, 1H), 2.88 (q, *J* = 6.9 Hz, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.69 (s, 3H), 1.23 (s, 3H), 0.81 (t, *J* = 7.6 Hz, 3H), 0.60 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 170.8, 167.7, 162.9, 145.1, 144.2, 143.9, 142.4, 139.4, 129.5, 127.3, 126.5, 120.3, 107.6, 104.1, 101.4, 97.3, 87.0, 54.6, 52.5, 51.1, 49.6, 31.5, 22.7, 17.1, 12.5, 10.8 ppm; **HRMS (ESI)**: calcd for $C_{30}H_{31}NO_7SNa$: $[M+Na]^+$ 572.1713, found 572.1722.



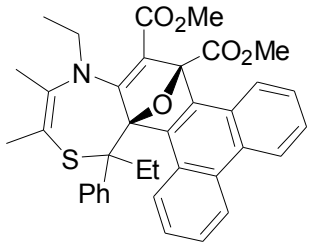
7g

Compound **7h**: 90 % yield, pale yellow solid; m.p.175–178 ^{o}C; **IR** (KBr) ν_{max} 3057, 2951, 2918, 1754, 1686, 1572, 1439, 1205, 754, 700 cm^{-1}; **^{1}H NMR** (400 MHz**,** d_6-Acetone, 25 ^{o}C, tetramethylsilane) δ = 7.74 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.27-7.11 (m, 8H), 6.88–6.79 (m, 2H), 3.89 (s, 3H), 3.70 (s, 3H), 2.78 (s, 3H), 1.85 (s, 3H), 1.21 ppm (s, 3H); **^{13}C NMR** (100 MHz, d_6-Acetone, 25 ^{o}C, tetramethylsilane) δ = 169.0, 167.2, 162.4, 148.8, 148.3, 144.3, 143.2, 142.4, 130.6, 127.0, 127.0, 126.7, 126.5, 125.3, 125.0, 124.2, 121.1, 120.4, 116.8, 96.0, 87.1, 58.5, 52.0, 50.7, 43.2, 22.1, 16.7 ppm; **HRMS (ESI)**: calcd for $C_{32}H_{29}NO_5SNa$: $[M+Na]^+$ 562.1659, found 562.1658.



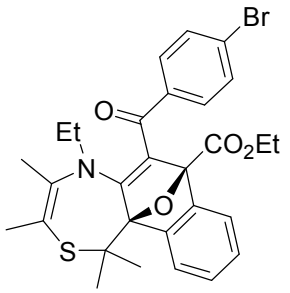
7h

Compound **7i**: 97 % yield, pale yellow solid; m.p.227–231 ^{o}C; **IR** (KBr) ν_{max} 3084, 2976, 2946, 1751, 1705, 1589, 1437, 1206, 756, 721 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 9.87 (d, *J* = 8.0 Hz, 1H), 8.78–8.72 (m, 2H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.66–7.54 (m, 6H), 7.29 (q, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 3.72 (s, 3H), 3.27 (q, *J* = 6.8 Hz, 1H), 2.81 (q, *J* = 7.2 Hz, 1H), 2.69 (q, *J* = 7.2 Hz, 1H),2.52 (q, *J* = 6.7 Hz, 1H), 1.87 (s, 3H), 1.08 (s, 3H), 0.82 (t, *J* = 7.6 Hz, 3H), 0.30 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 169.8, 167.8, 165.5, 149.7, 149.3, 142.5, 140.5, 130.3, 129.8, 129.6, 128.8, 128.3, 127.0, 126.8, 126.5, 126.1, 125.9, 125.8, 125.7, 125.0, 123.5, 123.0, 120.8, 102.6, 88.6, 53.6, 53.0, 51.2, 47.2, 30.5, 21.9 15.5, 12.9, 11.1 ppm; **HRMS (ESI)**: calcd for $C_{37}H_{35}NO_5SNa$: $[M+Na]^+$ 628.2128, found 628.2126.



7i

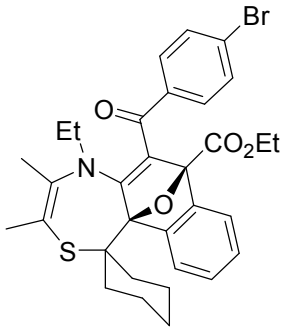
Compound **12a**: 85 % yield, pale yellow oil; **IR** (film) ν_{max} 3048, 2950, 2922, 1761, 1684, 1572, 1438, 1204, 752 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 7.87 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.60 (dd, J_1 = 12.8 Hz, J_2 = 8.4 Hz, 4H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.25–4.23 (m, 2H), 2.71–2.67 (m, 1H), 2.29–2.24 (m, 1H), 2.09 (s, 3H), 1.74 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.23 ppm (t, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 190.2, 167.2, 166.7, 149.0, 147.1, 138.8, 138.4, 131.8, 131.6, 130.2, 127.3, 126.0, 124.5, 123.4, 121.2, 119.5, 99.2, 88.4, 61.7, 52.3, 42.8, 25.7, 25.0, 24.4, 16.8, 13.9, 13.2 ppm; **HRMS (ESI)**: calcd for $C_{29}H_{30}BrNO_4SNa$: $[M+Na]^+$ 590.0971, found 590.0966.



12a

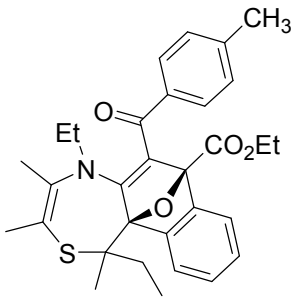
Compound **12b**: 87 % yield, pale yellow solid; m.p.193–195 ^{o}C; **IR** (KBr) ν_{max} 3059, 2970, 2954, 1760, 1692, 1575, 1436, 1211, 746, 695 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C,

tetramethylsilane) δ = 7.89 (d, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.60 (dd, J_1 = 12.8 Hz, J_2 = 8.4 Hz, 4H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 4.29–4.23 (m, 2H), 2.67 (q, *J* = 6.8 Hz, 1H), 2.26 (q, *J* = 6.8 Hz, 1H), 2.12 (s, 3H), 2.05–1.71 (m, 10H),1.59 (d, *J* = 12.0 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.42 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane) δ = 190.0, 168.0, 166.8, 149.0, 146.7, 139.4, 138.4, 131.7, 131.3, 130.2, 127.2, 125.9, 124.3, 124.0, 121.3, 118.4, 99.7, 80.0, 61.7, 52.8, 48.3, 30.8, 30.4, 25.5, 24.5, 21.5, 21.1, 17.1, 13.9, 13.2 ppm; **HRMS (ESI)**: calcd for $C_{32}H_{34}BrNO_4SNa$: $[M+Na]^+$ 630.1284, found 630.1272.



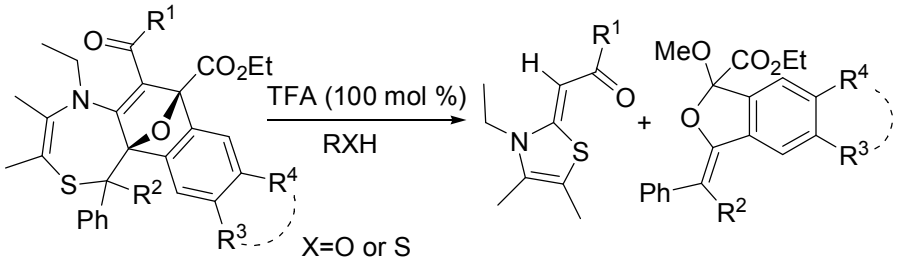
12b

Compound **12c**: 90 % yield, pale yellow solid; m.p.171–174 ^{o}C; **IR** (KBr) ν_{max} 3059, 2977, 2932, 1750, 1618, 1468, 1223, 1055, 770, 696 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-Acetone, 25 ^{o}C, tetramethylsilane) δ = 7.92 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 3.5 Hz, 1H), 7.02 (t, *J* = 7.0 Hz, 1H),4.21–4.16 (m, 2H), 2.66 (t, *J* = 6.8 Hz, 1H), 2.41 (s, 3H), 2.19 (t, *J* = 7.0 Hz, 1H), 2.10 (s, 3H), 1.97–1.95 (m, 1H), 1.77 (s, 3H), 1.61–1.58 (m, 1H), 1.37 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.35 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, d_6-Acetone, 25 ^{o}C, tetramethylsilane) δ = 190.6, 166.3, 165.1, 149.7, 148.0, 143.4, 140.1, 137.2, 132.0, 129.3, 128.7, 125.4, 124.2, 123.3, 121.4, 117.4, 100.1, 88.4, 61.0, 52.2, 47.4, 27.6, 23.6, 20.8, 19.2, 16.5, 13.4, 12.6, 7.8 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{35}NO_4SNa$: $[M+Na]^+$ 540.2179, found 540.2171.



12c

General procedure for the Brønsted acid catalyzed rearrangements of 2a–k

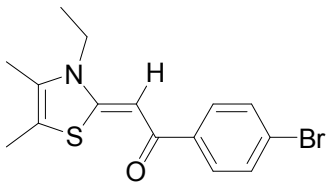


2 **3** **4** and **6**

To a solution of **2** (0.13 mmol) in 2 ml CH_2Cl_2/alcohol (5:1) was added TFA (0.13 mmol), and the resulting solution was stirred at RT for indicated time. On completion of the reaction, the solvent was removed under vacuum. The residue was chromatographed on a silica gel column with a hexane–ethyl acetate mixture (10:1) to afford the desired products **4a–i, 5** or **6a–e**, then with a hexane–ethyl acetate mixture (2:1) to afford the products **3a–b**.

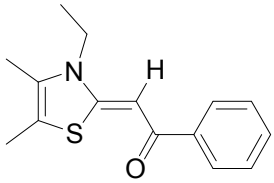
Characterization data for the compounds 3a–d, 4a–i, 5 and 6a–e

Compound **3a**: Yellow solid; m.p.128–130 ^oC; **IR** (film) ν_{max} 3062, 2985, 2929, 1686, 1596, 1472, 1186, 896, 728 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.82 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.28 (s, 1H), 3.95 (q, *J* = 7.2 Hz, 2H), 2.18 (s, 3H), 2.16 (s, 3H), 1.34 ppm (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 180.0, 161.9, 139.4, 131.1, 130.1, 128.4, 124.1, 114.2, 84.5, 41.8, 12.9, 11.5, 11.1 ppm; **HRMS (ESI)**: calcd for $C_{15}H_{16}BrNOSNa$: $[M+Na]^+$ 360.0028, found 360.0027.



3a

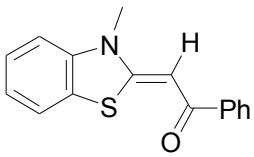
Compound **3b**: Yellow solid; m.p.116–118 ^oC; **IR** (film) ν_{max} 3061, 2985, 2929, 1689, 1597, 1471, 1188, 1086, 895, 796, 717 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^0C, tetramethylsilane): δ = 7.83 (s, 2H), 7.418 (t, J_1 = 6.4 Hz, J_2 = 8.0 Hz, 3H), 4.12 (s, 2H), 2.24 (s, 6H), 1.36 ppm(s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 162.4, 137.8, 133.2, 130.8, 128.3, 127.2, 119.9, 43.1, 13.3, 11.5, 11.2 ppm; **HRMS (ESI)**: calcd for $C_{15}H_{17}NOSNa$: $[M+Na]^+$ 282.0923, found 282.0928.



3b

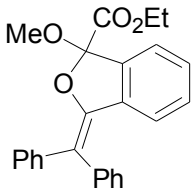
Compound **3d**: Yellow solid; m.p.134–136 ^oC; **IR** (film) ν_{max} 3060, 2983, 2927, 1596, 1568, 1483, 1424, 1347, 1221, 887, 728 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC,

tetramethylsilane): δ = 7.94–7.91 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.40–7.34 (m, 3H), 7.32–7.28 (m, 1H), 7.16–7.09 (m, 2H), 6.43 (br, 1H), 3.56 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 184.4, 162.6, 139.8, 139.3, 130.9, 128.3, 127.1, 127.1, 126.5, 123.0, 122.3, 109.9, 87.3, 32.5 ppm; **HRMS (ESI)**: calcd for $C_{16}H_{13}NOSNa$: $[M+Na]^+$ 290.0610, found 290.0611.



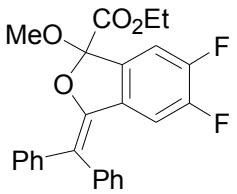
3d

Compound **4a**: White solid; m.p.88–90 ^{o}C; **IR** (KBr) ν_{max} 3055, 2980, 2938, 1754, 1466, 1250, 1041, 762, 702 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 7.65 (d, *J* = 7.6 Hz, 2H), 7.53–7.46 (m, 4H), 7.36–7.25 (m, 5H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.08 (d, *J* = 8.4 Hz, 1H), 4.33–4.28 (m, 2H), 3.30 (s, 3H), 1.32 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 167.1, 149.3, 139.1, 138.9, 136.4, 135.1, 131.2, 130.1, 129.6, 129.2, 128.7, 127.8, 126.4, 123.6, 123.2, 116.6, 107.4, 62.3, 51.6, 14.1 ppm; **HRMS (ESI)**: calcd for $C_{25}H_{22}O_4Na$: $[M+Na]^+$ 409.1410, found 409.1411.



4a

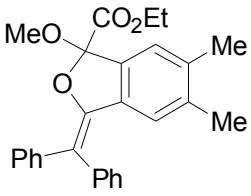
Compound **4b**: Colorless oil; **IR** (film) ν_{max} 3058, 2981, 2939, 1755, 1494, 1351, 1044, 804, 703 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 7.63 (d, *J* = 7.2 Hz, 2H), 7.50–7.49 (m, 3H), 7.34–7.30 (m, 5H), 7.23–7.21 (m, 1H), 5.76–5.71 (m, 1H), 4.32 (q, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 3.32 (s, 3H), 1.35 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 166.3, 151.6 (dd, *J* = 249, 13 Hz), 150.6 (dd, *J* = 252, 15 Hz), 147.5 (q, J^3 = 1.9 Hz), 138.4 (d, J^2 = 33.4 Hz), 132.4 (q, J^3 = 3.1 Hz), 131.6 (d, J^3 = 3.0 Hz), 131.5 (d, J^3 = 3.0 Hz), 130.9, 129.40, 129.35, 128.2, 127.8, 126.7, 117.3 (d, J^3 = 1.1 Hz), 112.2 (d, J^2 = 41.4 Hz), 112.1, 106.7 (d, J^3 = 1.9 Hz), 62.5, 51.6, 13.9 ppm; **HRMS (ESI)**: calcd for $C_{25}H_{20}F_2O_4Na$: $[M+Na]^+$ 445.1222, found 445.1221.



4b

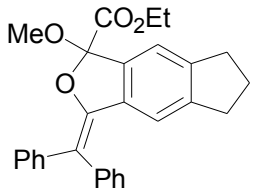
Compound **4c**: Colorless oil; **IR** (film) ν_{max} 3055, 2977, 2938, 1751, 1493, 1264, 1040, 767, 702 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 7.65 (d, *J* = 7.6 Hz, 2H), 7.47–7.45 (m, 3H), 7.35–7.26 (m, 5H), 7.16 (t, *J* = 7.2 Hz, 1H), 5.76 (s, 1H), 4.35–4.22 (m, 2H), 3.23 (s, 3H), 2.22 (s, 3H), 1.96 (s, 3H), 1.32 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 167.5, 149.8, 139.4, 139.3,

139.1, 138.3, 134.5, 133.3, 131.5, 129.6, 129.2, 127.9, 127.7, 126.2, 124.7, 123.7, 115.4, 107.6, 62.3, 51.5, 20.4, 20.2, 14.2 ppm; **HRMS (ESI)**: calcd for $C_{27}H_{26}O_4Na$: $[M+Na]^+$ 437.1723, found 437.1720.



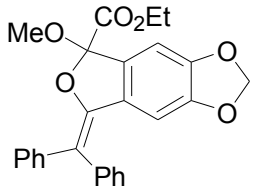
4c

Compound **4d**: Colorless oil; **IR** (film) ν_{max} 3054, 2939, 2841, 1751, 1442, 1261, 1040, 880, 732, 702 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.63 (d, *J* = 7.2 Hz, 2H), 7.46–7.44 (m, 3H), 7.35–7.27 (m, 5H), 7.18–7.16 (m, 1H), 5.85 (s, 1H), 4.31 (q, J_1 = 7.2 Hz, J_2 = 14.4 Hz, 2H), 3.29 (s, 3H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.02–1.98 (m, 2H), 1.33 ppm (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 167.4, 149.6, 147.0, 146.0, 139.4, 139.2, 135.2, 133.6, 131.3, 129.4, 129.0, 127.6, 127.6, 126.0, 119.2, 118.6, 115.2, 107.4, 62.1, 51.3, 32.5, 32.4, 25.6, 14.0 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{26}O_4Na$: $[M+Na]^+$ 449.1723, found 449.1709.



4d

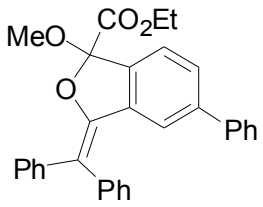
Compound **4e**: White solid; m.p.140–143 ^oC; **IR** (film) ν_{max} 3052, 2973, 2934, 1748, 1471, 1277, 1036, 866, 764, 701 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.61 (d, *J* = 7.6 Hz, 2H), 7.47–7.44 (m, 3H), 7.34–7.25 (m, 4H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.91 (s, 1H), 5.92 (d, *J* = 4.0 Hz, 2H), 5.39 (s, 1H), 4.35–4.25 (m, 2H), 3.29 (s, 3H), 1.34 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 167.1, 149.6, 149.1, 148.8, 139.2, 138.9, 131.3, 130.9, 129.6, 129.4, 129.2, 127.9, 127.8, 126.2, 115.0, 107.0, 103.4, 103.0, 101.9, 62.3, 51.3, 14.1 ppm; **HRMS (ESI)**: calcd for $C_{26}H_{22}O_6Na$: $[M+Na]^+$ 453.1309, found 453.1307.



4e

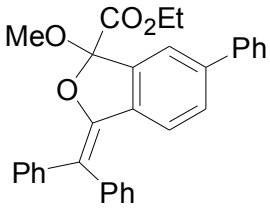
Compound **4f:** White solid; m.p.152–154 ^oC; **IR** (film) ν_{max} 3055, 2978, 2930, 1746, 1463, 1262, 1045, 858, 763, 699 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.58–7.46 (m, 5H), 7.41 (d, *J* = 6.8 Hz, 2H), 7.36–7.29 (m, 5H), 7.23–7.20 (m, 3H), 6.21 (s, 1H), 4.33 (q, *J* = 7.6 Hz, 2H), 3.34 (s, 3H), 1.34 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 167.1, 149.3, 142.9, 139.9, 139.0, 138.9, 136.0, 135.3, 131.4, 129.5, 129.3, 128.7, 127.9, 127.7, 127.7, 126.9, 126.5, 123.5, 122.4, 116.7, 107.5, 62.4, 51.6, 14.1 ppm; **HRMS (ESI)**: calcd for

$C_{31}H_{26}O_4Na$: $[M+Na]^+$ 485.1723, found 485.1728.



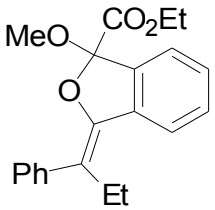
4f

Compound **4g:** White solid; m.p.158–160 °C; **IR** (film) ν_{max} 3053, 2978, 2932, 1745, 1468, 1265, 1044, 860, 764, 700 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 7.75 (d, *J* = 1.2 Hz, 1H),7.67 (d, *J* = 8.8 Hz, 2H), 7.55-7.48 (m, 5H), 7.41–7.30 (m, 8H), 7.21–7.20 (m, 1H), 6.12 (d, *J* = 8.8 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.35 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 167.2, 149.2, 141.9, 139.7, 139.2, 139.0, 137.4, 134.1, 131.4, 129.6, 129.2, 128.9, 127.9, 127.9, 127.0, 126.5, 124.0, 121.5, 116.7, 107.5, 62.4, 51.7, 14.1 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{26}O_4Na$: $[M+Na]^+$ 485.1723, found 485.1726.



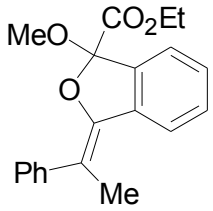
4g

Compound **4h**: Colorless oil; **IR** (film) ν_{max} 3054, 2968, 2936, 1751, 1464, 1252, 1126, 1050, 763, 698 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 7.78 (d, *J* = 8.4 Hz, 1H), 7.62–7.49 (m, 4H), 7.42–7.34 (m, 3H), 7.25–7.23 (m, 1H), 4.30–4.20 (m, 2H), 3.16 (s, 3H), 2.86 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.19 ppm (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 167.3, 147.8, 139.9, 136.9, 134.5, 130.6, 128.8, 128.4, 127.8, 126.3, 123.6, 123.1, 118.0, 106.3, 62.0, 51.2, 24.5, 13.9, 13.4 ppm; **HRMS (ESI)**: calcd for $C_{21}H_{22}O_4Na$: $[M+Na]^+$ 361.1410, found 361.1422.



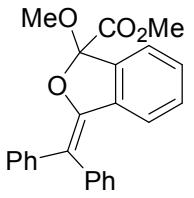
4h

Compound **4i**: Colorless oil; **IR** (film) ν_{max} 3053, 2980, 2937, 1751, 1466, 1249, 1124, 1045, 763, 698 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.58–7.49 (m, 4H), 7.42–7.34 (m, 3H), 7.25–7.22 (m, 1H), 4.27 (q, *J* = 6.8 Hz, 2H), 3.16 (s, 3H), 2.43 (s, 3H), 1.28 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 167.4, 147.9, 141.2, 136.9, 135.2, 130.5, 128.6, 128.4, 127.8, 126.3, 123.6, 123.6, 110.5, 106.7, 62.1, 51.2, 17.9, 14.0 ppm; **HRMS (ESI)**: calcd for $C_{20}H_{20}O_4Na$: $[M+Na]^+$ 347.1254, found 347.1247.



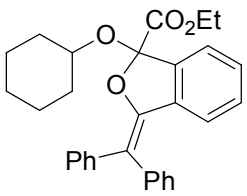
4i

Compound **5**: White solid; m.p.136–138 ^{o}C; **IR** (KBr) ν_{max} 3051, 2951, 2934, 1749, 1639, 1469, 1253, 1050, 763, 707, 633 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 7.63 (d, *J*= 7.6 Hz, 2H), 7.51–7.45 (m, 4H), 7.36–7.25 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.29 ppm (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 167.7, 149.3, 139.1, 138.9, 136.4, 135.2, 131.3, 130.2, 129.6, 129.2, 128.8, 127.9, 126.5, 123.8, 123.2, 116.8, 107.5, 53.2, 51.6 ppm; **HRMS (ESI)**: calcd for $C_{24}H_{20}O_4Na$: $[M+Na]^+$ 395.1254, found 395.1252.



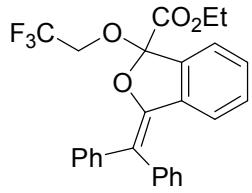
5

Compound **6a**: Colorless oil; **IR** (film) ν_{max} 3055, 2935, 2857, 1748, 1628, 1466, 1249, 762, 702 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 6.03 (d, *J* = 8.4 Hz, 1H), 4.26 (q, J_1 = 7.2 Hz, J_2 = 2.8 Hz, 2H), 3.57–3.51 (m, 1H), 1.97 (d, *J* = 10.8 Hz, 1H), 1.77–1.61 (m, 3H), 1.47–1.42 (m, 3H), 1.29 (t, *J* = 7.2Hz, 3H), 1.25–1.11 ppm (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 167.7, 149.2, 139.3, 139.1, 138.0, 135.1, 131.4, 129.8, 129.4, 129.2, 128.5, 127.7, 126.2, 123.6, 123.5, 116.3, 107.7, 74.9, 62.0, 33.9, 33.8, 25.3, 24.5, 24.3, 14.0 ppm; **HRMS (ESI)**: calcd for $C_{30}H_{30}O_4Na$: $[M+Na]^+$ 477.2036, found 477.2050.



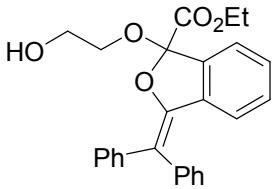
6a

Compound **6b**: Colorless oil; **IR** (film) ν_{max} 3057, 2983, 1753, 1467, 1285, 1166, 1053, 762, 701 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 7.60–7.55 (m, 3H), 7.49–7.46 (m, 3H), 7.36–7.28 (m, 5H), 7.25–7.21 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.11 (d, *J* = 8.0 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.98–3.93 (m, 1H), 3.77–3.74 (m, 1H), 1.32 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 ^{o}C, tetramethylsilane): δ = 166.0, 148.6, 138.8, 138.5, 135.6, 134.8, 131.1, 130.6, 129.6, 129.2, 129.1, 128.0, 127.9, 126.7, 123.7, 123.5, 123.4 (d, J^1 = 280 Hz), 117.8, 106.6, 62.6, 61.6 (q, J^2 = 36.5 Hz), 14.0 ppm; **HRMS (ESI)**: calcd for $C_{26}H_{21}F_3O_4Na$: $[M+Na]^+$ 477.1284, found 477.1302.



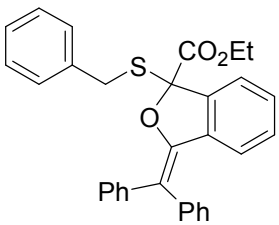
6b

Compound **6c**: Colorless oil; **IR** (film) ν_{max} 3640, 3055, 2983, 1748, 1626, 1466, 1250, 1050, 760, 702 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.62 (d, *J* = 7.6 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 6.4 Hz, 3H), 7.35–7.26 (m, 5H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.11(d, *J* = 8.0 Hz, 1H), 4.31–4.24 (m, 2H), 3.73(s, 2H), 3.68–3.56 (m, 2H), 2.63 (br, 1H), 1.30 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 167.3, 149.0, 139.0, 138.8, 136.7, 134.8, 131.1, 130.1, 129.5, 129.1, 128.8, 127.8, 127.2, 126.4, 123.6, 123.2, 116.9, 107.0, 66.2, 62.3, 61.4, 14.0 ppm; **HRMS (ESI)**: calcd for $C_{26}H_{24}O_5Na$: $[M+Na]^+$ 439.1516, found 439.1512.



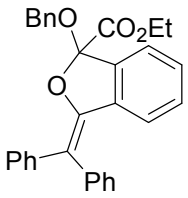
6c

Compound **6d**: Colorless oil; **IR** (film) ν_{max} 3058, 3028, 2981, 1740, 1626, 1494, 1233, 1051, 761, 700 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.66 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.47–7.43 (m, 3H), 7.35–7.30 (m, 4H), 7.24–7.15 (m, 7H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.06 (d, *J* = 7.6 Hz, 1H), 4.21–4.13 (m, 2H), 3.88 (q, J_1 = 12.8 Hz, J_2 = 27.2 Hz, 2H), 1.29 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 167.4, 149.9, 139.3, 139.0, 139.0, 136.7, 133.8, 131.3, 129.5, 129.4, 129.2, 128.9, 128.4, 127.8, 127.1, 126.3, 123.4, 116.7, 94.5, 62.5, 34.6, 14.0 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{26}O_3SNa$: $[M+Na]^+$ 501.1495, found 501.1491.



6d

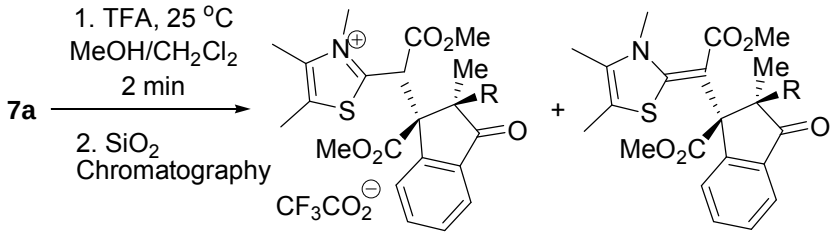
Compound **6e**: Colorless oil; **IR** (film) ν_{max} 3058, 3028, 2981, 1740, 1626, 1494, 1233, 1051, 761, 700 cm^{-1}; **^{1}H NMR** (400 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ 7.63–7.57 (m, 3H), 7.48–7.44 (m, 3H), 7.37–7.18 (m, 11H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 4.63 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 167.2, 149.2, 139.2, 139.0, 137.2, 137.1, 135.1, 131.3, 130.1, 129.6, 129.2, 128.8, 128.3, 127.9, 127.8, 127.8, 127.7, 126.4, 123.7, 123.5, 116.8, 107.4, 66.7, 62.3, 14.1 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{26}O_4Na$: $[M+Na]^+$ 485.1723, found 501.1730.



6e

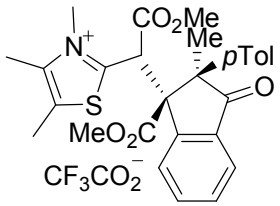
General procedure for the skeletal rearrangements of thiazepine-fused 7-oxanorbornadienes 7a–h

Preparation and characterization data for the intermediate 8a



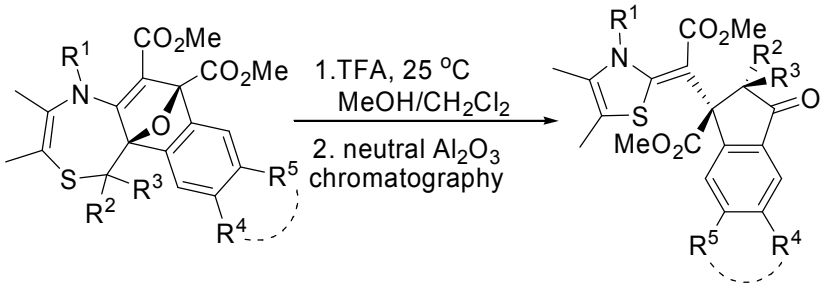
To a solution of **7a** (0.13 mmol) in 2 ml CH_2Cl_2/MeOH (5:1) was added TFA (0.13 mmol), and the resulting solution was stirred at RT for 30 min. The solvent was removed under vacuum. The residue was chromatographed on a silica gel column with a CH_2Cl_2–MeOH mixture (20:1) to afford a mixture of compounds **8a** and **9a** (c.a. 10:1, monitored by TLC). The mixture was dissolved in 3 ml ethyl acetate/ethyl ether (1:1) with 5 drops of CH_2Cl_2 and stood at 5 °C overnight, the colorless crystals were collected as a pure form of the intermediate **8a** (52% yield).

Compound **8a**: White solid; m.p.118–1120 °C; **IR** (KBr) ν_{max} 3072, 2954, 2873, 1754, 1730, 1426, 1336, 1011, 752, 708 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 25 °C, tetramethylsilane): δ = 8.04–7.92 (m, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.94 (s, 1H), 4.27 (s, 3H), 3.69 (s, 3H), 3.08 (s, 3H), 2.43 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H), 1.50 ppm (s, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 25 °C, tetramethylsilane): δ = 205.3, 169.6, 167.3, 161.2, 147.8, 144.5, 140.0, 138.7, 137.4, 137.0, 133.0, 132.6, 131.5, 128.7, 127.8, 124.3, 64.7, 59.9, 54.9, 52.6, 51.7, 39.6, 20.9, 19.0, 12.8, 12.1 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{30}NO_5S$: $[M\text{-}CF_3CO_2^-]^+$ 492.1839, found 492.1834.



8a

Rearrangements of 7a–h

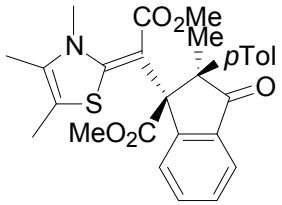


7a-h **9a-h**

To a solution of **7a**–**h** (0.13 mmol) in 2 ml CH_2Cl_2/MeOH (5:1) was added TFA (0.13 mmol), and the resulting solution was stirred at RT for 30 min. The solvent was removed under vacuum. The residue was chromatographed on a short pad of neutral Al_2O_3 column with a hexane–ethyl acetate mixture (1:1) to afford the desired products **9a**–**h**.

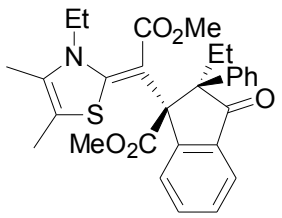
Characterization data for the compounds 9a–h and 10

Compound **9a**: Yellow solid; m.p.205–207 °C; **IR** (film) ν_{max} 3024, 2924, 2854, 1722, 1621, 1475, 1346, 1252, 1033, 755, 734 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 7.68 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 5.5 Hz, 2H), 7.45 (br, 1H), 6.88 (s, 4H), 3.47 (s, 3H), 3.19 (s, 3H), 2.99 (s, 3H), 2.23 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H), 1.69 ppm (s, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 204.8, 171.6, 169.9, 163.1, 152.5, 140.5, 137.9, 135.1, 135.0, 133.4, 128.1, 127.9, 127.7, 127.4, 121.5, 116.4, 78.2, 68.7, 61.1, 51.1, 48.6, 38.9, 20.3, 12.0, 11.1 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{30}NO_5S$: $[M+H]^+$ 492.1839, found 492.1834.



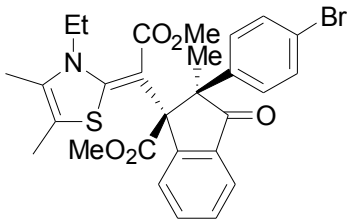
9a

Compound **9b**: Yellow solid; m.p.192–194 °C; **IR** (film) ν_{max} 3030, 2987, 2942, 1731, 1716, 1614, 1419, 1336, 1224, 1036, 745, 700 cm^{-1}; **^{1}H NMR** (500 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane): δ = 7.92 (s, 1H), 7.51–7.43 (m, 4H), 7.28 (d, *J* = 7.0 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 4.32 (q, *J* = 7.5 Hz, 1H), 3.92 (s, 1H), 3.27 (s, 3H), 3.06 (s, 3H), 2.46 (q, *J* = 7.0 Hz, 1H), 2.20 (s, 3H), 2.07 (s, 3H), 1.67 (s, 1H), 1.35 (t, *J* = 7.0 Hz, 3H), 0.68 ppm (s, 3H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane): δ = 203.3, 174.1, 166.8, 166.4, 148.1, 136.9, 133.1, 132.3, 132.3, 131.5, 129.4, 128.3, 126.2, 125.7, 124.6, 114.5, 83.4, 70.5, 68.7, 51.9, 49.8, 45.8, 30.6, 13.4, 12.6, 11.7, 8.6 ppm; **HRMS (ESI)**: calcd for $C_{29}H_{32}NO_5S$: $[M+H]^+$ 506.1996, found 506.1972.



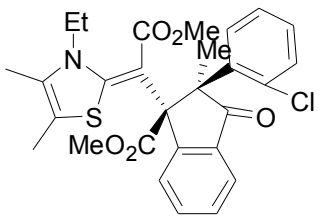
9b

Compound **9c**: Yellow solid; m.p.223–225 °C; **IR** (KBr) ν_{max} 3068, 2950, 1738, 1723, 1601, 1426, 1229, 1008, 848, 707 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 2H), 7.46 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 4.30 (q, *J* = 7.5 Hz, 1H), 3.95 (q, *J* = 7.0 Hz, 1H), 3.18 (s, 3H), 3.03 (s, 3H), 2.27 (s, 3H), 2.18 (s, 3H), 1.71 (s, 3H), 1.31 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 204.3, 171.7, 171.6, 151.9, 143.0, 135.0, 133.6, 131.1, 130.6, 130.1, 129.7, 128.6, 128.3, 127.9, 122.7, 121.7, 119.5, 68.9, 61.6, 51.2, 48.7, 46.0, 20.9, 13.3, 12.0, 11.3 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{29}BrNO_5S$: $[M+H]^+$ 570.0944, found 570.0940.



9c

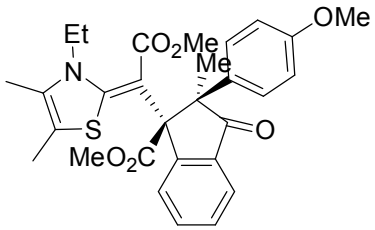
Compound **9d**: Yellow solid; m.p.217–220 °C; **IR** (KBr) ν_{max} 3061, 2983, 2946, 1747, 1713, 1644, 1433, 1236, 1177, 763, 736 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 25 °C, tetramethylsilane): δ = 7.56–7.54 (m, 2H), 7.48–7.35 (m, 4H), 7.08 (s, 2H), 4.15–4.13 (m, 1H), 3.78 (br, 1H), 3.42 (s, 3H), 3.28 (s, 3H), 2.02 (s, 3H), 1.82 (s, 3H), 1.34 (s, 3H), 1.13 ppm (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 206.2, 171.6, 171.1, 137.6, 135.6, 134.6, 132.1, 132.1, 131.8, 131.4, 129.8, 129.2, 129.0, 128.3, 127.9, 127.2, 125.4, 123.3, 121.1, 71.2, 51.4, 49.5, 46.4, 25.6, 18.8, 13.7, 11.9, 11.0 ppm; **HRMS (ESI)**: calcd for $C_{28}H_{29}ClNO_5S$: $[M+H]^+$ 526.1449, found 526.1432.



9d

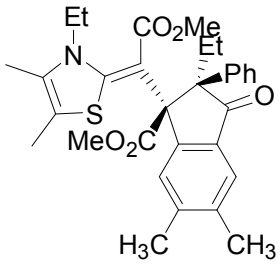
Compound **9e**: Yellow solid; m.p.214–216 °C; **IR** (KBr) ν_{max} 3060, 2946, 1715, 1618, 1421, 1338, 1225, 1032, 950, 758 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 7.67–7.58 (m, 3H), 7.41 (t, *J* = 7.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.5 Hz, 2H), 4.30 (q, *J* = 7.0 Hz, 1H), 3.92 (q, *J* = 7.0 Hz, 1H), 3.72 (s, 3H), 3.13 (s, 3H), 2.97 (s, 3H), 2.26 (s, 3H), 2.19 (s, 3H), 1.72 (s, 3H), 1.30 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 205.3, 172.2, 163.1, 158.3, 152.8, 138.8,

136.3, 135.6, 133.8, 130.9, 129.8, 128.9, 128.4, 128.0, 121.7, 114.1, 113.2, 69.4, 61.6, 55.7, 51.6, 49.1, 46.6, 20.2, 13.9, 12.6, 11.9 ppm; **HRMS (ESI)**: calcd for $C_{29}H_{32}NO_6S$: $[M+H]^+$ 522.1945, found 522.1929.



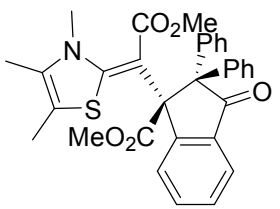
9e

Compound **9f**: Yellow solid; m.p.223–225 °C; **IR** (film) ν_{max} 3032, 2945, 1735, 1715, 1615, 1427, 1379, 1230, 1032, 748, 704 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 7.40 (s, 1H), 7.18 (d, *J* = 6.0 Hz, 2H), 7.07–6.97 (m, 4H), 4.05 (t, *J* = 7.0 Hz, 1H), 3.85 (t, *J* = 7.0 Hz, 1H), 3.08 (s, 3H), 3.01 (s, 3H), 2.30-2.28 (m, 1H), 2.27 (t, 3H, *J* = 7.0 Hz), 2.16 (s, 3H), 2.13 (s, 3H), 1.99 (s, 3H), 1.81 (br, 1H), 1.22 (t, *J* = 7.0 Hz, 3H), 0.60 ppm (s, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 203.3, 172.6, 164.909, 142.0, 138.5, 136.8, 135.1, 133.9, 131.0, 129.7, 129.3, 128.6, 126.6, 126.0, 125.5, 123.2, 122.5, 70.1, 66.9, 51.3, 49.0, 45.9, 27.4, 20.3, 19.2, 13.0, 12.0, 11.1, 9.0 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{36}NO_5S$: $[M+H]^+$ 534.2309, found 534.2294.



9f

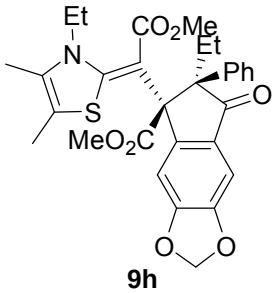
Compound **9g**: Yellow solid; m.p.188–190 °C; **IR** (KBr) ν_{max} 3055, 2946, 1749, 1733, 1643, 1492, 1350, 1212, 972, 762, 704 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 8.08 (s, 1H), 7.30–7.10 (m, 9H), 6.66 (d, *J* = 6.5 Hz, 1H), 3.59 (s, 3H), 3.55 (s, 3H), 3.30 s, 3H), 2.06 (s, 3H), 2.04 ppm (s, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 171.2, 168.3, 165.1, 150.9, 141.9, 140.2, 139.6, 135.3, 134.3, 131.3, 130.6, 129.3, 129.0, 128.4, 127.5, 127.1, 126.2, 125.6, 123.6, 122.7, 116.5, 79.6, 69.0, 52.4, 49.6, 38.9, 11.6, 11.0 ppm; **HRMS (ESI)**: calcd for $C_{32}H_{30}NO_5S$: $[M+H]^+$ 540.1839, found 540.1836.



9g

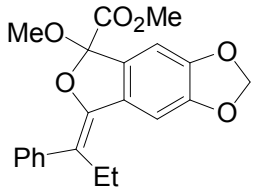
Compound **9h**: Yellow solid; m.p.238–240 °C; **IR** (film) ν_{max} 3053, 2972, 2943, 1753, 1648, 1521, 1312, 1163, 941, 766 cm^{-1}; **^{1}H NMR** (500 MHz**,** d_6-DMSO, 80 °C, tetramethylsilane): δ = 7.16 (d, *J* = 7.0 Hz, 2H), 7.07–7.01 (m, 4H), 6.60 (s, 1H), 6.05 (d, *J* = 14.0 Hz, 2H),

4.04 (q, *J* = 7.0 Hz, 1H), 3.90–3.84 (m, 1H), 3.13 (s, 3H), 3.03 (s, 3H), 2.28 (q, *J* = 7.0 Hz, 1H), 2.13 (s, 4H), 2.01 (s, 3H), 1.19 (t, *J* = 7.0 Hz), 0.62 ppm (s, 3H); **^{13}C NMR** (125 MHz**,** d_6-DMSO, 80 ^{o}C, tetramethylsilane): δ = 202.3, 172.3, 171.6, 152.3, 148.5, 147.0, 138.8, 134.1, 131.8, 130.9, 129.3, 128.4, 126.7, 126.1, 125.6, 107.5, 102.3, 101.1, 70.0, 66.8, 51.4, 49.1, 45.9, 28.9, 13.1, 12.1, 11.2, 9.1 ppm; **HRMS (ESI)**: calcd for $C_{30}H_{32}NO_7S$: $[M+H]^+$ 550.1894, found 550.1882.



9h

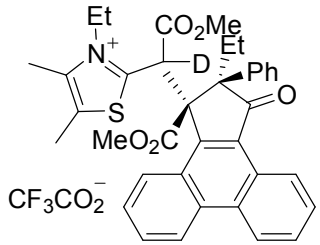
Compound **10**: White solid; m.p.112–114 ^{o}C; **IR** (KBr) ν_{max} 3054, 2967, 2907, 1743, 1650, 1502, 1479, 1374, 1105, 868, 770, 706 cm^{-1}; **^{1}H NMR** (400 MHz, d_6-Acetone, 25 ^{o}C, tetramethylsilane): δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.28 (s, 1H), 7.23–7.19 (m, 1H), 6.96 (s, 1H), 6.17 (d, *J* = 4.8 Hz, 2H), 3.74 (s, 3H), 3.12 (s, 3H), 2.82–2.79 (m, 2H), 1.15 ppm (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz**,** d_6-Acetone, 25 ^{o}C, tetramethylsilane): δ = 167.3, 150.7, 148.8, 147.7, 140.3, 131.5, 128.8, 128.3, 127.7, 126.2, 115.8, 106.1, 103.4, 102.7, 102.6, 52.1, 50.3, 24.0, 13.0 ppm; **HRMS (ESI)**: calcd for $C_{21}H_{20}O_6Na$: $[M+Na]^+$ 391.1152, found 391.1144.



10

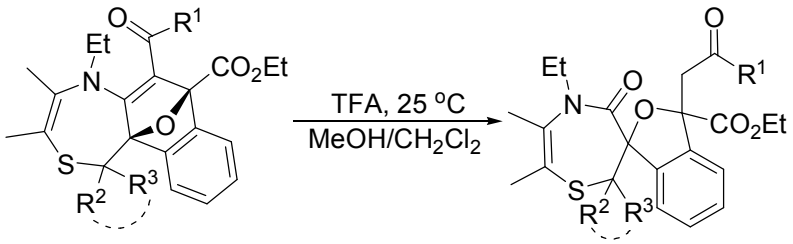
Characterization data for the compound [D_1]11

Compound [D_1]**11**: **^{1}H NMR** (500 MHz, $CDCl_3$ + d_4-Methanol (2:1), 25 ^{o}C, tetramethylsilane): δ = 8.74 (q, *J* = 8.0 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.78–7.64 (m, 5H), 7.45–7.34 (m, 5H), 4.66 (q, *J* = 7.5 Hz, 1H), 4.42 (q, *J* = 7.5 Hz, 1H), 3.54 (s, 3H), 2.96 (s, 3H), 2.91 (q, *J* = 7.5Hz, 1H), 2.69 (q, *J* = 7.5 Hz, 1H), 2.40 (s, 3H), 2.27 (s, 3H), 1.47 (t, *J* = 7.5 Hz, 3H), 1.15 ppm (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$ + d_4-Methanol (2:1), 25 ^{o}C, tetramethylsilane): δ = 169.8, 164.1, 161.8, 159.5 (d, J^2 = 38.8 Hz), 141.2, 140.3, 148.7, 134.2, 132.8, 132.2, 131.7, 131.0, 130.2, 128.4, 128.3, 128.1, 127.4, 127.0, 126.5, 125.5, 125.4, 124.1, 123.8, 123.0, 122.3, 116.4 (q, J^1 = 291 Hz), 88.9, 54.1, 53.2, 46.8, 26.2, 14.0, 12.3, 11.7, 11.5 ppm; **HRMS (ESI)**: calcd for $C_{37}H_{35}DNO_5S$: $[M\text{-}CF_3CO_2^-]^+$ 607.2371, found 607.2348.



[D_1]**11**

General procedure for the skeletal rearrangements of thiazepine-fused 7-oxanorbornadienes 12a–c

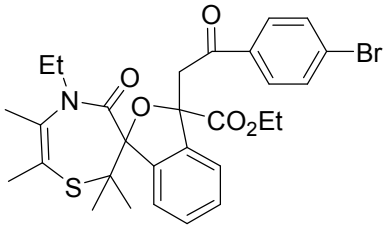


12a-c **13a-c**

To a solution of **12a–c** (0.13 mmol) in 2 ml CH_2Cl_2/MeOH (5:1) was added TFA (0.13 mmol), and the resulting solution was stirred at RT for 12 h. On completion of the reaction, the solvent was removed under vacuum. The residue was chromatographed on a silica gel column with a hexane–ethyl acetate mixture (3:1) to afford the desired products **13a–c**.

Characterization data for the compounds 13a–c

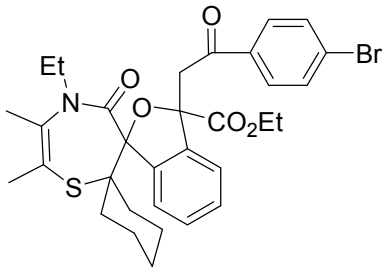
Compound **13a**: White solid; m.p.166–168 °C; **IR** (KBr) ν_{max} 3062, 2974, 2930, 1756, 1618, 1462, 1220, 1055, 776, 694 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, tetramethylsilane): δ = 7.87 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 9.2 Hz, 2H), 7.59 (d, *J* = 9.2 Hz, 2H), 7.42–7.34 (m, 3H), 4.30 (q, *J* = 7.4 Hz, 2H), 3.68–3.60 (m, 2H), 3.37 (d, *J* = 18.0 Hz, 1H), 3.15 (q, *J* = 6.8 Hz, 1H), 2.17 (d, *J* = 1.2 Hz, 3H), 1.66 (d, *J* = 1.2 Hz, 3H), 1.64 (s, 3H), 1.39 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.08 ppm (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 °C, tetramethylsilane): δ = 194.1, 172.7, 170.4, 141.1, 139.8, 137.2, 134.9, 132.0, 129.3, 128.8, 128.7, 127.9, 121.8, 98.4, 87.3, 69.6, 61.4, 50.8, 39.9, 28.7, 27.0, 23.5, 17.5, 14.1, 12.1 ppm; **HRMS (ESI)**: calcd for $C_{29}H_{32}BrNO_5SNa$: $[M+Na]^+$ 608.1077, found 608.1086.



13a

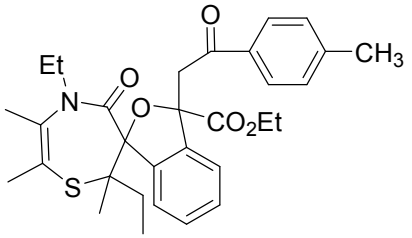
Compound **13b**: White solid; m.p.140–142 °C; **IR** (KBr) ν_{max} 3060, 2977, 2926, 1753,

1610, 1468, 1215, 1054, 775, 698 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.91 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.37–7.31 (m, 3H), 4.28–3.24 (m, 2H), 3.63–3.54 (m, 2H), 3.67 (d, *J* = 17.5 Hz, 1H), 3.14 (q, *J* = 7.0 Hz, 1H), 2.49 (t, *J* = 10.5 Hz, 2H), 2.11 (s, 3H), 1.97–1.84 (m, 2H), 1.65 (s, 3H), 1.57–1.48 (m, 4H),1.28 (t, *J* = 7.3 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H), 0.93–0.90 ppm (m, 2H); **^{13}C NMR** (125 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 194.7, 173.4, 170.7, 141.9, 140.2, 137.4, 135.3, 132.3, 130.0, 129.6, 129.03, 129.00, 127.9, 122.1, 121.6, 99.9, 87.5, 76.5, 61.7, 51.2, 40.1, 35.8, 32.5, 25.6, 24.0, 22.6, 21.7, 17.6, 14.3, 12.4 ppm; **HRMS (ESI)**: calcd for $C_{32}H_{36}BrNO_5SNa$: $[M+Na]^+$ 648.1390, found 648.1384.



13b

Compound **13c**: White solid; m.p.160–162 ^oC; **IR** (KBr) ν_{max} 3057, 2972, 2920, 1755, 1615, 1464, 1218, 1056, 776, 696 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 7.88–7.83 (m, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.41–7.33 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 2H), 4.30 (d, *J* = 7.2 Hz, 2H), 3.65–3.56 (m, 2H), 3.41 (d, *J* = 17.6 Hz, 1H), 3.17 (t, *J* = 5.8 Hz, 1H), 2.54 (br, 0.8H), 2.38 (s, 3H), 2.16 (s, 3H), 1.83–1.78 (m, 1.2H), 1.69 (s, 3H), 1.54 (s, 0.8H), 1.37 (s, 2.2H), 1.30 (t, *J* = 6.8 Hz, 3H), 1.09–1.03 ppm (m, 6H); **^{13}C NMR** (100 MHz**,** $CDCl_3$, 25 ^oC, tetramethylsilane): δ = 190.5, 173.2, 170.5, 144.3, 142.1, 141.3, 140.3, 137.1, 133.9, 129.3, 128.7, 128.0, 127.6, 122.0, 121.1, 99.2, 87.4, 75.1, 74.2, 61.3, 51.0, 39.8, 31.8, 23.7, 21.6, 17.3, 14.1, 12.3, 9.4 ppm; **HRMS (ESI)**: calcd for $C_{31}H_{37}NO_5SNa$: $[M+Na]^+$ 558.2285, found 558.2276.



13c

References

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(2) D. Pena, D. Perez, E. Guitian, L. Castedo, *J. Am. Chem. Soc.* **1999,** *121,* 5827–5828.
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(4) H. Yoshida, J. Ikadai, M. Shudo, J. Ohshita, A. Kunai, *J. Am. Chem. Soc.* **2003**, *125*, 6638–6639.
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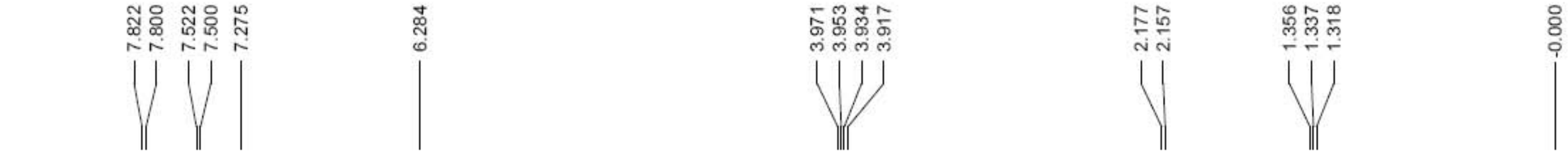
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7.522
7.500
7.275
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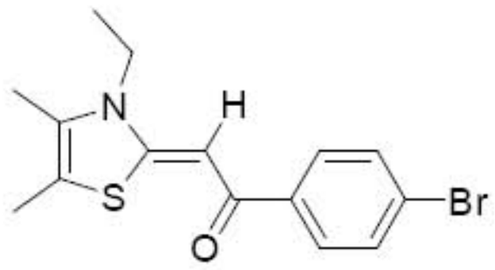
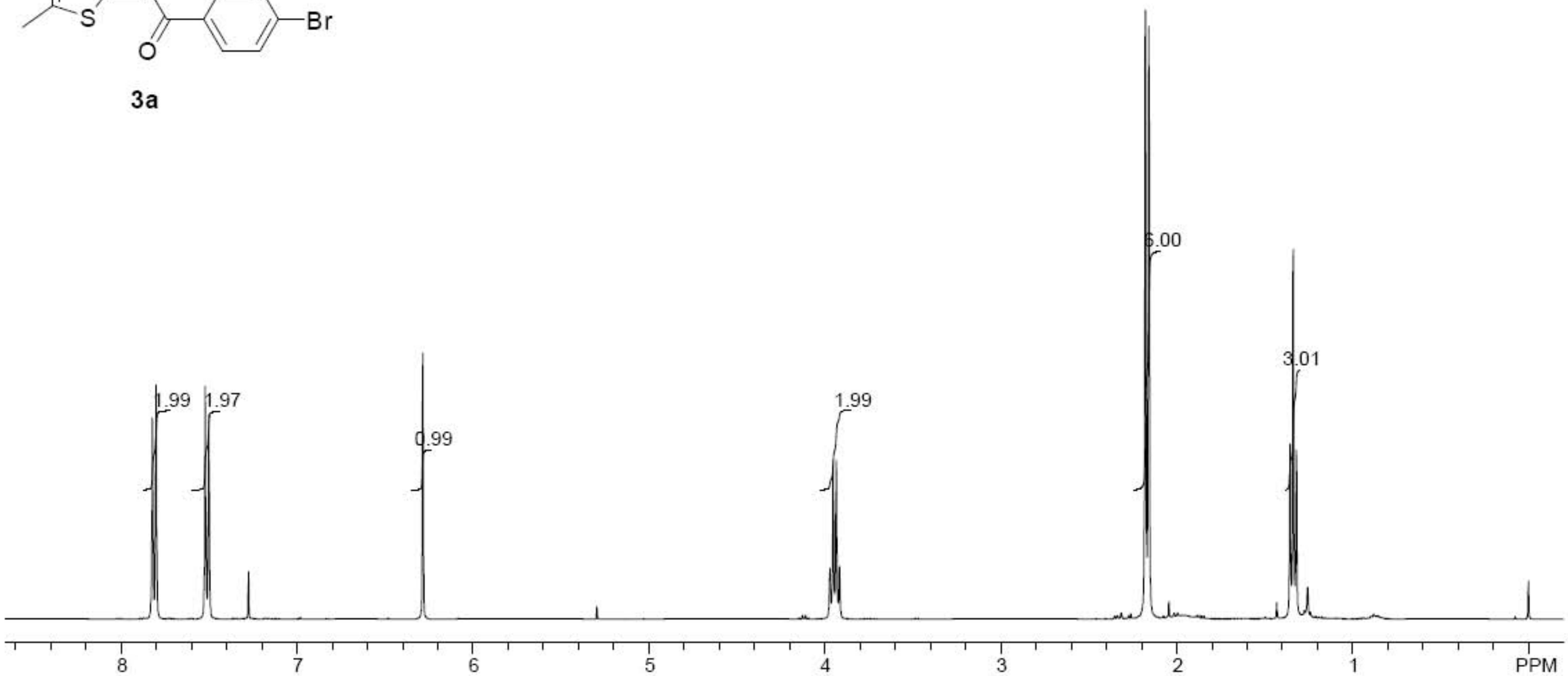
3.953
3.934
3.917
2.177
2.157
1.356
1.337
1.318
-0.000


N
H
S
O
Br

3a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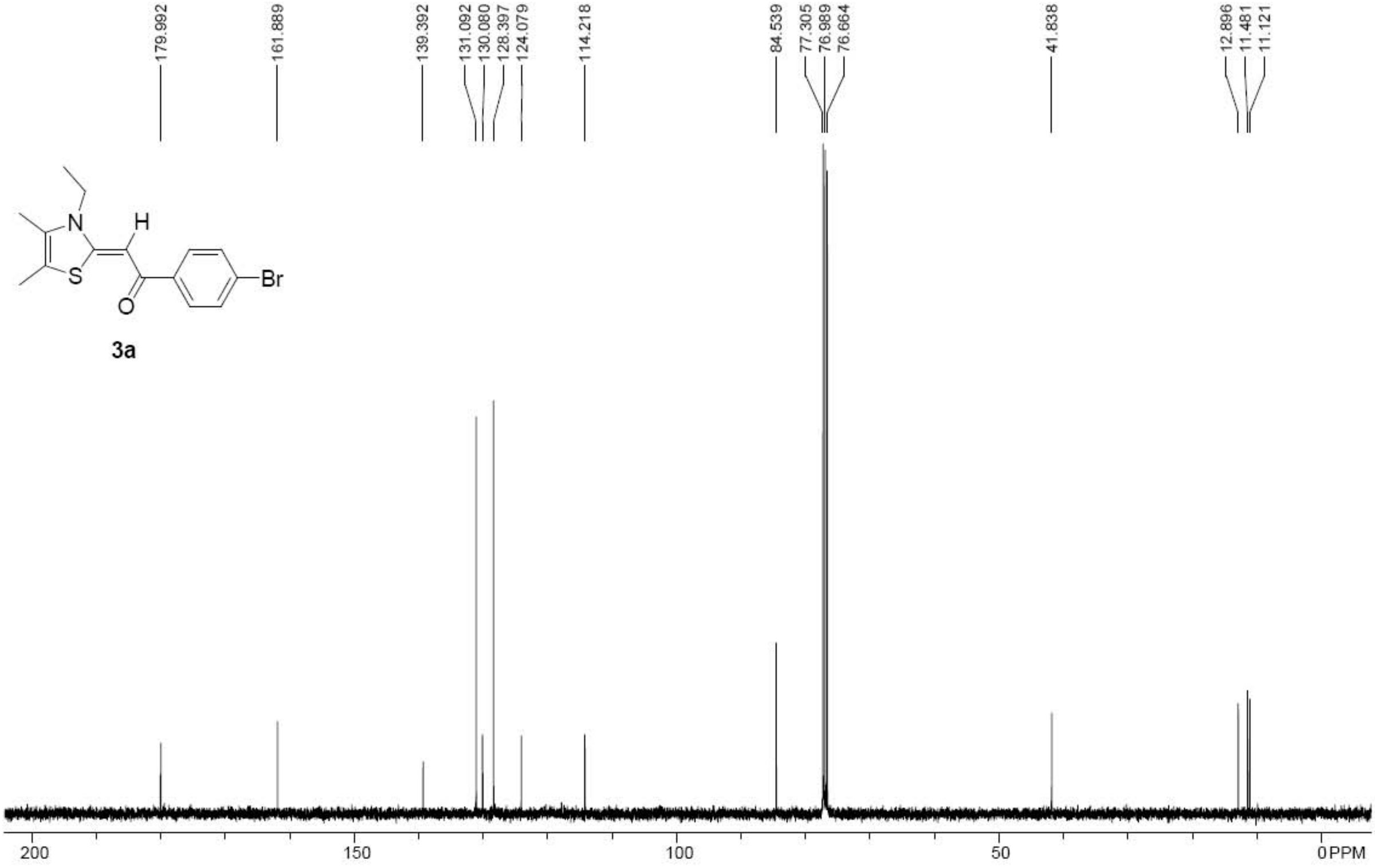
0.99
1.99
6.00
3.01
8
7
6
5
4
3
2
1
PPM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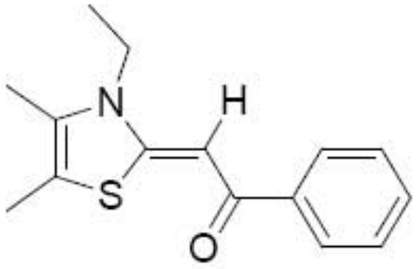
131.092
130.080
128.397
124.079
114.218
84.539
77.305
76.989
76.664
41.838
12.896
11.481
11.121
N
H
S
O
Br
200
150
100
50
0 PPM

3a


N
H
S
O

3b

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7.418
7.398
7.272
4.119
2.238
1.361
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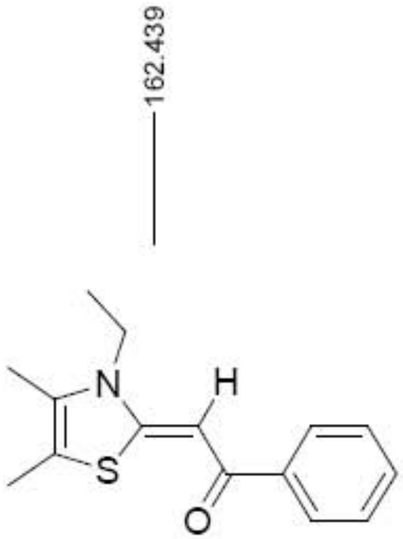
3.13
3.04
2.00
2.00
8
7
6
5
4
3
2
1
0 PPM


N
H
S
O

3b

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128.309
127.202
119.939
77.409
76.902
76.672
43.089
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11.467
11.193
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120
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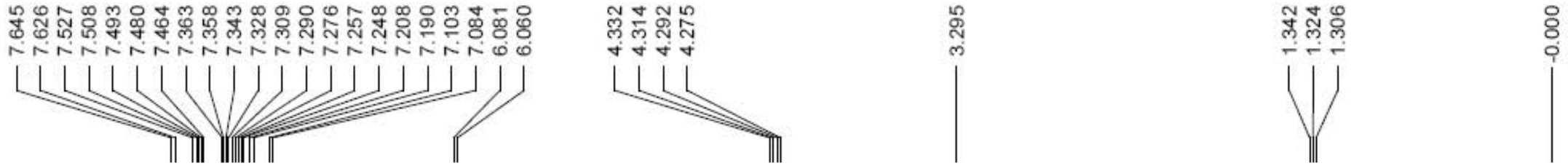
80
60
40
20
0
PPM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7.363
7.358
7.343
7.328
7.309
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7.276
7.257
7.248
7.208
7.190
7.103
7.084
6.081
6.060
4.332
4.314
4.292
4.275
3.295
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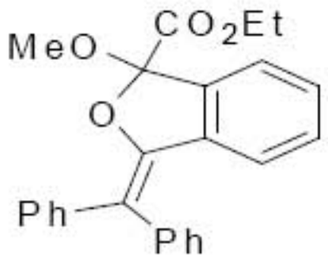
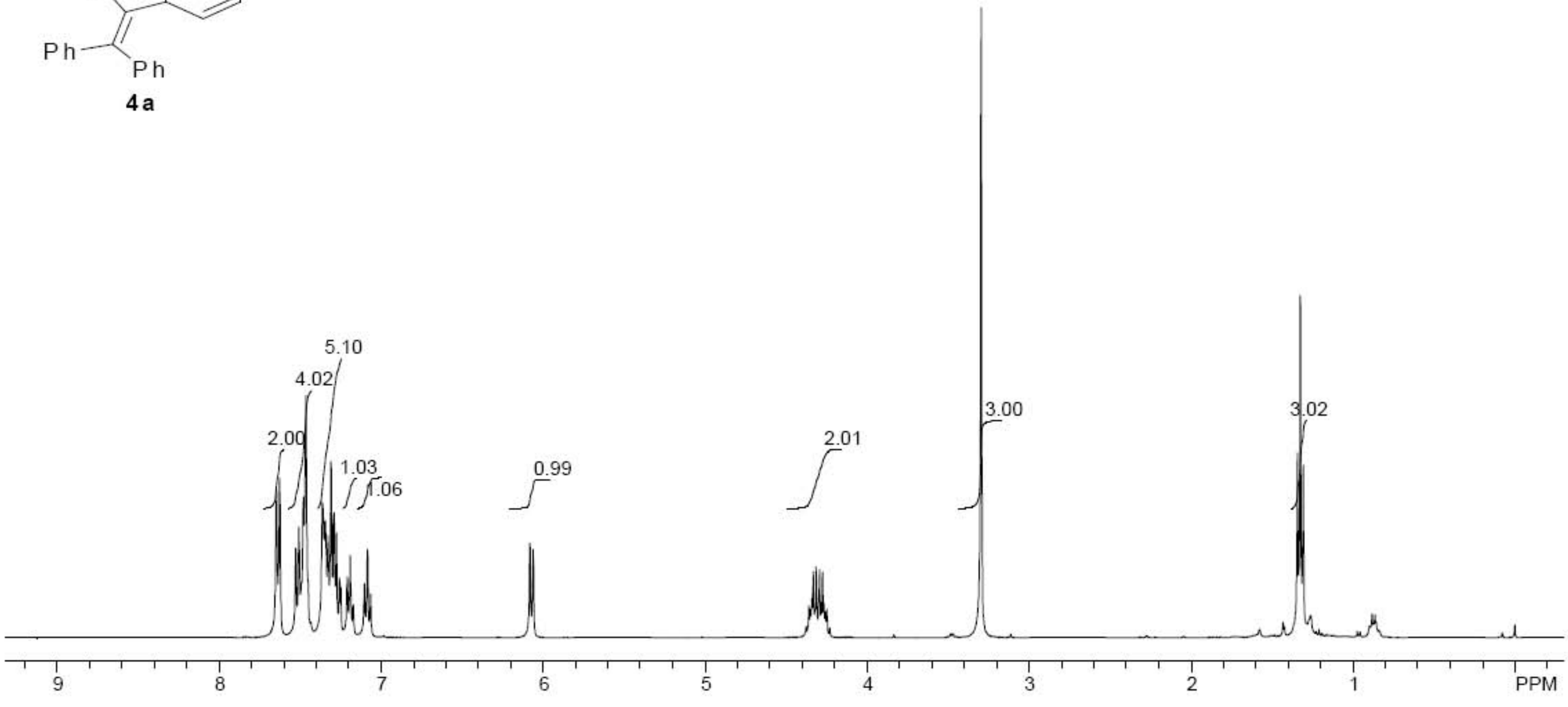
1.324
1.306
-0.000


MeO
CO2Et
O
Ph
Ph

4a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4.02
2.00
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1.06
0.99
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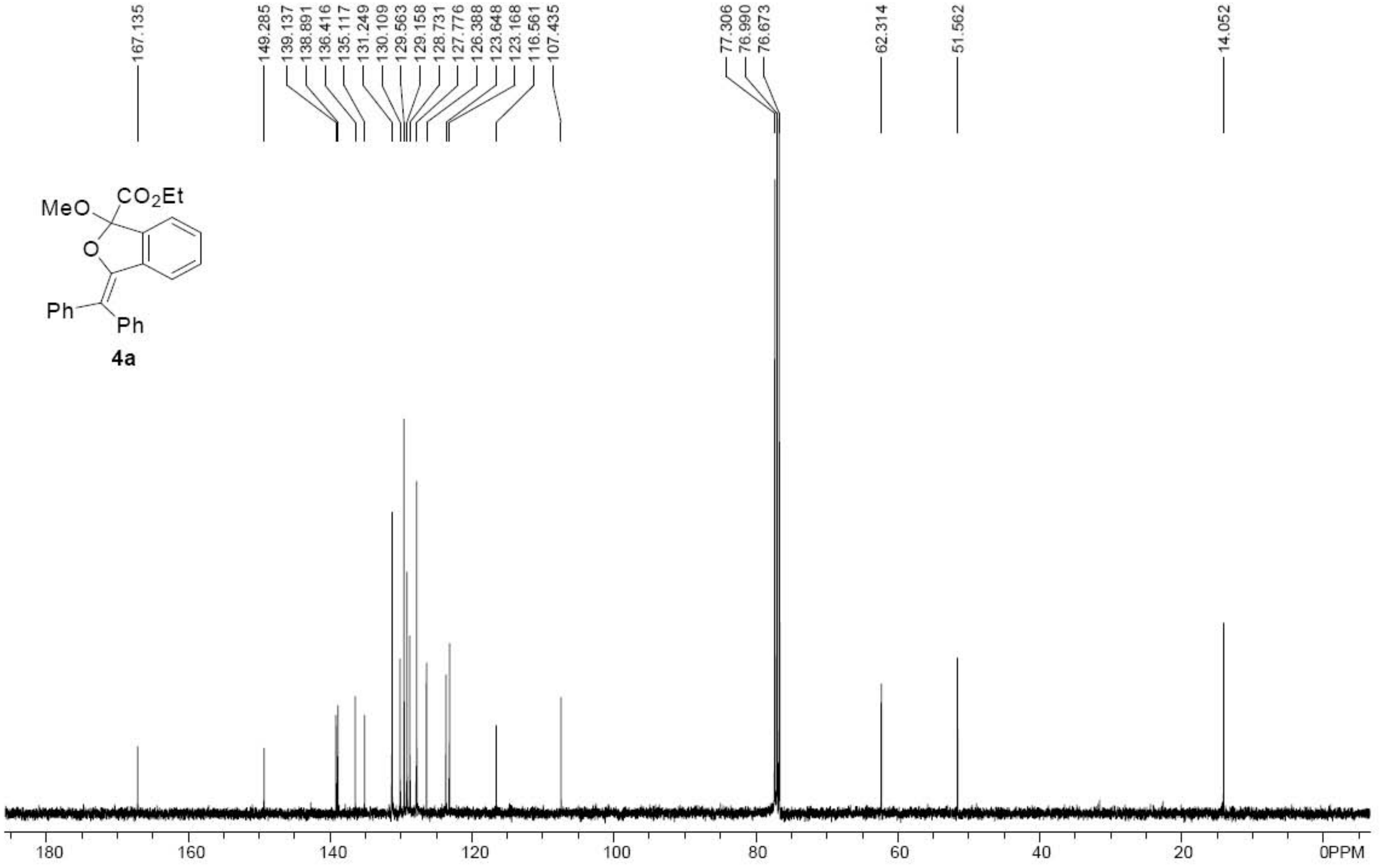
3.00
3.02
9
8
7
6
5
4
3
2
1
PPM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131.249
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128.731
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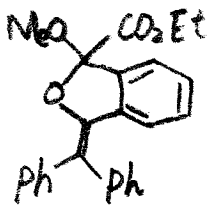
123.648
123.168
116.561
107.435
77.306
76.990
76.673
62.314
51.562
14.052
MeO
CO2Et
O
Ph
Ph
180
160
140
120
100
80
60
40
20
0PPM

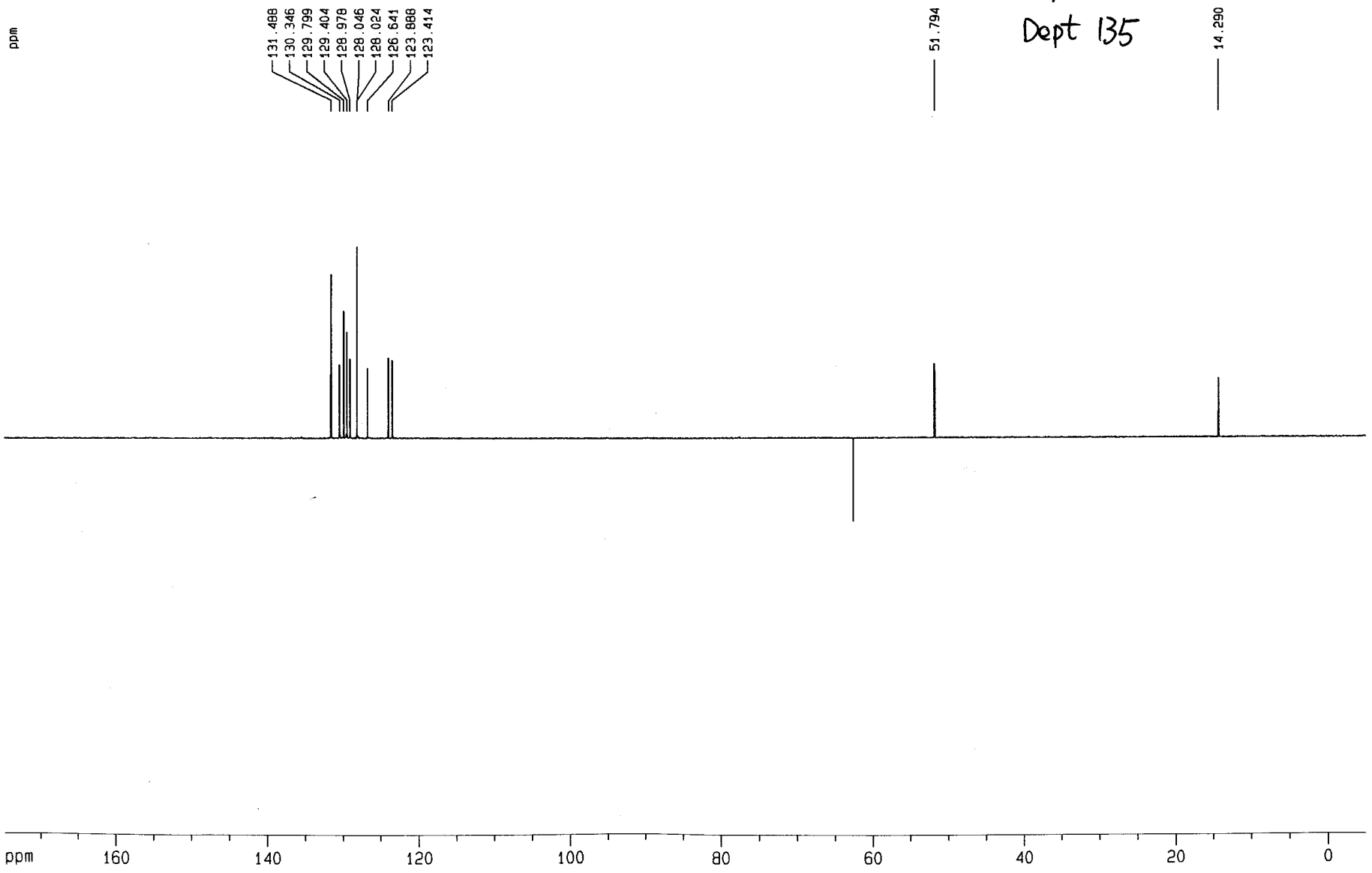
4a

Zhejiang University Avance DMX 500
DMP 5mm Smaple: dhf070104 in CDCL3

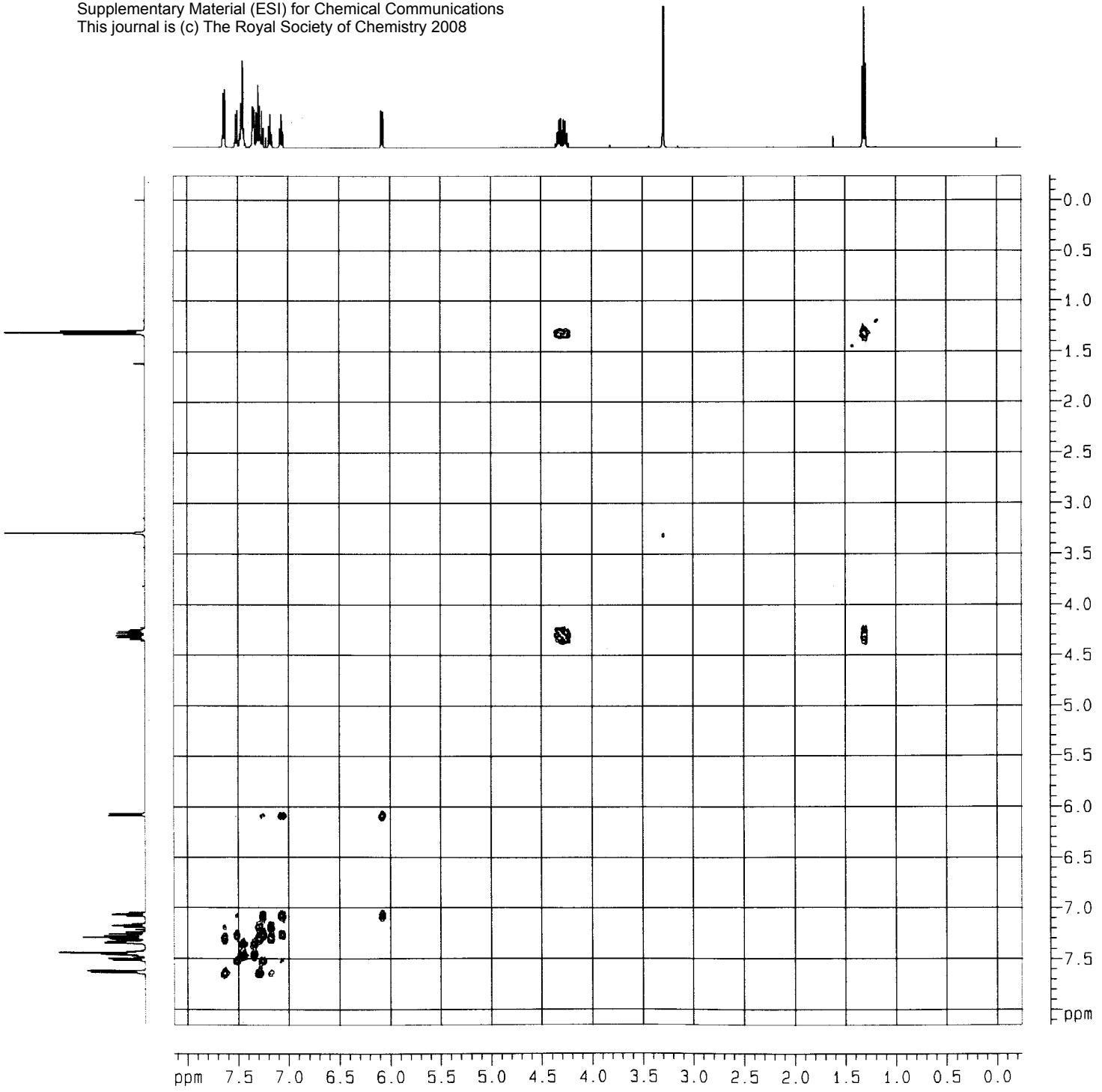


4a

Dept 135



1H-1H COSY



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NS	4
DS	8
SWH	4194.631 Hz
FIDRES	2.048180 Hz
AQ	0.2442908 sec
RG	512
DW	119.200 usec
DE	6.00 usec
TE	298.0 K
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D1	2.00000000 sec
d13	0.00000400 sec
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MCREST	0.00000000 sec
MCWRK	2.00000000 sec

******** CHANNEL f1 ********

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PL1	4.00 dB
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****** GRADIENT CHANNEL *****

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GPNAM2	SINE.100
GPNAM3	SINE.100
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GPX2	0.00 %
GPX3	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPY3	0.00 %
GPZ1	16.00 %
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FnMODE	QF

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SSB	0
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GB	0
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F1 - Processing parameters

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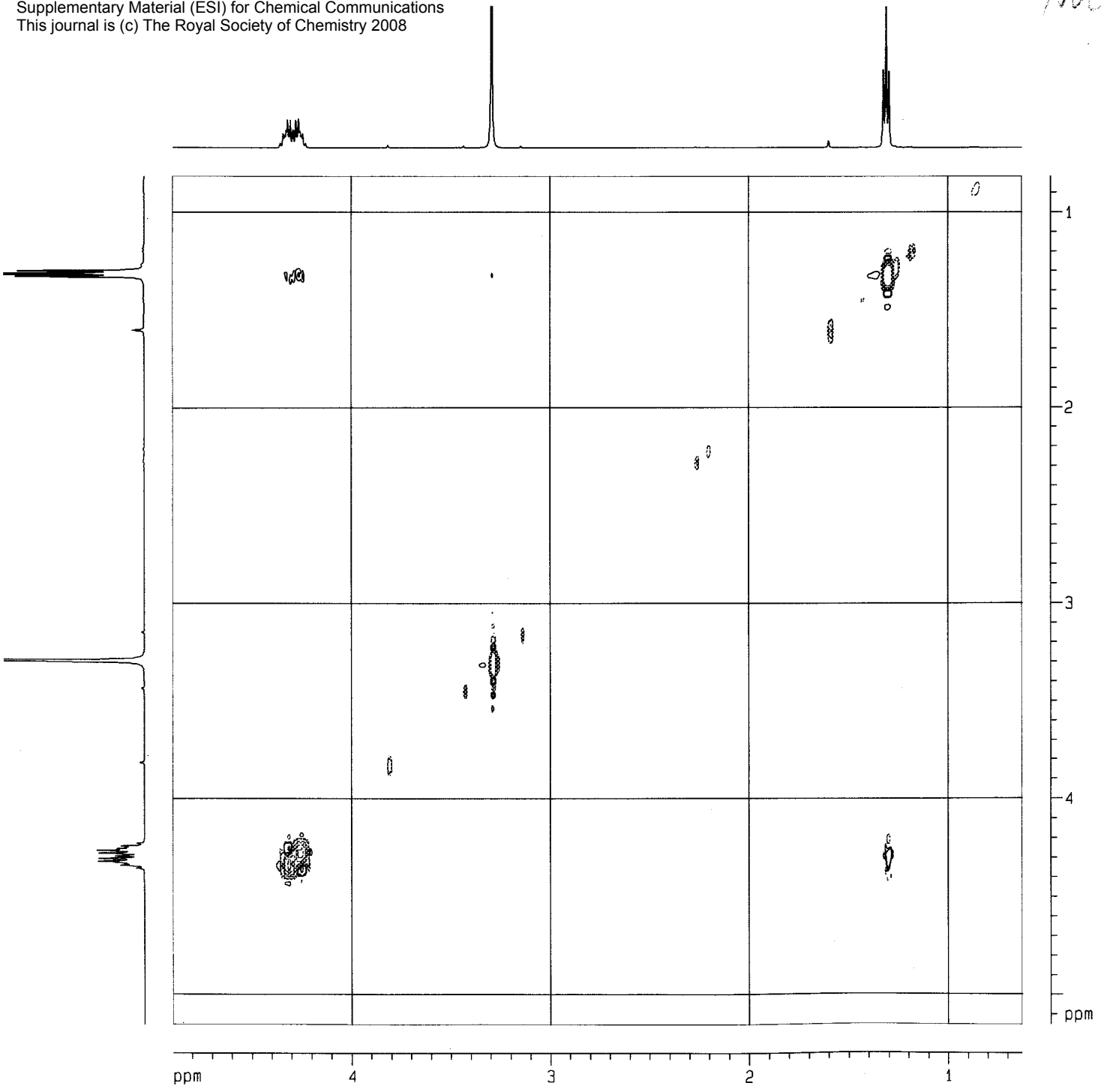
F2PHI	-0.247 ppm
F2HI	-123.60 Hz
F1PLO	8.148 ppm
F1LO	4075.28 Hz
F1PHI	-0.242 ppm
F1HI	-120.89 Hz
F2PPMCM	0.55914 ppm/cm
F2HZCM	279.64206 Hz/cm
F1PPMCM	0.55934 ppm/cm
F1HZCM	279.74475 Hz/cm

NOESY 4a

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d1                  1.50000000 sec
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MCWRK               0.75000000 sec
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PL1                    4.00 dB
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SW                      9.200 ppm
FnMODE              States-TPPI

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SSB                         2
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GB                          0
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              F1 - Processing parameters
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MC2                 States-TPPI
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GB                          0

              2D NMR plot parameters
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F2HI                  313.27 Hz
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F1LO                 2577.66 Hz
F1PHI                   0.815 ppm
F1HI                  407.40 Hz
F2PPMCM              0.28476 ppm/cm
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F1PPMCM              0.28929 ppm/cm
F1HZCM             144.68419 Hz/cm
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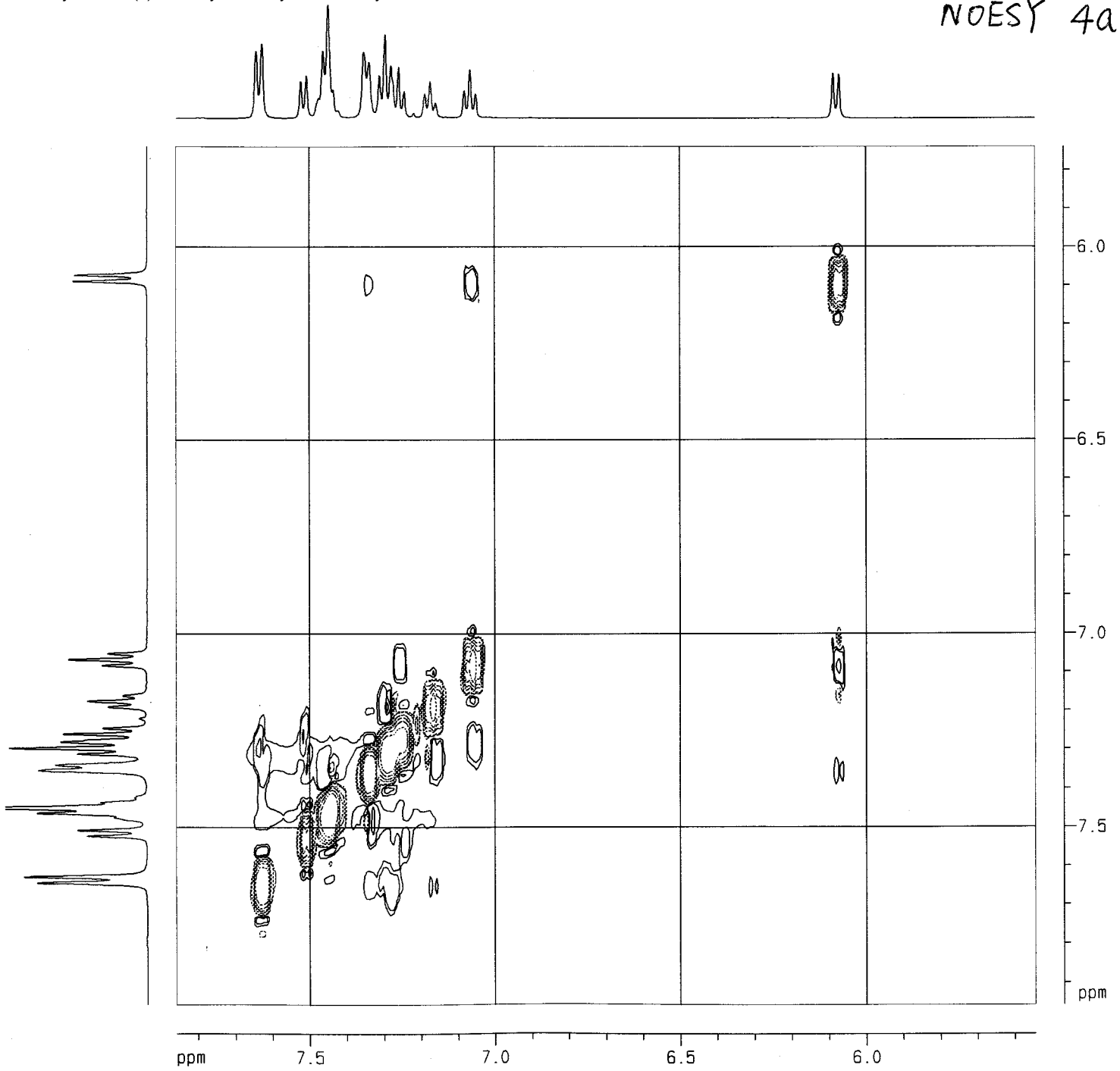
NOESY 4a



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F1 - Processing parameters

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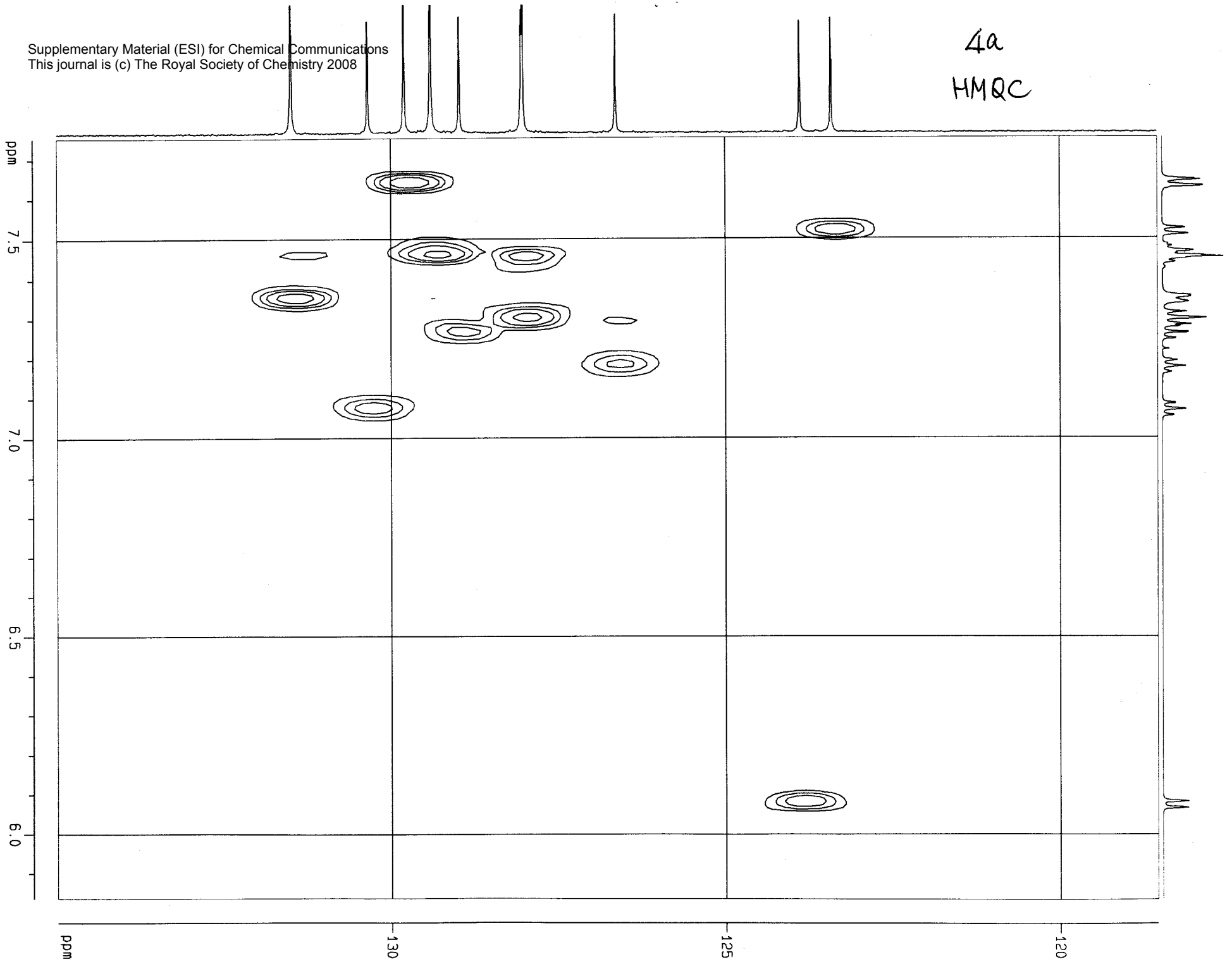
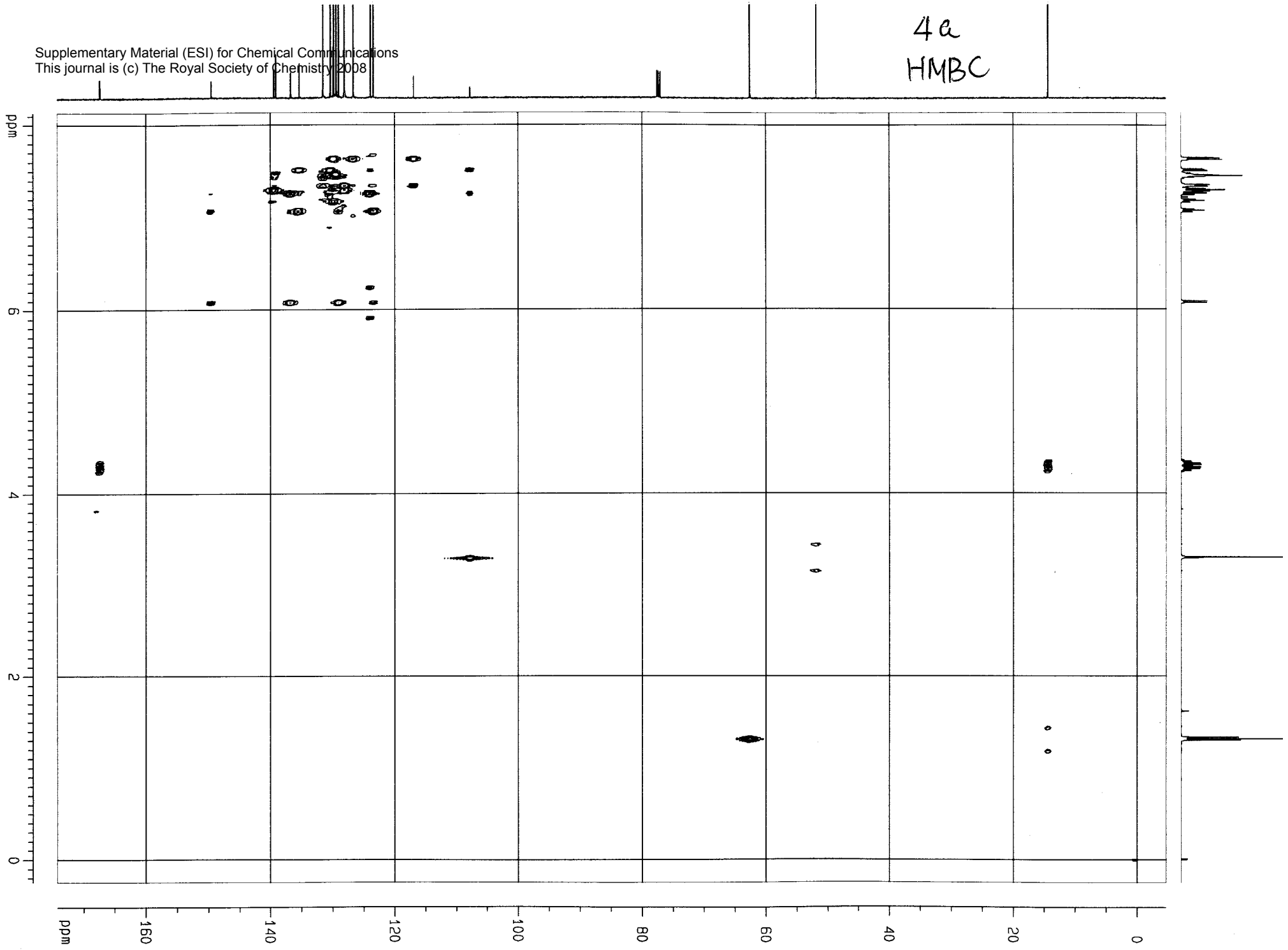
F1LO	3979.57 Hz
F1PHI	5.738 ppm
F1HI	2869.72 Hz
F2PPMCM	0.15434 ppm/cm
F2HZCM	77.19149 Hz/cm
F1PPMCM	0.14794 ppm/cm
F1HZCM	73.98963 Hz/cm

2.3.

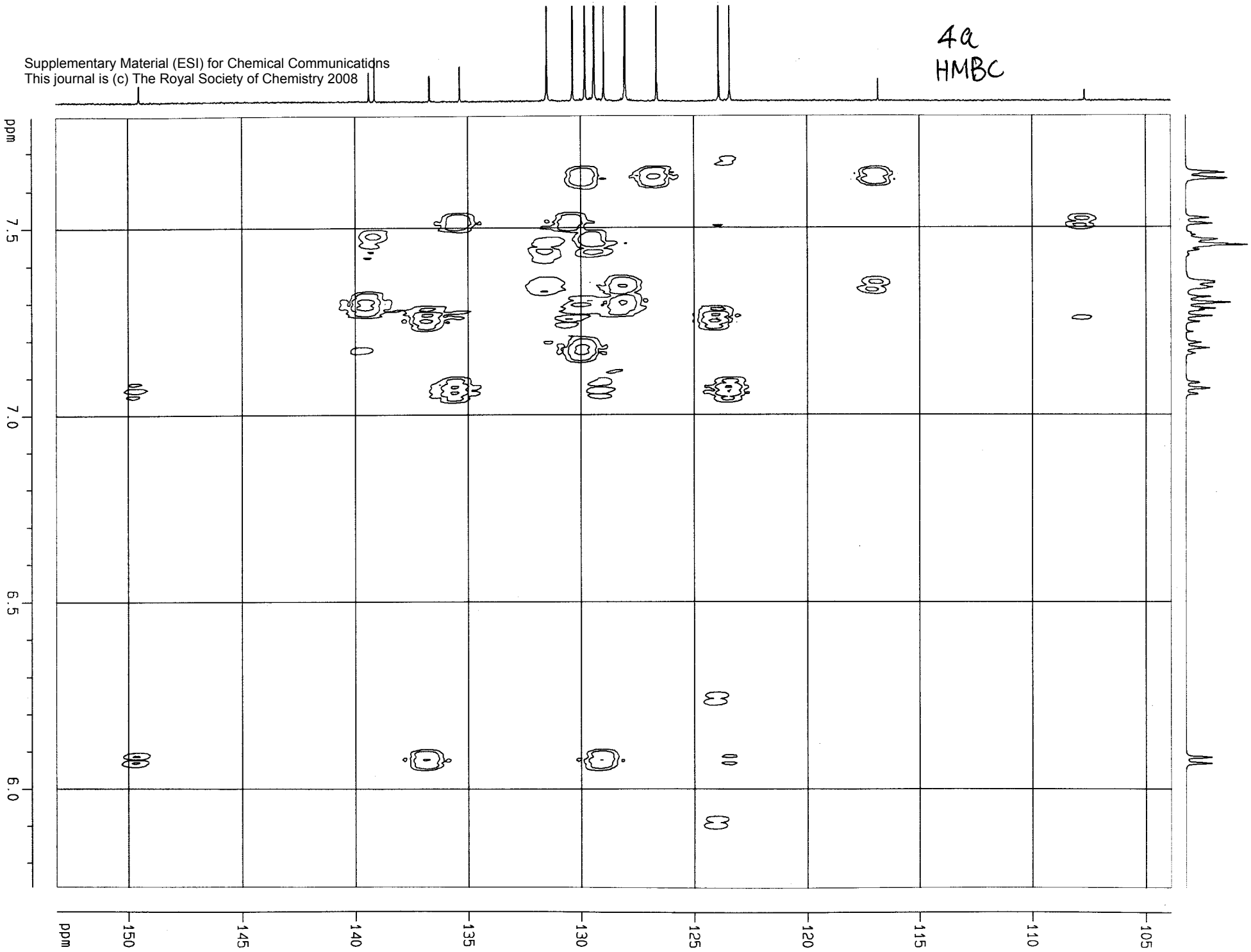
4a

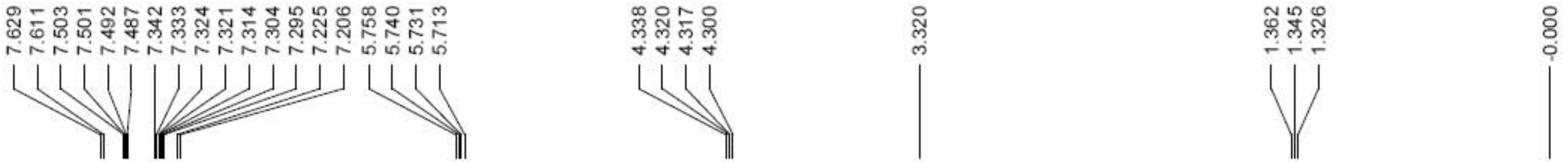
HMQC





4a
HMBC

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7.501
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7.487
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7.333
7.324
7.321
7.314
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7.295
7.225
7.206
5.758
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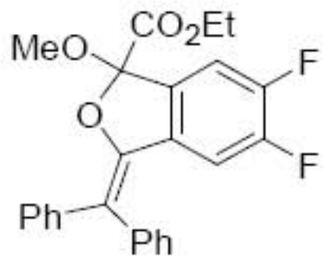
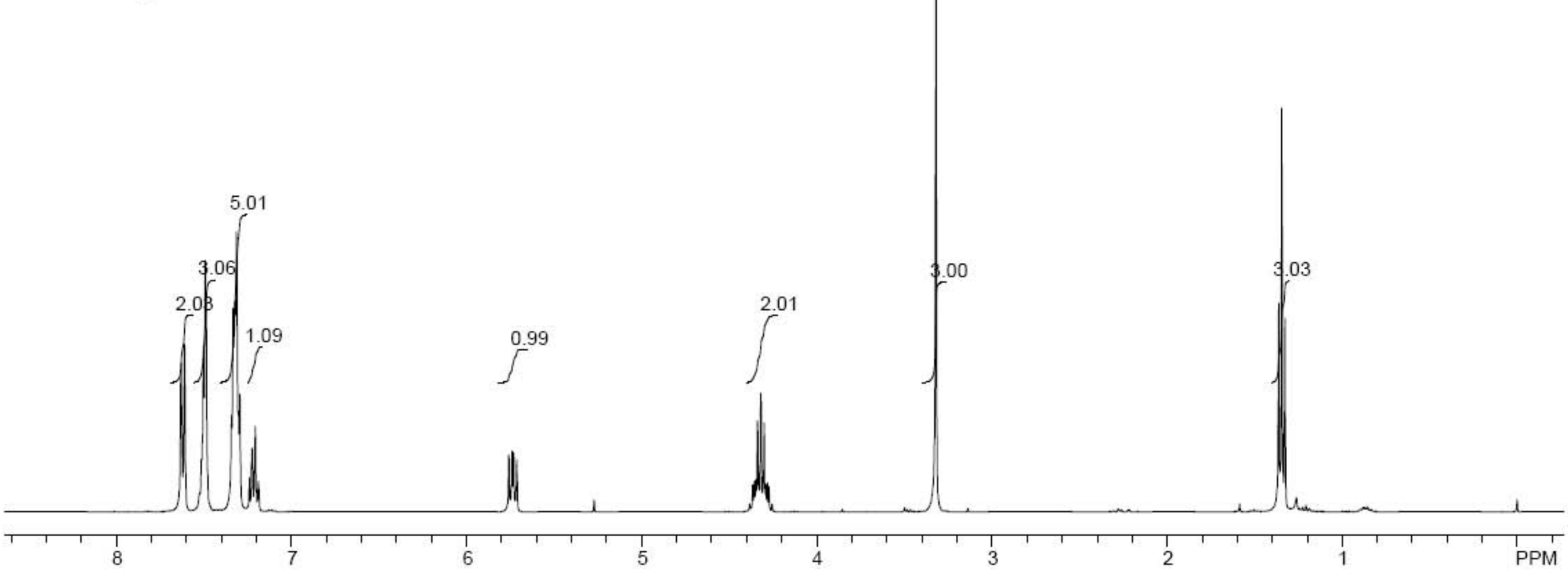
4.300
3.320
1.362
1.345
1.326
0.000


MeO
CO2Et
O
F
F
Ph
Ph

4b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3.06
2.08
1.09
0.99
2.01
3.00
3.03
8
7
6
5
4
3
2
1
PPM

166.340
152.826
152.694
152.009
151.867
150.334
150.208
149.489
149.341
147.551
147.511
147.494
138.367
138.033
132.430
132.399
132.367
132.336
131.573
131.543
131.492
131.462
130.862
129.403
129.350
128.204
127.799
126.703
117.323
117.312
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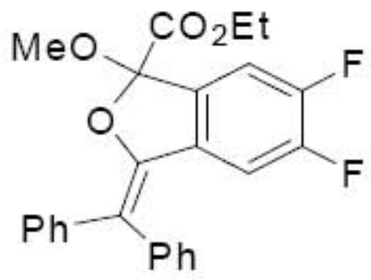
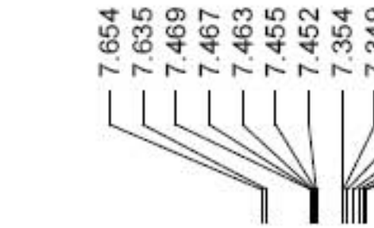
111.952
106.702
106.683
77.229
76.906
76.593
62.511
51.616
13.945



4b

200
150
100
50
PPM


MeO
CO2Et
Me
O
Me
Ph
Ph

4c

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7.635
7.469
7.467
7.463
7.455
7.452
7.354
7.349
7.336
7.311
7.292
7.272
7.264
7.179
7.161
7.143
5.756
4.351
4.334
4.325
4.306
4.287
4.269
4.250
4.241
4.224
3.277
2.222
1.963
1.336
1.318
1.300
-0.000
2.00
3.05
5.04
1.06
0.99
2.00
3.00
3.09
3.01
3.04
8
7
6
5
4
3
2
1
PPM

167.529
149.769
139.390
139.318
139.055
138.281
134.471
133.255
131.542
129.562
129.158
127.868
127.728
126.246
124.662
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107.554
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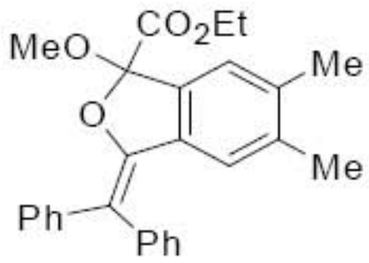
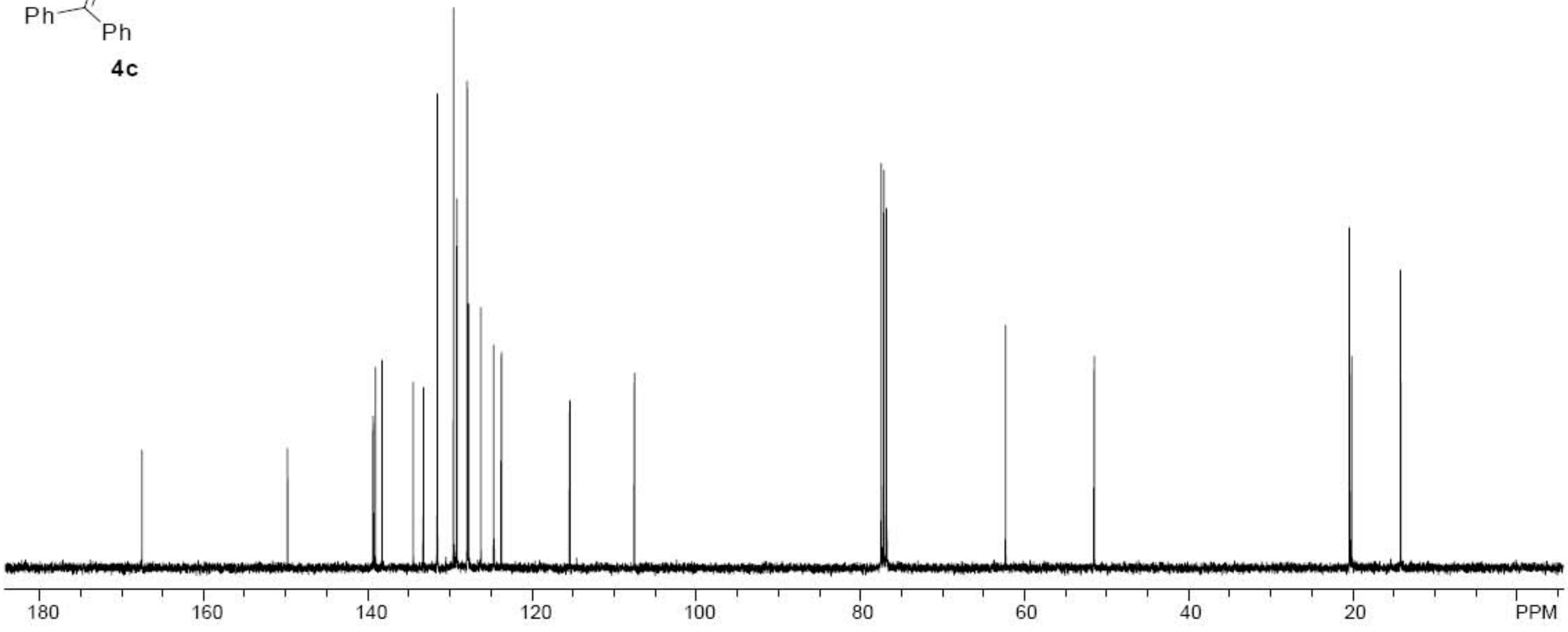
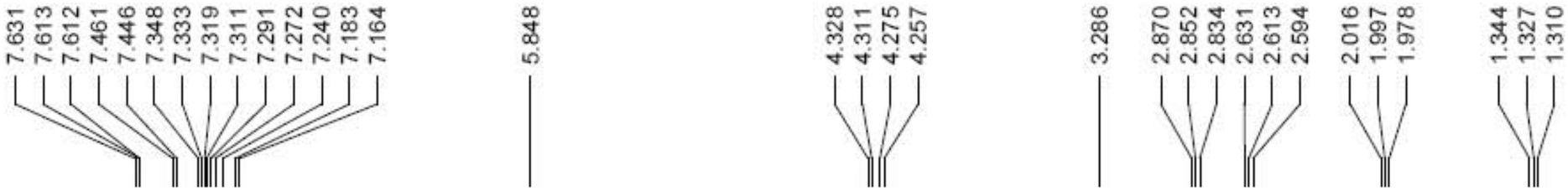
77.144
76.830
62.339
51.531
20.440
20.166
14.189



4c

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7.446
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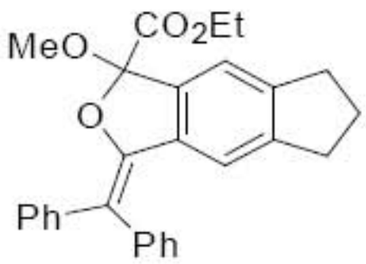
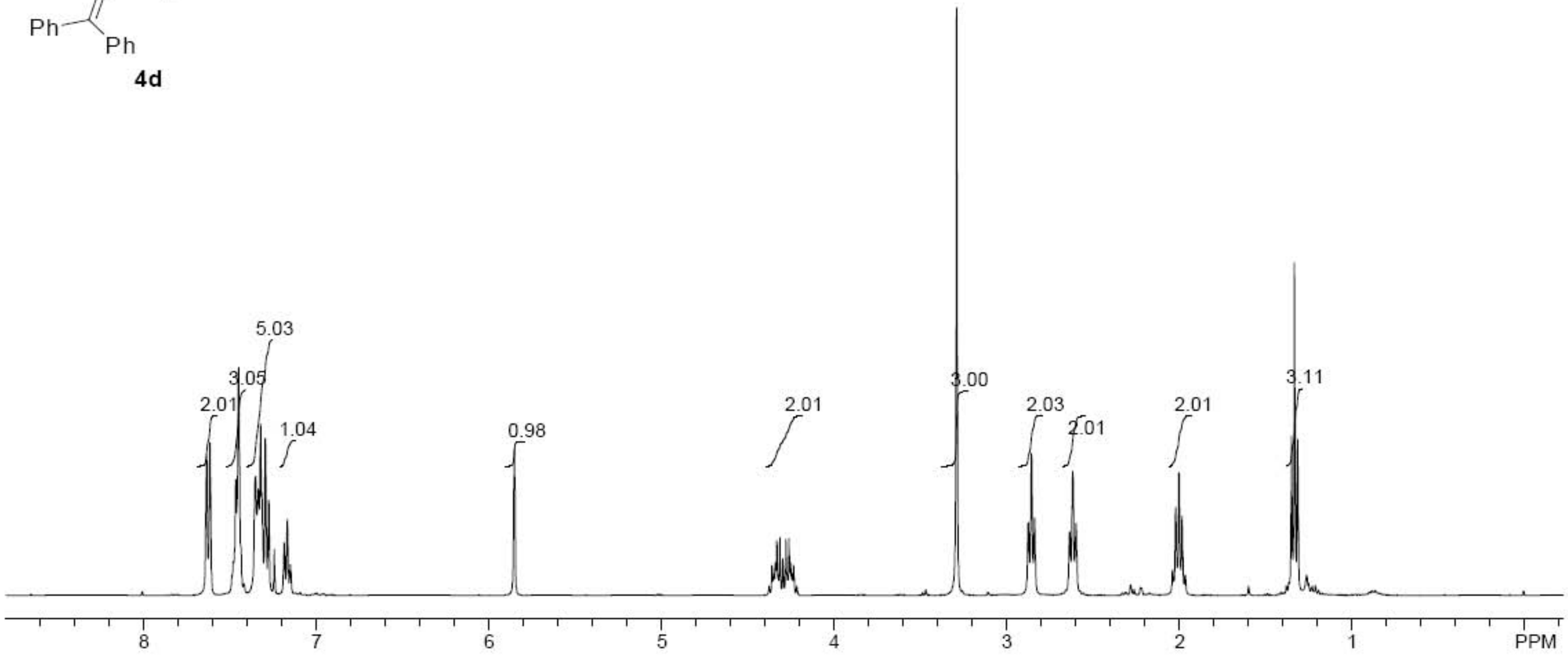
7.333
7.319
7.311
7.291
7.272
7.240
7.183
7.164
5.848
4.328
4.311
4.275
4.257
3.286
2.870
2.852
2.834
2.631
2.613
2.594
2.016
1.997
1.978
1.344
1.327
1.310


MeO
CO2Et
O
Ph
Ph

4d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3.05
5.03
1.04
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2.01
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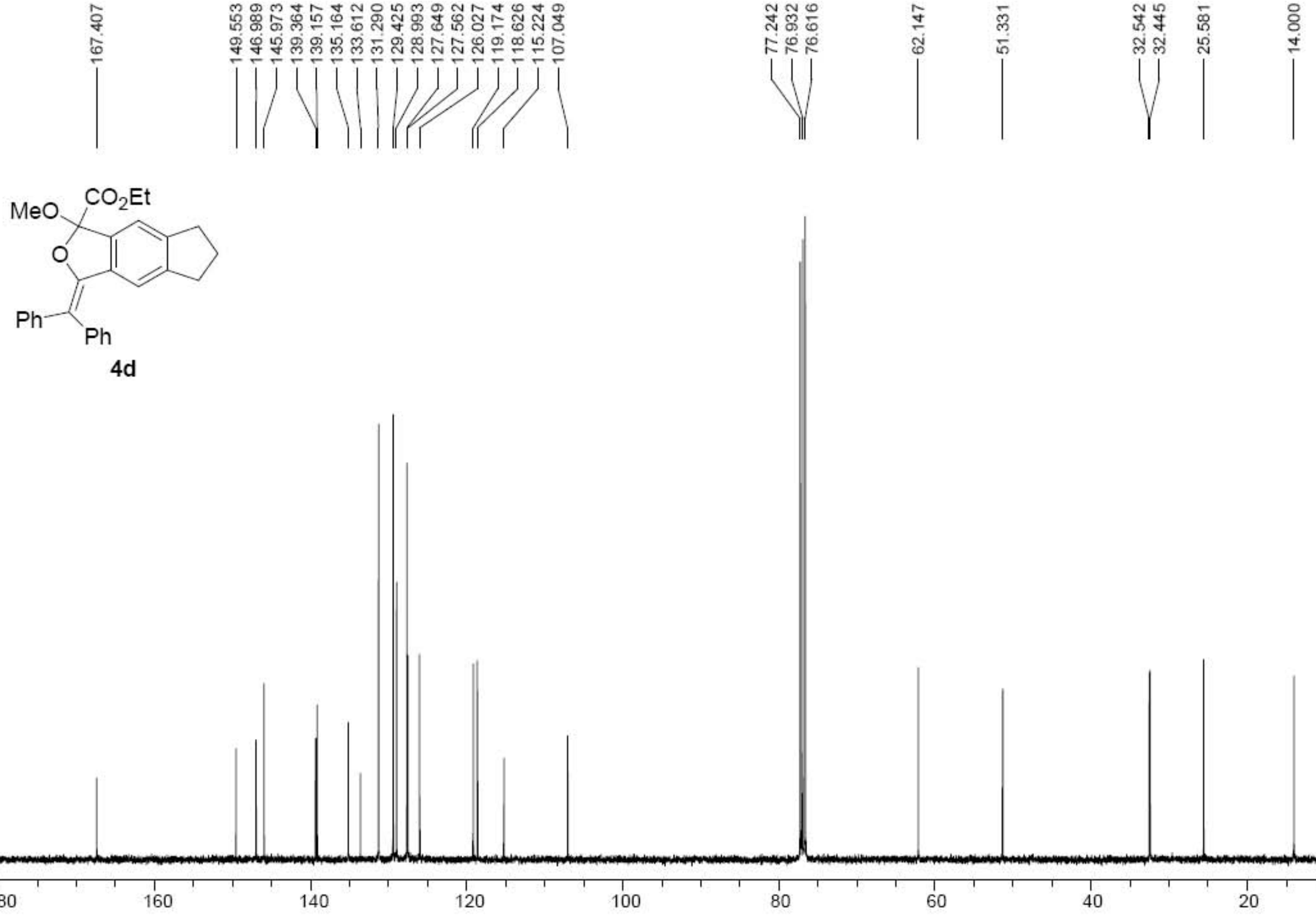
2.03
2.01
2.01
3.11
8
7
6
5
4
3
2
1
PPM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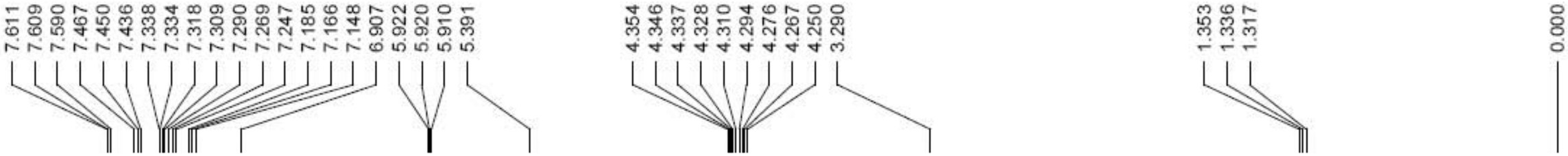
139.157
135.164
133.612
131.290
129.425
128.993
127.649
127.562
126.027
119.174
118.626
115.224
107.049
77.242
76.932
76.616
62.147
51.331
32.542
32.445
25.581
14.000
MeO
CO2Et
O
Ph
Ph
4d
180
160
140
120
100
80
60
40
20
PPM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7.609
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7.450
7.436
7.338
7.334
7.318
7.309
7.290
7.269
7.247
7.185
7.166
7.148
6.907
5.922
5.920
5.910
5.391
4.354
4.346
4.337
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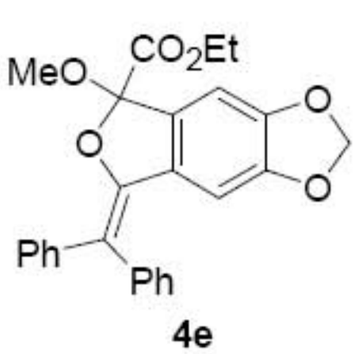
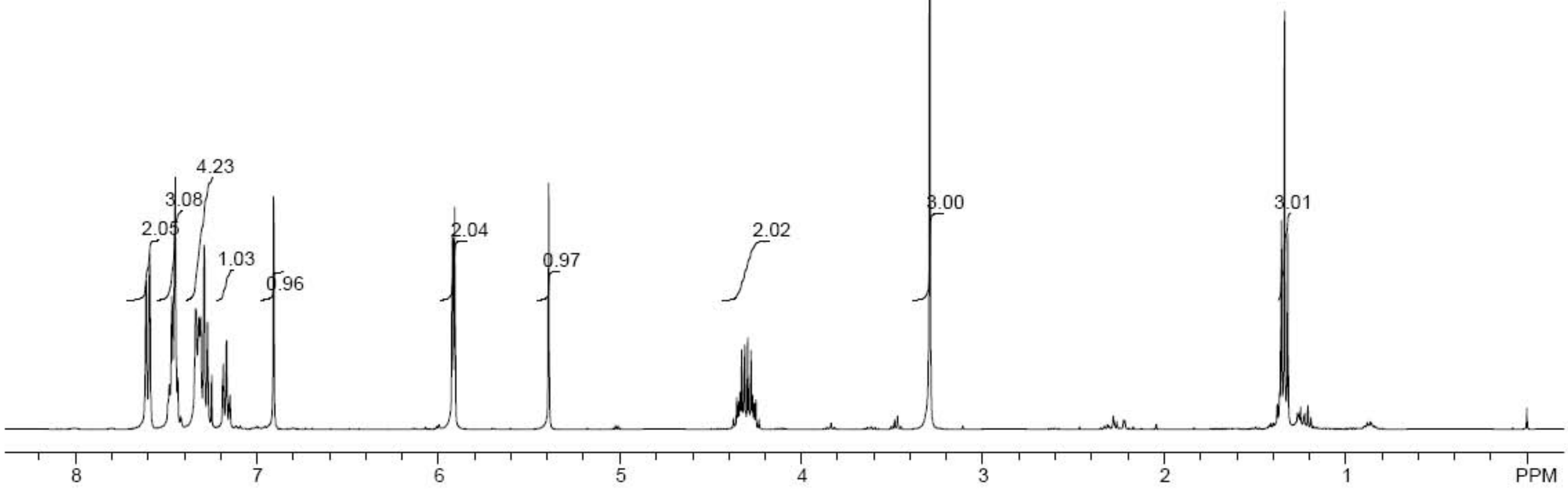
4.267
4.250
3.290
1.353
1.336
1.317
0.000


MeO
CO2Et
O
O
O
Ph
Ph

4e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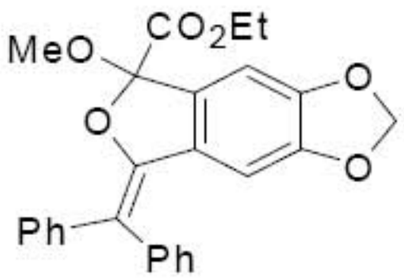
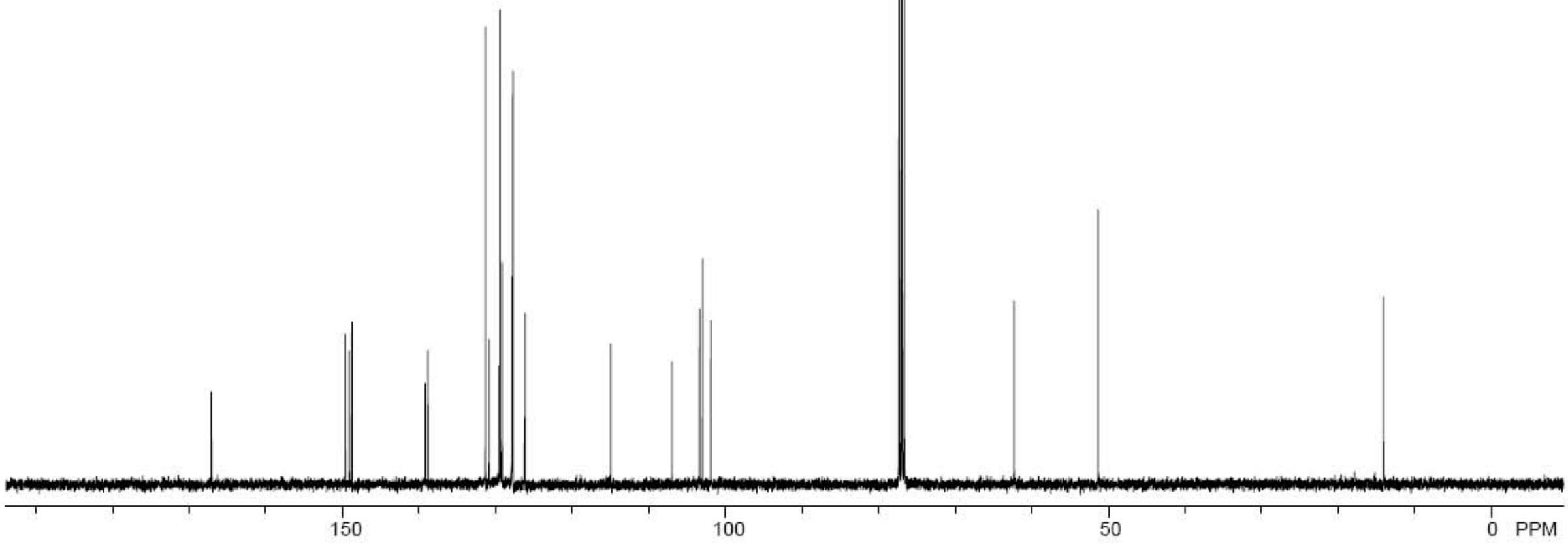
3.08
2.05
1.03
0.96
2.04
0.97
2.02
3.00
3.01
8
7
6
5
4
3
2
1
PPM


167.112
149.628
149.124
148.795
139.188
138.865
131.346
130.850
129.570
129.442
129.193
127.882
127.779
126.196
114.992
106.996
103.374
102.994
101.928
77.326
77.014
76.697
62.344
51.339
14.083


MeO
CO2Et
O
O
O
Ph
Ph

4e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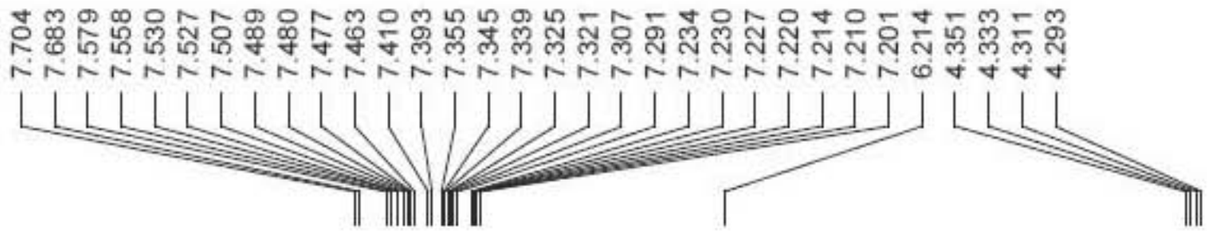
100
50
0 PPM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7.489
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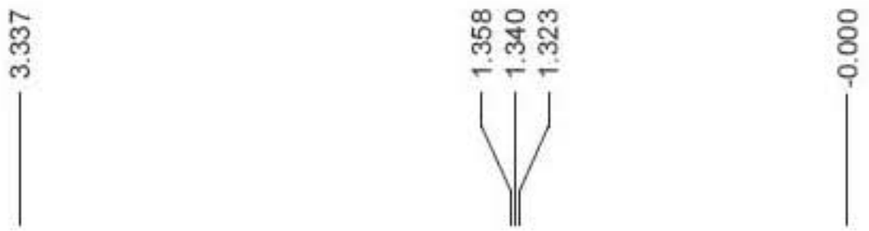
7.477
7.463
7.410
7.393
7.355
7.345
7.339
7.325
7.321
7.307
7.291
7.234
7.230
7.227
7.220
7.214
7.210
7.201
6.214
4.351
4.333
4.311
4.293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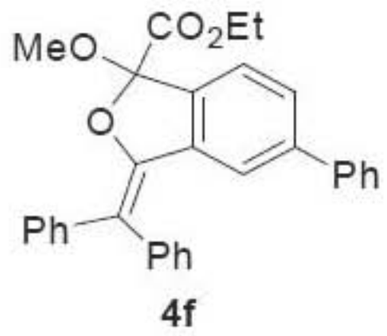
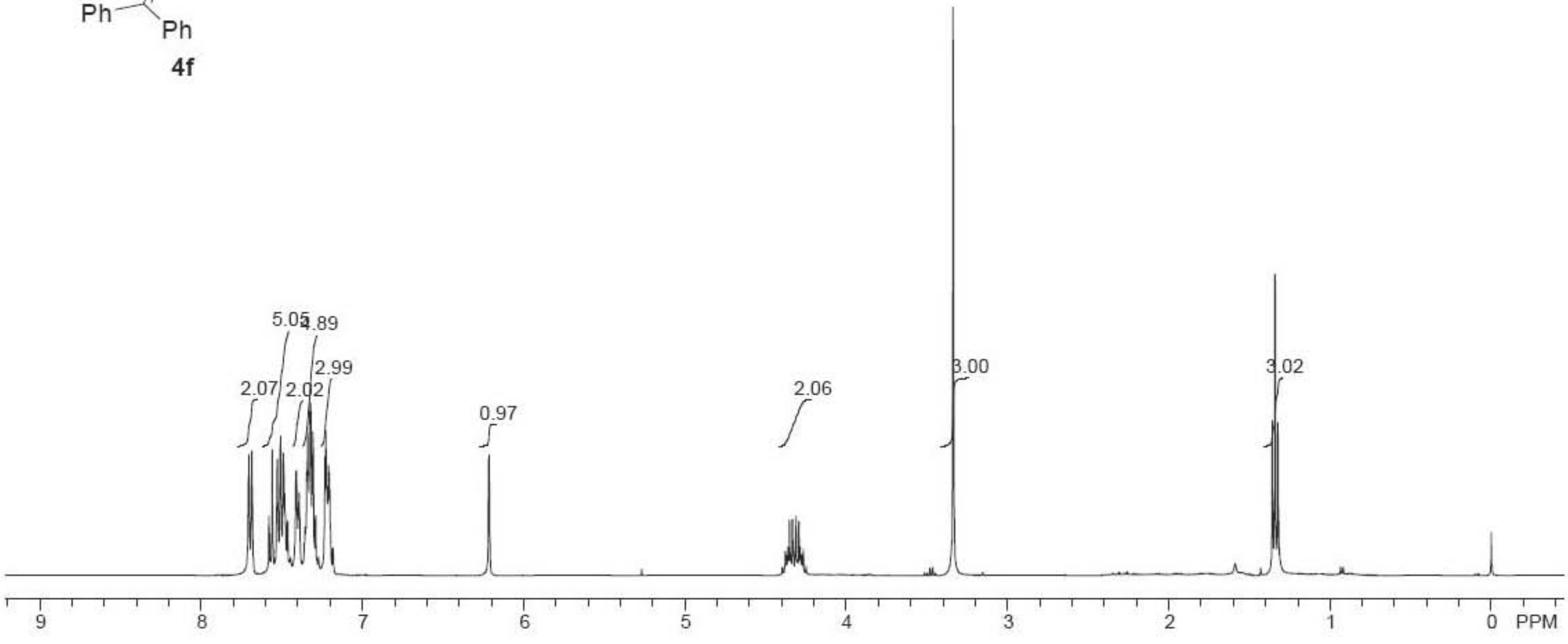

MeO
CO2Et
O
Ph
Ph
Ph

4f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2.99
2.07
2.02
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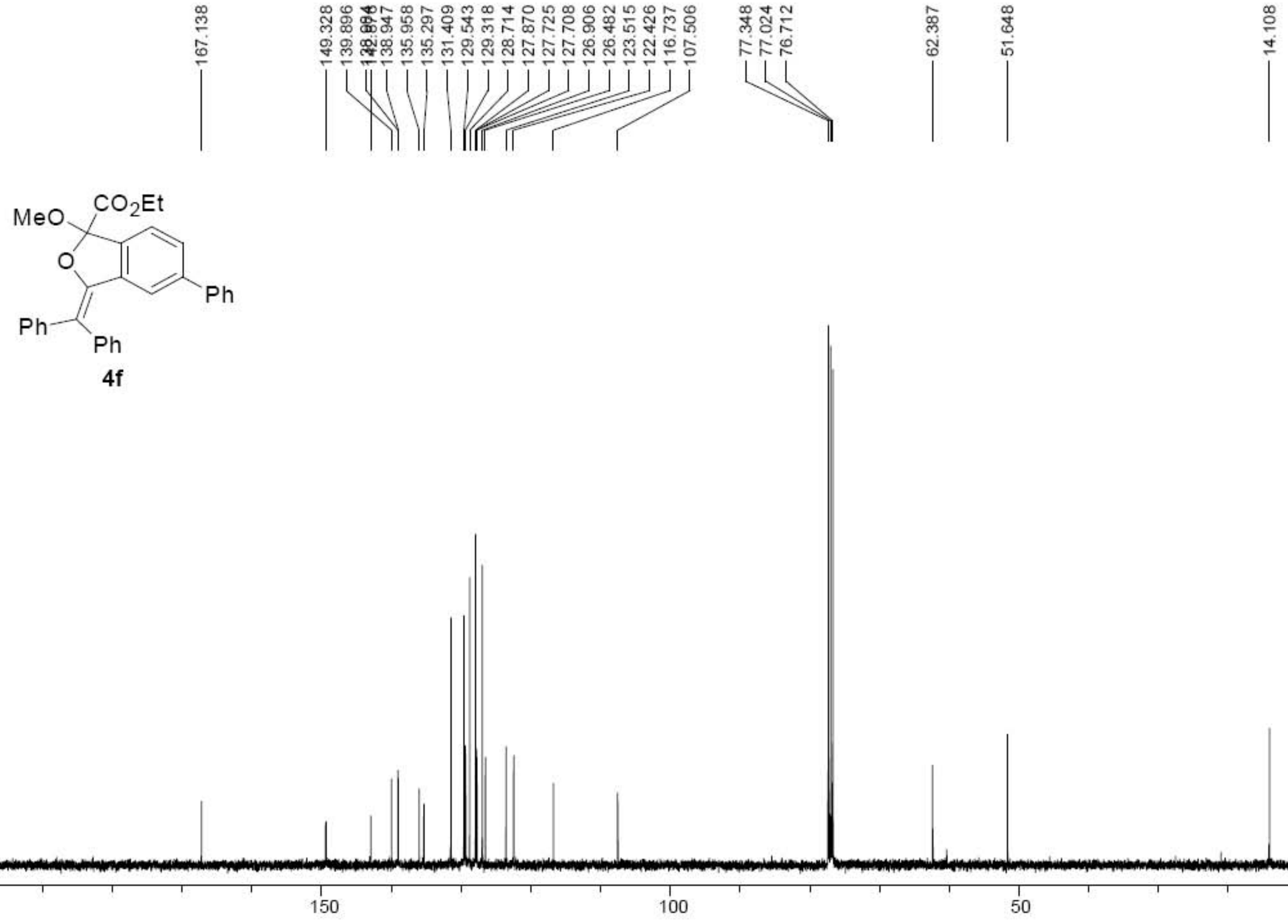
2.06
3.00
3.02
9
8
7
6
5
4
3
2
1
0
PPM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135.297
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129.543
129.318
128.714
127.870
127.725
127.708
126.906
126.482
123.515
122.426
116.737
107.506
77.348
77.024
76.712
62.387
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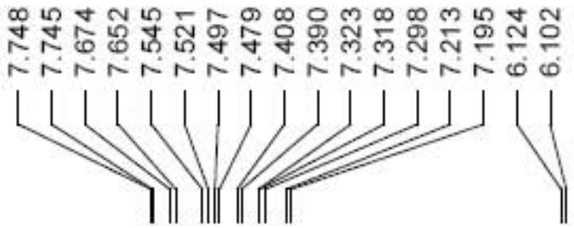
14.108
MeO
CO2Et
O
Ph
Ph
Ph
4f
200
150
100
50
PPM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7.298
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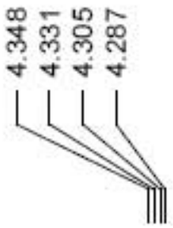
6.102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4.305
4.287


3.353


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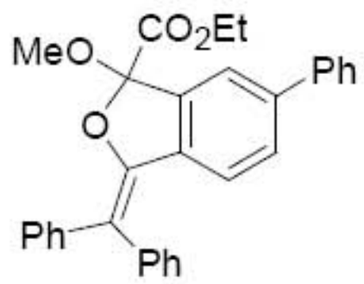
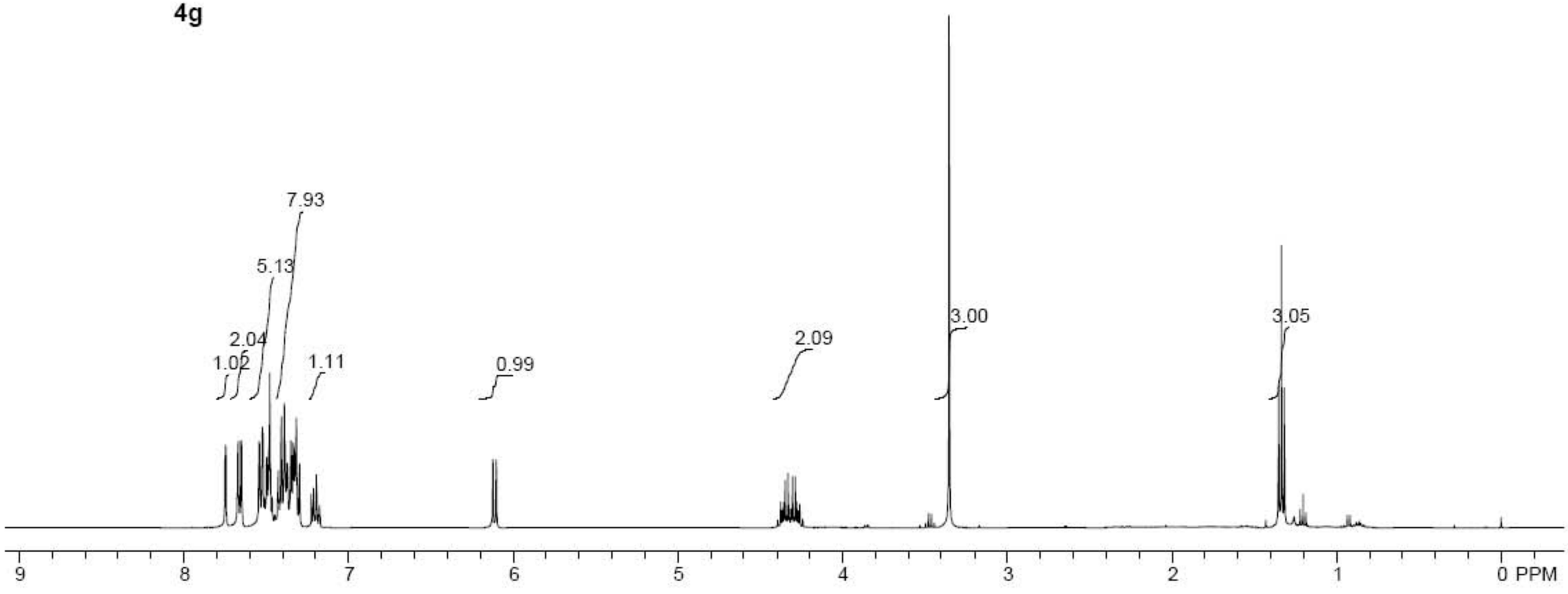
1.334
1.317


MeO
CO2Et
Ph
O
Ph
Ph

4g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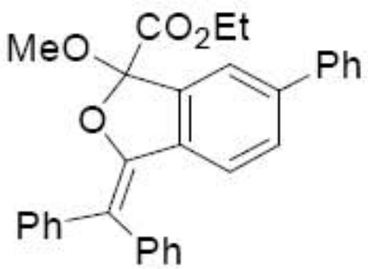
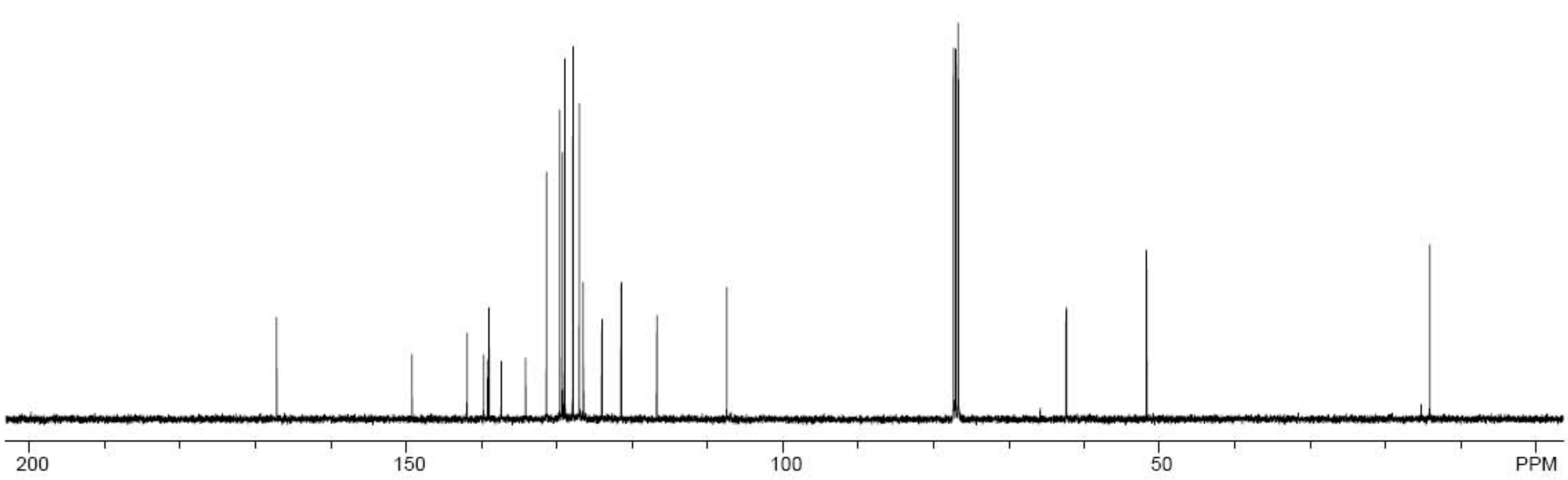
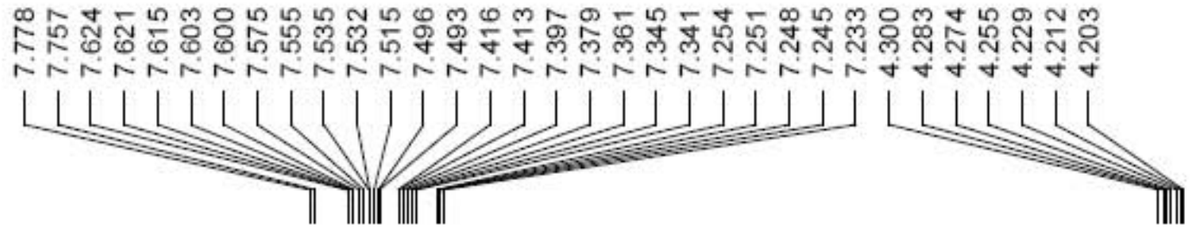
1.11
0.99
2.09
3.00
3.05
9
8
7
6
5
4
3
2
1
0 PPM

167.188
141.905
149.222
139.708
139.158
138.984
137.358
134.135
131.360
129.599
129.231
128.915
127.884
127.856
127.013
126.467
124.011
121.460
116.737
107.445
77.353
77.041
76.725
62.396
51.722
14.143



4g

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7.535
7.532
7.515
7.496
7.493
7.416
7.413
7.397
7.379
7.361
7.345
7.341
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7.251
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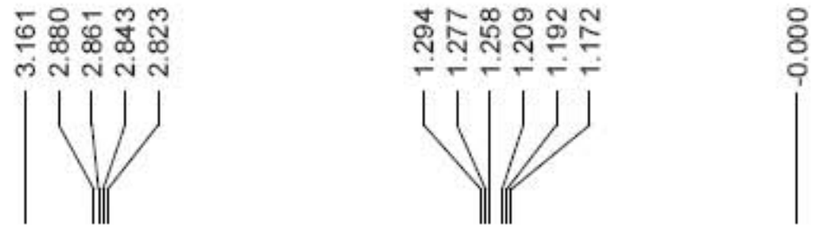
4.274
4.255
4.229
4.212
4.203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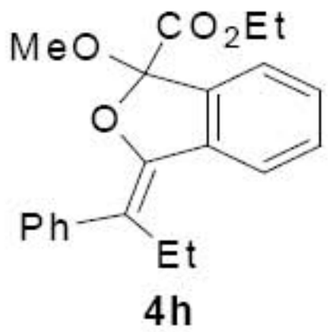
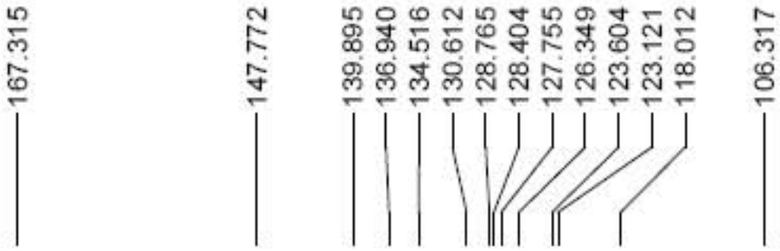
1.277
1.258
1.209
1.192
1.172
-0.000


MeO
CO2Et
O
Ph
Et

4h

4.01
3.05
1.01
1.13
2.01
3.00
2.00
3.06
3.02
9
8
7
6
5
4
3
2
1
PPM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127.755
126.349
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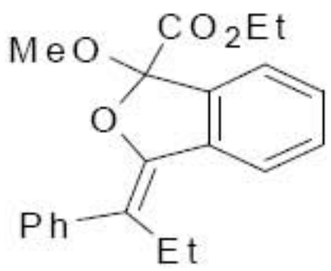
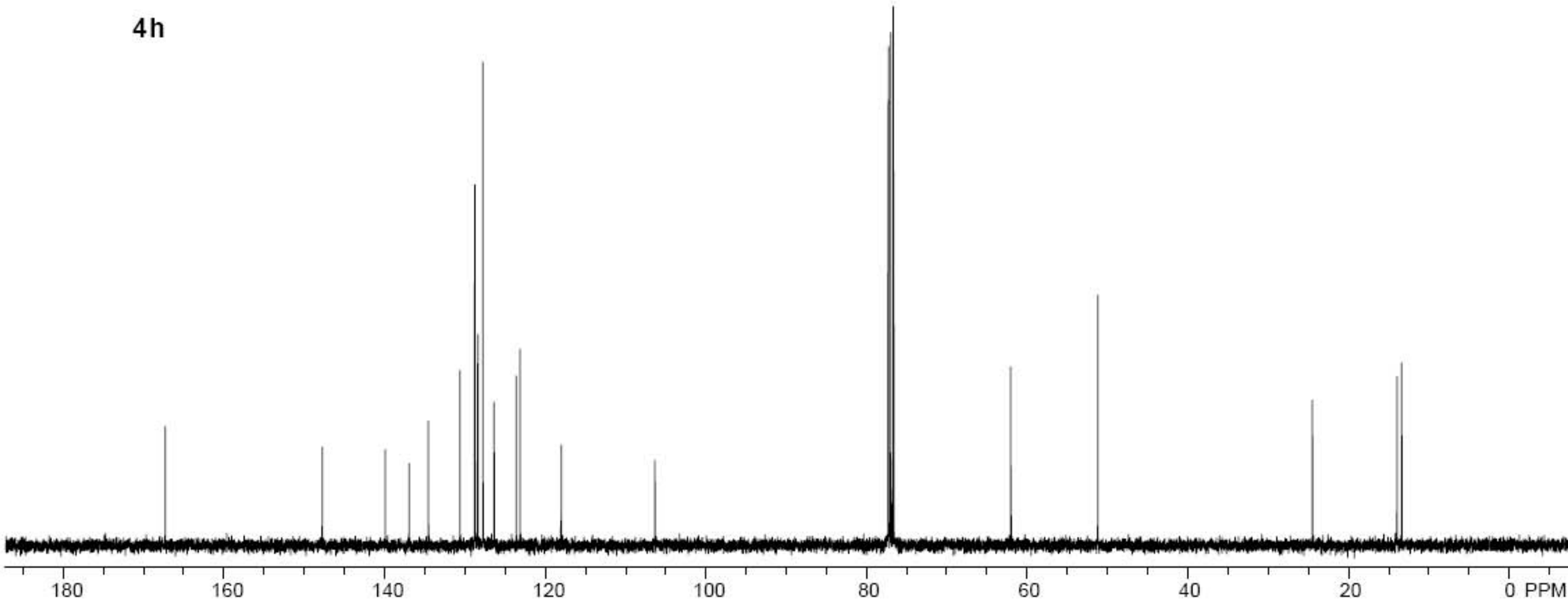
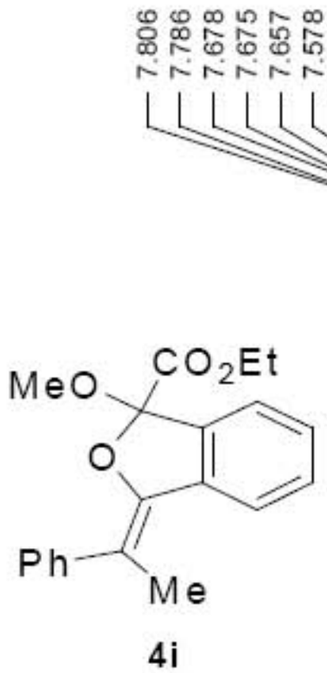
51.183
24.473
13.946
13.366


MeO
CO2Et
O
Ph
Et

4h


180
160
140
120
100
80
60
40
20
0 PPM


MeO
CO2Et
O
Ph
Me

4i

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7.657
7.578
7.559
7.534
7.531
7.512
7.496
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7.417
7.398
7.379
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7.218
4.285
4.268
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4.224
3.162
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1.300
1.282
1.265
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2.00
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3.04
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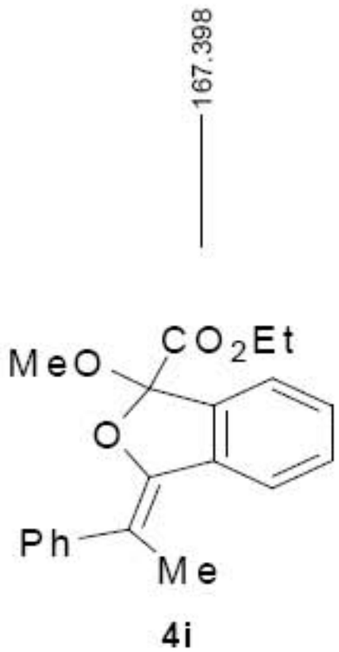
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CO2Et
O
Ph
Me

4i

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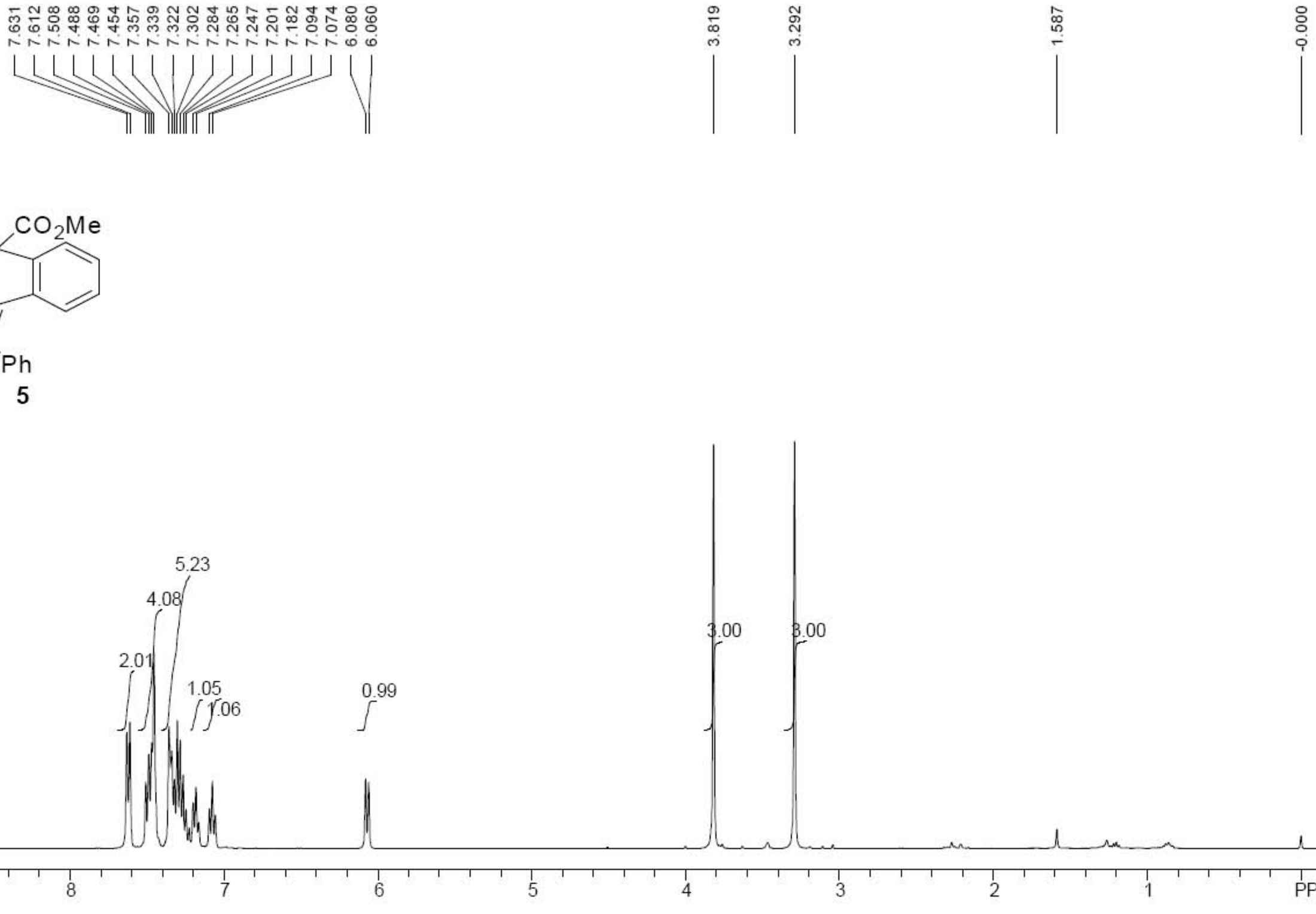
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7.201
7.182
7.094
7.074
6.080
6.060
3.819
3.292
1.587
-0.000
MeO
CO2Me
O
Ph
Ph
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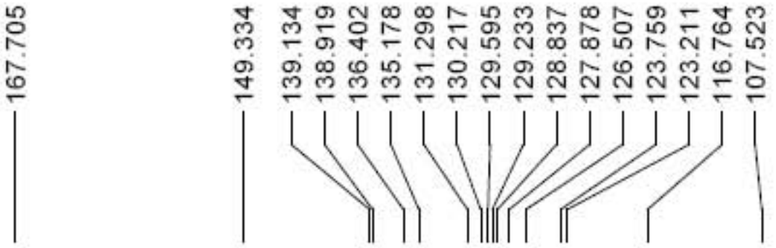
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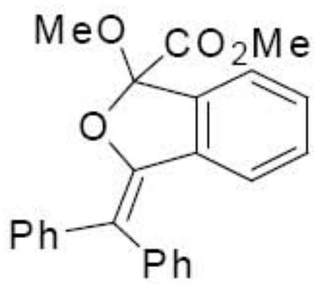
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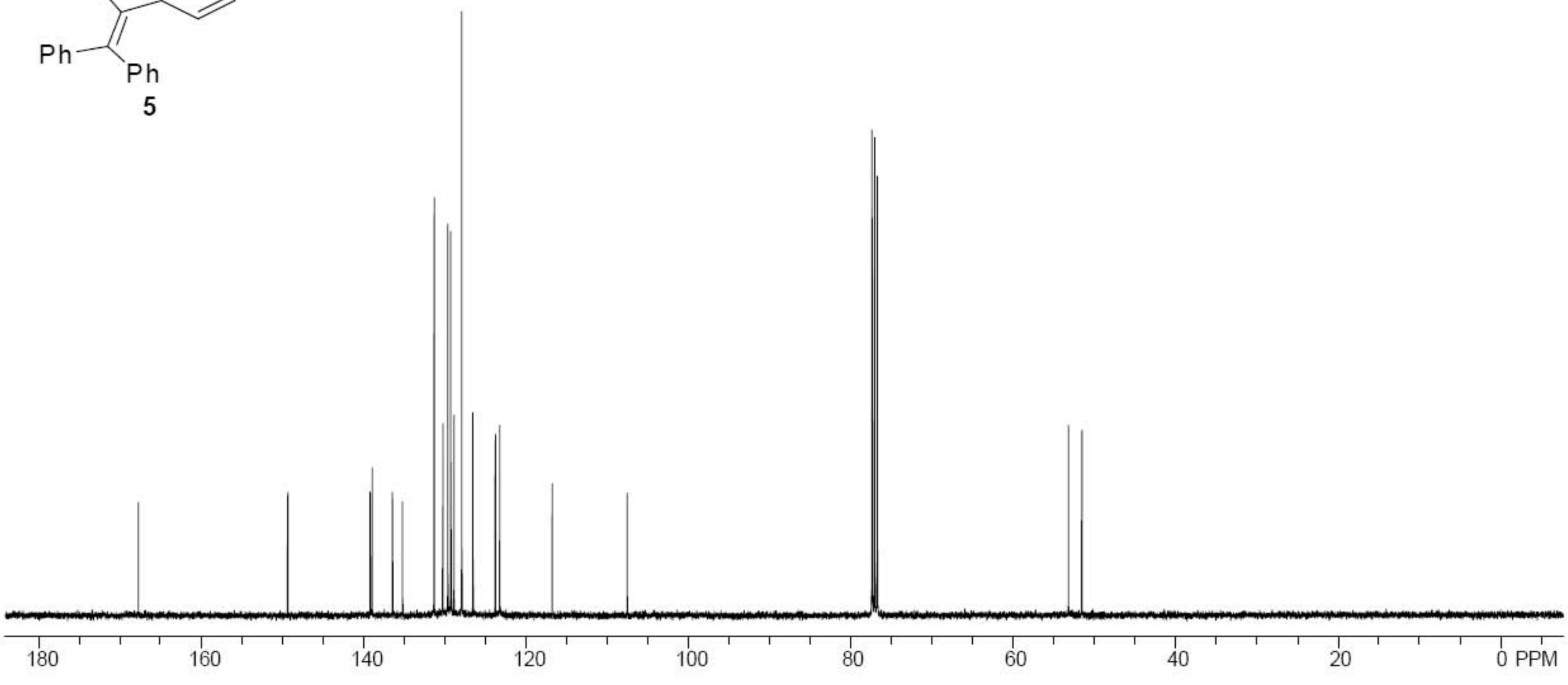
CO2Me
O
Ph
Ph

5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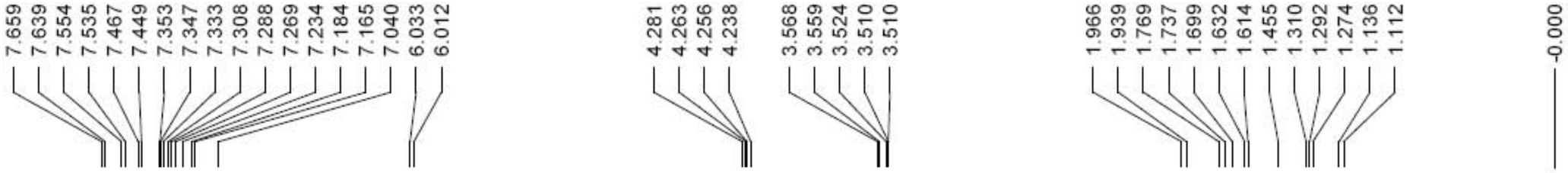

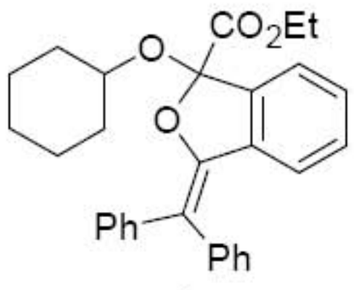

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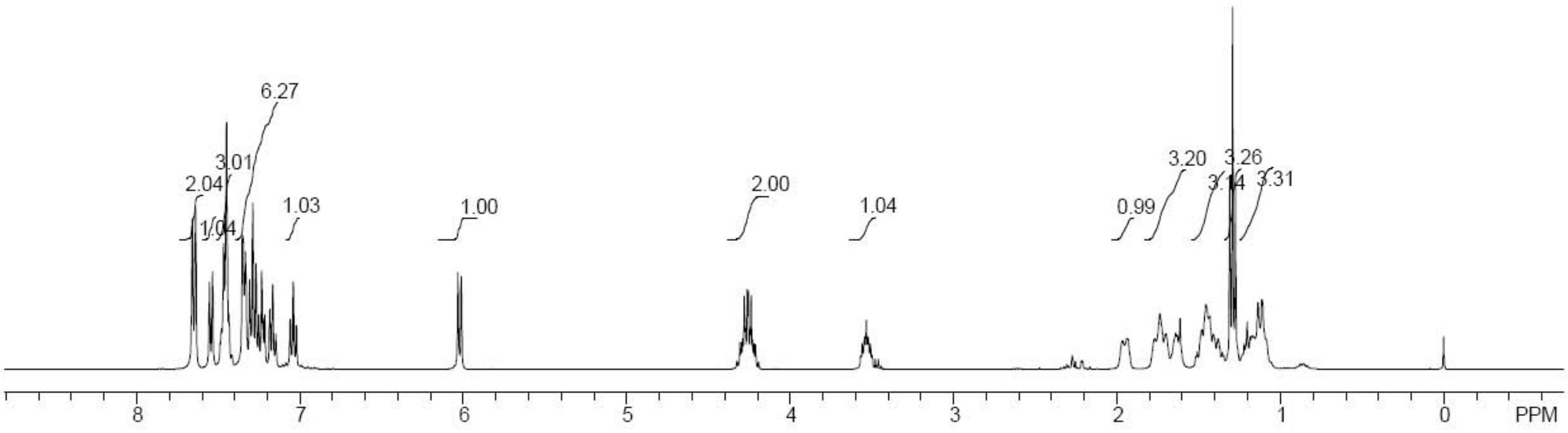

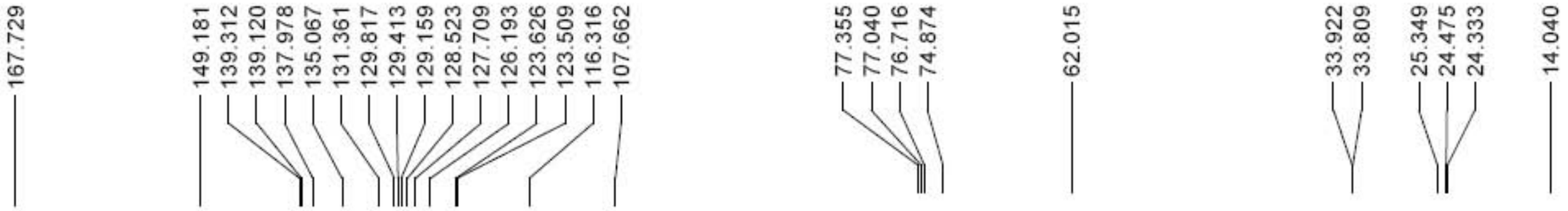
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129.159
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123.509
116.316
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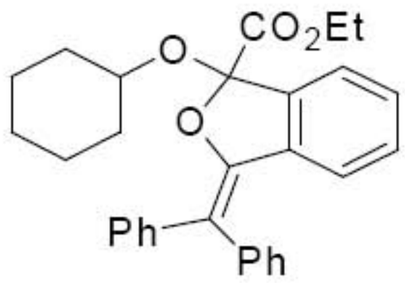
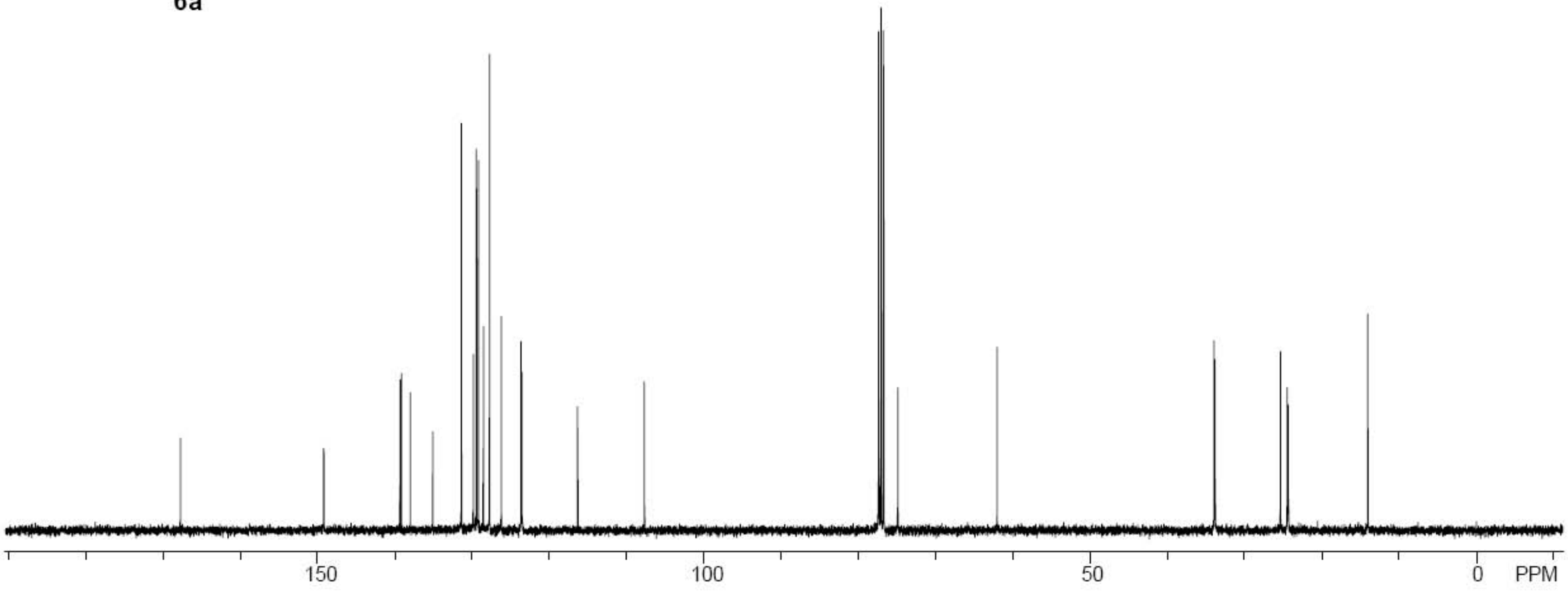
24.475
24.333
14.040


CO2Et
O
O
Ph
Ph

6a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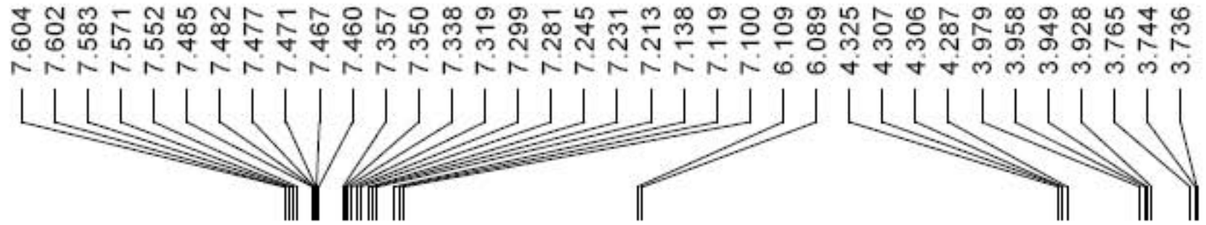
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7.319
7.299
7.281
7.245
7.231
7.213
7.138
7.119
7.100
6.109
6.089
4.325
4.307
4.306
4.287
3.979
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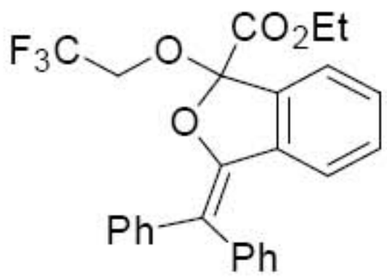
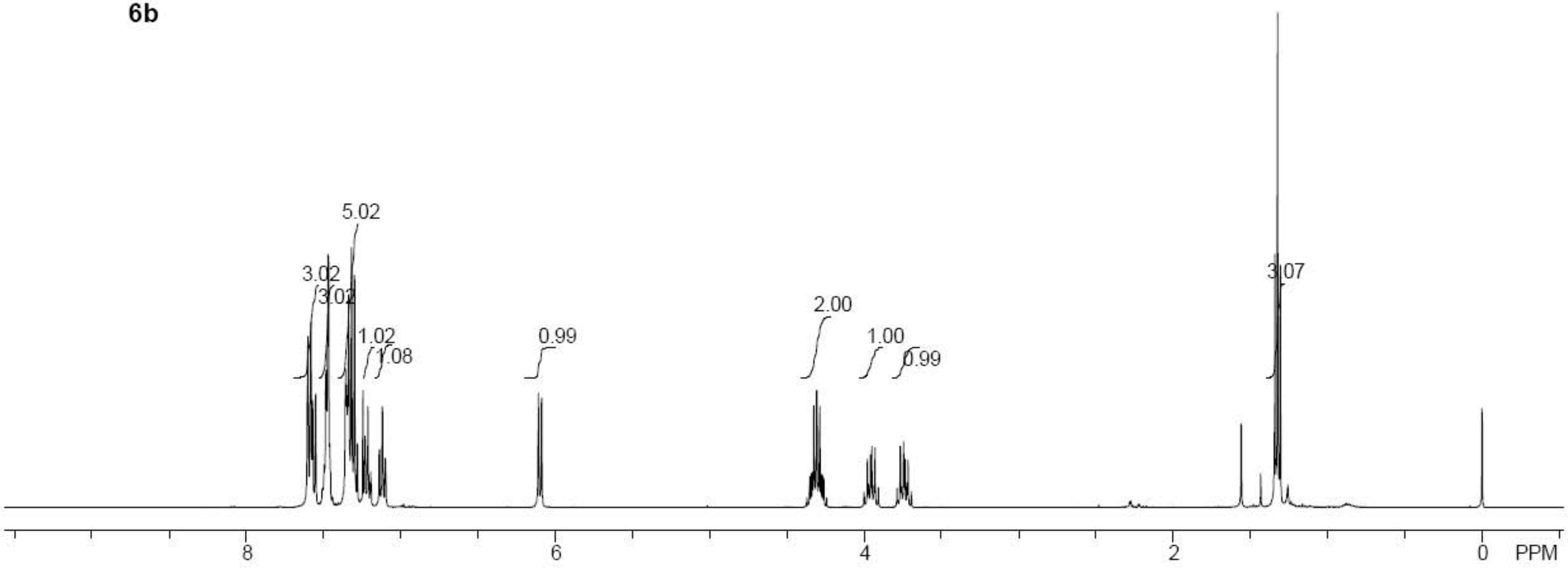

F3C
O
CO2Et
O
Ph
Ph

6b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1.00
0.99
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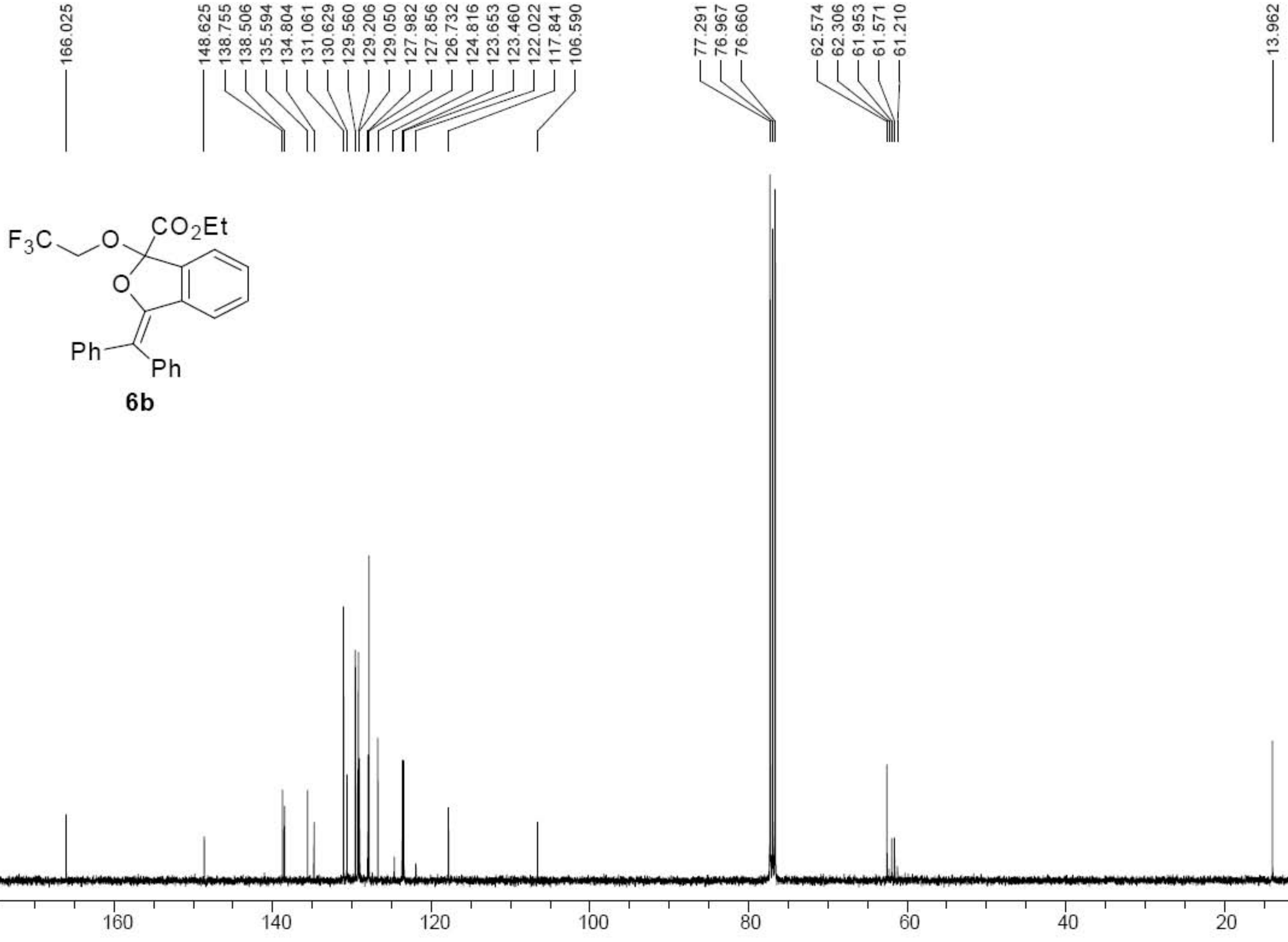
0
PPM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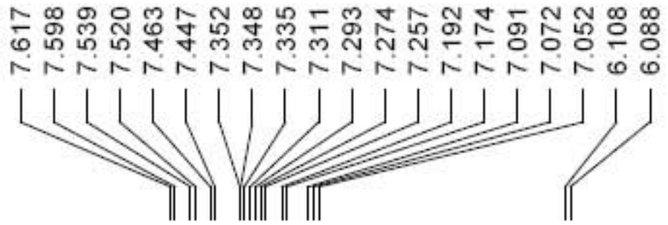
126.732
124.816
123.653
123.460
122.022
117.841
106.590
77.291
76.967
76.660
62.574
62.306
61.953
61.571
61.210
13.962
F3C
O
CO2Et
O
Ph
Ph
160
140
120
100
80
60
40
20
0 PPM

6b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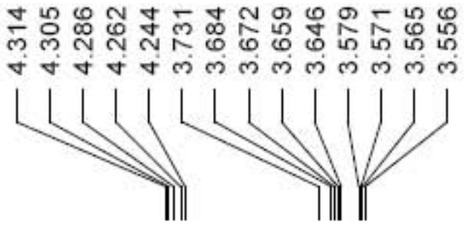
7.072
7.052
6.108
6.088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3.571
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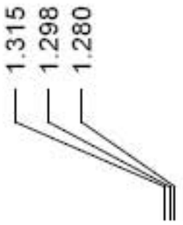
3.556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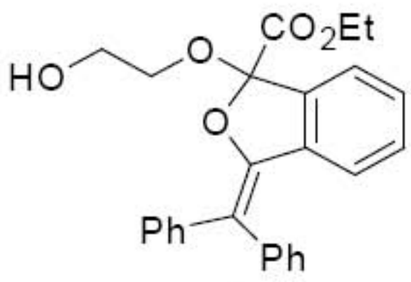
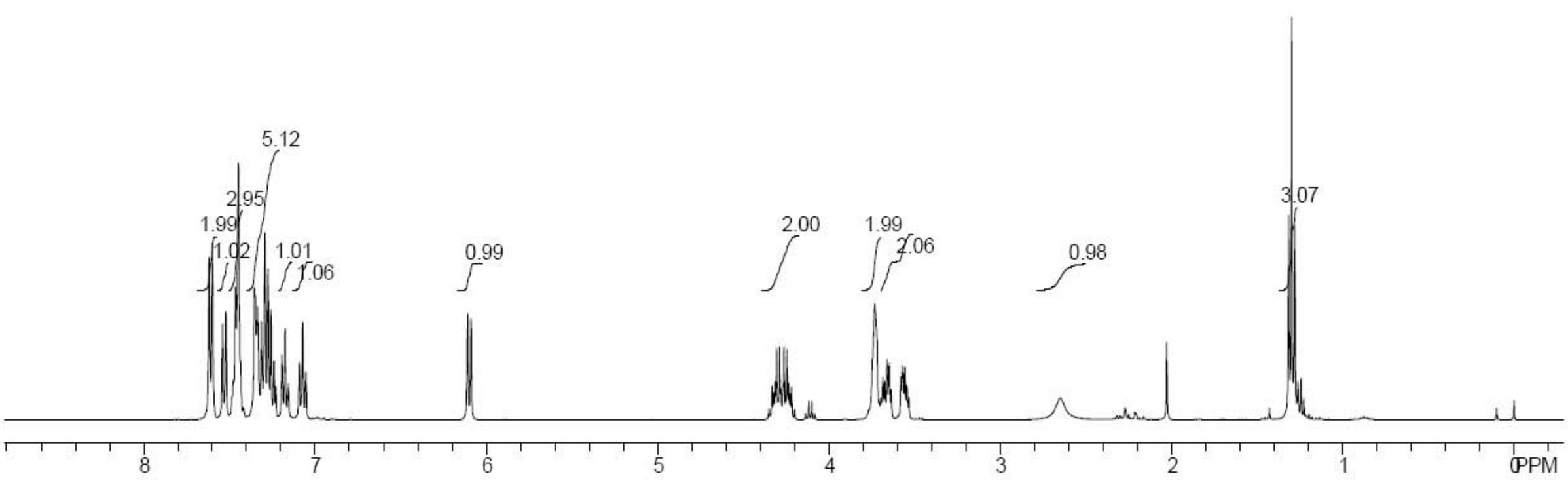

HO
O
CO2Et
O
Ph
Ph

6c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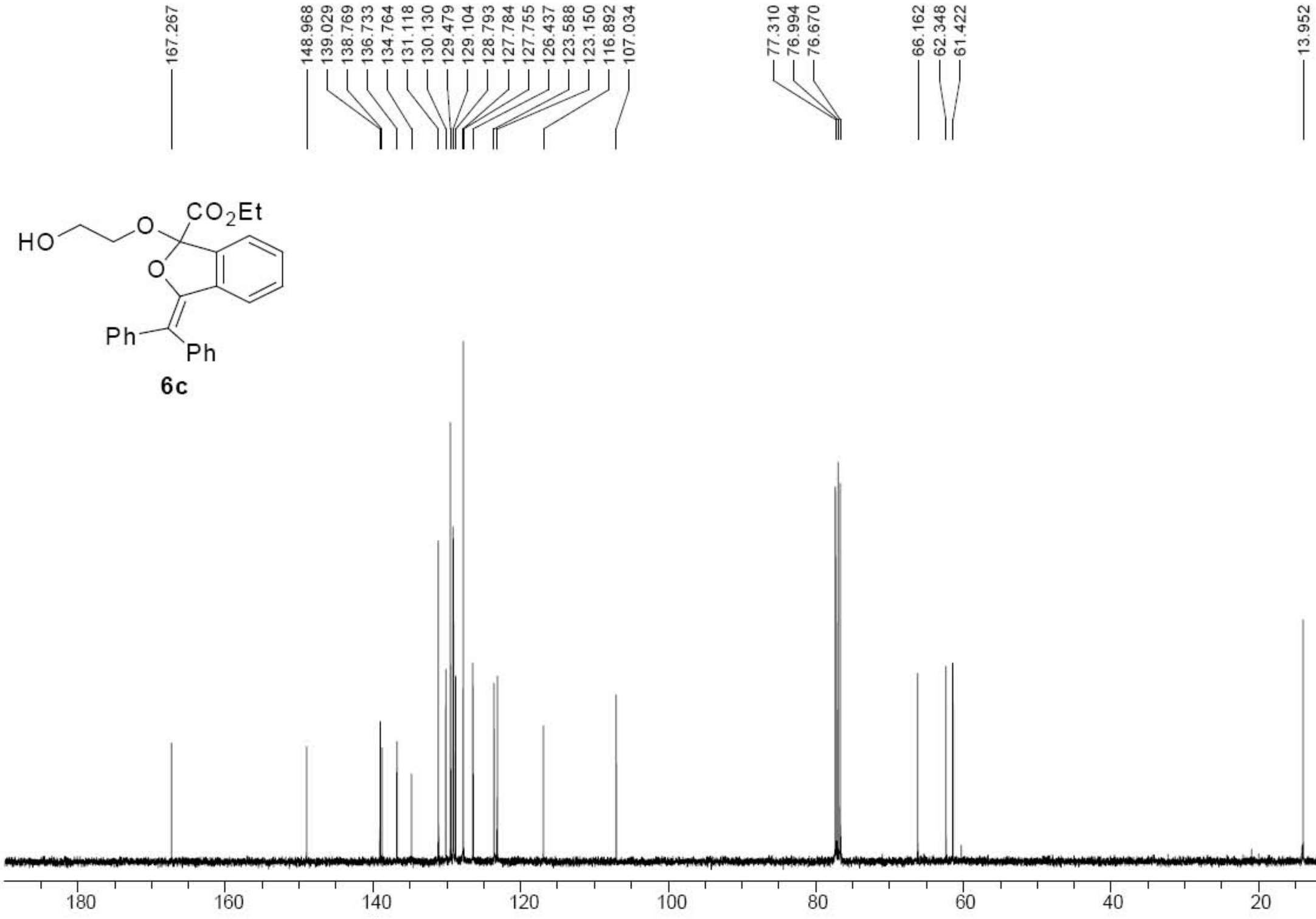
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123.150
116.892
107.034
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76.994
76.670
66.162
62.348
61.422
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HO
O
CO2Et
O
Ph
Ph
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80
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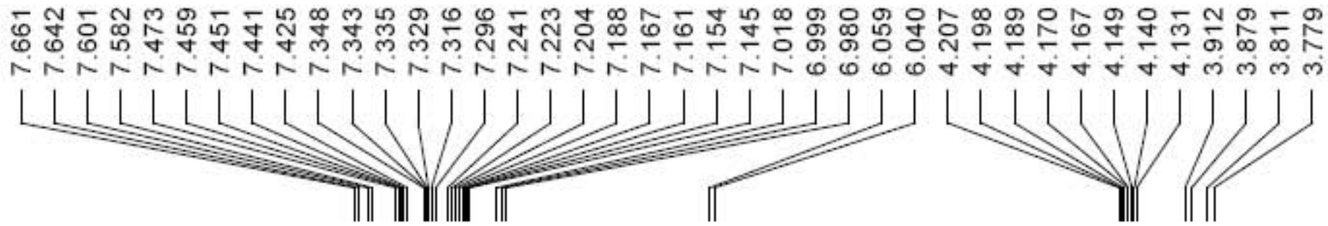
40
20
0
PPM

6c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7.204
7.188
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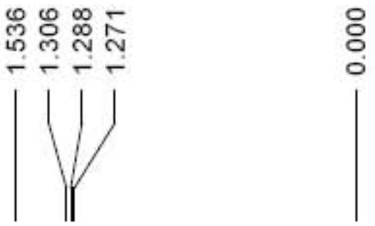
3.779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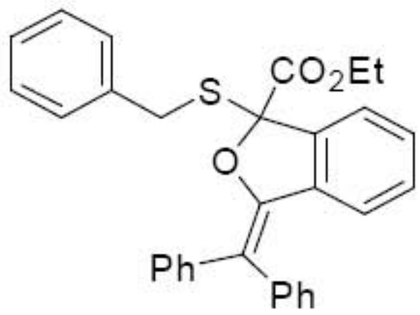
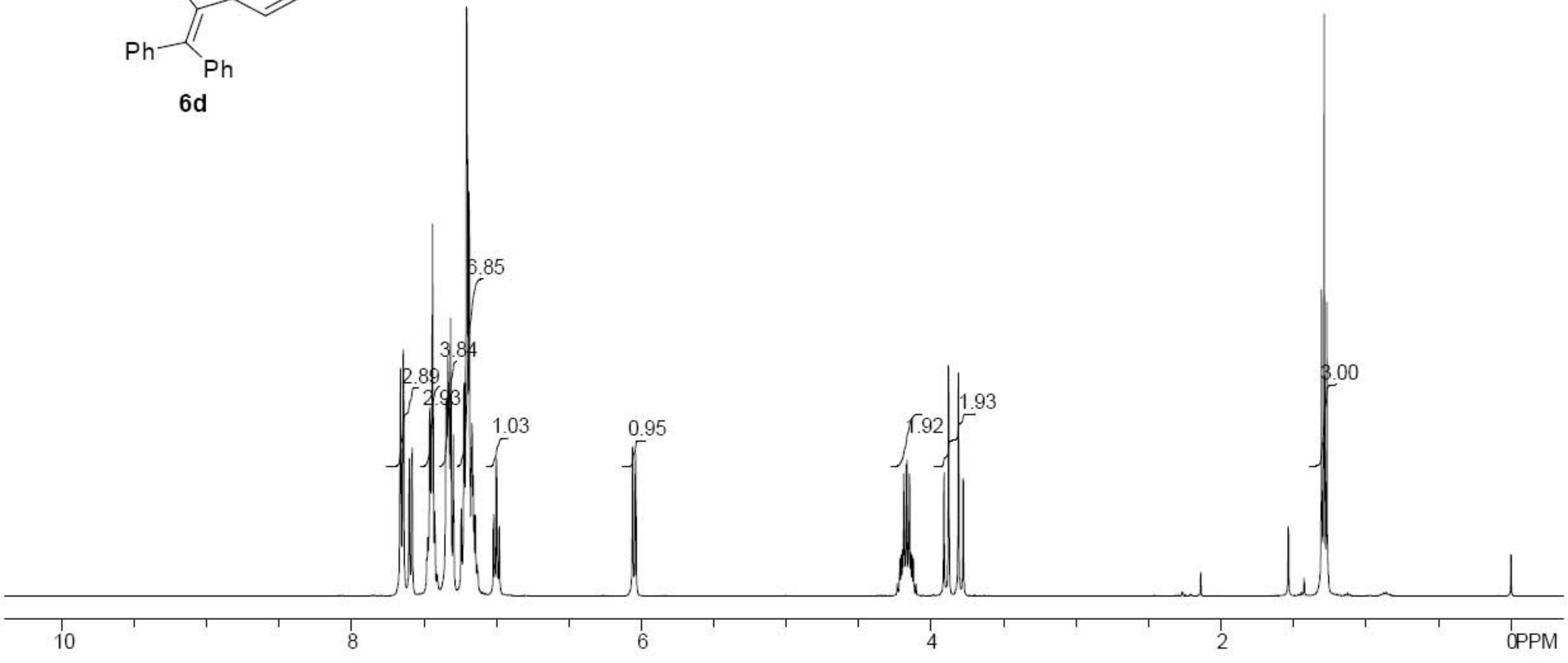

S
CO2Et
O
Ph
Ph

6d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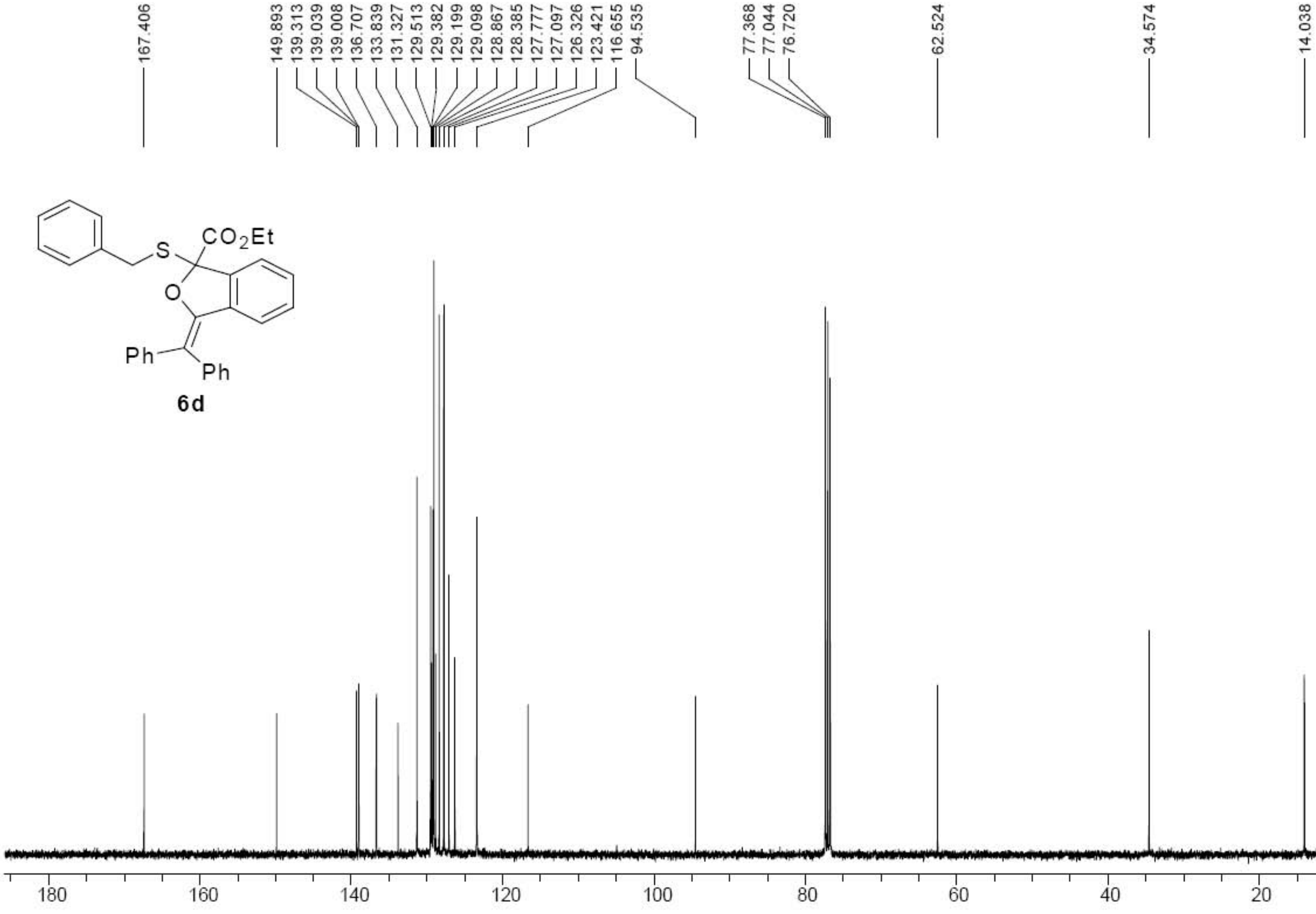
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128.385
127.777
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126.326
123.421
116.655
94.535
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76.720
62.524
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S
O
Ph
Ph
6d
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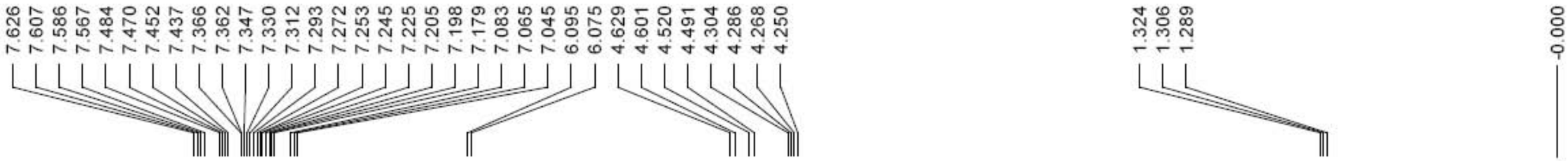
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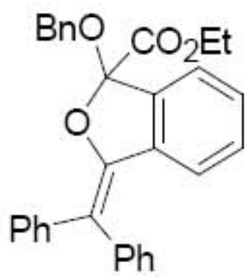
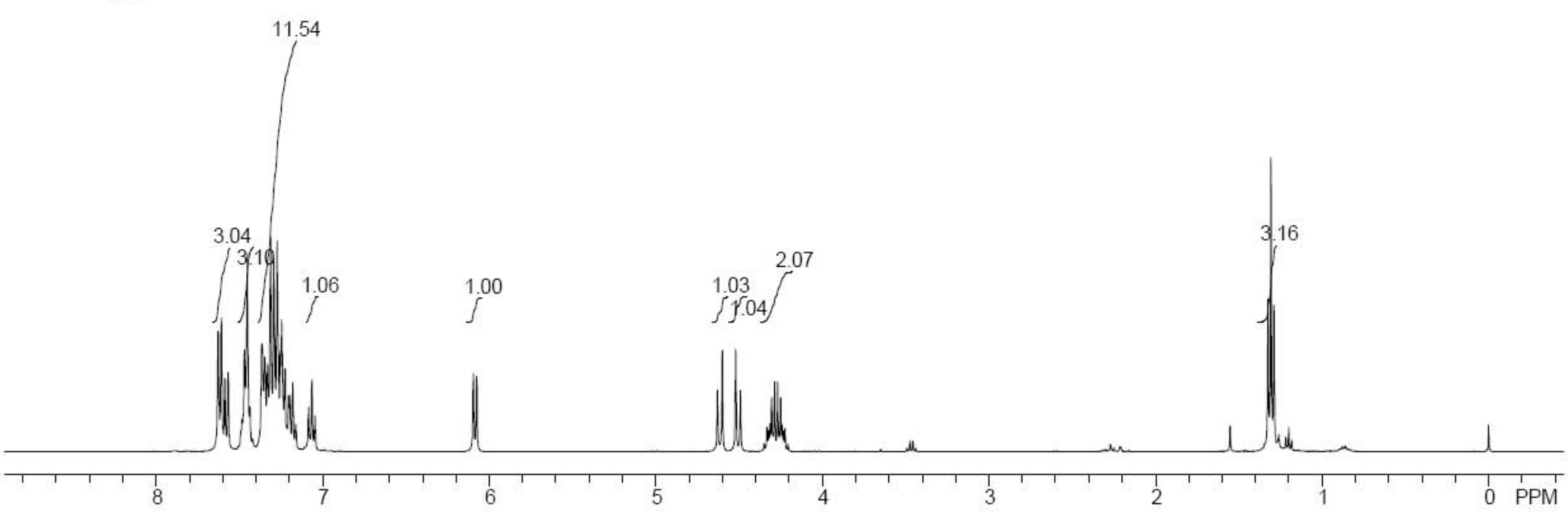

BnO
CO2Et
O
Ph
Ph

6e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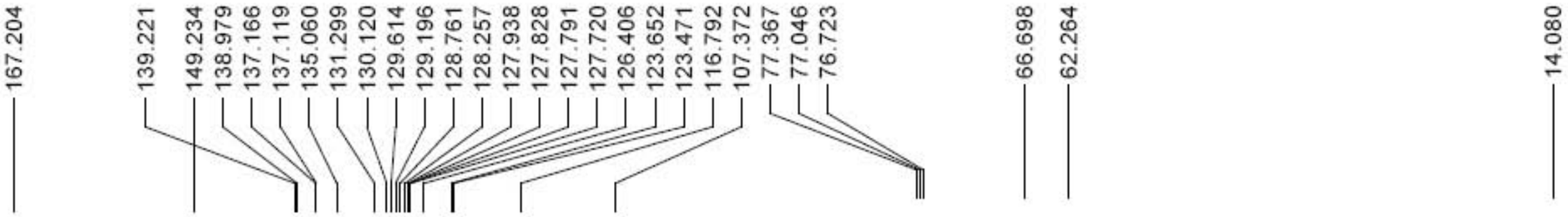
PPM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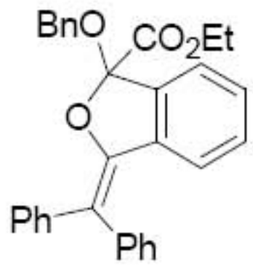
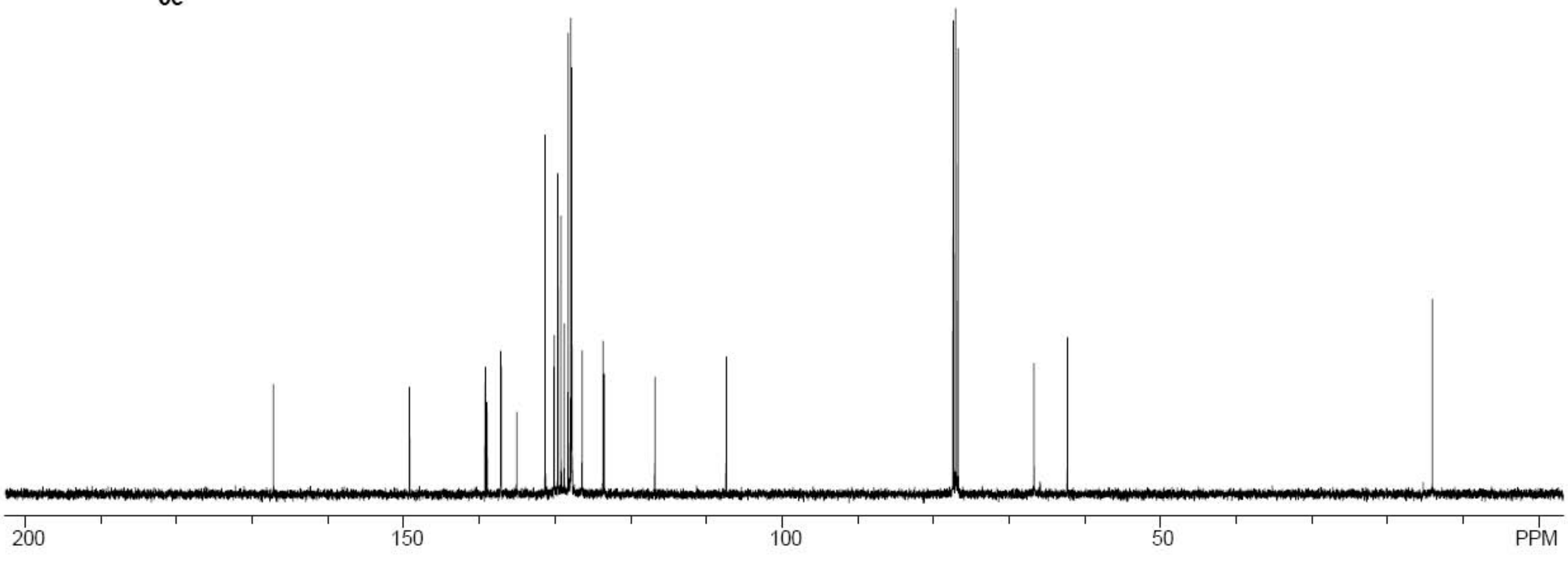

BnO
CO2Et
O
Ph
Ph

6e


200
150
100
50
PPM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7.033
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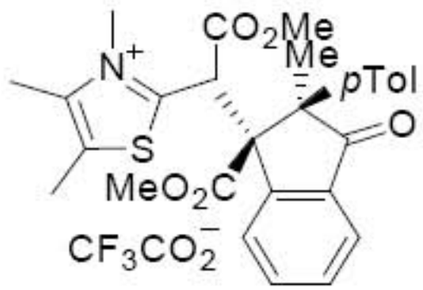
2.211
1.504


CO2Me
Me
pTol
O
N+
S
MeO2C
CF3CO2−

8a

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2.00
2.02
1.01
3.02
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3.00
9
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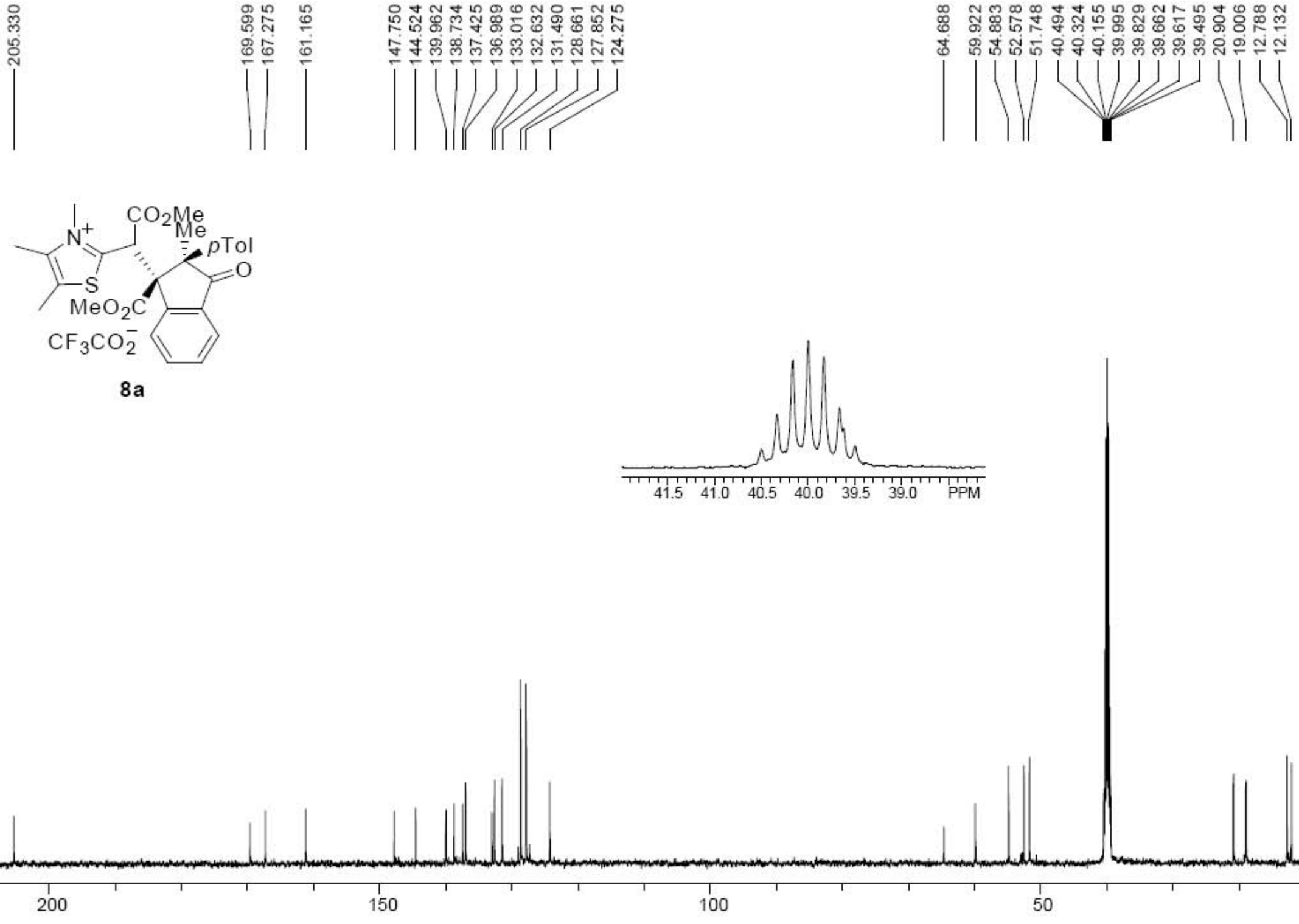
7
6
5
4
3
2
1
0 PPM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39.995
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39.662
39.617
39.495
20.904
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12.788
12.132
CO2Me
Me
pTol
O
N+
S
MeO2C
CF3CO2−
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40.0
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39.0
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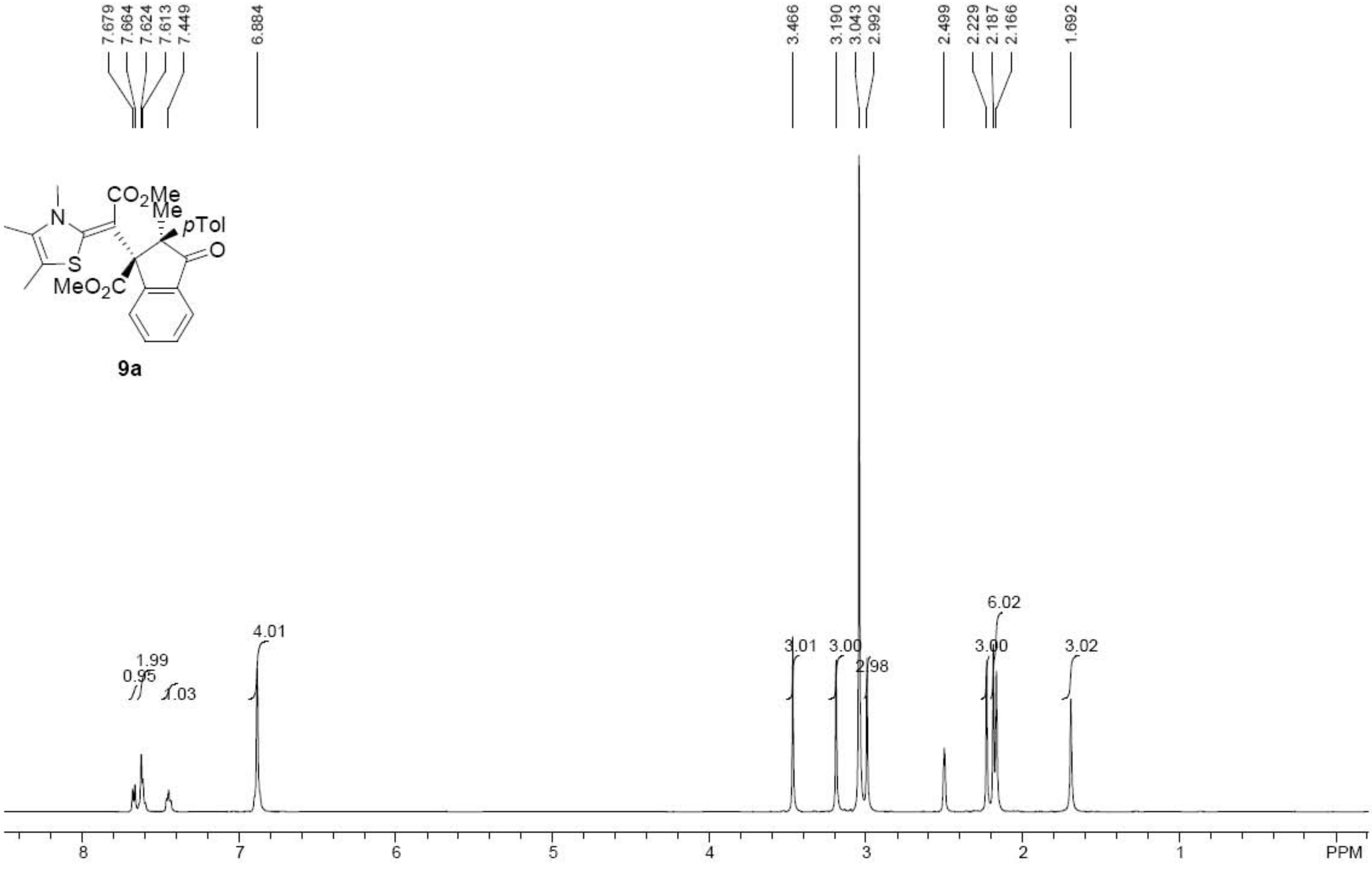
100
50
PPM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CO2Me
Me
pTol
O
N
S
MeO2C
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3.00
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7
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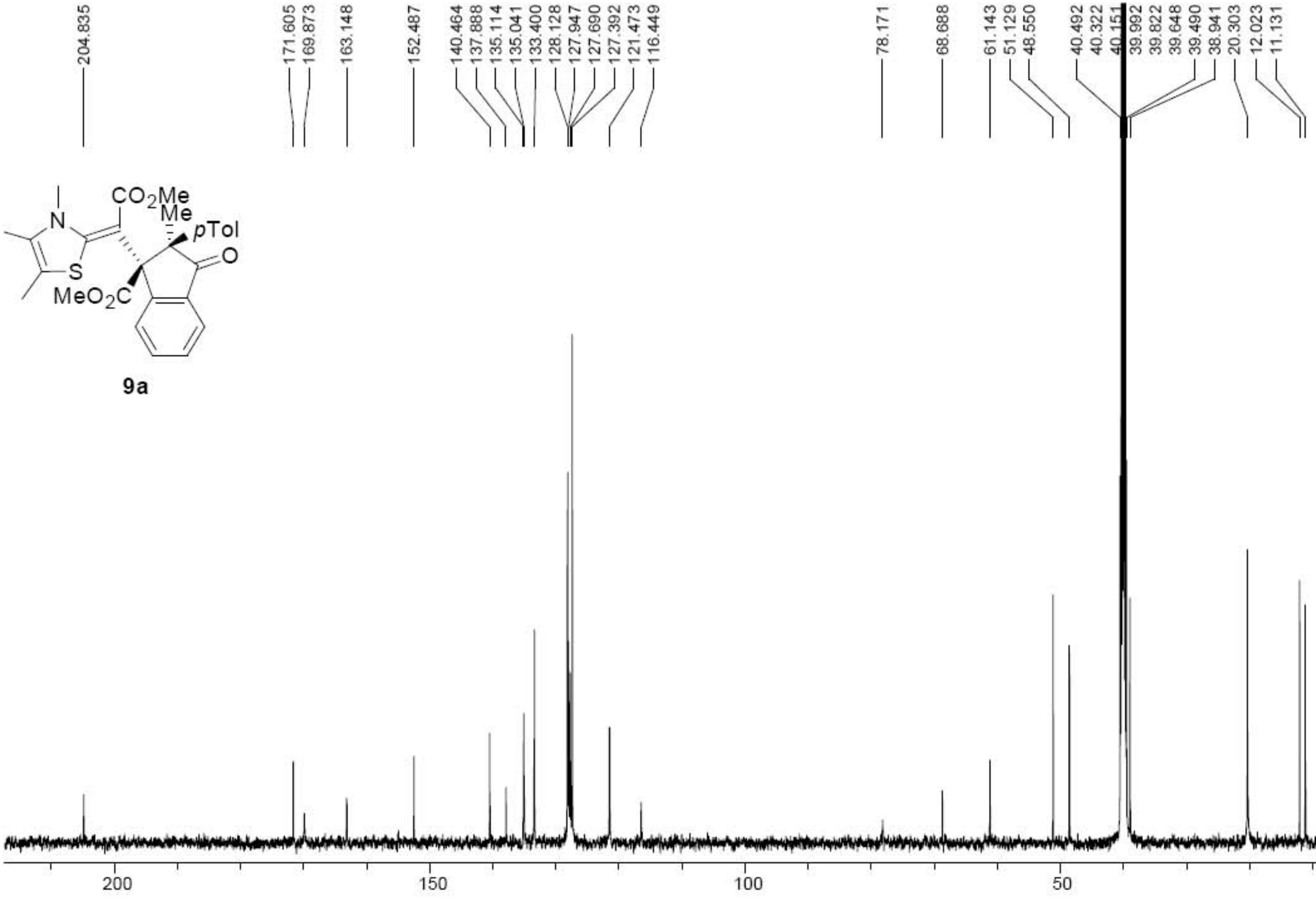
2
1
PPM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40.322
40.151
39.992
39.822
39.648
39.490
38.941
20.303
12.023
11.131
CO2Me
Me
pTol
O
N
S
MeO2C
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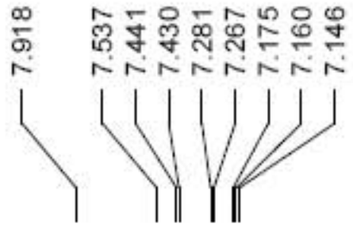
150
100
50
PPM

9a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7.430
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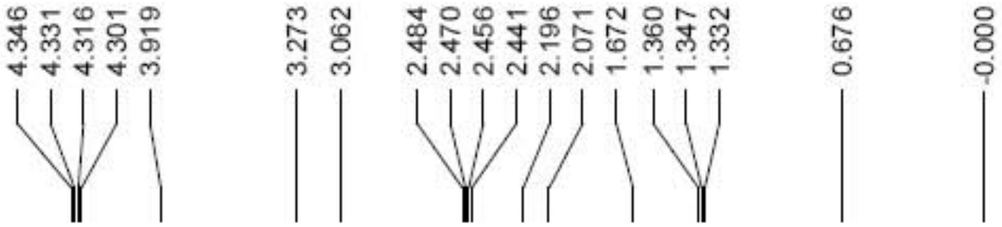
7.267
7.175
7.160
7.146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4.316
4.301
3.919
3.273
3.062
2.484
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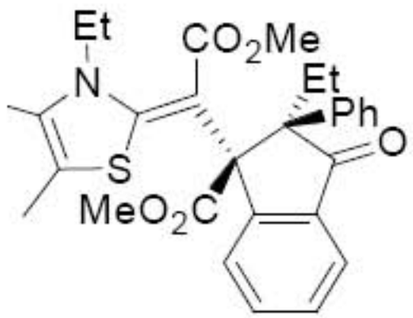
2.441
2.196
2.071
1.672
1.360
1.347
1.332
0.676
-0.000


Et
CO2Me
N
Et
Ph
O
S
MeO2C

9b

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4.06
2.21
1.82
1.00
0.98
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1.02
3.08
3.02
1.08
3.03
2.96
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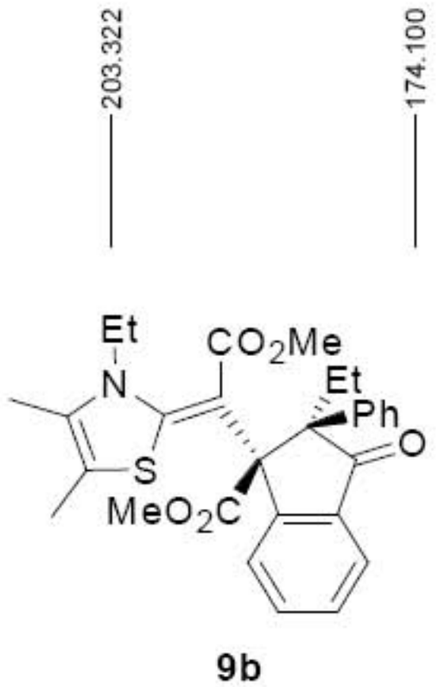
0
PPM


Et
N
CO2Me
Et
Ph
O
S
MeO2C

9b

203.322
174.100
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166.380
148.131
133.123
136.898
132.295
132.259
131.473
129.413
128.320
126.233
125.715
124.582
114.457
83.419
76.989
76.666
70.466
68.694
51.926
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45.838
30.625
13.387
12.574
11.660
8.635
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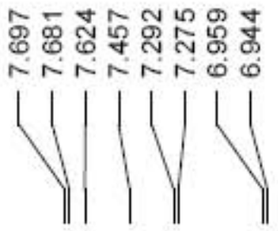
150
100
50
0 PPM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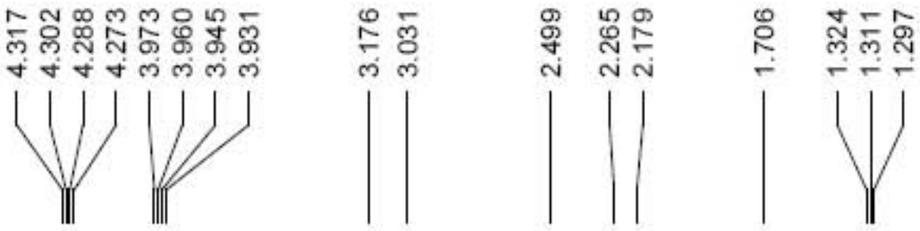
6.959
6.944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4.302
4.288
4.273
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3.931
3.176
3.031
2.499
2.265
2.179
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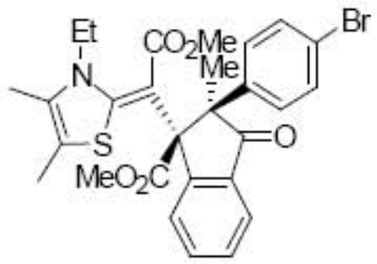
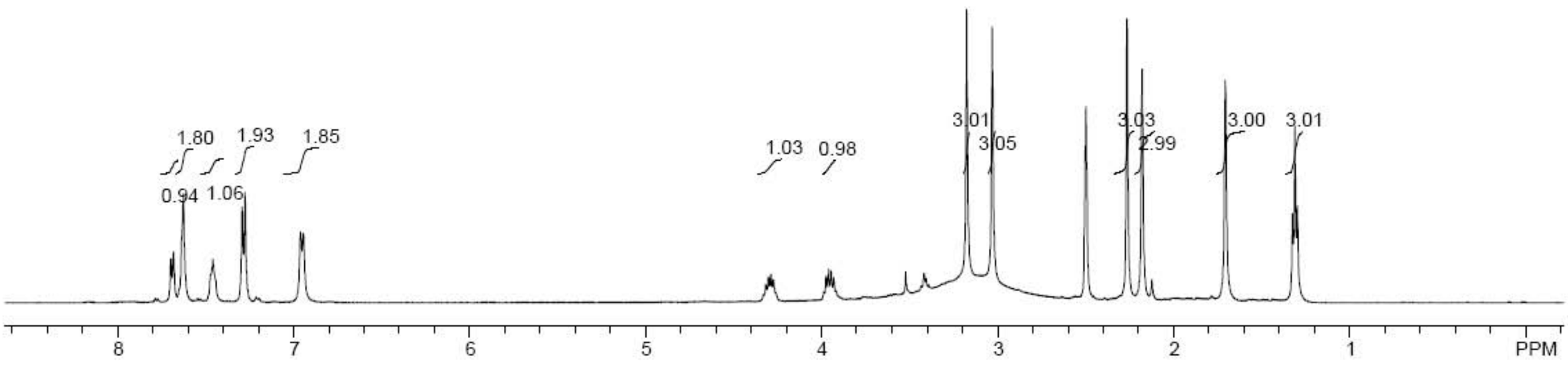
1.324
1.311
1.297


Et
N
S
CO2Me
Me
Br
O
MeO2C

9c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1.06
1.03
0.98
3.01
3.05
3.03
2.99
3.00
3.01
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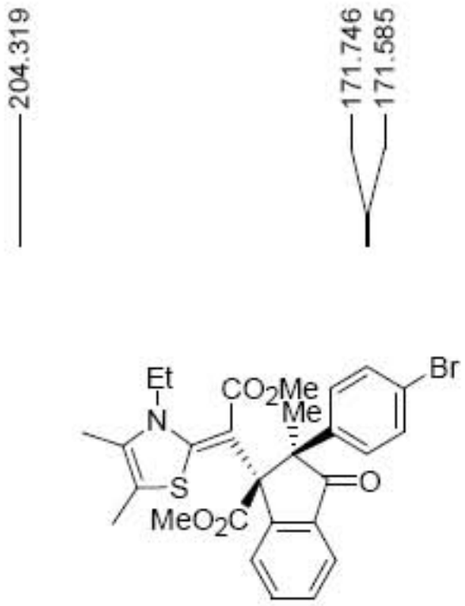
7
6
5
4
3
2
1
PPM


Et
N
S
CO2Me
Me
Br
O
MeO2C

9c

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151.893
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134.980
133.639
131.086
130.572
130.057
129.700
128.576
128.302
127.887
122.694
121.659
119.499
68.914
61.580
51.215
48.674
46.001
40.494
40.323
39.992
39.823
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39.488
20.894
13.281
11.977
11.266
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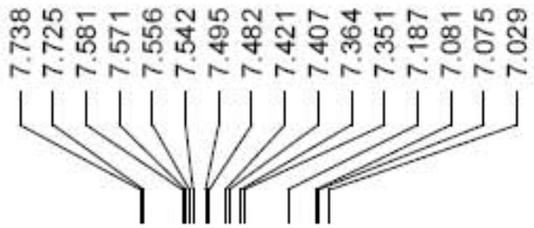
150
100
50
0
PPM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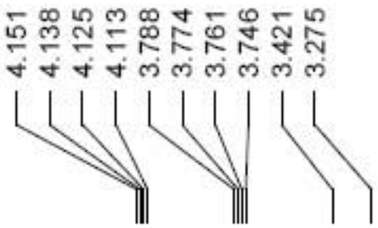
7.725
7.581
7.571
7.556
7.542
7.495
7.482
7.421
7.407
7.364
7.351
7.187
7.081
7.075
7.029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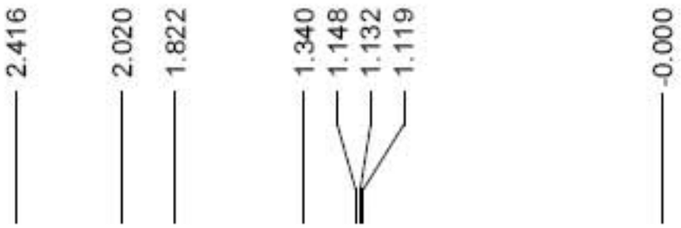
4.125
4.113
3.788
3.774
3.761
3.746
3.421
3.275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1.340
1.148
1.132
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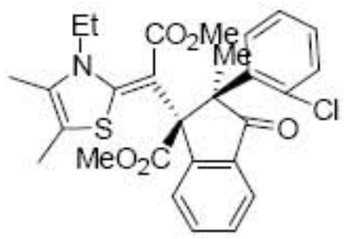
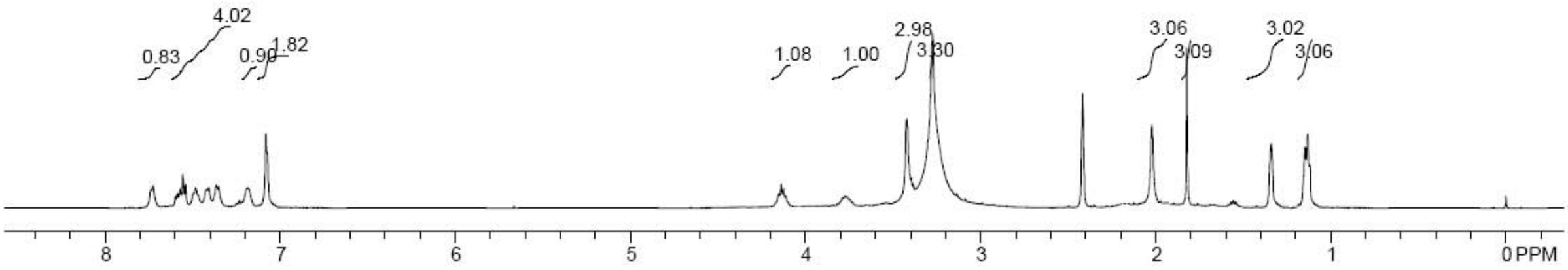
-0.000


Et
N
CO2Me
Me
Cl
S
O
MeO2C

9d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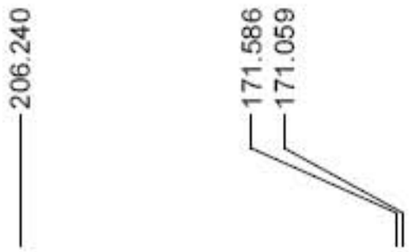
0.90
1.82
1.08
1.00
2.98
3.30
3.06
3.09
3.02
3.06
8
7
6
5
4
3
2
1
0 PPM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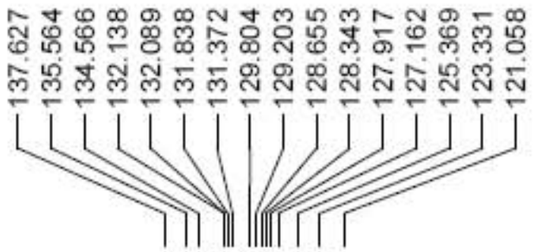
171.586
171.059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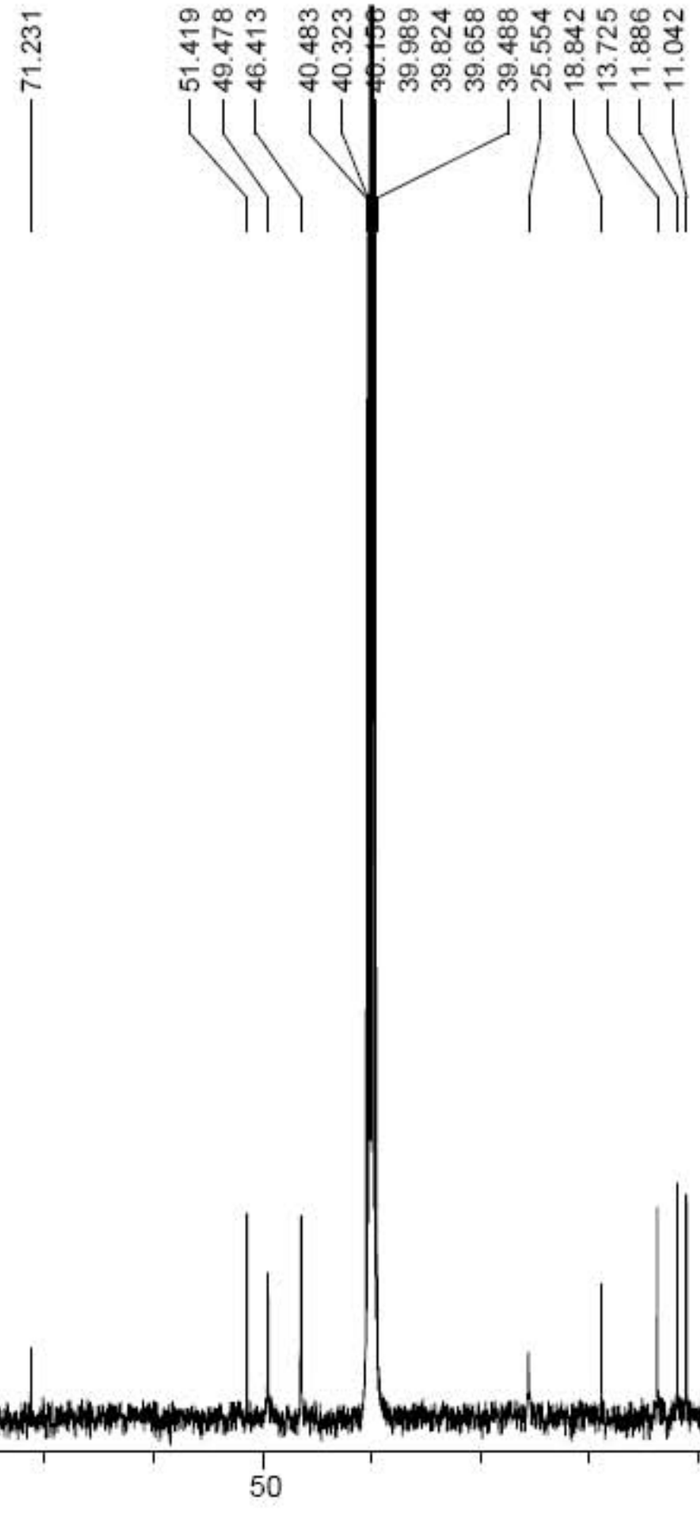
132.138
132.089
131.838
131.372
129.804
129.203
128.655
128.343
127.917
127.162
125.369
123.331
121.058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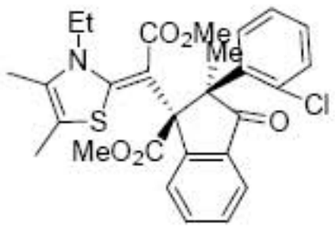
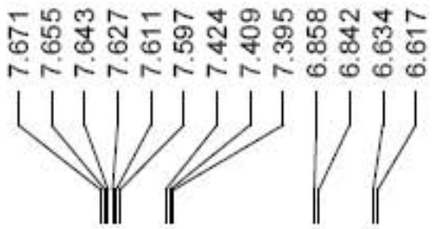
49.478
46.413
40.483
40.323
39.989
39.824
39.658
39.488
25.554
18.842
13.725
11.886
11.042
200
150
100
50
PPM


Et
N
CO2Me
Me
Cl
O
S
MeO2C

9d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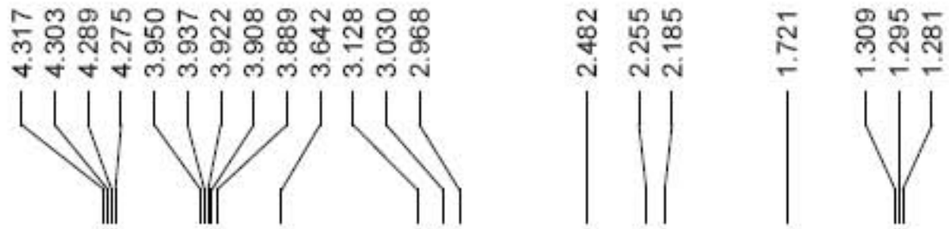
7.643
7.627
7.611
7.597
7.424
7.409
7.395
6.858
6.842
6.634
6.617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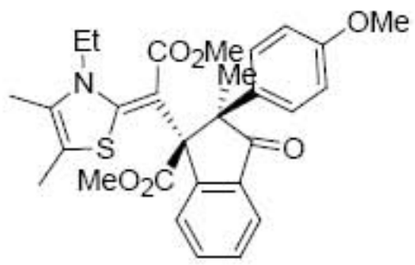
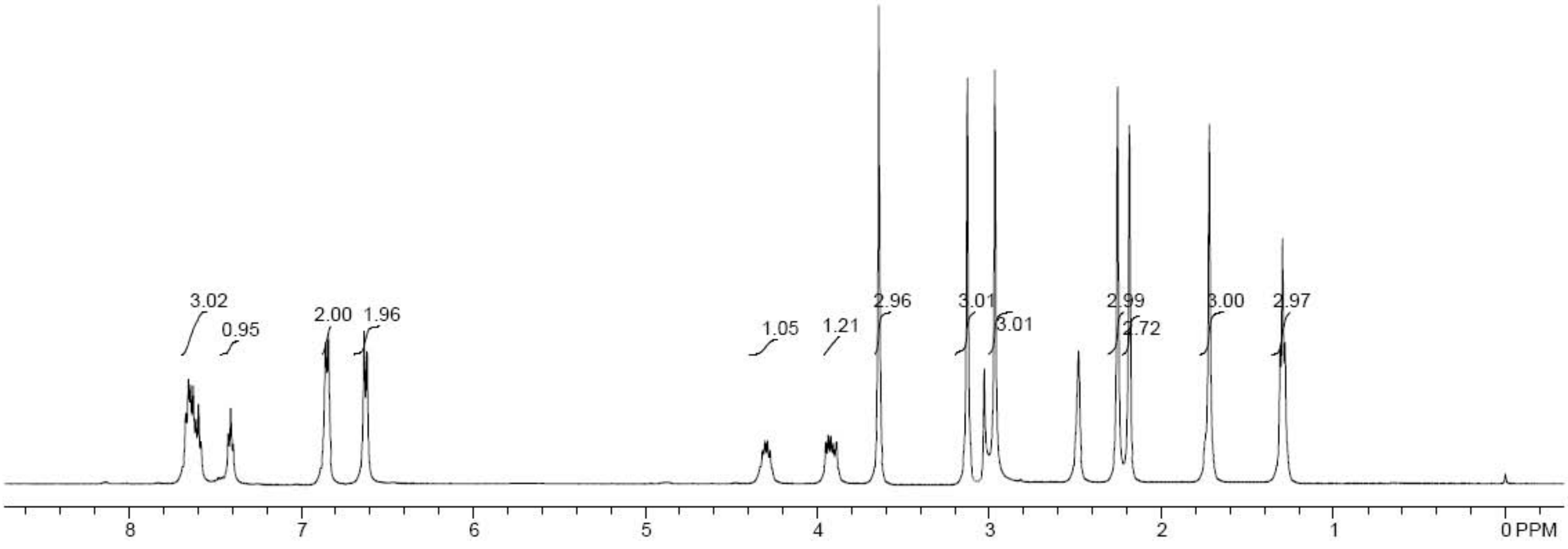
4.303
4.289
4.275
3.950
3.937
3.922
3.908
3.889
3.642
3.128
3.030
2.968
2.482
2.255
2.185
1.721
1.309
1.295
1.281


Et
N
CO2Me
Me
OMe
S
O
MeO2C

9e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1.96
1.05
1.21
2.96
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3.01
2.99
2.72
3.00
2.97
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2
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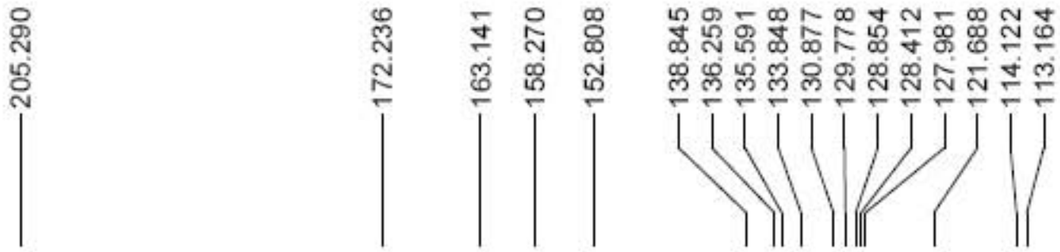
0 PPM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172.236
163.141
158.270
152.808
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133.848
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129.778
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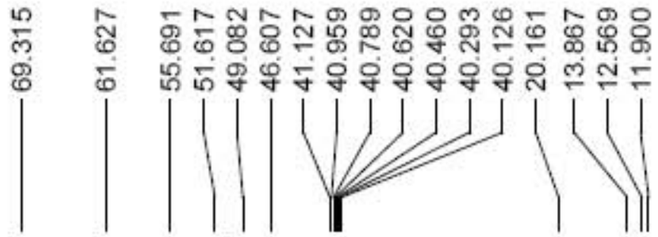
128.412
127.981
121.688
114.122
113.164


69.315
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55.691
51.617
49.082
46.607
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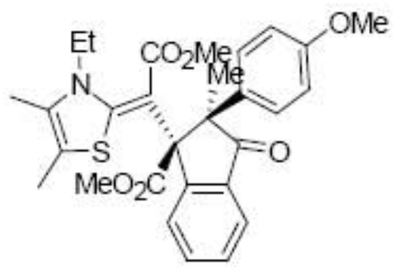
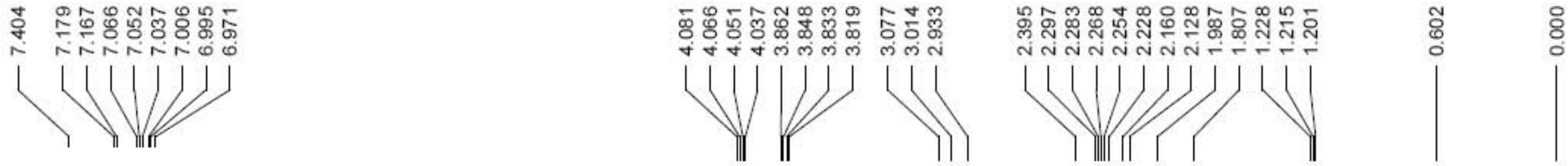
40.789
40.620
40.460
40.293
40.126
20.161
13.867
12.569
11.900


Et
N
S
CO2Me
Me
OMe
O
MeO2C

9e

200
150
100
50
PPM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4.051
4.037
3.862
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3.077
3.014
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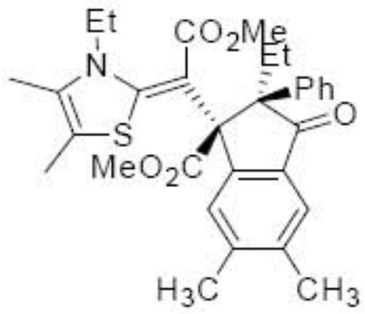
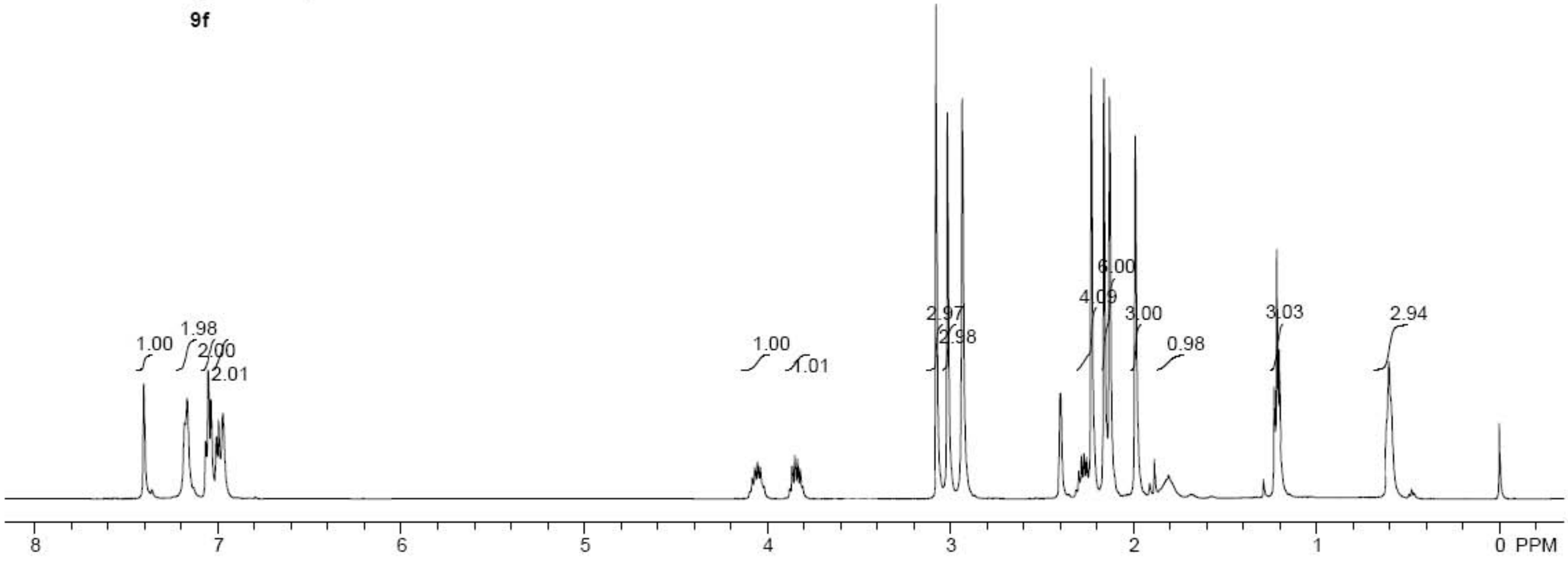
0.602
0.000


Et
N
CO2Me
Et
Ph
O
S
MeO2C
H3C
CH3

9f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2.00
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1.01
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2.98
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0.98
3.03
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7
6
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4
3
2
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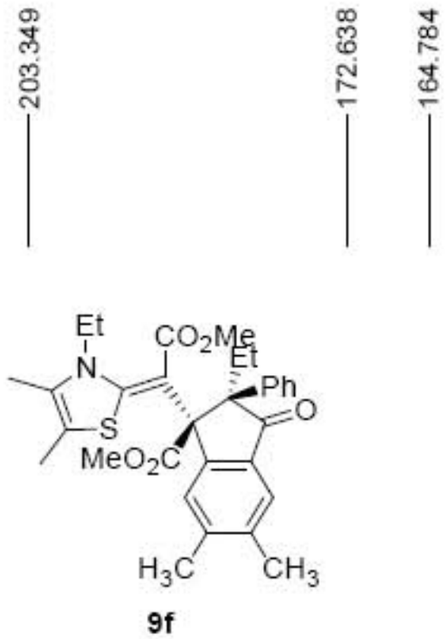
0 PPM


Et
N
CO2Me
Et
Ph
O
S
MeO2C
H3C
CH3

9f

203.349
172.638
164.784
138.594
136.839
142.020
135.125
133.850
131.017
129.685
129.265
128.614
126.649
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123.232
122.467
70.100
66.853
51.304
48.988
45.869
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8.965
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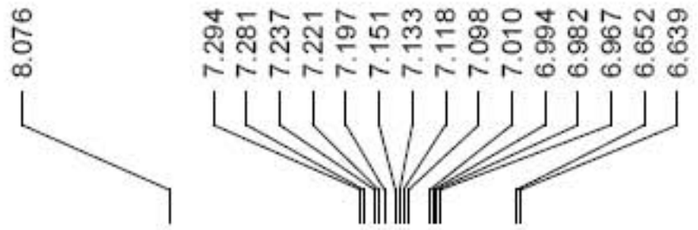
100
50
0 PPM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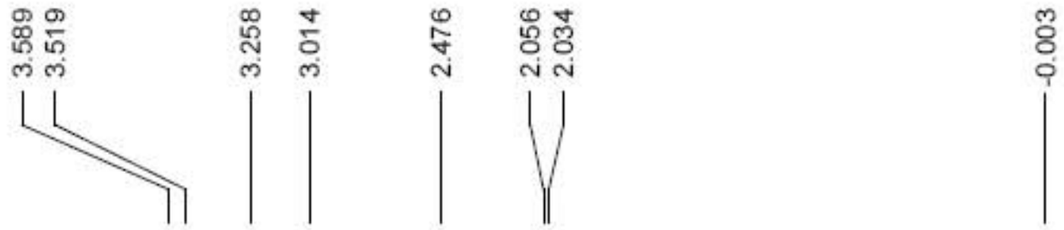
6.982
6.967
6.652
6.639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3.014
2.476
2.056
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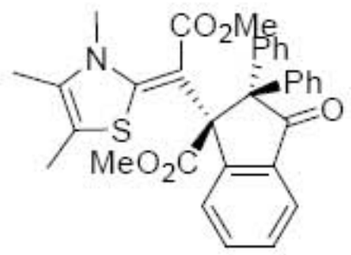
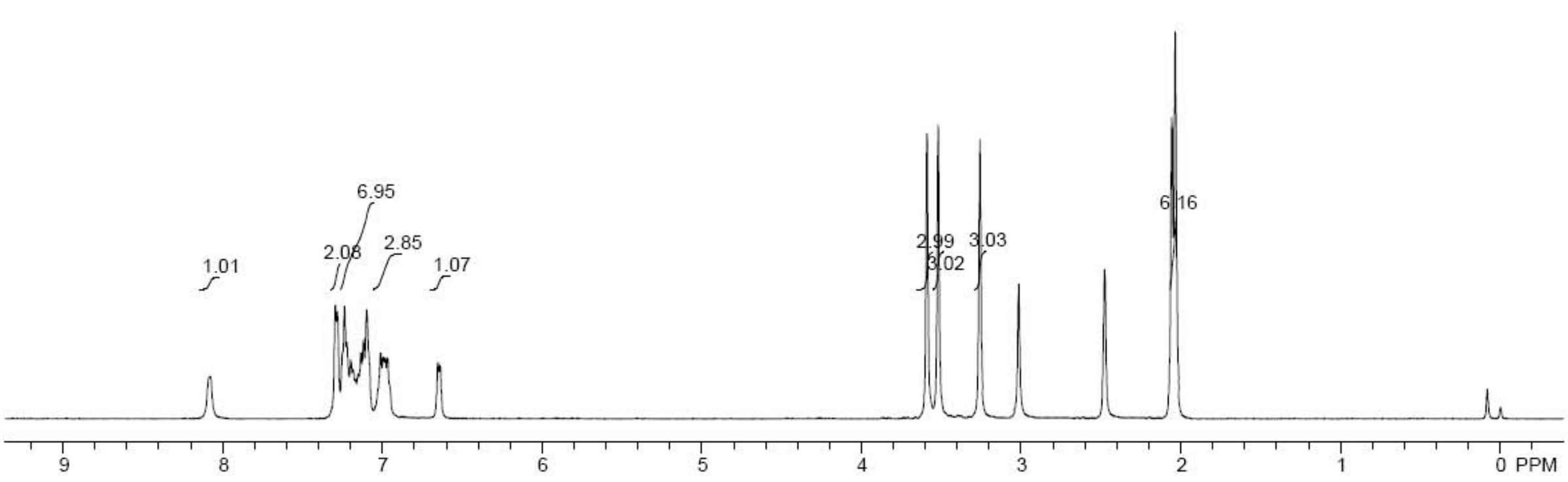
-0.003


N
CO2Me
Ph
Ph
O
S
MeO2C

9g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3.03
6.16
9
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7
6
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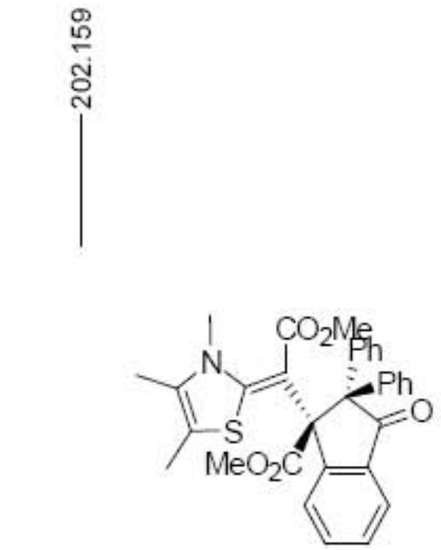
4
3
2
1
0 PPM


N
CO2Me
Ph
Ph
O
S
MeO2C

9g

202.159
168.294
165.122
150.880
141.857
140.168
139.628
135.286
134.264
131.293
130.567
129.268
129.032
128.408
127.542
127.109
126.176
125.552
123.645
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116.523
79.565
69.127
52.387
49.598
40.501
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39.837
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39.578
38.931
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11.003
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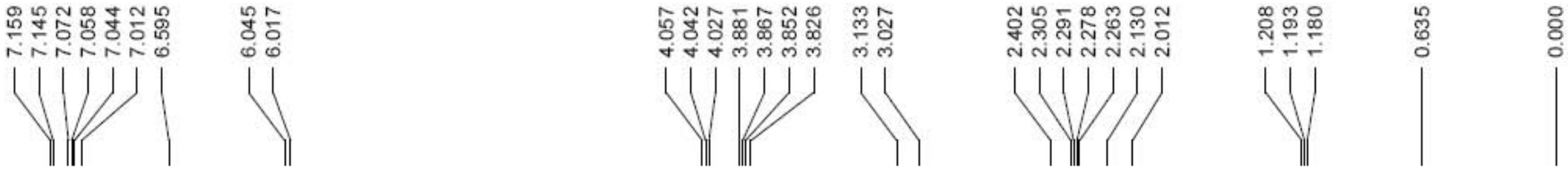
150
100
50
PPM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7.012
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6.045
6.017
4.057
4.042
4.027
3.881
3.867
3.852
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3.133
3.027
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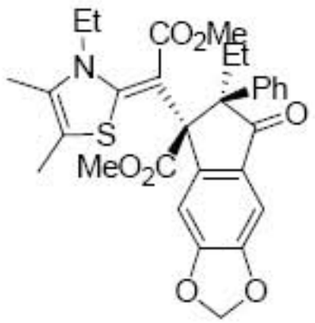
Et
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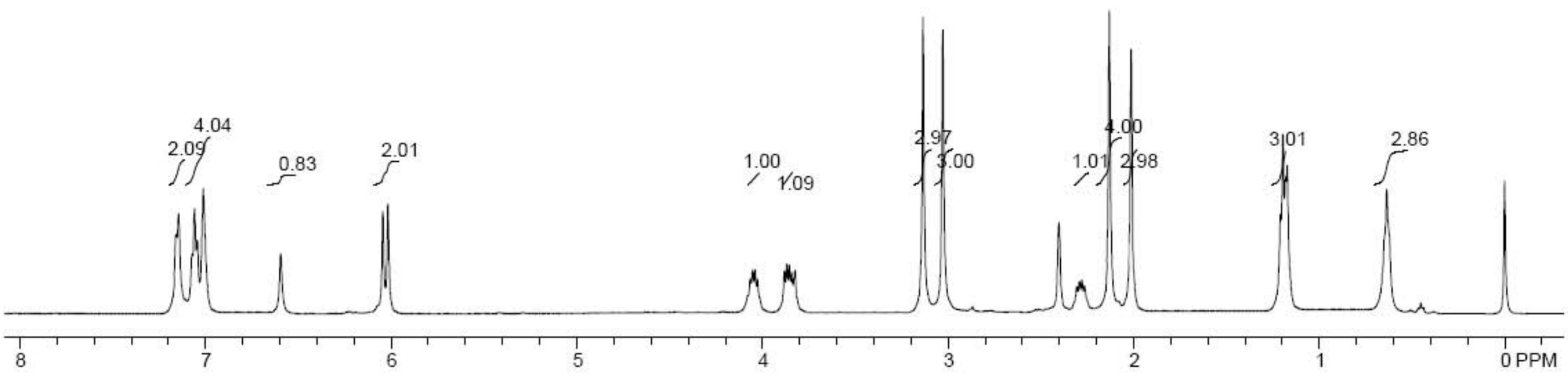
CO2Me
Et
Ph
O
S
MeO2C
O
O

9h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1.00
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4.00
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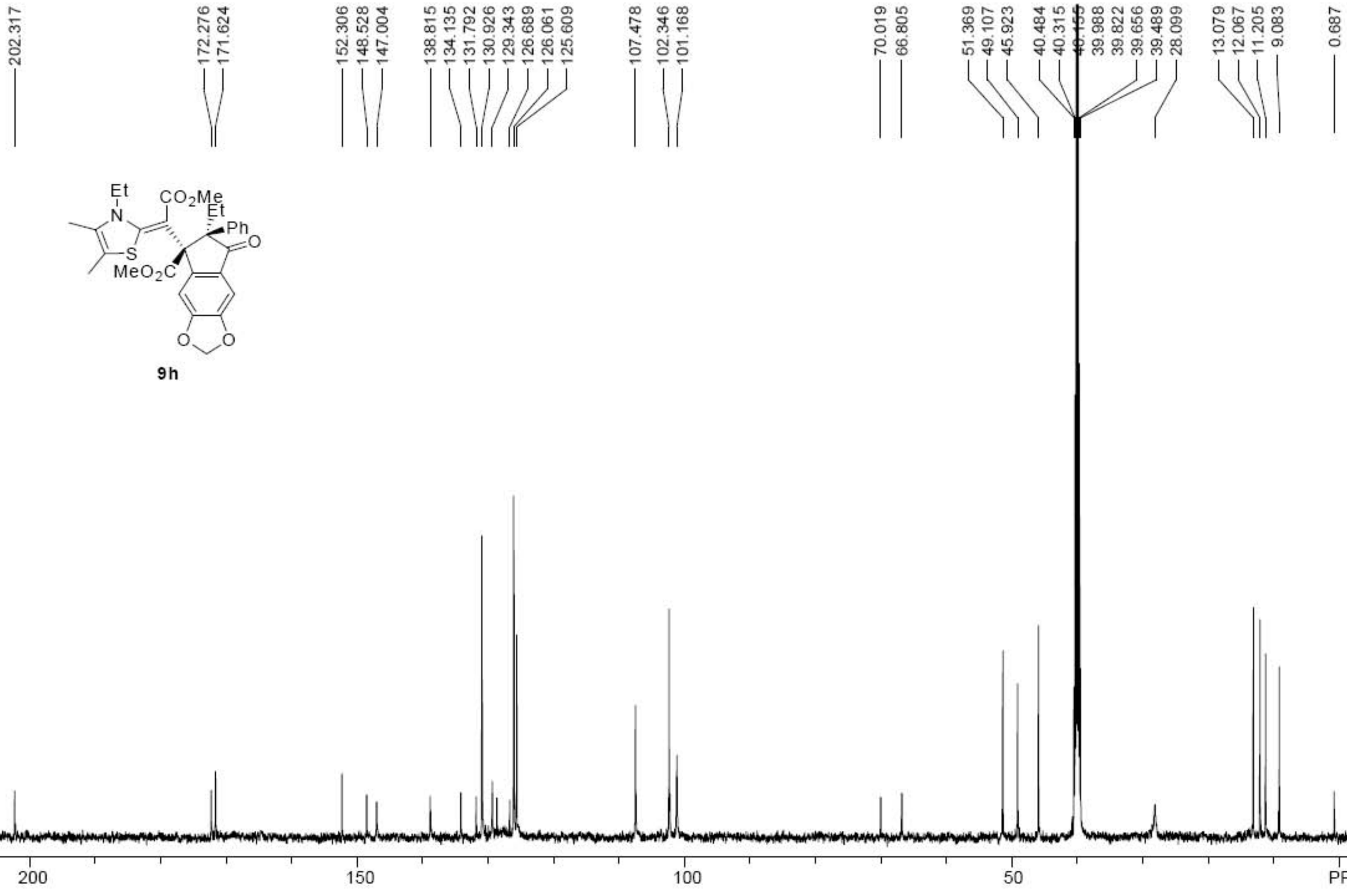
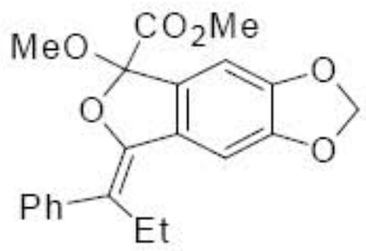
2.86
8
7
6
5
4
3
2
1
0 PPM


202.317
172.276
171.624
152.306
148.528
147.004
138.815
134.135
131.792
130.926
129.343
126.689
126.061
125.609
107.478
102.346
101.168
70.019
66.805
51.369
49.107
45.923
40.484
40.315
39.988
39.822
39.656
39.489
28.099
13.079
12.067
11.205
9.083
0.687
Et
N
CO2Me
Et
Ph
O
S
MeO2C
O
O
200
150
100
50
PPM

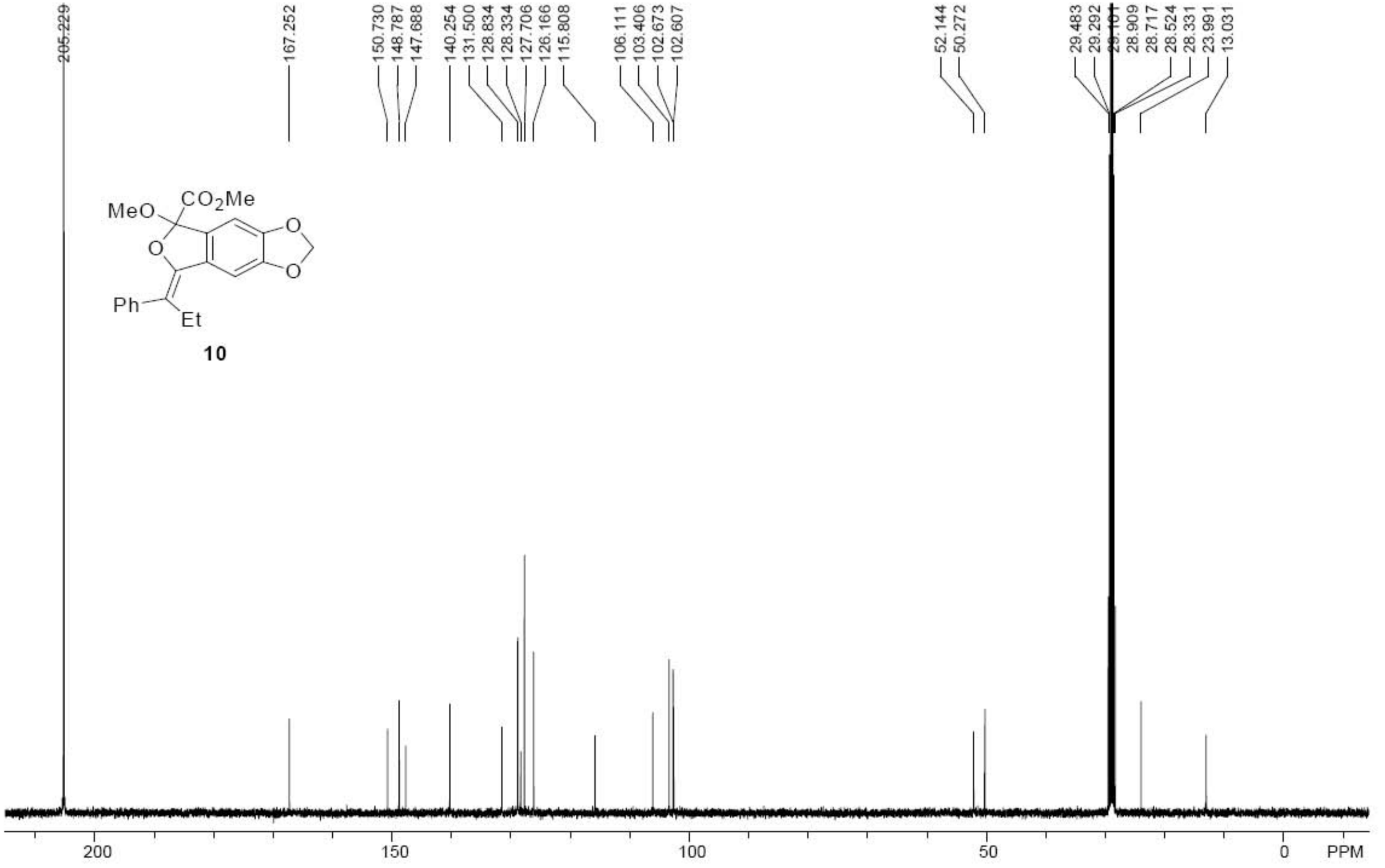
9h


7.610
7.607
7.589
7.587
7.365
7.346
7.326
7.279
7.229
7.211
6.955
6.170
6.158
3.737
3.124
2.822
2.818
2.812
2.803
2.794
2.047
1.165
1.147
1.127
0.000


MeO
CO2Me
O
O
O
Ph
Et

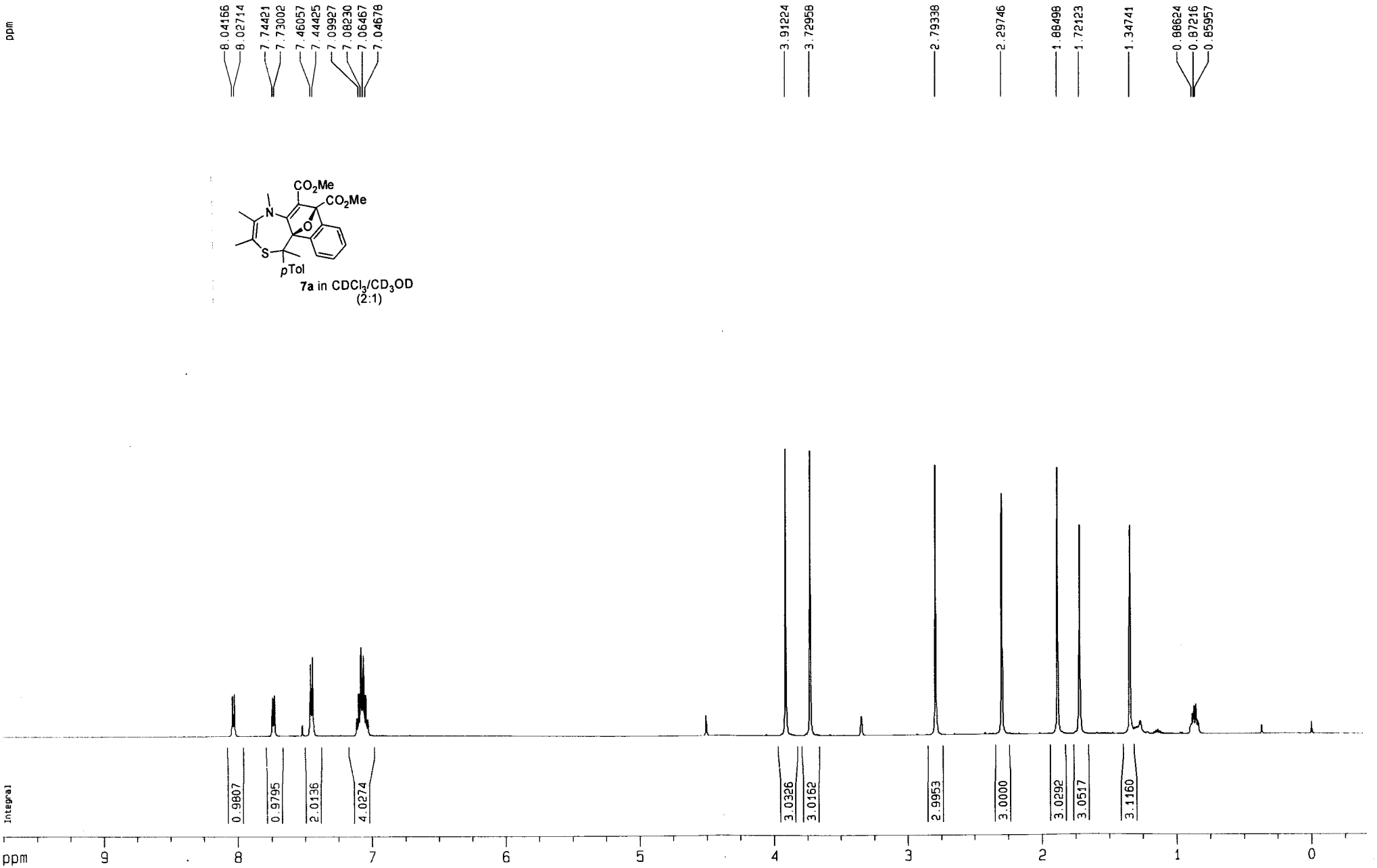
10

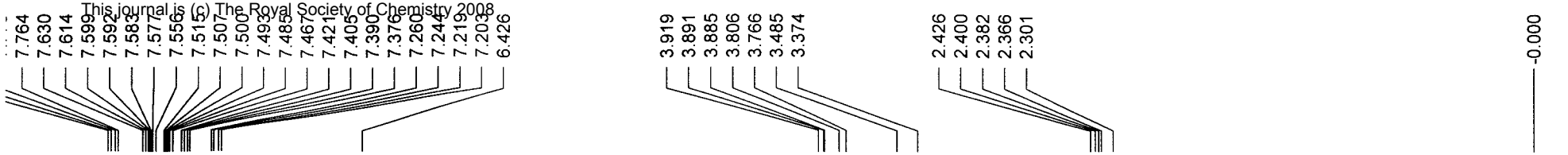
1.99
2.01
1.03
1.01
0.98
2.01
3.00
3.00
2.01
3.07
8
7
6
5
4
3
2
1
0
PPM

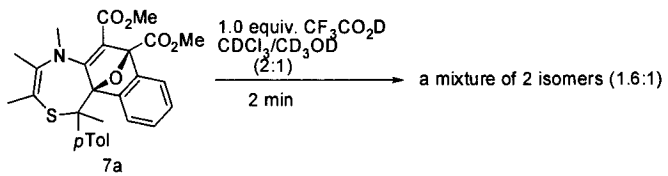

205.229
167.252
150.730
148.787
147.688
140.254
131.500
128.834
128.334
127.706
126.166
115.808
106.111
103.406
102.673
102.607
52.144
50.272
29.483
29.292
28.909
28.717
28.524
28.331
23.991
13.031
MeO
CO2Me
O
O
O
Ph
Et
200
150
100
50
0
PPM

10

Zhejiang University Avance DMX 500
DMF Exp: Sample: DB102 in CDCL3+CD3OD

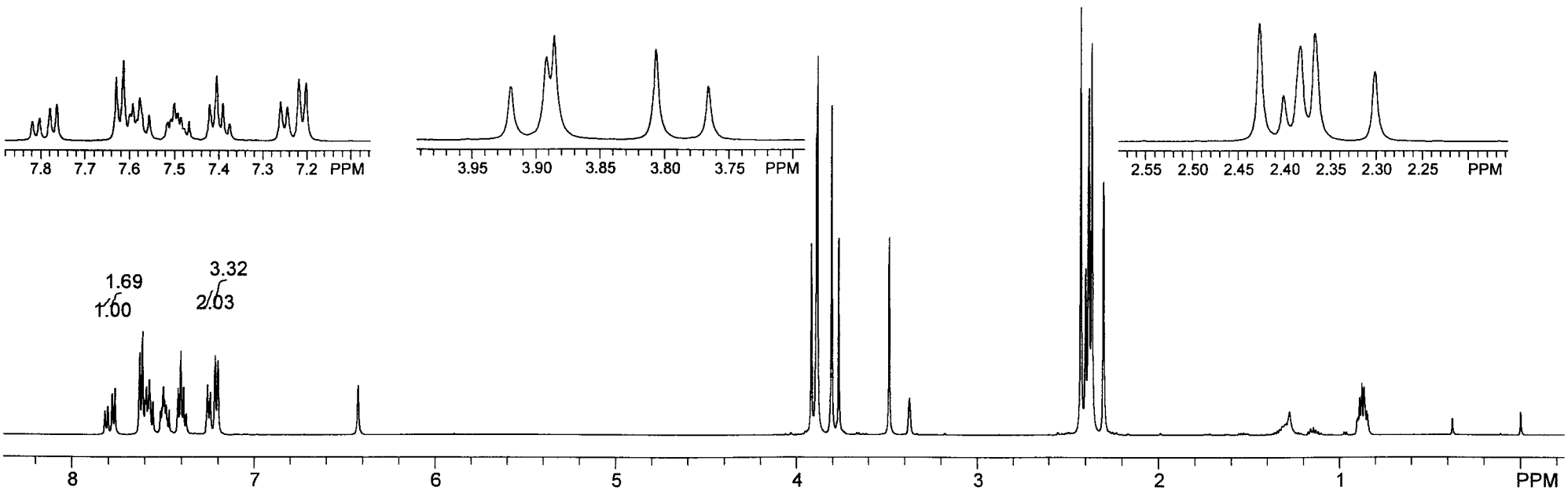


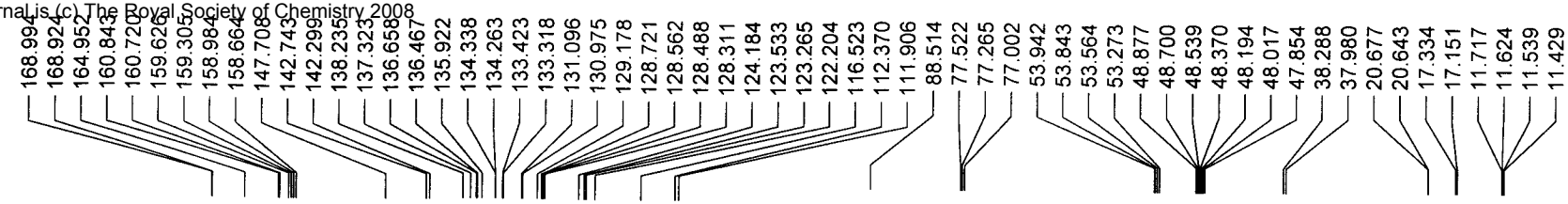


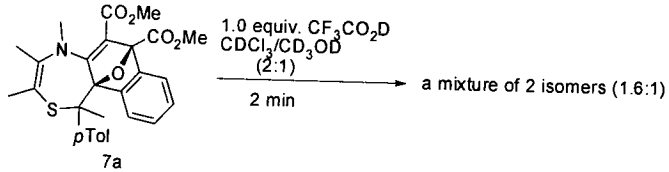


1.0 equiv. CF_3CO_2D
$CDCl_3/CD_3OD$ (2:1)
2 min

→ a mixture of 2 isomers (1.6:1)





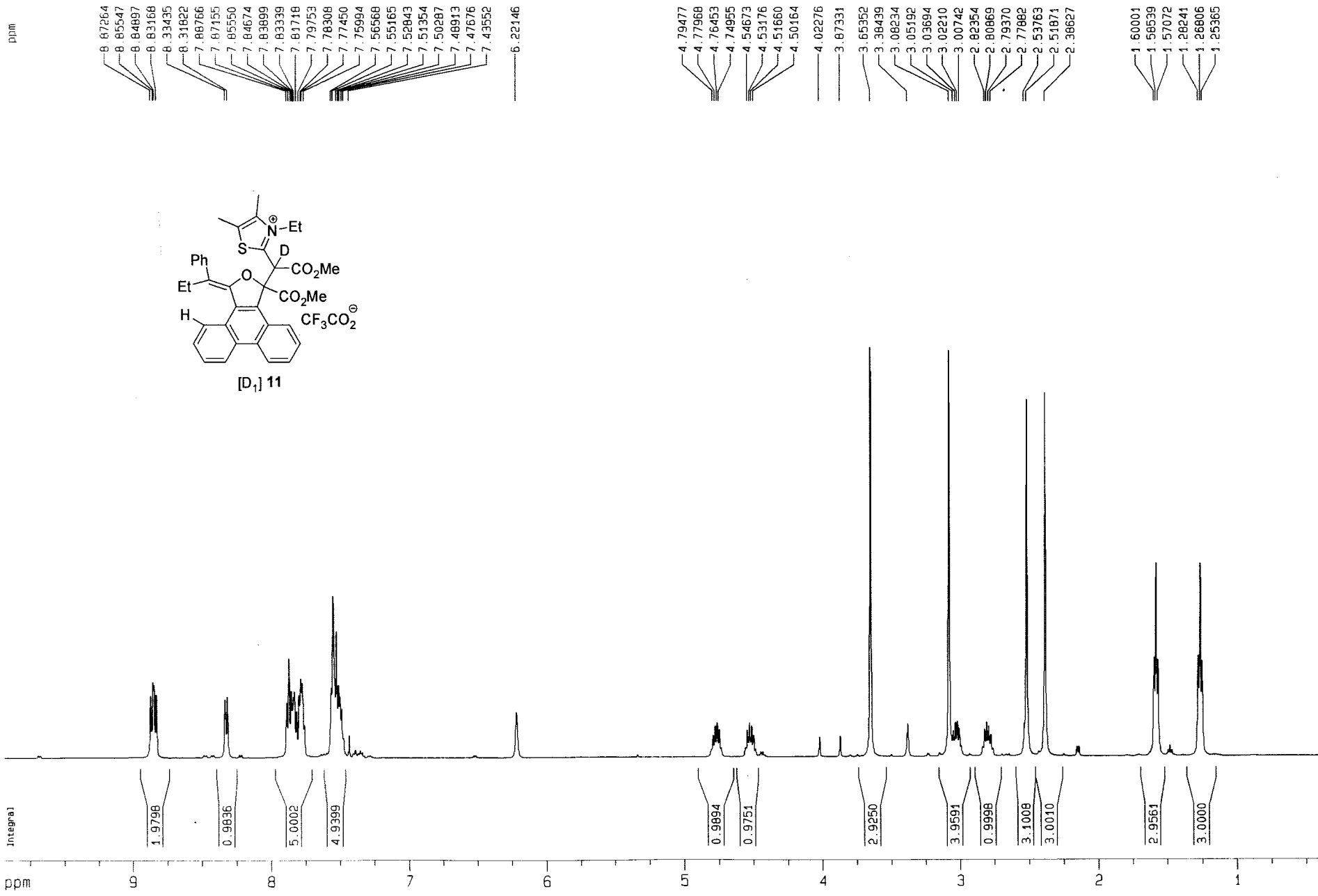


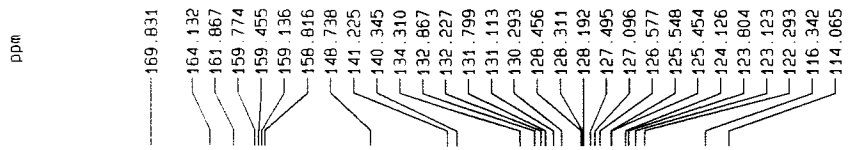
7a

1.0 equiv. CF_3CO_2D
$CDCl_3/CD_3OD$
(2:1)
2 min

→ a mixture of 2 isomers (1.6:1)

Zhejiang University Avance DMX 500
DMF 5mm Sample: DC108A in CDCL3 + CD_3OD




ppm
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164.132
161.867
159.774
159.455
159.136
158.816
148.738
141.225
140.345
134.310
132.867
132.227
131.799
131.113
130.293
128.456
128.311
128.192
127.495
127.096
126.577
125.548
125.454
124.126
123.804
123.123
122.293
116.342
114.065
77.530
77.273
77.017
54.154
53.298
49.068
48.896
48.725
48.553
48.382
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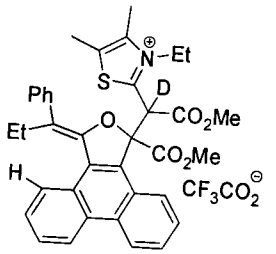
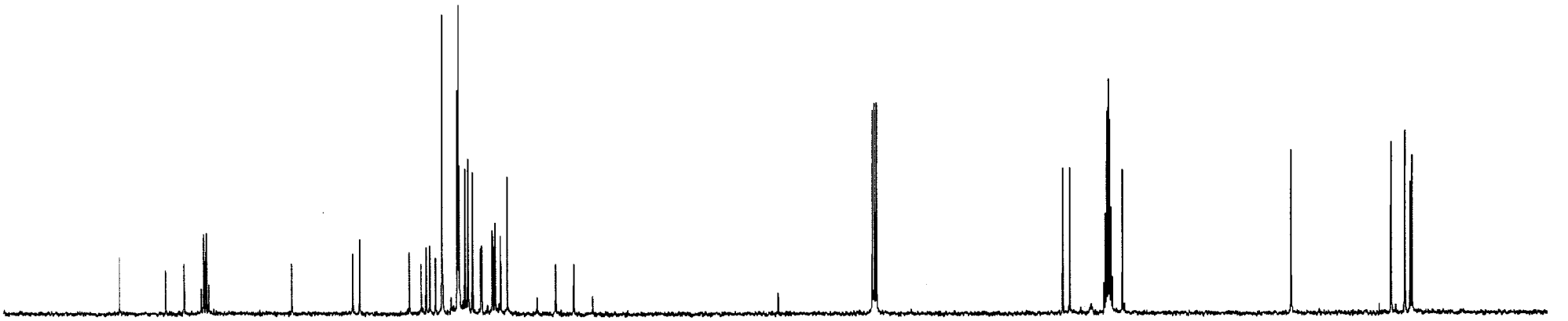
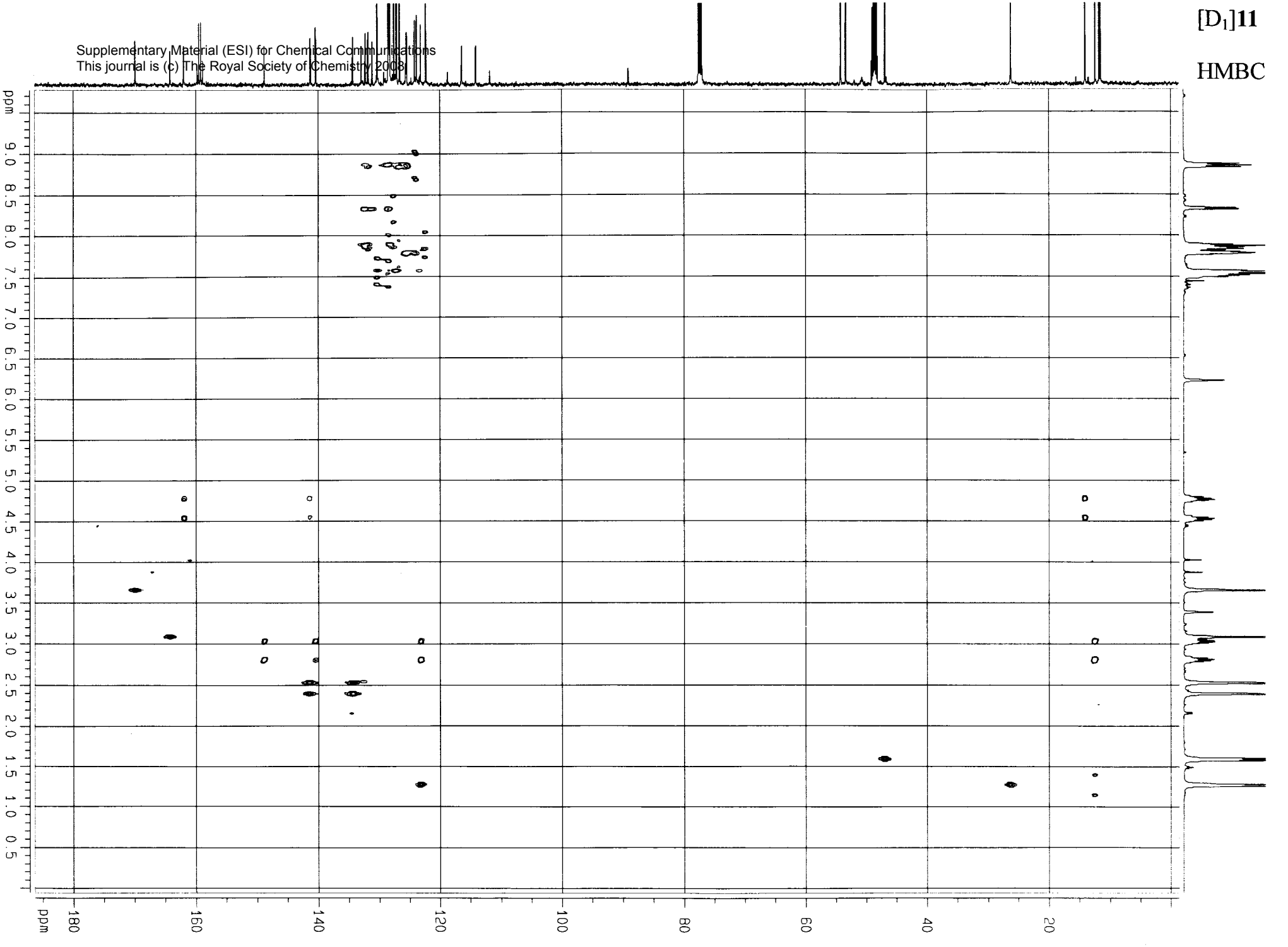
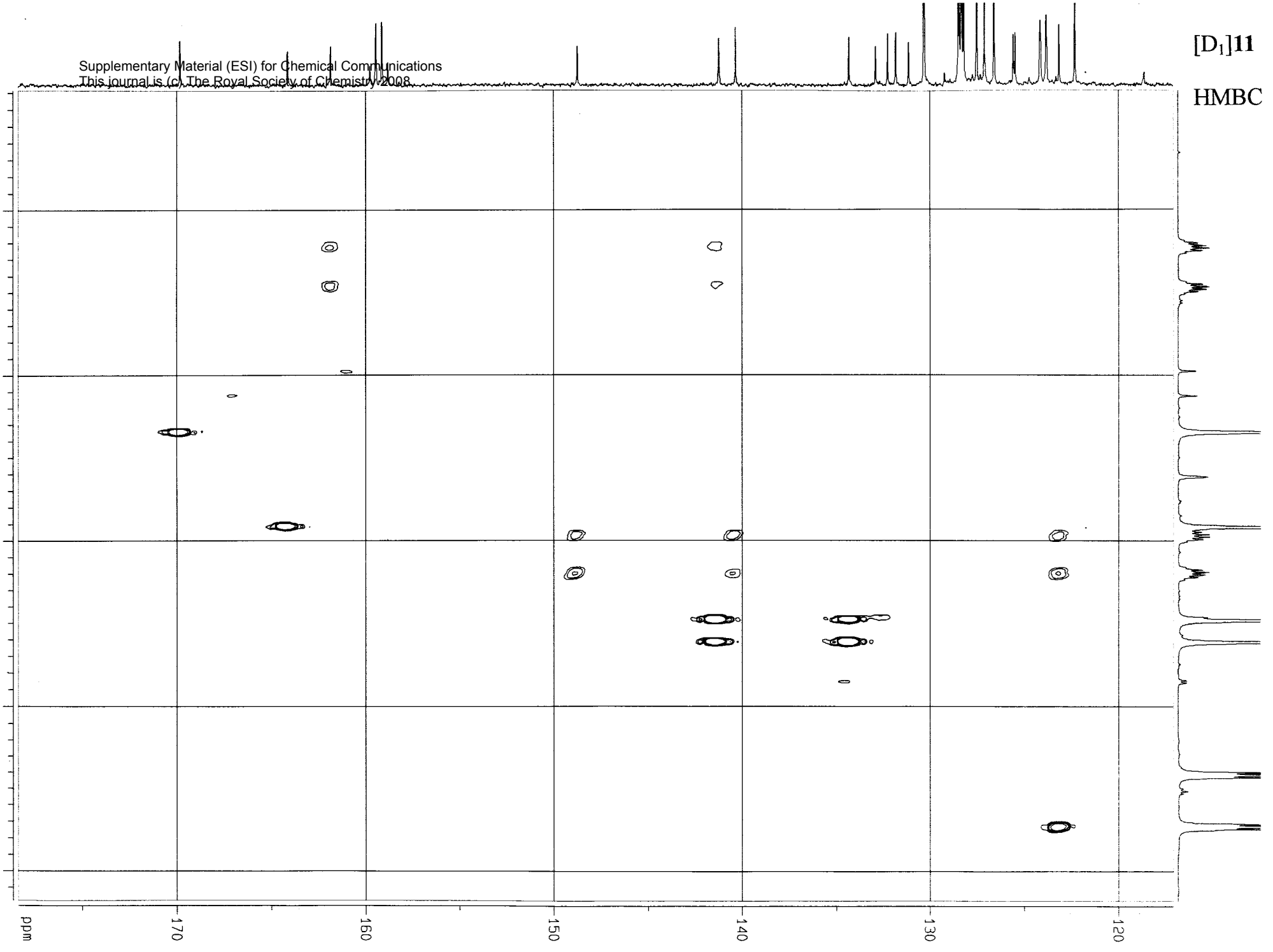
26.209
14.026
12.371
11.699
11.503


N
Et
S
D
Ph
Et
O
CO_2Me
CO_2Me
H
$CF_3CO_2^{\ominus}$

$[D_1]$ **11**

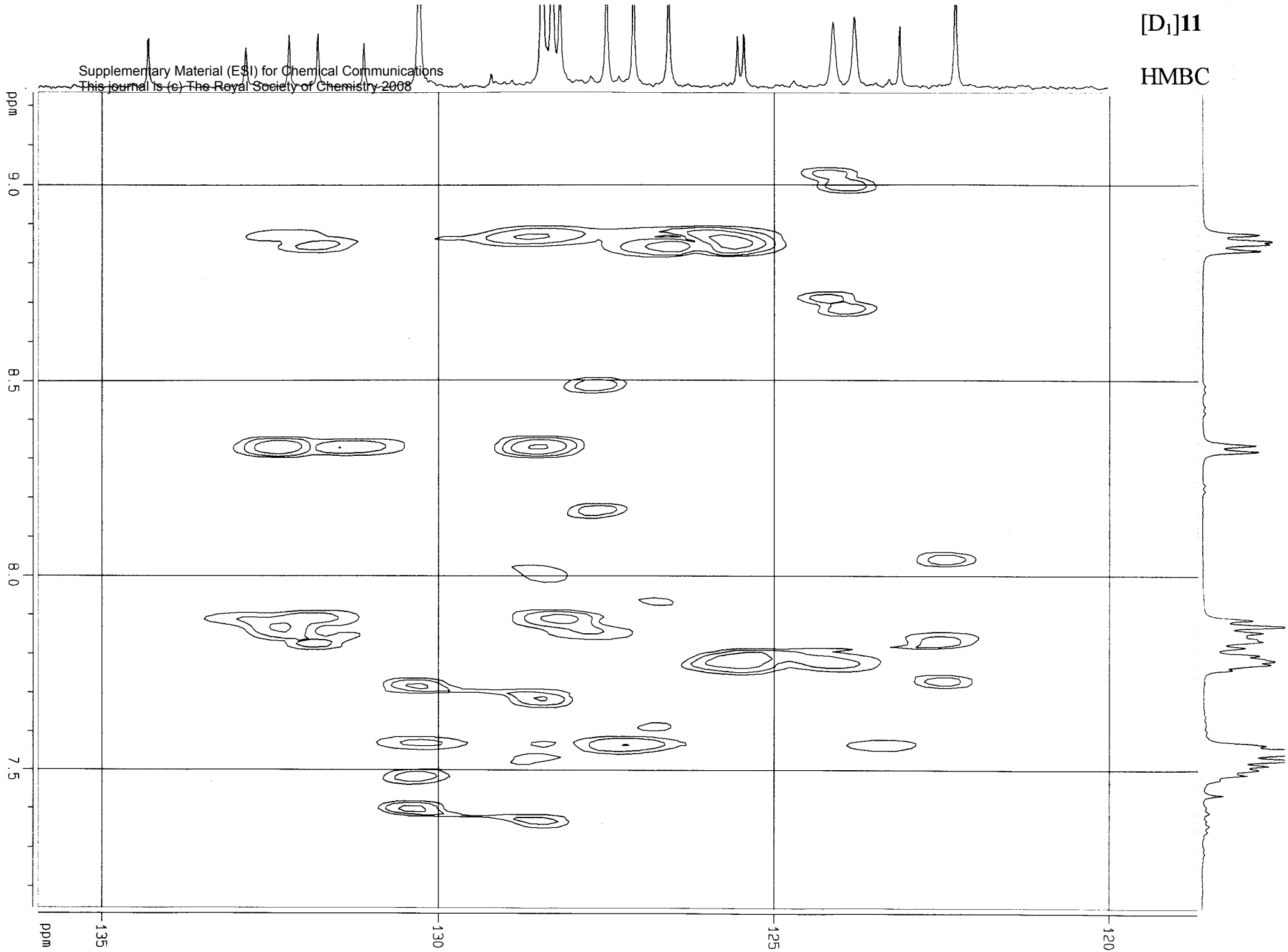






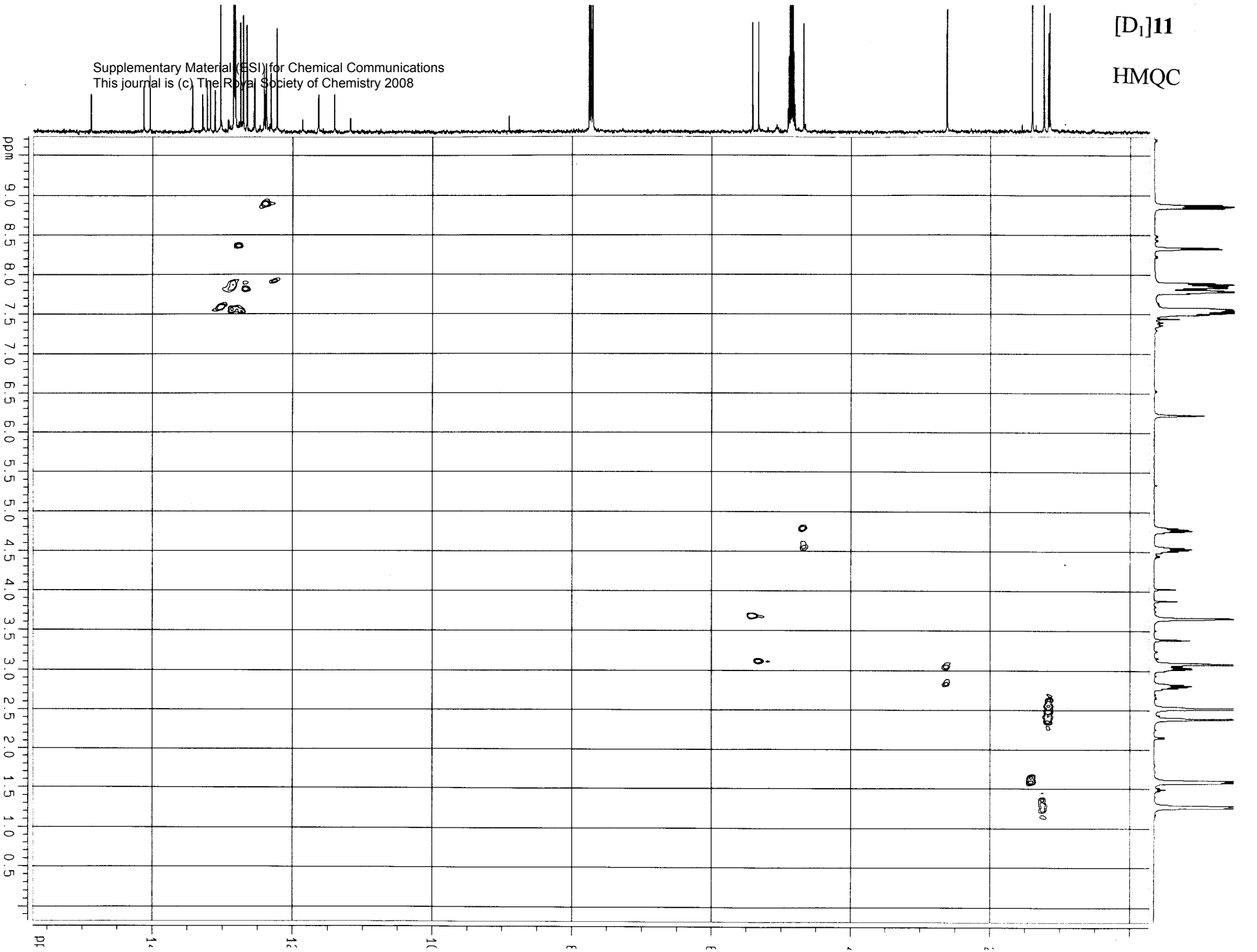
[D$_1$]11

HMBC



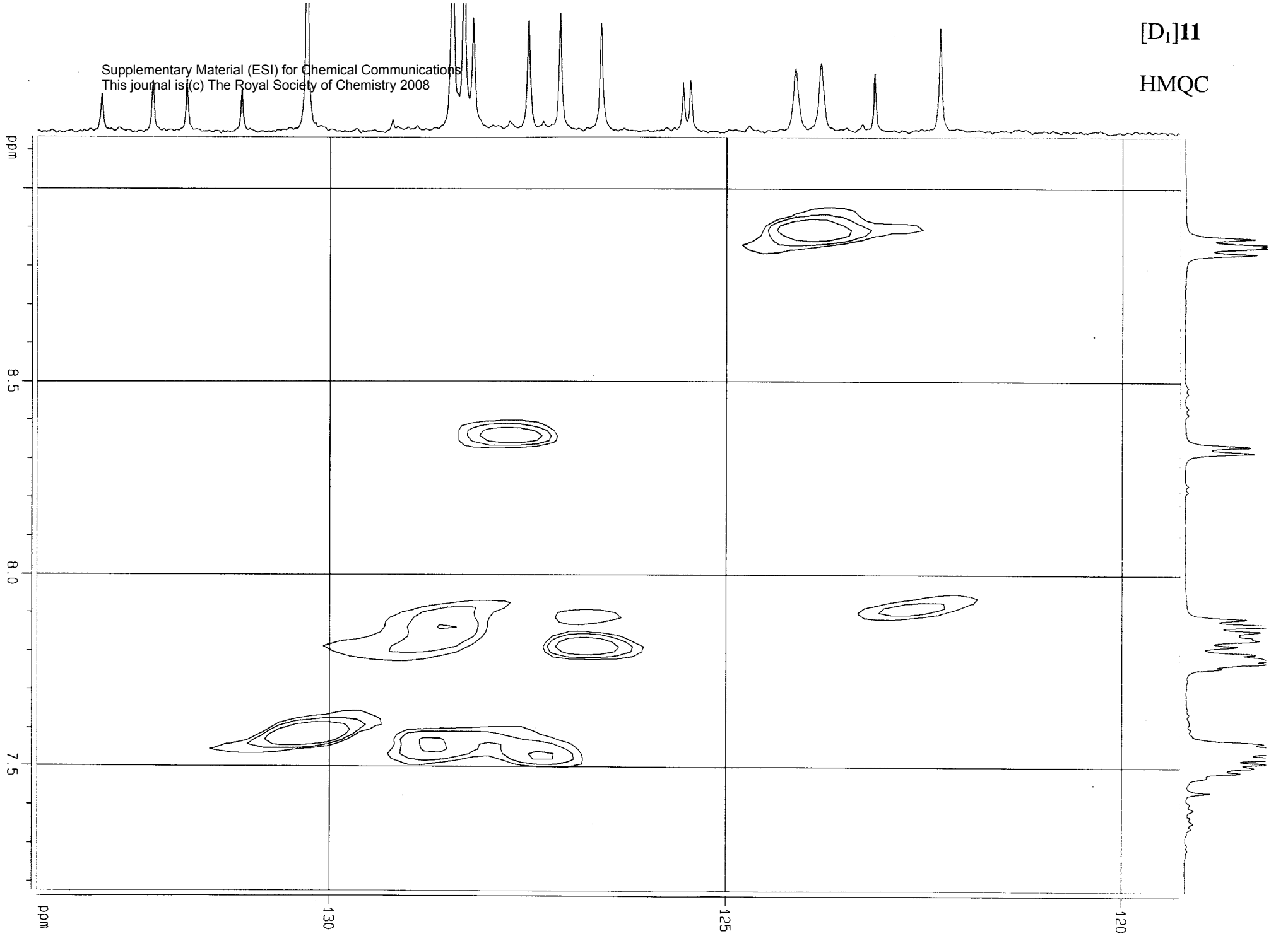
[D_1]**11**

HMQC



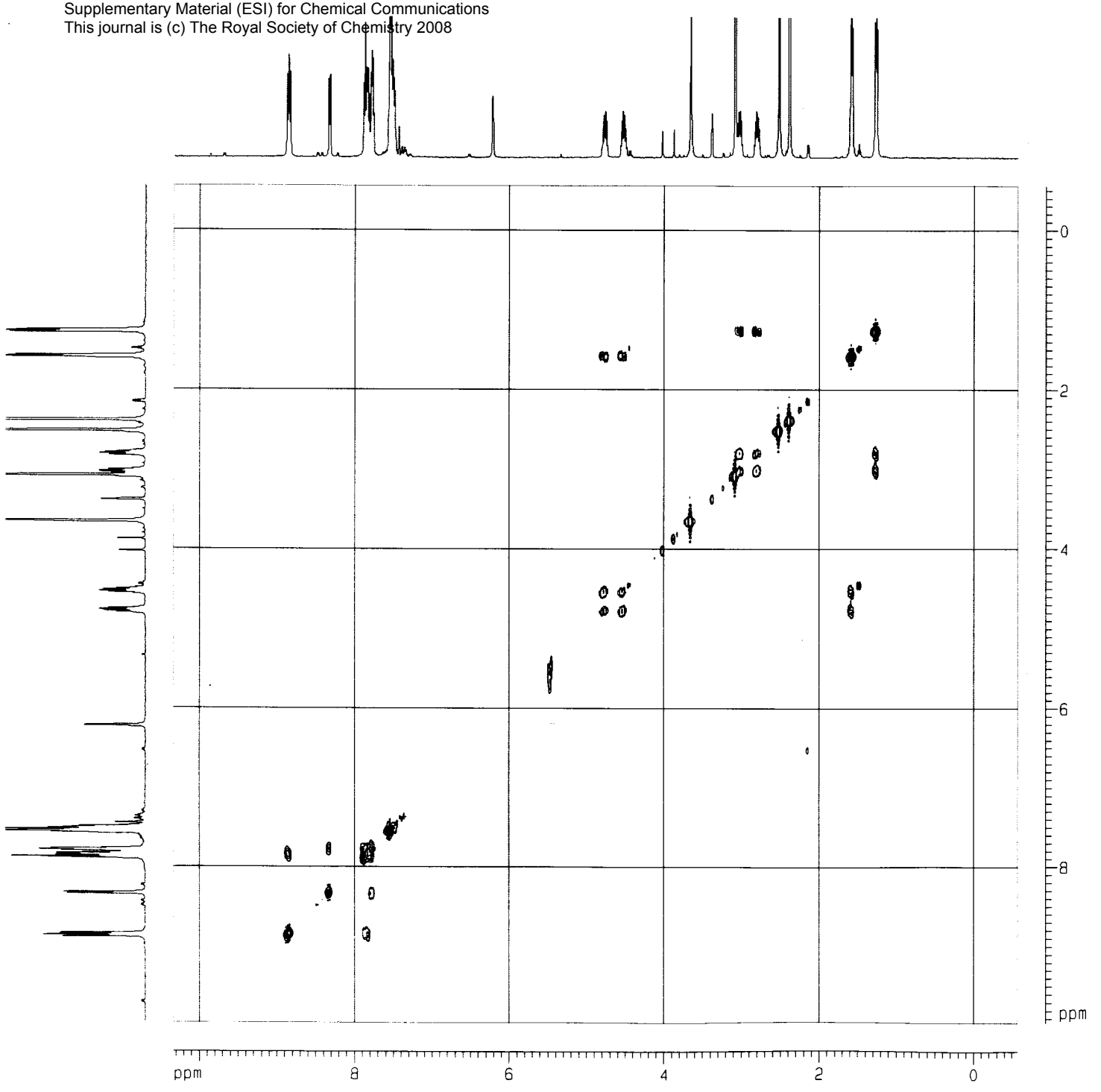
[D$_1$]**11**

HMQC



[D$_1$]11

COSY



Current Data Parameters

NAME	he2007-2
EXPNO	492
PROCNO	1

F2 - Acquisition Parameters

Date_	20070923
Time	14.51
INSTRUM	dmx500
PROBHD	5 mm QNP 1H/15
PULPROG	cosygpqf
TD	2048
SOLVENT	CDCl3
NS	8
DS	8
SWH	6510.417 Hz
FIDRES	3.178914 Hz
AQ	0.1574132 sec
RG	128
DW	76.800 usec
DE	6.00 usec
TE	299.0 K
d0	0.00000300 sec
D1	1.48689198 sec
d13	0.00000400 sec
D16	0.00020000 sec
DNO	0.00015360 sec
MCREST	0.00000000 sec
MCWRK	1.48689198 sec

======== CHANNEL f1 ========

NUC1	1H
P0	8.70 usec
P1	8.70 usec
PL1	4.00 dB
SF01	500.1340460 MHz

====== GRADIENT CHANNEL =====

GPNAM1	SINE.100
GPNAM2	SINE.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	10.00 %
GPZ2	10.00 %
P16	1000.00 usec

F1 - Acquisition parameters

NDO	1
TD	128
SFO1	500.134 MHz
FIDRES	50.795490 Hz
SW	13.000 ppm
FnMODE	QF

F2 - Processing parameters

SI	1024
SF	500.1319480 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

F1 - Processing parameters

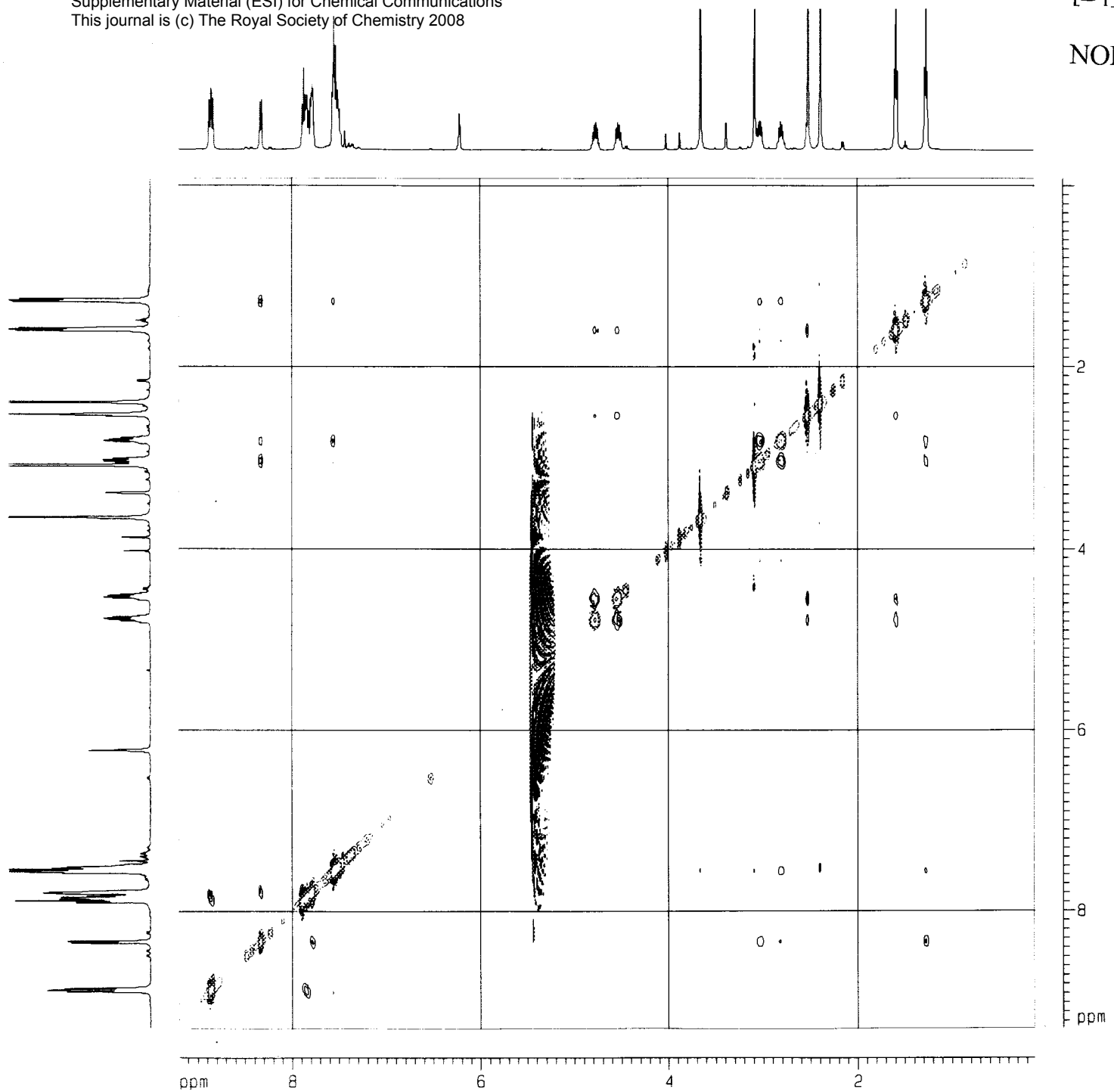
SI	2048
MC2	QF
SF	500.1319485 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	10.335 ppm
F2LO	5168.86 Hz
F2PHI	-0.572 ppm
F2HI	-286.17 Hz
F1PLO	9.951 ppm
F1LO	4977.02 Hz
F1PHI	-0.561 ppm
F1HI	-280.42 Hz
F2PPMCM	0.72714 ppm/cm
F2HZCM	363.66821 Hz/cm
F1PPMCM	0.70081 ppm/cm
F1HZCM	350.49615 Hz/cm

$[D_1]$**11**

NOESY



Current Data Parameters

NAME	ne2007-2
EXPNO	493
PROCNO	1

F2 - Acquisition Parameters

Date_	20070923
Time	15.20
INSTRUM	dmx500
PROBHD	5 mm QNP 1H/15
PULPROG	noesyph
TD	2048
SOLVENT	CDCl3
NS	32
DS	4
SWH	5482.456 Hz
FIDRES	2.676980 Hz
AQ	0.1869188 sec
RG	16
DW	91.200 usec
DE	6.00 usec
TE	298.7 K
d0	0.00007981 sec
D1	1.50000000 sec
D8	0.60000002 sec
IN0	0.00018178 sec
MCREST	0.00000000 sec
MCWRK	0.75000000 sec
ST1CNT	128

======== CHANNEL f1 ========

NUC1	1H
P1	8.70 usec
PL1	4.00 dB
SFO1	500.1338920 MHz

F1 - Acquisition parameters

ND0	1
TD	256
SFO1	500.1339 MHz
FIDRES	21.489479 Hz
SW	11.000 ppm
FnMODE	States-TPPI

F2 - Processing parameters

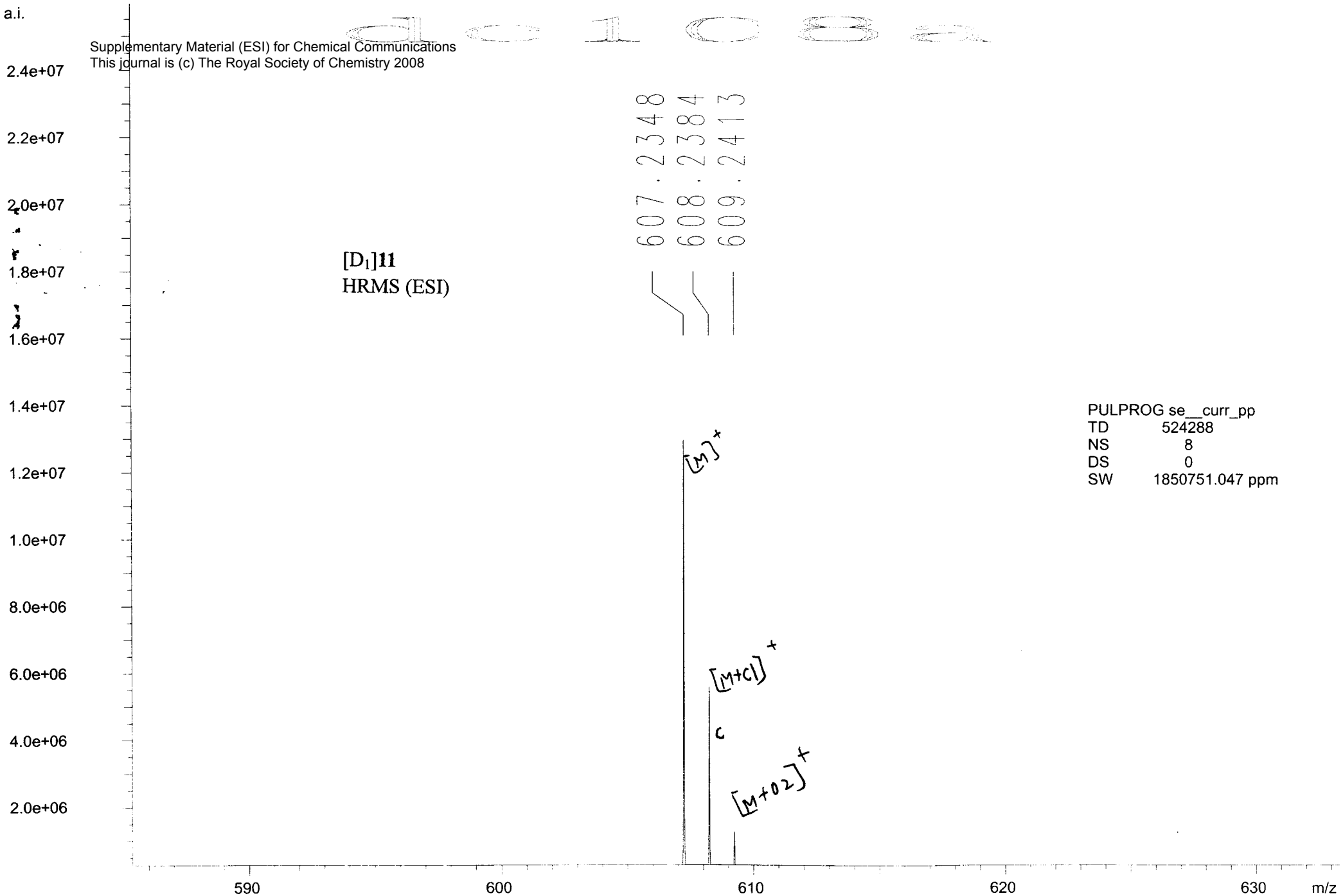
SI	1024
SF	500.1319469 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

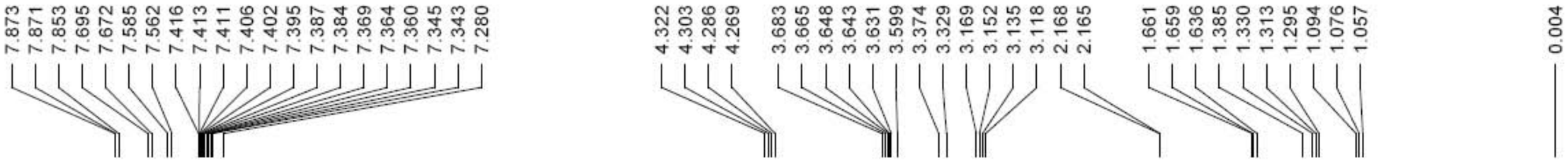
F1 - Processing parameters

SI	1024
MC2	States-TPPI
SF	500.1319471 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	9.199 ppm
F2LO	4600.68 Hz
F2PHI	0.121 ppm
F2HI	60.52 Hz
F1PLO	9.281 ppm
F1LO	4641.83 Hz
F1PHI	-0.086 ppm
F1HI	-42.88 Hz
F2PPMCM	0.60520 ppm/cm
F2HZCM	302.67758 Hz/cm
F1PPMCM	0.62446 ppm/cm
F1HZCM	312.31409 Hz/cm

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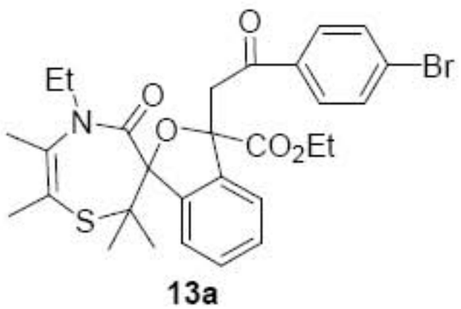
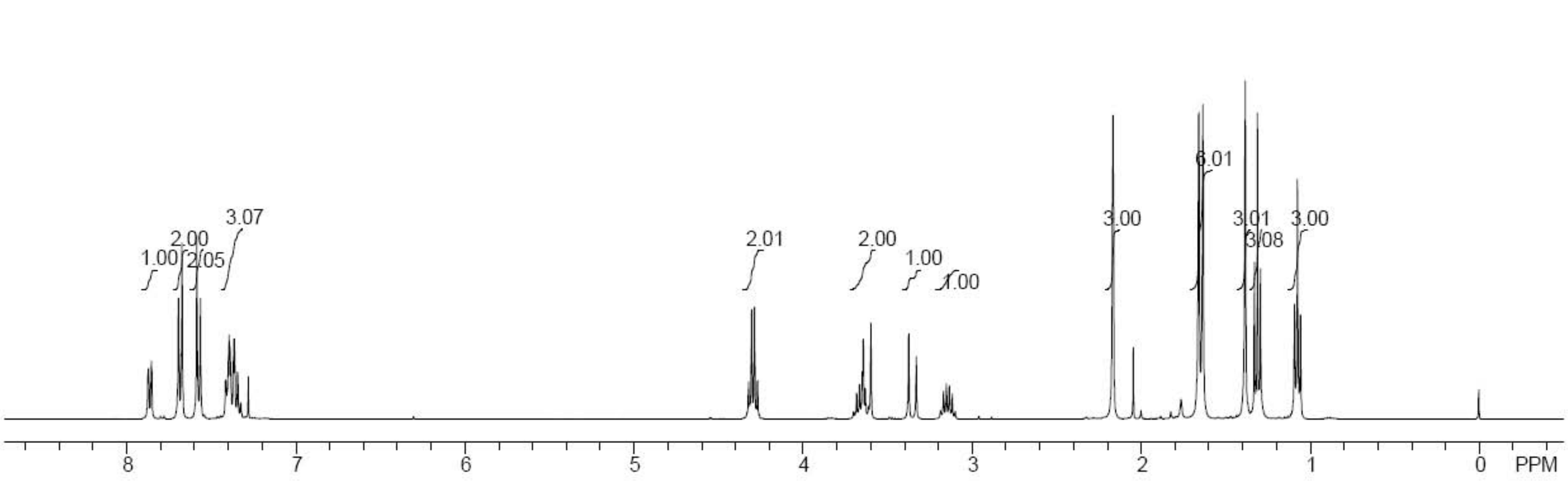
7.871
7.853
7.695
7.672
7.585
7.562
7.416
7.413
7.411
7.406
7.402
7.395
7.387
7.384
7.369
7.364
7.360
7.345
7.343
7.280
4.322
4.303
4.286
4.269
3.683
3.665
3.648
3.643
3.631
3.599
3.374
3.329
3.169
3.152
3.135
3.118
2.168
2.165
1.661
1.659
1.636
1.385
1.330
1.313
1.295
1.094
1.076
1.057
0.004


Et
N
O
O
O
CO2Et
Br
S

13a


1.00
2.00
2.05
3.07
2.01
2.00
1.00
1.00
3.00
6.01
3.01
3.08
3.00
8
7
6
5
4
3
2
1
0
PPM

194.312
172.738
170.400
141.122
139.783
137.201
134.924
132.000
129.323
128.836
128.721
127.944
121.759
98.433
87.272
77.319
76.996
76.686
69.600
61.392
50.795
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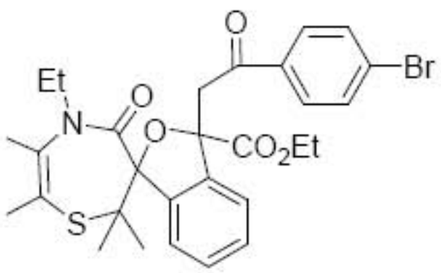
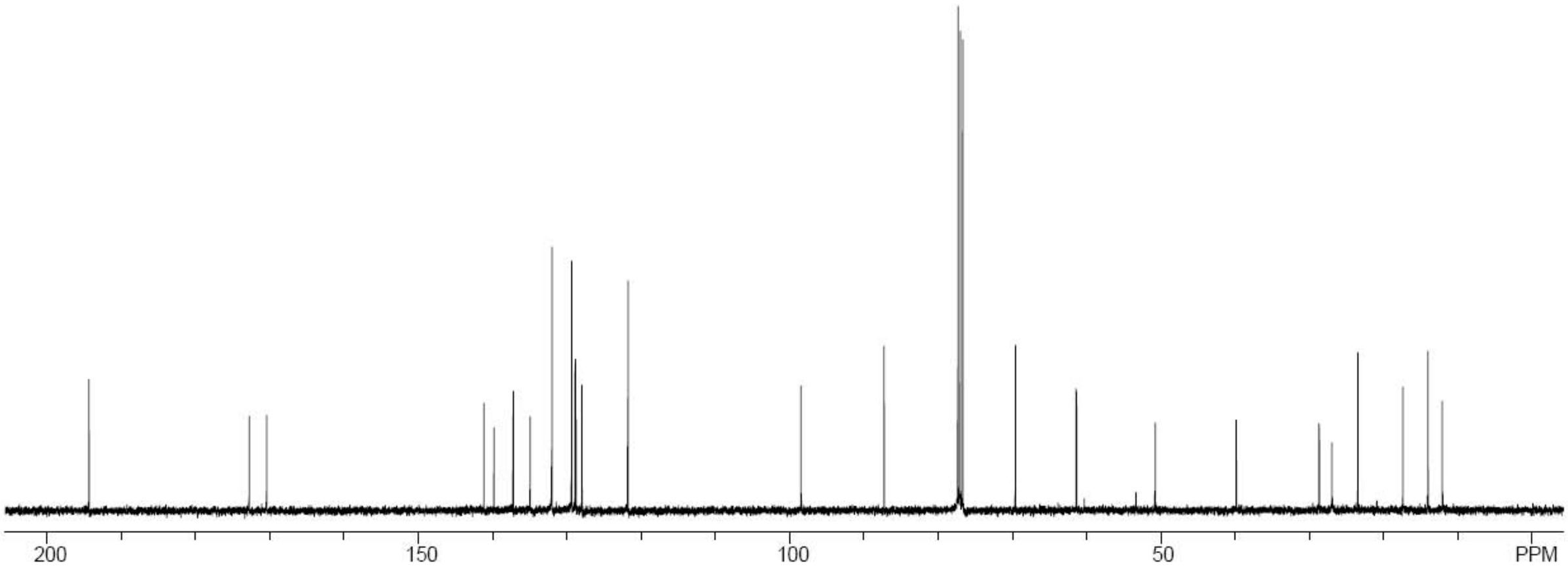
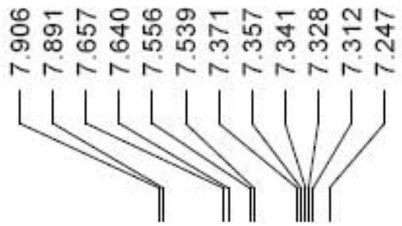
26.973
23.499
17.458
14.063
12.117



13a

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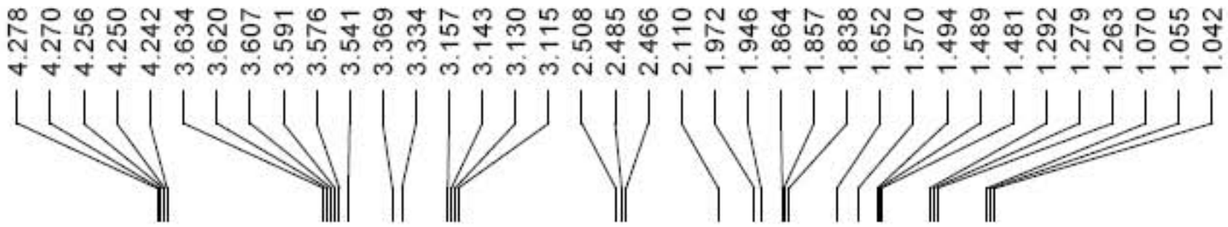
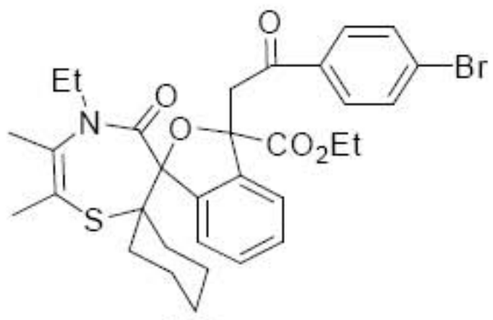
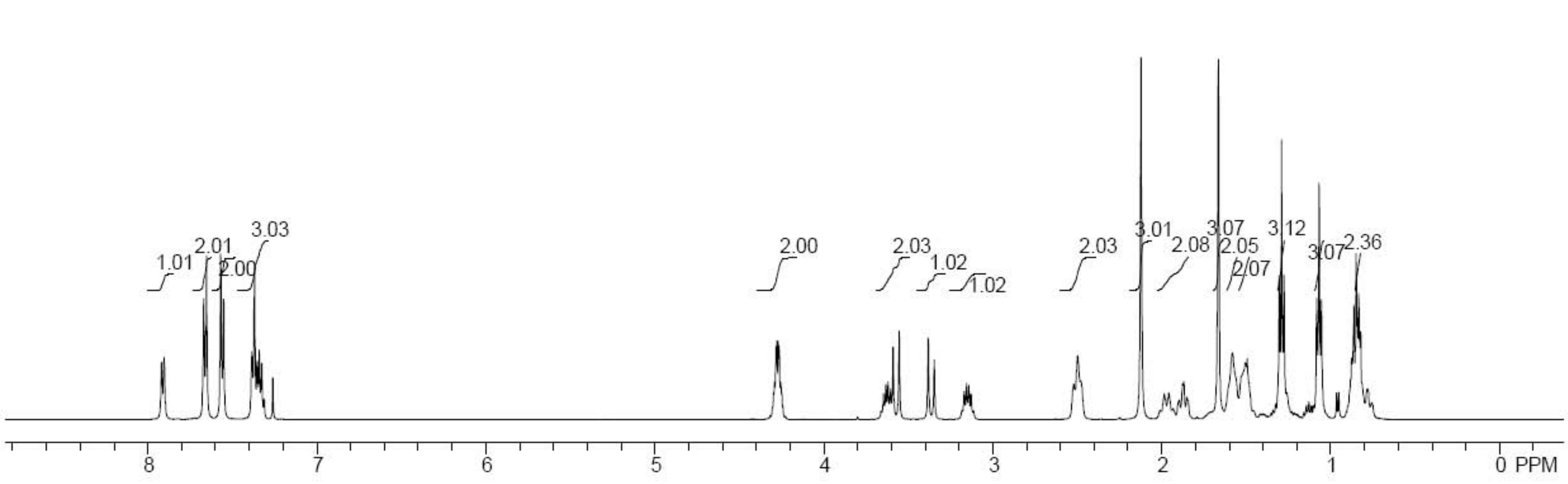
7.657
7.640
7.556
7.539
7.371
7.357
7.341
7.328
7.312
7.247


4.278
4.270
4.256
4.250
4.242
3.634
3.620
3.607
3.591
3.576
3.541
3.369
3.334
3.157
3.143
3.130
3.115
2.508
2.485
2.466
2.110
1.972
1.946
1.864
1.857
1.838
1.652
1.570
1.494
1.489
1.481
1.292
1.279
1.263
1.070
1.055
1.042


O
Br
Et
N
O
O
CO2Et
S

13b


1.01
2.01
2.00
3.03
2.00
2.03
1.02
1.02
2.03
3.01
2.08
3.07
2.05
2.07
3.12
3.07
2.36
8
7
6
5
4
3
2
1
0 PPM

194.703
173.386
170.689
141.858
140.225
137.408
135.274
132.292
130.019
129.611
129.026
128.996
127.903
122.107
121.624
99.889
87.521
77.515
77.262
77.007
76.495
61.651
51.163
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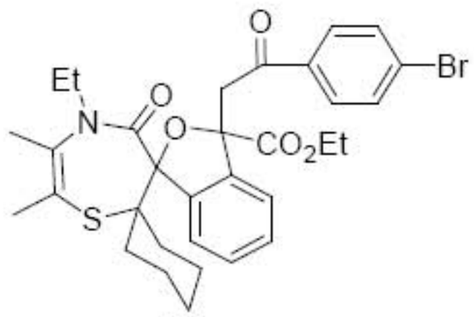
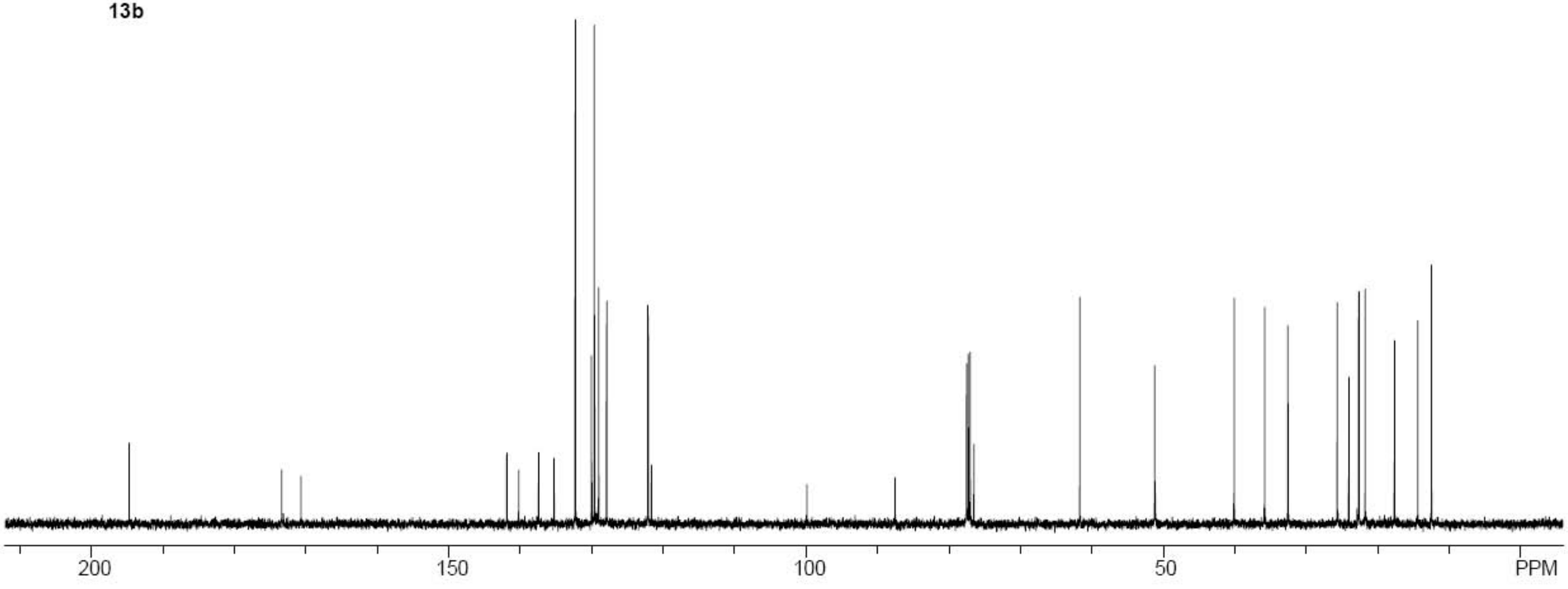
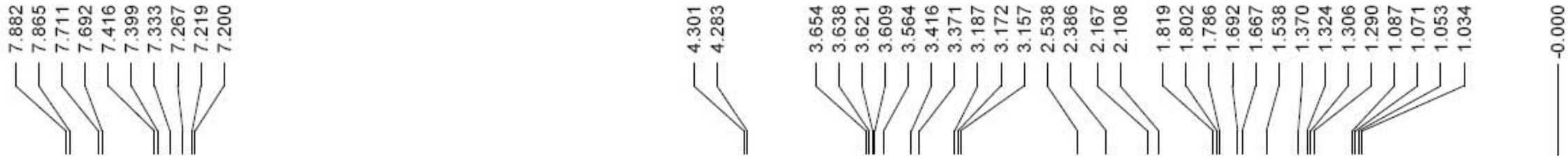
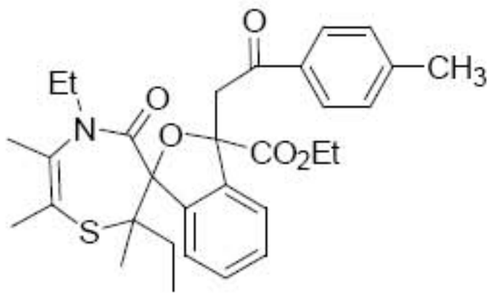
35.802
32.544
25.629
24.013
22.610
21.710
17.614
14.345
12.448



13b




7.882
7.865
7.711
7.692
7.416
7.399
7.333
7.267
7.219
7.200
4.301
4.283
3.654
3.638
3.621
3.609
3.564
3.416
3.371
3.187
3.172
3.157
2.538
2.386
2.167
2.108
1.819
1.802
1.786
1.692
1.667
1.538
1.370
1.324
1.306
1.290
1.087
1.071
1.053
1.034
-0.000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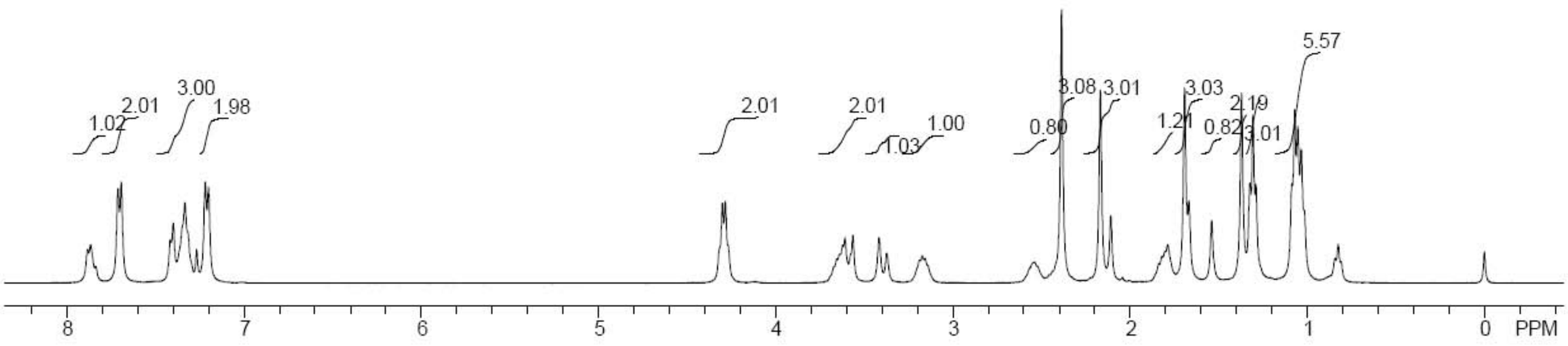
CO2Et
CH3
S

13c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8
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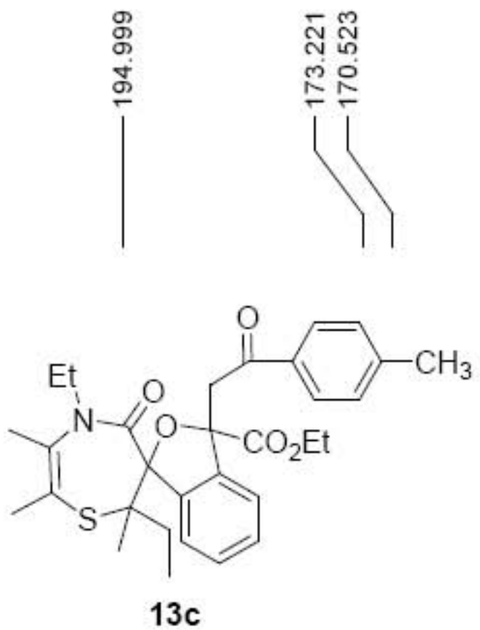
PPM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13c

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200
150
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50
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